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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Zinc Acrylate Polymer in RC3707 and RC3708

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Director
NICNAS

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Zinc Acrylate Polymer in RC3707 and RC3708

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
Akzo Nobel Pty Limited (ABN: 59 000 119 424)
115 Hyde Rd
YERONGA QLD 4104

NOTIFICATION CATEGORY
Limited: Polymer with NAMW ≥ 1000 (more than 1 tonne per year).

EXEMPT INFORMATION (SECTION 75 OF THE ACT)
Data items and details claimed exempt from publication:
Chemical Name(s)
Other Name(s)
CAS Number
Molecular Formula
Structural Formula
Means of Identification
Molecular weight
Reactive Functional Groups
Charge Density
Polymer Constituents
Residual Monomers and Impurities
Import volumes
Detailed use information

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)
Variation to the schedule of data requirements is claimed as follows:
Boiling Point
Vapour Pressure
Water Solubility
Hydrolysis as a Function of pH
Partition Co-efficient
Absorption/Desorption
Dissociation Constant
Flammability Limits
Autoignition Temperature
Explosive Properties

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
None.

NOTIFICATION IN OTHER COUNTRIES
None.

2. IDENTITY OF CHEMICAL

MARKETING NAME(S)
RC3707 Zinc Acrylate (Deep Sea) and RC3708 Zinc Acrylate (Coastal) (solutions of the notified polymer, < 50% by weight in solvents).

MOLECULAR WEIGHT (MW)
Number Average Molecular Weight (Mn) >1000

METHODS OF DETECTION AND DETERMINATION

Remarks An IR reference spectrum was provided.

3. COMPOSITION

DEGREE OF PURITY
90 - 100%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS
All hazardous impurities and residual monomers are present at below the relevant cut-offs for classification of the notified polymer solution as a hazardous substance.

DEGRADATION PRODUCTS
The polymer may combust to form carbon dioxide, carbon monoxide and nitrogen oxide.

LOSS OF MONOMERS, OTHER REACTANTS, ADDITIVES, IMPURITIES
Volatile impurities may be lost during reformulation and application processes. Non-volatile impurities are expected to be trapped within the cured paint and slowly released to the environment in a diffuse manner.

4. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS
The notified polymer will not be manufactured in Australia, but will be reformulated in Australia.

The products containing the notified polymer (< 50% by weight) will be imported in 205 L steel drums.

MAXIMUM INTRODUCTION VOLUME OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

Year	*1*	*2*	*3*	*4*	*5*
Tonnes	< 30	< 30	< 50	< 50	< 50

USE
The notified polymer is used as an additive in the manufacture of anti-fouling paint to be used on ships. The notified polymer solution RC3707 Zinc Acrylate is used in the Deep Sea paint formulations, while RC3708 Zinc Acrylate is used in the Coastal paint formulations.

5. PROCESS AND RELEASE INFORMATION

5.1. Distribution, transport and storage

PORT OF ENTRY
The notified polymer will be imported through Queensland by wharf.

IDENTITY OF MANUFACTURER/RECIPIENTS
Paint manufacturer in Queensland.
TRANSPORTATION AND PACKAGING

The products containing the notified polymer (< 50%) in 205 L steel drums will be transported from the dockside by road directly to the Akzo Nobel site, where it will be stored in a chemical warehouse, in bunded area, until required for paint manufacture.

The finished paint products (< 20% notified polymer) will be transported in 20 L epoxy lined steel cans to customer sites by road.

5.2. Operation description

Reformulation

Factory operators are involved in transferring the polymer solutions (< 50% notified polymer) from the 205 L steel drums into open stainless steel floor pots (1,000 L capacity), which are under local exhaust ventilation. The transfer operation involves removing the two inch bungs on the drum and then pouring the notified polymer using drum lifts into the open floor pots. Solvents are added to dissolve the notified polymer and this mixture is used as a concentrate in a high speed dispersion along with fillers, colourants and solvents in the open floor pot. During dispersion the pots are covered. The blend is then reduced with solvent and binders to the finished form.

