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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in Acrylic Resin RC-0714

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Director Chemicals Notification and Assessment

FULL PUBLIC REPORT

RC29757

1. APPLICANT

DuPont (Australia) Ltd of 49-59 Newton Rd WETHERILL PARK NSW 2164 has submitted a limited notification statement in support of their application for an assessment certificate for a polymer with number average molecular weight (NAMW) > 1000 RC29757.

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 exact import volume have been exempted from publication in the Full Public Report and the Summary Report.

Trade Name: RC29757

Method of Detection infrared spectroscopy (spectrum supplied)

and Determination:

3. PHYSICAL AND CHEMICAL PROPERTIES

The polymer will be imported in solution; some of the physical and chemical properties provided by the notifier are those of the solution.

Appearance at 20°C transparent and colourless solution

and 101.3 kPa:

Melting Point: the notified polymer will not melt below the estimated

decomposition temperature of 360°C

Specific Gravity: 1.05 (for the polymer)

1.00 (for the solution)

Water Solubility: < 1 mg/L at 25°C

Dissociation Constant: the notified polymer contains no acidic or basic

functional groups

Flammability Limits: Upper Explosive Limit = 10.7 %

Lower Explosive Limit = 0.9 % (for the solution)

Autoignition Temperature: 370°C (for the solution)

Explosive Properties: the polymer is not expected to be explosive

Reactivity/Stability: the polymer is not expected to be highly reactive at

room temperature

Comments on Physico-Chemical Properties

The density given above was estimated from previous experience with similar acrylic resins. However, the resin solution in which the polymer will be imported has a density 1.0 ± 0.05 g/cm³.

A water solubility study was not submitted. The notifier claims that the notified polymer is estimated to have water solubility very much less than 1 mg/L, as the polymer is predominantly hydrophobic. The notified polymer is of high molecular weight, with the notifier claiming that as a constituent of vehicle finishing paints it is designed to be chemically and environmentally inert. While the new polymer contains groups which are inherently susceptible to hydrolytic cleavage, the polymer will be securely bound into a cured resin matrix in the paint. This will preclude contact between the potentially reactive functionalities and water (as well as other reactants in the environment), and hence the possibility for hydrolysis in the environmental pH region (4<pH<9) or other reactions would be extremely small.

No partition coefficient data was supplied, but the polymer is predominantly hydrocarbon in nature and contains no other highly polar groups. Consequently, the polymer is hydrophobic, and would be expected to partition into the oil phase.

Similarly, while no adsorption/desorption data was provided with the notification, the predominantly hydrocarbon nature of the polymer indicates that it would have a large value for Koc, and hence a high affinity for the organic component of soils and sediments. The polymer contains no groups capable of ionising in aqueous media, so dissociation constant data are not relevant.

4. **PURITY OF THE CHEMICAL**

Degree of Purity: up to 70 % in solution

Toxic or Hazardous Impurities:

> Chemical name: solvent naphtha, petroleum, light aromatic

Synonyms: petroleum distillate

CAS No.: 64742-95-6

Weight percentage: 20 - 30 %

On the List of Designated Hazardous Substances (National Occupational Health and Safety Commission, *Toxic properties:*

draft, 1997)

T cutoff 0.1 %

R45(2) 'May cause cancer'

R65 'May cause lung damage if swallowed'

kidney damage and kidney or liver tumours were seen in

studies on rats

the R45(2) notation does not apply if the solvent

contains less than 0.1 % benzene

Chemical name: 1-butanol

Synonyms: n-butyl alcohol

Weight percentage: 1 - 10 %

71-36-3 CAS No.:

On the List of Designated Hazardous Substances (National Occupational Health and Safety Commission, *Toxic properties:*

1994b)

Xn cutoff 25 % R10 'Flammable'

R20 'Harmful by inhalation'

Non-hazardous Impurities

(> 1% by weight):

none

Maximum Content

of Residual Monomers:

< 1 % total; the polymer is not considered hazardous on

the basis of residual monomer content

5. USE, VOLUME AND FORMULATION

RC29757 is an automotive binder resin for use in Original Automobile Manufacturer topcoat paints cured in high temperature ovens. During the next five years, it is expected that hundreds of tonnes of the notified polymer will be imported per year. The notified polymer will not be manufactured in Australia.

