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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Acrylic copolymer in BYK-381

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Director Chemicals Notification and Assessment

FULL PUBLIC REPORT

Acrylic copolymer in BYK-381

1. APPLICANT

A C Hatrick Chemicals Pty Ltd of 49-61 Stephen Rd BOTANY NSW 2019 has submitted a limited notification statement with their application for an assessment certificate for acrylic copolymer in BYK-381.

2. IDENTITY OF THE CHEMICAL

Acrylic copolymer in BYK-381 is not considered to be hazardous based on the nature of the polymer and the data provided. Therefore the chemical name, CAS number, molecular and structural formulae and spectral data have been exempted from publication in the Full Public Report and the Summary Report.

Trade name: BYK-381 (52% notified chemical in dipropylene

glycol methylether)

Number-average

molecular weight (NAMW): 3 584

Weight-average

molecular weight: 18 956

Maximum percentage of low molecular weight species

Molecular weight < 500: 2.6% Molecular weight < 1000: 5.9%

Method of detection

and determination: infrared spectroscopy

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C

and 101.3 kPa: yellow solid

Boiling Point: not determined

Specific Gravity: not determined

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Vapour Pressure: not determined

Water Solubility: soluble

Partition Co-efficient

(n-octanol/water): not determined

Hydrolysis as a function

of pH: not determined

Adsorption/Desorption: not determined

Dissociation Constant: not determined

Flash Point: > 100°C

Flammability Limits: does not form flammable vapours

Explosive Properties: not explosive

Reactivity/Stability: does not decompose at temperatures below 250°C

Comments on Physico-Chemical Properties

The notifier states that the polymer is soluble in water. An estimate of the water solubility of the polymer was attempted using the preliminary test in OECD Method 105 {Organisation for Economic Co-operation and Development, 1995-1996 #15} for the determination of water solubility. The notifier states that this test gave a value for solubility in the range of 0.1 g/L to 1 000 g/L. The polymer contains approximately 35% of a carboxylic acid salt functionality and hence the water solubility of the polymer will depend on the pH of the medium. At low pH values, at which the polymer will exist predominantly in the free carboxylic acid form, the solubility in water is expected to be very low. However, at higher pH the carboxylic acid groups will be deprotonated and the resulting water solubility of the polymer will be higher (further discussed under Environmental Fate). The polymer is in the deprotonated form in the formulated product, BYK-381.

It is unclear whether the notified polymer is likely to undergo hydrolytic decomposition in the environmental pH range of 4-7, due to its solubility, however it is noted that the exposure to the aquatic compartment is expected to be low.

Due to the complex nature of the polymer the partition coefficient, dissociation constant, and adsorption/desorption will be difficult to measure.

The polymer will have a high partition coefficient in carboxylic acid form again due to low water solubility.

The polymer contains dissociable carboxylic acid groups and the pKa is expected to be in the range of 3 to 5. In the polymer formulated product, BYK-381, an amine

cation is added to neutralise the carboxylic acid groups within the polymer and is therefore present as the corresponding ammonium cation.

Adsorptivity has a strong negative correlation with solubility. Low solubility of the carboxylic acid form of the polymer suggests that they will have high absorptivity coefficients. As the water and the amine are lost from the polymer formulation, it will become viscous and tacky and the polymer will bind to soil and become fixed.

4. PURITY OF THE CHEMICAL

Degree of purity: 96.9%

Toxic or hazardous one residual monomer, present at a relatively low concentration, is moderately toxic by ingestion

concentration, is moderately toxic by ingestion {Sax, 1989 #16} and may cause skin and eye irritation {National Occupational Health and Safety

Commission, 1994 #10}

Non-hazardous impurities

(> 1% by weight): none

Maximum content

of residual monomers: 3.1%

Additives/adjuvants: none

5. USE, VOLUME AND FORMULATION

The notified polymer is to be used as a leveling agent in automotive basecoats. The estimated quantity of BYK-381 (52% solution of the notified chemical in dipropylene glycol methyl ether) to be imported into Australia is 500 kg in the first year to 2 tonnes per year by the fifth year.

6. OCCUPATIONAL EXPOSURE

The notified polymer will be imported in steel drums. Exposure during transport and handling is unlikely and should only occur in the event of an accident.