Sampling

Personnel sample and test the imported polymer solutions and the final paint formulations containing the notified polymer. Samples are taken from the open floor pots by cups and poured into sealable 500 mL steel containers. Laboratory equipment used in testing includes equipment for spectroscopy and determination of physicochemical properties such as pH and viscosity.

Filling

Filling line staff operate and clean the automated guarded filling equipment. The finished product (< 20% notified polymer) is filled from the floor pots via funnels (termed hoppers) into 20 L epoxy lined steel cans. This process is performed by gravity feed. Each filling line has a ventilation extraction system.

Warehousing

Paint products are held in the warehouse before they are picked and packed to go to customers. The warehouse staff will normally take one hour to handle one order.

Paint Application

Paint applicators will use the finished anti-fouling paint for the protection of ship structures below the waterline. The paint will normally be applied either via brushes, rollers or airless spraying. The ship will be in dry dock (outdoor area) during the paint process. Typically the spray painter will measure the appropriate amounts of the different components required in a particular formulation into an open container and pour this mixture into a spray gun (if used). Solvent drying from the spray may result in overspray, which will be confined in the dock, predominantly as dust on the ground. Where possible, overspray will be collected through the use of protective sheeting on surrounding surfaces which will be collected and disposed of by licensed waste contractors. Residual paint mixture is likely to be washed from the equipment manually using recycled paint solvent, and the washings disposed of by solvent recyclers.

5.3. Occupational exposure

Number and Category of Workers

Category of Worker	*Number*	*Exposure Duration*	*Exposure Frequency*
Waterside and transport workers	5-10	5-10 hours/day	10-20 days/year
Factory Operators	6-10	1.5 hours/day	4-6 days/year
Laboratory technicians/Chemist	2	0.25 hours/day	4-6 days/year
Filling Line Staff	2	1 hour/day	4-6 days/year
Warehouse Workers	2	1 hour/day	4-6 days/year
Customers - Paint Applicators	10/site	4-8 hours/day	200 days/year

Exposure Details

Transport and storage
Transport and storage workers are not expected to be exposed to the imported notified polymer, as they will be handling closed containers. The notified polymer solutions will be supplied in 205 L steel drums and transported in secure pallets. Exposure is possible only in the event of an accidental spill where the packaging is breached.

Factory Operators and Filling line staff
The predominant route of exposure during formulation will be dermal. Ocular exposure may occur to a lesser degree. Inhalation of solvent vapour and mist (generated during decanting the notified polymer from steel drums) is also possible.

Local and general exhaust ventilation systems are located within the formulation plant, each filling line has a ventilation extraction system and the pots are covered during blending and dispersion. Formulation workers will wear impervious gloves, coveralls, and goggles. Filling line staff have access to disposable latex gloves, safety glasses, uniforms and safety shoes.

Laboratory Technician and Chemists
Incidental dermal contact with the notified polymer solutions may occur during the dilution stage of the notified polymer with other ingredients and QC sampling and testing. Laboratory technicians and chemists will wear laboratory coats, gloves and eye protection during sampling and testing.

Paint Application
Paint application will take place at several sites (dry docks). There is potential for dermal, ocular and inhalation exposure to the notified polymer (< 20% concentration) in the paint while painting (spray painting and application by brush and/or roller) and when cleaning painting equipment and the work area. Workers are expected to wear respiratory protection, chemical goggles or face shield, protective overalls and impermeable gloves and follow the National Guidance Material for Spray Painting (NOHSC, 1999b).

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

5.4. Release

RELEASE OF CHEMICAL AT SITE
The notified polymer is imported into Australia and is added to paint formulations. Approximately 1% (500 kg/annum) of the notified polymer mixture remains as residue in the steel drums. The empty steel drums and residue are sent to a licensed waste disposal company and are not recycled. Disposal will take place at the premises of licensed waste contractors.