The notified polymer will be imported both as a resin concentrate solution containing 50-70 % (w/w) resin and as prepared automobile paints containing 10-36 % resin. The polymer (as resin solution or paint) will be imported in 208.2 L (55 US gallon) drums or 3.78 L (1 US gallon) steel cans. The steel cans will be packed into cardboard boxes in lots of four.

The resin concentrate solution will be reformulated in existing plants which manufacture automobile paints by the addition of solvents, additives and ground, pigmented mill base to prepare paints for use by Original Equipment Manufacturers (OEMs).

6. OCCUPATIONAL EXPOSURE

The notified polymer will be imported in solution, and will be reformulated to produce automobile paints, which will be applied by robot or manual spraying then cured by high temperature baking. The use of these paints will be restricted to automobile manufacture plants.

Workers may be exposed to the solutions of resin or paint containing the resin solution dermally, by direct contact with drips or spills of the liquids, or by inhalation of paint aerosols containing the polymer.

Transport and storage

The notifier did not provide details of the worker exposure during unloading, storage or transport of the import containers containing the notified polymer. The containers used for importation are expected to provide protection for these workers except in the case of an accident involving rupture of the steel containers.

Reformulation

Production of automobile paints will be restricted to several plants with the appropriate facilities to prepare the final paints. Typically two workers will be involved in handling the resin concentrate solution in the preparation of a paint batch. The notifier states that the addition of the resin solution is the last stage in the paint preparation and handling of the notified polymer in the reformulation process is therefore minimised.

The resin solution will be poured from the imported drum into a 5000, 10000 or 20000 L mixing tank using pneumatic drum handling equipment. The area over the mixing tank has a high volume exhaust fan to remove solvent vapours. The mixed paint will be filled into 200 L closed head drums for transport to the OEM sites.

The notifier states that typically the manufacturing workers are supplied with overalls, gloves and eye protection. Only dermal exposure to the polymer is probable at this stage.

OEM vehicle painting

The notified polymer will be contained in the paint topcoat, which will be applied by robot spray in up to three OEM vehicle manufacturing plants in Australia. In around 15-20 % of cases, manual touchup is required after the robot spraying. The vehicle body is then baked at a high temperature which cures the polymer, producing crosslinking and hardening of the paint coat.

An estimate of the number of workers exposed to the polymer at each plant has been provided. It is likely that approximately 2 workers will be required to service the robots as required; approximately three shifts each of 4 workers will apply the manual touchup of the paint.

The notifier did not provide details of the processes involved in transferring the paint from the transport drums to the robot sprayers, but a highly automated process would be expected; exposure would therefore be limited to drips while connecting lines to fresh paint drums. The manual spray painters would be expected to manually fill the spray equipment and skin contamination could occur. Maintenance workers would also potentially be dermally exposed to residual paint in the robots.

Touchup workers will be trained spray painters using the high quality facilities of the OEM site. Manual spraying will be done in a purpose designed area with appropriate ventilation. Workers in this area will be supplied with air fed respirators and full protective equipment. The paints used contain many other components apart from the notified polymer, and many of these, particularly solvents, require the use of a high level of engineering controls and personal protective equipment. The notifier states that the engineering controls are such as to allow the air quality to comply with AS1668.2 *The use of mechanical ventilation and air-conditioning in buildings - Mechanical ventilation for acceptable indoor-air quality.* Inhalation of aerosols containing the notified polymer is expected to be minimised by the use of these controls.

Once painted, the vehicles move automatically to the preheat oven and baking oven, where they are heated at 160 °C for 4 hours to cure the resin. This process reduces the reactivity of the polymer and increases the molecular weight by cross linking. Following this process, anyone touching the cured paint would not experience separate exposure to the resin, which in any case would not be bioavailable.