The steel drums will be delivered to a single paint manufacturer. Typically the polymer solution is pumped from the drum into a mixer for blending into a paint. The paint is then filtered and filled into 200 L steel drums. The notifier states that there is limited scope for accidental spillage to occur during the paint manufacturing and packaging processes. Typically, closed systems are used to limit exposure to solvents and local exhaust ventilation is used to remove volatiles. The most likely point of exposure to the polymer is expected to be during pumping operations when connecting and disconnecting lines.

At the paint manufacturing site, there may be limited exposure to workers involved in laboratory development and paint application in spray booths.

The paint containing the notified polymer will be used at an automobile manufacturing plant and applied by a combination of electrostatic and air atomised spray. There is potential for spillage during stirring of the paint and during its addition to a circulation tank. The spray painting will be conducted in down draft spray booths and the overspray will be collected by a high efficiency water scrubbing system so that exposure during spray painting is likely to be low.

7. PUBLIC EXPOSURE

In the case of accidental spillage during transport, the public may be exposed to the notified polymer, however public exposure resulting from transport and disposal is expected to be negligible.

The paint containing the notified polymer is applied to the exterior of car bodies and will be part of an inert, fully cured and hardened paint film. The potential for public exposure is thus considered to be very low.

8. ENVIRONMENTAL EXPOSURE

Release

Releases to the environment will be limited to those that occur during formulation and when the paint containing the polymer is applied.

The single paint manufacturer has developed a process whereby waste resin and paint are processed to reclaim the solvents in which they are dissolved, and the residue converted to an inert solid which will be landfilled or incinerated. Waste generated in this manner is expected to be less than 250 kg per annum. If a spill occurs during formulation it will be limited to an on-site sealed surface and contained to the plant by bunding. Spills will be cleaned up according to the Material Safety Data Sheet (MSDS).

Paint containing the polymer is expected to be used by only one automotive manufacturer and applied in spray booths. The spray booths are down draft self contained units with a water curtain which uses recycled water. The paint products are applied by a combination of electrostatic and air atomised spray. Transfer efficiencies range from 35% to 75% depending on the application method. The water from the spray booth is treated by flocculation, which will remove most of the waste paint, with the 'clean' water returned to the spray booth. Solid residue from the flotation tanks, expected to be less than 1 300 kg per annum (65% overspray), will be disposed of to landfill.

The painted vehicles are baked to cure the polymer into a paint film. The cured polymer will be effectively inert and be disposed of with the vehicles. Releases of the cured polymer during vehicle repairs etc. will be diffuse and limited to small

quantities.

Transportation of the paint containing the polymer will be over short distances (within the Melbourne metropolitan area). During transport risk of environmental release is limited to accidents where the drums containing the polymer are ruptured, releasing a maximum of 1 L per drum of the notified polymer.

Fate

Excess paints, residues from drums, cleaning of spray equipment, scrubber apparatus, filters and empty drums will be disposed of to landfill where the polymer would be immobilised in the dry paint.

After application the paint dries to form a protective coating. Any waste product of the dry paint produced through chipping or flaking will be inert and form part of the soil and sediments.

The notified polymer is a water-reducible polymer. Water-reducible polymers generally contain pendant carboxylic acid groups along the polymer backbone. Although the polymer in carboxylic acid form is water insoluble, the pendant carboxylic acid groups can be neutralised with basic compounds to produce water-soluble soaps of the polymer. In this case the basic compound used is an amine. The presence of the amine is critical to the water solubility of the polymer. Loss of amine, or insufficient amine, can lead to a decrease in solubility resulting in precipitation of the polymer from aqueous solution {Browning, 1983 #35}. Therefore, in landfill, as the solvents and amine are lost from the polymer formulation, the polymer is likely to become viscous and tacky, binding to the soil and becoming immobilised.

9. EVALUATION OF TOXICOLOGICAL DATA

Toxicological data are not required for polymers of NAMW greater than 1 000 according to the Act. However, data on acute oral toxicity, skin and eye irritation were supplied and are evaluated below.