It is estimated that 1% of the notified polymer is lost through spillage and cleaning resulting in up to 500 kg/annum. All spillages are usually covered with a blanket of foam and then washed down into a sludge pit. After each batch, all equipment is washed with a suitable solvent, which is normally a recycled mixture of aromatic, ketone and alcohol solvents, and washings are pumped into a sludge pit, then pumped into 200 L steel drums and removed from the site by a licensed waste disposal company. There is no on-site effluent treatment plant at Akzo Nobel.

RELEASE OF CHEMICAL FROM USE
Paint Application
Major releases to the environment will be likely to occur during paint application of the anti-fouling paint. The notified polymers comprises < 20% of the final paint product. Once applied, it is cured within the paint film and becomes inert. It is recommended that the paint be applied by airless spraying. It will be used to paint below the waterline of ships, which will take place in dry dock, at several sites.

During application of the coating mix, wastage is likely to occur through overspray and residual

material left in the paint containers. Wastage due to spillage is expected to be negligible. It is estimated that 1% of the coating mixture would remain in the 20 L pail following application, and it would generally dry out into its cured form within one hour at room temperature. Approximately 500 kg/annum of notified polymer will remain as residual in steel cans.

Wastage is also likely to occur through overspray, the degree of which is dependent mainly on the prevailing atmospheric conditions. Typical estimates of losses for overspray under different atmospheric conditions are presented below:

- 5% - indoor, well ventilated
- 5-10% - outdoor, calm conditions
- >20% - outdoor, windy conditions

Application takes place outdoors and will not occur under windy conditions. Therefore, assuming moderate conditions, 15% resulting in a maximum of 7.5 tonnes would be a reasonable "worst case scenario" estimate of loss through overspray. Where possible overspray will be collected through the use of protective sheeting on surrounding surfaces which will be collected and disposed of by licensed waste contractors. Some release of the notified polymer is expected to occur through washing of spray equipment. It is expected that this would be approximately 1%, resulting in approximately 500 kg per annum being released to sewer.

After application to ships, the polymer is expected to slowly release to the marine environment during use in a very diffuse manner.

5.5. Disposal

At Akzo Nobel all spills and washings from equipment cleaning are pumped into a sludge pit, then pumped into 200 L steel drums and removed from the site by a licensed waste disposal company.

Any remaining paint in the 20 L paint cans will be allowed to cure prior to disposal. The 20 L paint cans and residues will be disposed to licensed commercial landfill sites.

5.6. Public exposure

The notified polymer will only be used by industrial spray painters and will not be sold to the public. Once applied to ships, the notified polymer are cured within the paint film and become inert. Public exposure to the notified polymer through dried paint on ships is unlikely.

6. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa Translucent, pale amber liquid (< 50% polymer solutions).

Melting Point/Freezing Point Not determined.

Remarks The notified polymer is never isolated from the manufacturing solution.

Boiling Point Not determined.

Remarks The notified polymer is never isolated from the manufacturing solution.

Density 997 kg/m^3 (< 50% polymer solution)

Remarks Temperature not specified. Value given on technical specification sheet. Study report not provided.

Viscosity 80 poise (maximum value for < 50% polymer solutions)

Remarks Value given on technical specification sheet. Study report not provided.

Vapour Pressure Not determined.

Remarks The notified polymer is never isolated from the manufacturing solution. The notified polymer is expected to have low volatility on the basis of the molecular weight and structure. The vapour pressure of the major solvent in the imported product (xylene) was provided: 0.8 kPa at 20°C.

Water Solubility Not miscible.

Remarks The water solubility of the notified polymer was not determined. The notifier states that the notified polymer is not miscible with water. From the structure of the notified polymer and its molecular weight it is likely that the water solubility would be < 1 mg/L. However, the notified polymer contains a polyethylene glycol derivative, which may impart some solubility. However, the non-polar part of the polymer would not be expected to be soluble.

