File No: PLC/144

July 2000

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Epoxy Acrylic Block Polymer 99 R 9545

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.

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Director
Chemicals Notification and Assessment

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1. APPLICANT

The Valspar (Australia) Corporation Pty Ltd of 203 Power St Glendenning NSW 2761 has submitted a Polymer of Low Concern notification statement in support of their application for an assessment certificate for Epoxy Acrylic Block Polymer 99 R 9545.

2. IDENTITY OF THE CHEMICAL

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

Marketing Name:	99 R 9545
Other Names:	Epoxy Acrylic Block Polymer

Characterisation as a Synthetic Polymer of Low Concern

Number-Average Molecular Weight (NAMW):	3653
Weight-Average Molecular Weight:	7624
Polydispersity:	2.09
Maximum Percentage of Low Molecular Weight Species	
Molecular Weight < 500:	0.0 %
Molecular Weight < 1 000:	3.3 %
Polymer Stability	expected to be stable under normal environmental conditions
Reactivity	The notified polymer nominally contains epoxy groups at a higher level than is permissible in a Synthetic Polymer of Low Concern; however, the polymer

	contains an excess of methacrylic acid, and is produced and stored in aqueous solution in the presence of a tertiary amine. The $t_{1/2}$ values for hydrolysis to the diols of the related epoxides ethylene oxide (IPCS, 1985a), propylene oxide (IPCS, 1985b) and epichlorohydrin (IPCS, 1984) in neutral water are 14 days, 12 days and 148 hours, respectively, at 25°C (ref EHCs 55, 56, 33, respectively). Hydrolysis of epichlorohydrin is base catalysed, with $t_{1/2}$ of 62 hours in basic solution; hydrolysis of ethylene oxide is also stated to be base catalysed. The reaction of the epoxy groups of the notified polymer to form a diol would also be expected to be base catalysed. Accordingly, the terminal epoxy groups are expected to be in hydrolysed form after storage. Carboxylate groups, considered to be low concern reactive functional groups, are also present.
Charge Density	anionic, functional group equivalent weight of 784 per carboxylate group

The polymer meets the criteria for assessment as a synthetic polymer of low concern under Regulation 4A of the *Industrial Chemicals (Notification and Assessment) Act 1989*.

Method of Detection and Determination:	infrared spectroscopy
Spectral Data:	3466(br), 3040, 2974, 2940, 2888, 1726, 1610, 1584, 1512, 1466, 1387, 1366, 1297, 1251, 1186, 1133, 1044, 1015, 956, 832, 703 cm^{-1}

3. PHYSICAL AND CHEMICAL PROPERTIES

The notified polymer is produced in aqueous solution, in the presence of an amine and other co-solvents to aid solubility. As the notified polymer is never isolated, limited data on the physical and chemical properties are available.

Appearance at 20°C and 101.3 kPa:	clear yellow solution, with a slight fishy and solvent odour
Glass Transition Temperature:	79.5°C
Specific Gravity:	1.12 - 1.13
Water Solubility:	0.24 % soluble species at 21 - 23°C
Particle Size:	not applicable as the notified polymer is produced and

	used in liquid form
Partition Co-efficient (n-octanol/water):	not determined, see comments below
Dissociation Constant:	not determined, see comments below
Flammability Limits:	not flammable
Autoignition Temperature:	> 300°C
Explosive Properties:	not explosive
Reactivity/Stability:	resistant to hydrolysis and thermal degradation

3.1. Comments on Physico-Chemical Properties

The polymer is not expected to have a clearly defined melting point, but a glass transition temperature has been provided by the notifier.

The water solubility was determined by smearing a sample of the polymer solution onto a weighed glass plate and drying it overnight. After determining the combined weight of plate and polymer, the plate was immersed in water for 24 h, removed, dried and reweighed. This test was also performed on the polymer mixture final product (which will be sold to the public), and both the notified polymer and the polymer mixture had a water extractable fraction of 0.24 % under these conditions. The water solubility of the polymer cannot be directly determined from these results, but it is expected to be moderate due to the presence of ionisable groups.

The notified polymer contains a high proportion of carboxylic acid groups which are likely to have typical acidity, and is water soluble in the presence of amine. The partition co-efficient was not measured, as the notified polymer has low water solubility in the absence of co-solvents.