Disposal

Solvent wash, spray gun cleanup solvent and waste paint residues will be handled by a solvent reclamation company. These workers routinely handle complex mixtures and would be expected to use protective measures appropriate to the more hazardous components of the mixtures.

7. PUBLIC EXPOSURE

The notified polymer is not available for sale to the general public and will be used in the automobile coating industry. The potential for public exposure to the notified polymer during transport, reformulation and automobile coating operations or from disposal is assessed as negligible. Although members of the public will make dermal contact with automobiles coated with paints containing the notified polymer, exposure will be negligible because of the cured state and high molecular weight of the notified polymer.

8. ENVIRONMENTAL EXPOSURE

Release

From figures provided by the notifier, it is possible to calculate that around 20 tonnes of uncured resin, in the form of imported resin solution or of uncured paint, will be released to the environment as residues in drums and cans after emptying. In addition, the notifier states that up to half of the import volume will be lost as overspray during paint application. Most of this would be contained within the control equipment, and would be collected and disposed of, probably via incineration, or possibly by deposition to landfill.

The notifier indicates that paint and solvent residues removed from spray equipment and the spray booths would be collected and reprocessed by a solvent reclamation company. It is assumed that the entrained polymer solids would be recovered during this process and sent to landfill or incinerated.

Fate

The notifier expects that, if any of the uncured resin formulation containing the new polymer were spilt, it would be expected to associate with and become assimilated into the organic component of soils and sediments because of its predominantly hydrophobic nature. Biological membranes are not permeable to polymers of very large molecular size, consequently bioaccumulation of the notified polymer would not be expected if quantities of the uncured polymer were to be released into the water compartment.

Once applied to the metal panels of vehicles and baked, the notified polymer will be incorporated in a hardened paint matrix and bound the surface of metal panels on vehicles. Any fragments, chips or flakes of the dried paint will be of little concern as they are expected to be inert. At the end of their useful life, metal panels coated with the polymer are likely to be either recycled for steel reclamation or placed into landfill. When recycled the paint, would be destroyed in the blast furnaces and converted to water vapour and oxides of carbon and nitrogen, as well as ash which would remain with the slag. When deposited into landfill with used paint tins or on discarded panels, the organic components of the cured paint including the new polymer would be inert and immobile, but could nevertheless be expected to be very slowly degraded through the biological and abiotic processes operative in these facilities.

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

No acute toxicology data were submitted, which is acceptable for a limited notification of a polymer with NAMW > 1000.

9.2 Repeated Dose Toxicity (Kelly, 1991)

A repeat dose toxicity study on a related polymer (acrylic copolymer RC-P-10037) has been supplied by the notifier. The study was a 90 day inhalation toxicity study in rats. The analogue polymer contains a side group similar to the group of greatest toxicological interest in the notified polymer. The analogue polymer comprised 62 % (w/w) of the solution used for the study, along with butyl acetate (34 % (w/w)), xylene (3.5 % (w/w) and toluene (0.5 % (w/w)). The mixture was further diluted with twice the volume of butyl acetate to facilitate aerosol formation. A solvent comparison test using butyl acetate alone at a concentration equivalent to the solvent concentration for the highest polymer dose used was included in the study.

Species/strain: rat/Crl CDBR

Number/sex of animals: 10/sex/group

Method of administration: nose only exposure, 6 hours/day, 5 days/week; the liquid

was nebulised directly into the exposure chamber for the high dose study; a portion of the nebulised mixture was directed to the exposure chamber along with dilution air for

the lower doses.