Hydrolysis as a Function of pH Not determined

Remarks Hydrolysis of the notified polymer was not determined. The notified polymer contains ester group side chains that could be expected to undergo hydrolysis under extreme pH conditions. However, due to the expected low water solubility, this is unlikely in the environmental pH range of between 4 and 9.

Partition Coefficient (n-octanol/water) Not determined

Remarks The presence of a metal ion precludes the determination of this coefficient. The notifier states that the notified polymer is expected to partition into n-octanol rather than water.

Adsorption/Desorption Not determined

Remarks The presence of a metal ion precludes the determination of this coefficient. The notifier states that it is expected to be immobile in soil due to the large molecular weights and low water solubility.

Dissociation Constant Not determined

Remarks The notified polymer is not isolated from the manufacturing solution. Structurally related zinc complexes have pKas in the range 7-9.

Particle Size Not applicable.

Remarks The notified polymer is introduced in solution.

Flash Point 22ºC (< 50% polymer solution)

METHOD Setaflash closed cup method.
Remarks Value given on technical specification sheet. Study report not provided. Considered to be due to the solvent content. Based on the expected low volatility of the polymer, the notified polymer is not expected to form a flammable air/vapour mixture.

Flammability Limits Not determined.

Remarks The notified polymer is not isolated from the manufacturing solution. Based on the expected low volatility of the polymer it would also be expected to have limited flammability. The flammability limits of the major solvent (xylene) were provided

by the notifier:
Upper Explosive Limit = 7.0 %
Lower Explosive Limit = 1.4%

Autoignition Temperature Not determined.

Remarks The notified polymer is never isolated from the manufacturing solution. The notified polymer is not expected to autoignite under normal conditions of use.

Explosive Properties

Remarks Expected to be stable under normal conditions of use. The notified polymer contains no functional groups that would infer explosive properties.

Reactivity

Remarks The notified polymer is stable under normal environmental and operating conditions.

7. TOXICOLOGICAL INVESTIGATIONS

No toxicity data were submitted.

8. ENVIRONMENT

8.1. Environmental fate

No environmental fate data were submitted.

8.2. Ecotoxicological investigations

No ecotoxicity data were submitted.

9. RISK ASSESSMENT

9.1. Environment

9.1.1. Environment – exposure assessment

The intended use pattern of the notified polymer is expected to result in the majority of the polymer being released to the marine environment. However, this will be in an extremely diffuse manner as the notified polymer contained within the anti-fouling paint is designed to be slowly released during use. This slow release coupled to the large volume of seawater that will dilute the released paint layer will result in a very low environmental concentration.

Any remaining coating containing the notified chemical is likely to be removed from ships periodically by scraping or high pressure water blast before recoating. The spent coating is likely to be disposed of to landfill.

The only other release to the aquatic environment will be from release to sewer from cleaning of equipment after applying the paint, which amounts to a maximum 500 kg per annum. If this occurs at several sites, the worst case Predicted Environmental Concentration (PEC) is 6.41 µg/L. (250kg / (260 days × 15 ML/day × 10 (ocean dilution factor)) assuming the following realistic worst case scenario:

- half (250 kg) of the notified polymer is used at one site at a major regional centre;
- release to sewer occurs over several working days throughout the year with 260 days assumed as the standard number of work days per annum; and
- the release to sewer occurs to one major regional sewage treatment plant with an ocean outfall.

This is a worst case scenario where it is assumed that none of the chemical is adsorbed to sludge. Realistically it is expected that due to the polymer's low water solubility and high molecular weight, that it would mostly adsorb to sludge.

Any residual polymer in empty containers is likely to be immobile and is likely to eventually undergo in –situ degradation by biotic and abiotic processes.