9.1 Acute Toxicity

Summary of the acute toxicity of acrylic copolymer in BYK-381

Test	Species	Outcome	Reference
acute oral toxicity	rat	LD ₅₀ > 5 000 mg/kg	{Heisler, 1993 #36}
skin irritation	rabbit	slight irritant	{Heisler, 1993 #38}
eye irritation	rabbit	slight to moderate irritant	{Heisler, 1993 #37}

9.1.1 Oral Toxicity {Heisler, 1993 #36}

Species/strain: rat/Wistar

Number/sex of animals: 5/sex

Observation period: 14 days

Method of administration: by gavage with distilled water as the vehicle;

dosages of 2 000, 3 000 and 5 000 mg/kg

were administered

Clinical observations: none

Mortality: none

Morphological findings: none

Test method: OECD Guidelines for Testing of Chemicals

Organisation for Economic Co-operation and

Development, 1995-1996 #15}

 LD_{50} : > 5 000 mg/kg

Result: the notified polymer exhibited low acute oral

toxicity in rats

9.1.2 Skin Irritation {Heisler, 1993 #38}

Species/strain: rabbit/New Zealand white

Number/sex of animals: 3 males

Observation period: 7 days

Method of administration: notified polymer in distilled water was applied

for 4 hours under a gauze dressing fixed with

adhesive plaster

Test method: OECD Guidelines for Testing of Chemicals

Organisation for Economic Co-operation and

Development, 1995-1996 #15}

Result: the notified polymer was a slight skin irritant in

rabbits: all animals exhibited slight erythema at 1, 24, 48 and 72 hours post-treatment but no erythema at day 7; 1 animal exhibited no oedema at any time point; 1 animal exhibited slight oedema at 1, 24 and 48 hours post-treatment; 1 animal exhibited slight oedema at

24 and 48 hours post-treatment

9.1.3 Eye Irritation (Heisler, 1993 #37)

Species/strain: rabbit/New Zealand White

Number/sex of animals: 3

Observation period: 7 days

Method of administration: 0.1 mL of the notified polymer in distilled water

into the conjunctival sac of one eye of each

rabbit

Draize scores (Draize, 1959 #4) of unirrigated eyes:

No corneal or iridal effects were seen in any animal at any time point

Time after instillation

Animal	1	hοι	ır	2	hou	rs	4	hou	rs	8	hou	rs		1 day	y
Conjunctiva	r a	C ^b	ď	rª	C ^b	ď	rª	C ^b	ď	rª	C _p	ď	ra	C ^b	d c
1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	1
2	1	1	2	1	2	2	2	2	2	2	2	2	2	2	2
3	1	1	2	1	2	2	2	2	2	2	2	2	2	2	1
	2	day	'S	3	day	'S	4-	7 da	ys						
1	1	1	0	1	0	0	0	0	0						
2	1	1	1	1	1	0	0	0	0						
3	1	1	0	1	0	0	0	0	0						

¹ see Attachment 1 for Draize scales

Test method: OECD Guidelines for Testing of Chemicals

{Organisation for Economic Co-operation and

Development, 1995-1996 #15}

Result: the notified polymer was a slight to moderate

eye irritant in rabbits

9.2 Overall Assessment of Toxicological Data

The notified polymer exhibited low acute oral toxicity in rats $(LD_{50} > 5\,000\,\text{mg/kg})$. It was not a skin irritant in rabbits, but was a slight to moderate eye irritant in this species.

The notified polymer has a NAMW greater than 1 000, so transmission across

a redness b chemosis c discharge

biological membranes leading to systemic effects should be precluded. One of the monomers, which is moderately toxic by ingestion, is present at a relatively low concentration. However, the polymer should not be rendered hazardous by residual monomers levels according to the concentration cutoffs recommended by the *Approved Criteria* for *Classifying Hazardous Substances* (Approved Criteria) {National Occupational Health and Safety Commission, 1994 #9}. The levels of low molecular weight species (5.9% below NAMW 1 000 with 2.6% below 500) are unlikely to render the polymer hazardous.

Based on the information provided by the notifier, the notified polymer would not be classified as hazardous according to the Approved Criteria {National Occupational Health and Safety Commission, 1994 #9}.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicology data were provided, which is acceptable for polymers of NAMW greater than 1 000 according to the Act.

Biological membranes are not permeable to polymers of very large molecular size and therefore bioaccumulation of the notified polymer is not expected {Anliker, 1988 #2; Gobas, 1986 #6}. The notified polymer is a polyanionic polycarboxylate. Polymers of this type are of environmental concern because of their precedented toxicity to green algae {Nabholz, 1993 #8}. This toxicity is most potent for polyacrylic acid. Polyacrylic acid would be released from the notified polymer should hydrolysis of the ester linkages within the polymer occur. The polymer also contains a quaternary ammonium counterion. Quaternary ammonium compounds have also been shown to exhibit acute toxic effects on algae and chronic effects to other aquatic organisms {Nabholz, 1993 #8}. The potential toxic effects of the polymer and counterion will be mitigated by the anticipated low environmental exposure of the notified polymer.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The polymer is unlikely to present a hazard to the environment when it is incorporated into the paint and applied to automobiles. The automobiles will be consigned to landfill or recycled at the end of their useful life and the paint containing the notified substance will share the fate of the automobile.