The polymer is expected to be stable under normal environmental conditions. Whilst it does contain a number of acid groups and ester linkages, hydrolysis in the environmental pH range of 4 - 9 is not expected when bound up in the paint matrix.

4. PURITY OF THE CHEMICAL

Degree of Purity:	not stated, produced as a 30 % aqueous solution
Hazardous Impurities:	none
Non-hazardous Impurities (> 1% by weight):	none

Maximum Content of Residual Monomers:	residual monomer identities and concentrations have been exempted from publication; concentrations of residual monomers are all below the relevant cutoffs for the notified polymer to be classified as hazardous

Additives/Adjuvants:

Chemical name:	water
CAS No.:	7732-18-5
Weight percentage:	30 - 60
Chemical name:	n-butanol
CAS No.:	71-36-3
Weight percentage:	10 - 30
Toxic properties:	R20 Harmful by inhalation (NOHSC, 1999a)
Regulatory Controls:	National exposure standard 50 ppm peak limitation with skin notation (NOHSC, 1995)
Chemical name:	diethylaminoethane
Synonyms:	triethylamine
CAS No.:	121-44-8
Weight percentage:	1 - 10
Toxic properties:	R35 Causes burns R20/21/22 Harmful by inhalation, in contact with skin and if swallowed (NOHSC, 1999a)
Regulatory Controls:	National exposure standard 3 ppm TWA, 5 ppm STEL (NOHSC, 1995)
Chemical name:	propanol, (2-methoxymethylethoxy)-
Synonyms:	dipropylene glycol monomethyl ether, DPGME
CAS No.:	34590-94-8
Weight percentage:	1 - 10
Toxic properties:	On the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999a); eye and respiratory system irritant and central nervous system depressant in humans (American Conference of Government Industrial Hygienists, 1998)
Regulatory Controls:	National exposure standard 100 ppm TWA, 150 ppm STEL with skin notation (NOHSC, 1995)

5. USE, VOLUME AND FORMULATION

The notified polymer will be used as a component of water based industrial surface coatings, for applications including the production of coated hard boards. It will be manufactured in Australia at one site. The polymer will be manufactured as an aqueous solution containing 30 % (w/w) notified polymer. It will then be reformulated at the site of manufacture to produce the final paint products. The paint will contain less than 10 % (w/w) notified polymer. The paint products will be transferred to 200 L drums, 1000 L intermediate bulk containers (IBCs) or possibly bulk tankers for sale to industrial users.

The notifier estimates the manufacture volumes to be 30 tonnes in the first year, 60 – 90 tonnes in the second year, and 120 tonnes per annum thereafter.

6. OCCUPATIONAL EXPOSURE

Transport and Storage
Warehouse workers and transport drivers will handle the drums and IBCs of finished paint, but no exposure is expected unless the packaging is ruptured.

Polymer Manufacture
The polymer manufacture will involve 4 reactor operators along with 2 quality control personnel, 3 supervisors (who are likely to have limited exposure) and 4 storage workers and forklift drivers. The notifier indicates that 6 to 10 batches will be manufactured per year.

The reactants will be added to an enclosed reactor, either by closed pipe from storage tanks, or by pumping from drums. The resultant polymer solution will be transferred to a thinning tank, then to a holding tank. Sampling for quality control will be carried out through a sampling valve using a tin with an extended handle. There is potential for dermal exposure to the polymer solution in the form of drips and spills during transfer, but normal practice will be transfer through a hard piped system. Exposure to the 30 % solution of the notified polymer may occur during sampling and quality control activities. These will involve the operators and quality control personnel. Store workers may have dermal exposure to the solution of notified polymer if small quantities have to be transferred from drums by pump.

Paint Manufacture
The paint production will involve 6 operators along with 7 personnel in the drumming off section, 2 quality control personnel, 3 supervisors, 5 storage workers and forklift drivers, and 2 truck drivers. The notifier indicates that paint production will occur approximately 70 times per year, in batches of either 20 or 50 tonnes. Only 2 operators and 2 drumming off personnel will be involved with each batch.