Dose: $0, 1, 10, 100 \text{ mg/m}^3 \text{ resin}$

780 mg/m³ butyl acetate

Study duration: 90 days

Previous studies:

A 14 day study with 14 day recovery period was referred to in the introduction to the 90 day study. This study used a related acrylic polymer with a different solvent system. An LC₅₀ value of approximately 1.6 mg/L was found. The major findings included dose related, reversible laryngeal lesions, as well as alveolar effects (at 330 mg/m³) which were markedly reduced after the 14 day recovery period. The latter included minimal alveolar macrophage and polymorphonuclear leukocyte infiltration and Type II pneumocyte hyperplasia.

Clinical observations:

All animals survived until the end of the study except one female of the low dose group, which was believed to have died from suffocation from being placed in an inadequately sized restrainer tube.

Body weight gains were similar for all groups throughout the study. No significant dose related differences were observed.

During the exposure period, ocular and nasal discharges were observed. This was considered to be common in subchronic inhalation studies. No clinical signs of toxicity were observed during the non-exposure periods.

Clinical chemistry/Haematology

No dose related differences were observed during the study. The values for all measured parameters were within expected ranges and, in the absence of clear dose response, any variations from controls were considered to be biologically unimportant.

Gross pathology

There was a significant increase in the lung weights of male rats in the 100 mg/m³ group. Four out of ten of the female rats of the 100 mg/m³ group showed pin head sized white foci in the pleural surface of the lungs. This was associated with enlarged mediastinal lymph nodes with white mottling, and also with nodules on the thymus.

Histopathology:

No exposure related histopathological changes were seen in rats of the 1 or 10 mg/m³ polymer groups or in the solvent exposed group.

All of the animals exposed to 100 mg/m³ showed aggregates of foamy alveolar macrophages with minimal neutrophilic infiltration adjacent to the alveolar duct regions. The alveolar walls enclosing foamy alveolar macrophages showed minimal Type II pneumocyte proliferation. Peribronchial lymphoid tissue contained apparently translocated foamy alveolar macrophage aggregates. Mediastinal lymph nodes also contained numerous apparently translocated foamy alveolar macrophage aggregates, but no inflammatory response was seen. The foamy alveolar macrophages were filled with vacuoles and tiny round reflective particulates thought to be phagocytised aerosol particles.

Comment:

On the basis of the results of an earlier study with 14 day exposure and 14 day recovery period, the lung changes were considered to be reversible; the lack of inflammatory response in the mediastinal lymph nodes was considered important as an inflammatory tissue response produced by dust-laden macrophages in the lymph nodes was stated to be possibly indicative of a potentially fibrogenic dust particle.

Result:

A no observable effect level (NOEL) of 10 mg/m³ was established in this study.

9.3 Overall Assessment of Toxicological Data

The notified polymer has a high molecular weight and is considered unlikely to cross the skin or other biological membranes. No acute toxicological studies were provided, as these are not usually required for a limited notification of a polymer with NAMW > 1000. The presence of moderately reactive functional groups in the polymer may however indicate potential for producing irritation or sensitisation when in contact with the skin or eyes.

The single toxicological study provided was a repeat dose inhalation toxicity study of an analogue polymer. This is appropriate to the exposure routes for the notified polymer, as aerosols are encountered in the end use as a spray paint. The main observations were similar to those frequently observed in rats after inhalation exposure to particulates. The effects included increased lung weights, enlarged lymph nodes, increased numbers of macrophages and Type II cell hyperplasia. These effects were only observed in the groups exposed to 100 mg/m^3 . A NOEL of 10 mg/m^3 was established in this study.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided, which is acceptable for a limited notification of a polymer with NAMW > 1000.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

It is possible that up to 50% (hundreds of tonnes) of the new polymer could be released as a consequence of paint preparation and application. Release is expected to occur primarily in dedicated paint manufacturing facilities or OEMs, with the majority of the released material collected and disposed of in responsible manner. The majority of the material would be encapsulated in a cured polymer matrix and is expected to be insoluble and inert. Most of this solid waste would be deposited into landfill or incinerated.

However, some of the cured waste paint may be released into sewers as a consequence of cleaning spray equipment or wash down of spray booths. It would become incorporated into sewerage treatment plant sludge and eventually either incinerated or placed into landfill.