The main environmental exposure arises from landfill disposal of recovered waste paint (up to 65% of that imported) containing the resin. Such material will be bound to soil and remain immobile in the environment. Hence, the overall environmental hazard is expected to be low.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The health risk posed to workers during transport and handling of the imported drums of solvent solution is negligible, as exposure is unlikely except in the event of an accident and the polymer is not expected to be hazardous.

The occupational health risk posed to workers involved in paint manufacture is likely to be low due to the use of automated systems for mixing and drum filling and the anticipated low hazard of the polymer. Exposure would be most likely to occur during transfer of the polymer solution to the mixing vessels.

Exposure to the notified polymer in the final paint at the application site is possible during transfer of the paint to a circulation tank and subsequent mixing. However, the concentration of polymer in the paint is less than 1% so exposure should be negligible.

The risk of adverse health effects to workers involved in transport, storage, use and disposal of the notified polymer is negligible because of the low predicted hazard of the notified polymer and the limited opportunity for exposure. The health risk to the public is negligible for the same reasons.

The polymer solution to be imported will contain dipropylene glycol methyl ether which has Worksafe exposure standards of 606 mg/m³ (time weighted average) and 909 mg/m³ (short term exposure limit) {National Occupational Health and Safety Commission, 1995 #14}. This substance also has a skin notation, which indicates that significant absorption through the skin can occur. Thus, skin and eye protection as outlined below should be worn during paint manufacture.

13. RECOMMENDATIONS

To minimise occupational exposure to acrylic copolymer in BYK-381 the following guidelines and precautions should be observed:

- It is good work practice to wear industrial clothing which conforms to the specifications detailed in Australian Standard (AS) 2919 {Standards Australia, 1987 #18} and occupational footwear which conforms to Australian and New Zealand Standard (AS/NZS) 2210 {Standards Australia/Standards New Zealand, 1994 #24} to minimise exposure when handling any industrial chemical;
- Spillage of products containing the notified polymer 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.

In addition, the Worksafe Australia document *Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National*

Exposure Standards (National Occupational Health and Safety Commission, 1995 #14) should be used as a guide in the control of workplace exposure to dipropylene glycol methyl ether, and appropriate personal protective equipment should be worn where necessary to minimise exposure to this chemical (see product MSDS). Workplace monitoring for these components should be carried out on a regular basis.

14. MATERIAL SAFETY DATA SHEET

The MSDS for a product containing the notified polymer was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* {National Occupational Health and Safety Commission, 1994 #13}.

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 polymer 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

Attachment 1

The Draize scale for evaluation of eye reactions is as follows:

CORNEA

Opacity	Rating	Area of Cornea involved	Rating
No opacity	0 none	25% or less (not zero)	1
Diffuse area, details of iris clearly visible	1 slight	25% to 50%	2
Easily visible translucent areas, details of iris slightly obscure	2 mild	50% to 75%	3
Opalescent areas, no details of iris visible, size of pupil barely discernible	3 moderate	Greater than 75%	4
Opaque, iris invisible	4 severe		

CONJUNCTIVAE

Redness	Rating	Chemosis	Rating	Discharge	Rating	
Vessels normal	0 none	No swelling	0 none	No discharge	0 none	
Vessels definitely injected above normal	1 slight	Any swelling above normal	1 slight	Any amount different from normal	1 slight	
More diffuse, deeper crimson red with individual vessels not	2 mod.	Obvious swelling with partial eversion of lids	2 mild	Discharge with moistening of lids and adjacent hairs	2 mod.	
easily discernible Diffuse beefy red	3	Swelling with lids half-closed	3 mod.	Discharge with moistening of lids and	3 severe	
	severe	Swelling with lids half-closed to completely closed	4 severe	hairs and considerable area around eye		

IRIS

Values	Rating
Normal	0 none
Folds above normal, congestion, swelling, circumcorneal injection, iris reacts to light	1 slight
No reaction to light, haemorrhage, gross destruction	2 severe