At the end of the useful life of ships on which the notified chemical will be used the metal will be sent to landfill or recycled. During recycling the polymer will be combusted in electric arc furnaces (or the like) to produce oxides of carbon and water vapour, with the metal oxide reporting to the slag.

9.1.2. Environment – effects assessment

Anionic polymers are known to be moderately toxic to algae. The mode of toxic action is overchelation of nutrient elements needed by algae for growth. The highest toxicity is when the acid is on alternating carbons of the polymer backbone. This is unlikely to apply to the notified polymer. The polymer contains chelated ions which is likely to negate the toxic action by overchelation. (Nabholz *et al*. 1993).

The polymer has a high molecular weight and is unlikely to cross biological membranes. The metal ions present in the polymer are not regarded as toxic to aquatic life.

9.1.3. Environment – risk characterisation

Although no risk quotient can be calculated, the release to the marine environment from use on ships will be extremely diffuse and unlikely to pose a significant risk to the aquatic environment. The release to the aquatic environment from other sources is expected to be minimal.

9.2. Human health

9.2.1. Occupational health and safety – exposure assessment

Transport and storage

During transport and storage workers are unlikely to be exposed to the notified polymer except when packaging is accidentally breached.

Factory Operators and Filling Line staff

Dermal and possibly ocular exposure to the notified polymer at a concentration of < 50% (pre-blending) and < 20% (post-blending) could occur during reformulation processes. Inhalation of mist (generated during decanting the notified polymer from steel drums) is also possible. Exposure will be limited by the use of control measures (exhaust ventilation) and the use of PPE.

Laboratory Technician and Chemists

There is potential for dermal exposure to the notified polymer at a concentration of < 20% during sampling and testing of the notified polymer. However, exposure is expected to be low due to the relatively small amounts involved and the use of PPE.

Paint Application

The extent and type of exposure to the notified polymer (< 20%) is likely to be related to the method of application. During mixing of the paint components and application by brush or roller, exposure will be primarily dermal. In addition to dermal exposure, spray application may also lead to inhalation and ingestion exposure through formation of aerosols. This method of application may also generate dust after drying of spray. Only natural ventilation is present. Exposure is expected to be limited due to the use of PPE, including respiratory protection.

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

9.2.2. Public health – exposure assessment

Paint products containing the notified polymers will only be used by industrial spray painters. Members of the public are not likely to make contact with the inert cured paint film on ships.

9.2.3. Human health – effects assessment

No toxicological data have been provided for the notified polymer and therefore the substance cannot be classified in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004).

The notified polymer is a zinc complex with a polymeric acid and monobasic organic acid. This complex is likely to dissociate to differing extents *in vivo* to give the polymeric acid ion, monobasic organic acid ion and the zinc ion. The notified polymer has a molecular weight greater than 1000 and less than 5% low molecular weight species (MW < 1000), which would reduce the possibility of its being absorbed across biological membranes. Therefore, any systemic effects are likely to be due to the dissociated monobasic organic acid ion and zinc ion. Local effects will be influenced by the functional groups present, including the zinc complex, although the severity of effects would be reduced due to the high molecular weight of the polymer.

The toxicity profile of the monobasic organic acid zinc complex is as follows (US EPA, 2006):

Endpoint	*Conclusion*
Acute toxicity (oral, dermal and inhalation)	low toxicity
Skin irritation	moderately irritating
Eye irritation	slightly irritating
Skin sensitisation	evidence of skin sensitisation
Repeat dose toxicity	low toxicity at the top dose tested
Genotoxicity	positive in 2/3 tests (*in vitro*)
Reproductive and developmental toxicity	no reproductive or teratogenic effects

Zinc is essential for human health and plays a key role in human metabolism, however excess intake may lead to adverse effects.