The polymer is unlikely to present a hazard to the environment when it has been incorporated into the paint, applied to solid substrates and cured. Such painted objects will be consigned to metal reclamation plants or landfill at the end of their useful lives and the paint containing the notified substance will share their fate.

The main environmental hazard would arise whereby spills in transport accidents may release small quantities of the polymer to drains and waterways. However, the polymer should quickly become immobile on association with the soil/sediment layer.

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

The notifier states that the aromatic hydrocarbon solvent contained in the resin solution RC29757 contains less than 0.1 % benzene, and, accordingly, the resin solution is not classified as a hazardous substance according to the NOHSC *Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1994a).

Transport and Storage

There is little potential for significant occupational exposure to the notified polymer in the transport and storage of the paint components containing this polymer. The greatest exposure is in the reformulation, use and disposal of the paints.

Reformulation

Workers involved in preparation of the finished paints containing the notified polymer may be dermally exposed to spills and drips of the polymer solutions. It is likely that the polymer will have irritant or sensitising properties. Dermal or ocular exposure should be prevented by engineering controls and the use of appropriate personal protective equipment. As exposure is likely to be infrequent, the risk of irritant or sensitising effects is likely to be low.

The paints containing this polymer could contain a wide variety of additional ingredients once fully mixed, and many of the solvents and additives used in paint manufacture have potential effects on human health. Therefore precautions should be taken to minimise exposure during their formulation and use.

End Use

The paints containing the notified polymer will only be used in OEM vehicle manufacturing plants, and the majority of the application will be done by robot spray. Touchup will be needed in up to 20 % of cases, and the touchup paint will be applied manually. The spraying

procedure produces a dense aerosol of paint particles which would adversely affect human health because of the solvent content. There is potential for respiratory, dermal and ocular exposure to the notified polymer.

The presence of many potential and actual hazards in spray paint formulations for automobile applications requires the use of stringent engineering controls and a high level of personal protective equipment. The use of the paint containing the notified polymer should be in accordance with the NOHSC *Draft National Code of Practice for Spray Painting* (National Occupational Health and Safety Commission, 1991). The level of protection from exposure afforded by the standard protective measures should provide adequate protection from the notified polymer.

Disposal

The wastes containing the notified polymer may be hazardous materials on the basis of the solvent content, and are likely to be mixed with other paint residues of varying hazards. The precautions required for the handling of these additional materials should be adequate for protection from the notified polymer. The notified polymer will not cross-link unless baked at high temperature and therefore cleanup and disposal will involve possible dermal exposure to uncured polymer.

After the paint film is baked at high temperature, crosslinking reactions which consume the reactive sites on the polymer chain occur. The potential to produce dermal irritation will be substantially removed by the curing process.

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 automobiles, 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. It is therefore considered that the notified polymer will not pose a significant hazard to public health.

13. RECOMMENDATIONS

To minimise occupational exposure to RC29757 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;
- The use of the paint containing the notified polymer should be in accordance with the NOHSC Draft National Code of Practice for Spray Painting (National Occupational Health and Safety Commission, 1991);
- 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 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, 1994c).

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. No other specific conditions are prescribed.

16. REFERENCES

Kelly, D. P. (1991) Ninety-Day Inhalation Toxicity Study in Rats with Acrylic Copolymer RC-P-10037, Project No. HLR 305-91, DuPont, Newark, Delaware, USA.

National Occupational Health and Safety Commission (1991) Draft National Code of Practice for Spray Painting. Australian Government Publishing Service, Canberra.

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

National Occupational Health and Safety Commission (1994b) List of Designated Hazardous Substances [NOHSC:10005(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994c) 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 (1997) List of Designated Hazardous Substances [draft]. Australian Government Publishing Service, Canberra.

Standards Australia (1987) Australian Standard 2919-1987, Industrial Clothing. Standards Association of Australia, Sydney.

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, Sydney.

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

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, Sydney/Wellington.

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

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