The solution of the notified polymer will be transferred from the holding tanks to a make-up tank, along with pigments and additives. The notifier states that the paint production is likely to occur in a dedicated tank, where the paint will be held until it is transferred to the containers for delivery to customers. Sampling for quality control will be performed using a manhole in the make-up tank.

The formulated product (less than 10 % notified polymer) is filled from the makeup tank via an open filter into 200 L drums or 1000 L IBCs. Skin contact with the paint may occur during filling, particularly if spillage occurs. The notifier states that the workers involved in drumming off will wear impervious gloves, overalls and safety boots. Facial protection will also be available.

Paint Application
The paints containing the notified polymer will only be available to industrial customers. The notifier has indicated that one application will be in the continuous production of coated hard boards. The curtain coater will be enclosed, with paint not used being recycled. Exposure to the paint containing the notified polymer will only occur during addition of paint to the recycling reservoir.

After application of the paint, it will cure and crosslink, and the notified polymer will no longer be separately available for exposure.

7. PUBLIC EXPOSURE

Paint products containing the notified polymer will only be used by industry. The potential for public exposure to the notified polymer during manufacture, reformulation, transport and coating operations or from disposal is assessed as negligible. Although members of the public will make dermal contact with articles coated with products containing the notified polymer, exposure will be negligible because of the high molecular weight and the cured state of the notified polymer in the coatings.

8. ENVIRONMENTAL EXPOSURE

8.1. Release

After the polymer resin manufacture, the notifier states that all tanks and lines will be cleaned with the co-solvent and these residues added to the thinning tank. This process will minimise the amount of waste resin released. Solvent used for a final wash will be stored in a drum and added to the next batch of resin. A small amount (2.5 kg per annum) of polymer will be lost as dry film adhering to the sides of the drum when it is disposed of to landfill.

The polymer residues produced during the paint manufacture will also be minimised by recovering and recycling most of the washings. However, there may be some release of the diluted paint to the sewer in the event that production is not in dedicated equipment. This is estimated by the notifier to be up to 100 kg polymer per annum. Spills may also contribute to the annual release.

The IBC tanks used to transport the final paint product to the customer factories will have the liners removed and slit, to allow the paint to dry on the inside of the liner, which is then disposed of to landfill.

The notifier is not yet able to specify the number and sites of the end users of the paint containing the notified polymer. However, they have provided information on the likely use

pattern and estimates on the predicted residues that will be released to the environment. Those provided below are based on the maximum expected manufacture volumes.

Summary Of Releases To The Environment (Landfill)

Resin Production-losses as dry film on drums	2.5 kg per annum
Paint Production-dry film on IBC liners	120 kg per annum

Summary Of Releases To The Environment (Sewers)

Resin Production-losses from spills/cleaning	20 kg per annum
Paint Production-cleaning of tanks and lines	100 kg per annum
Paint Production-spills, drips etc	60 kg per annum
Customer Use- cleaning of equipment	4 kg per annum
Customer Use-spills, drips etc	50 kg per annum

8.2. Fate

Waste polymer sent to landfill as a dry solid bound in the paint matrix is expected to remain associated with the soils and sediments and would not be expected to leach into the aquatic environment.

When released to the sewer, the notified polymer is expected to remain in solution in concentrations far below its saturation point because of the relatively high water solubility of the polymer.

The coating is expected to dry to form a solid inert film that after use will share the fate of the substrate and not present a significant hazard. Any fragments, chips or flakes of the paint will be of little environmental concern as they are expected to be inert.

Bioaccumulation of the polymer is unlikely due to the high molecular weight of the polymer, even before curing (Connell, 1990).

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicology data were submitted. Polymers of low reactivity and high molecular weight do not readily cross skin or other biological membranes, and the toxicity of the notified polymer is therefore expected to be low.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were submitted. Poly(aliphatic acid) polymers are known to be moderately toxic (96 h EC_{50} values between 8 to 50 mg/L) to green algae indirectly in that they chelate the calcium and magnesium ions that the algae require for growth. They exhibit consistently low toxicity to fish and aquatic invertebrates with LC_{50} values > 1000 mg/L (Hamilton, 1997).