9.2.4. Occupational health and safety – risk characterisation

The major route of exposure to workers involved in paint formulation and paint application is expected to be dermal. Dermal exposure, which may occur during transfer of polymer solution from steel drums to the mixing pots, quality assurance sampling, transfer of paint from containers to mixing vessel, filling spray gun, painting and cleaning spray equipment is expected to be limited by the use of PPE. In addition, the notified polymer is expected to have a low order of toxicity via the dermal route, due to the high number average molecular weight, and low percentage of low molecular weight species. Therefore the risk of toxic effects is expected to be low. However, due to the possibility of irritant and sensitisation effects, personal protective equipment, such as protective clothing and impervious gloves, should be worn during all operations where dermal exposure to the notified polymer is possible.

The notified polymer is expected to be of low acute toxicity via inhalation, but long term effects cannot be ruled out. However, the inhalation risk to workers is considered to be low if exposure is minimised by the use of respiratory protection during spray application.

9.2.5. Public health – risk characterisation

Public exposure to the notified polymer is expected to be negligible and therefore the risk to public health is also expected to be negligible.

10. CONCLUSIONS – ASSESSMENT LEVEL OF CONCERN FOR THE ENVIRONMENT AND HUMANS

10.1. Hazard classification

No toxicological data have been provided for the notified polymer and therefore the substance cannot be classified in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004)

Classification of notified polymer using the Globally Harmonised System for the Classification and Labelling of Chemicals (GHS) (United Nations 2003) cannot be undertaken as no toxicological or ecotoxicological data were available. This system is not mandated in Australia and carries no legal status but is presented for information purposes.

10.2. Environmental risk assessment

The polymer is not considered to pose a risk to the environment based on its reported use pattern.

10.3. Human health risk assessment

10.3.1. Occupational health and safety

There is Low Concern to occupational health and safety under the conditions of the occupational settings described.

10.3.2. Public health

There is Negligible Concern to public health when used as described.

11. MATERIAL SAFETY DATA SHEET

11.1. Material Safety Data Sheet

The MSDS of the notified polymer solutions RC3707 Zinc Acrylate (Deep Sea) and RC3708 Zinc Acrylate (Coastal) provided by the notifier were in accordance with the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC 2003). They are published here as a matter of public record. The accuracy of the information on the MSDS remains the responsibility of the applicant.

11.2. Label

The label for the notified polymer solutions RC3707 Zinc Acrylate (Deep Sea) and RC3708 Zinc Acrylate (Coastal) were in accordance with the NOHSC *National Code of Practice for the Labelling of Workplace Substances* (NOHSC 1994). The accuracy of the information on the label remains the responsibility of the applicant.

12. RECOMMENDATIONS

CONTROL MEASURES

Occupational Health and Safety

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified polymer as introduced, and as diluted for use in formulated paint products:
  - Avoid skin and eye contact
  - Avoid breathing spray
  - Collect and dispose of over-spray without exposing workers to dust

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer as introduced, and as diluted for use in formulated paint products:
  - Chemical resistant gloves
  - Protective clothing
  - Appropriate respiratory protection where there is potential exposure to spray or dust during end use

- Spray application of paint containing the notified polymer should be in accordance with the NOHSC *National Guidance Material for Spray Painting*.

  Guidance in selection of personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

- A copy of the MSDS should be easily accessible to employees.

- If products and mixtures containing the notified polymer are classified as hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

Disposal

- The notified polymer should be disposed of by authorised landfill.

Emergency procedures

- Spills or accidental release of the notified polymer should be handled by physical containment. Prevent entry into watercourses or drains. Remove sources of ignition do not turn lights or unprotected electrical equipment on or off. Adsorb with inert material (vermiculite, sand, earth etc.) and place in closed containers for disposal.

12.1. Secondary notification

The Director of Chemicals Notification and Assessment must be notified in writing within 28 days by the notifier, other importer or manufacturer:

(1) Under Section 64(1) of the Act; if
  - the polymer has a number-average molecular weight of less than 1000

or

(2) Under Section 64(2) of the Act:
  - if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

13. BIBLIOGRAPHY

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