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The notifier estimates that during paint manufacture and application approximately 122 kg per annum of notified polymer will be disposed of to landfill as solid waste and 234 kg per annum will be released to the sewer as aqueous waste. All solid residues will remain associated with the soil and sediment due to the high molecular weight and the stability of the cured paint matrix. The fate of the aqueous residues released to the sewer system is less predictable as the relatively high water solubility of the polymer may allow it to stay in solution at low concentrations.

The Sewage Treatment Plant servicing the manufacturing site has a daily capacity of 28 ML. A dilution of 1:3 upon entering receiving waters can be assumed for this plant and a worst case Predicted Environmental Concentration (PEC) for the paint manufacturing process is calculated as follows:

180 kg released to sewer/annum (~3.6 kg per batch @ 50 batches/annum)
28 ML discharge daily from sewage treatment plant
Concentration of notified polymer in discharge = 129 ppb
Further diluted 1:3 by receiving waters to 43 ppb

The PEC is several orders of magnitude less than concentrations expected to cause adverse effects in aquatic organisms, so the aquatic hazard is predicted to be low.

The majority of the notified polymer will be applied to various substrates (hard board and others not specified) and cured into a solid paint coating. The polymer will share the fate of the substrates and the eventual disposal of the article to landfill is unlikely to present a hazard to the environment, as it will be in a solid matrix not expected to biodegrade or leach. If the products coated with the notified polymer are incinerated, the environmental hazard is also expected to be low. The aqueous waste released to the sewer by end users will be widespread and at low levels that should not be an environmental hazard.

The main environmental hazard would occur through spillage in transport accidents. Small quantities of the polymer may be released to drains and waterways. It is difficult to predict the behaviour of the polymer in the natural aquatic environment.

The low environmental exposure of the polymer as a result of the proposed use indicates the overall environmental hazard should be low.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Hazard Assessment
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 is not expected to be hazardous by dermal exposure as the high molecular weight will preclude absorption through the skin.

The polymer solution containing 30 % notified polymer, as manufactured, is a hazardous

substance because of the solvent content (n-butanol and triethylamine). The Material Safety Data Sheet (MSDS) for the polymer solution lists a number of potential health effects, namely skin, eye and respiratory irritation, dermatitis, nausea and liver, kidney and blood disorders. These relate mainly to the solvents, n-butanol, dipropylene glycol monomethyl ether and triethylamine, rather than the notified polymer. Due to the high molecular weight and low reactivity of the polymer, the toxicological hazard of the notified polymer is expected to be low.

Occupational Health and Safety

There is little potential for significant occupational exposure to the notified polymer in the transport and storage of the polymer solution or the paint component containing this polymer. There may be exposure during the manufacture and reformulation of the polymer and during production of paint, and in the use and disposal of the paints.

During the manufacture, reformulation and application processes, the main exposure route for the notified polymer will be dermal. The paints and polymer solutions will be viscous, and ready formation of aerosols is not expected. Splashes are also not likely during filling operations. All processes involving the notified polymer are likely to be enclosed and automated except for filling the containers for transport to the customers and transfer from these containers to the recycling tank of the coating equipment. It is possible that paints including the notified polymer will also be used by other customers for other applications, and greater worker exposure may occur.

Due to the low toxicological hazard posed by the notified polymer, protective measures used to prevent exposure to the solvents should provide sufficient protection against the notified polymer.

Once the applied final paint mix, containing a maximum of 10 % notified polymer, has hardened, the polymer will not be separately available for exposure or absorption.

There are NOHSC exposure standards for n-butanol, dipropylene glycol monomethyl ether and triethylamine, identified as ingredients in the polymer solution. The employer is responsible for ensuring that these exposure standards are not exceeded in the workplace.

Public Health

Paint products containing the notified polymer will only be used by industry. Although members of the public will make dermal contact with articles coated with products containing the notified polymer, exposure will be negligible because of the high molecular weight and the cured state of the notified polymer in the coatings.

The notified polymer is not expected to pose a significant hazard to public health when used in the proposed manner.

13. RECOMMENDATIONS

To minimise occupational exposure to Epoxy Acrylic Block Polymer 99 R 9545 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.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the resin solution containing the notified polymer 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 subsection 64(1) of the Act, secondary notification may be required if the polymer characteristics cease to satisfy the criteria under which it has been accepted as a Synthetic Polymer of Low Concern. Secondary notification of the notified polymer may be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

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