File No: NA/381

Date: October 1996

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in Acumer 4161

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 Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment, Sport, and Territories and the assessment of public health is conducted by the Department of Health and Family Services

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, Worksafe Australia, 92-94 Parramatta Road, Camperdown NSW 2050, between the hours of 8.30 a.m. and 5.00 p.m. each week day except Thursday when opening is extended to 8.30 p.m. The library is not open on public holidays.

For Enquiries please contact the Administration Coordinator at:

Street Address: 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA

Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA Telephone: (61) (02) 9577-9466 **FAX (61) (02) 9577-9465**

Director Chemicals Notification and Assessment

FULL PUBLIC REPORT

Polymer in Acumer 4161

1. APPLICANT

Rohm and Haas Australia Pty Ltd of 969 Burke Rd CAMBERWELL VICTORIA 3124 has submitted a limited notification for assessment of Polymer in Acumer 4161.

2. IDENTITY OF THE CHEMICAL

Polymer in Acumer 4161 is not considered to be hazardous based on the nature of the chemical and the data provided, therefore the chemical identity, composition of the chemical including impurities and additives/adjuvants, methods of detection and determination, and spectral data have been granted exemption from publication in the Full Public Report and Summary Report

Trade Name: component of Acumer 4161

Number-Average

Molecular Weight: > 1 000

Weight-Average

Molecular Weight: > 1 000

Maximum Percentage of Low Molecular Weight Species

(molecular weight < 1000): < 5%

(molecular weight < 500): < 1%

Method of Detection

and Determination: infrared (IR) spectroscopy and gel permeation

chromatography

3. PHYSICAL AND CHEMICAL PROPERTIES

As the notified polymer is imported for use as an aqueous solution polymer, some physical and chemical properties have been determined solely for the solution and not for the polymer. This is indicated below:

Appearance at 20°C

and 101.3 kPa: clear, yellow liquid (aqueous solution)

Odour: low odour (agueous solution)

Melting Point: not determined

Glass-Transition Temperature: 105°C

Specific Gravity: 1.7 g/cm³

Vapour Pressure: not determined

Water Solubility: not stated, infinitely dilutable (aqueous solution)

Partition Co-efficient

(n-octanol/water) log Pow: not determined

Hydrolysis as a

Function of pH: not expected to hydrolyse on the basis of

chemical structure

Dissociation Constant: pKa 2.7-9.2 (titration)

Flash Point: not determined

Flammability Limits: not flammable

Combustion Products: oxides of carbon and hydrogen; incomplete

combustion may yield acrylic monomers

Pyrolysis Products: not determined

Decomposition Temperature: > 177°C

Decomposition Products: thermal decomposition may yield acrylic

monomers

Autoignition Temperature: not determined

Explosive Properties: not explosive

Reactivity/Stability: incompatible with alkaline substances

Particle Size Distribution: not applicable (liquid)

Comments on physico-chemical properties

Vapour pressure is not applicable as the polymer is a non volatile solid dissolved in water.

The limit of water solubility of the notified polymer is not known. However, Acumer 4161 is made to be fully soluble in water. When the system is dried to remove water (around 100°C), the polymer residue is still soluble and can be redissolved. At higher temperatures (>160°C), crosslinking occurs and water solubility diminishes.

The Polymer in Acumer 4161 does not contain functional groups which hydrolyse. Neither the backbone chain, nor the pendent groups will hydrolyse under the conditions of the OECD hydrolysis test (TG 111).

Partition coefficient is not applicable as the polymer is highly soluble in water.

No information is currently available for absorption/desorption. However the polymer is expected to bind to cations in soils as it contains ionisable groups.

4. PURITY OF THE CHEMICAL

Degree of purity: > 95%

Toxic impurities: < 0.1% poison by ingestion and skin contact;

severe skin and eye irritant (1); experimental teratogen (1); classified as hazardous (irritant) when in concentrations in excess of 5% (2)

Maximum content of

residual monomers: < 0.5%

Additives/Adjuvants: water 48-50% (formulation)

5. INDUSTRIAL USE

The notified chemical will be imported into Australia as a component of an aqueous solution polymer. This product has the appearance of a clear to hazy yellow liquid with an acrylic odour. It will be imported from the United States to Sydney or Melbourne in 205 litre drums, where dispatching to end users for reformulation will take place. The notified polymer is intended to be used as a de-scaling agent in water treatment systems. The aqueous solution will be sold directly to customers for formulating into products suitable for use in cooling water systems for large scale plants. The reformulated product will contain the notified polymer at 10-25%. This product is used at a concentration of 20-100 ppm in cooling towers.

It is estimated that approximately > 1 tonnes of the chemical will be imported during the first five years as Acumer 4161 (of which the notified polymer is present in a concentration of approximately 50% w/w).

6. OCCUPATIONAL EXPOSURE

The aqueous solution polymer will be supplied direct to Rohm and Haas's customers without repackaging. Occupational exposure during transportation and warehousing will be minimal and will only occur due to accidental spillage.

The aqueous solution polymer Acumer 4161, will be reformulated at Rohm and Haas's customers facilities. At each reformulation site approximately six employees will be exposed to the notified polymer. These staff will consist of three in the blending/mixing operation, 2 packaging workers, 1 quality control testing. These employees will be exposed to the notified polymer at concentrations ranging from 50-52% in the Acumer 4161 to 10-25% in the reformulated product. The blender/mixers may potentially be exposed to the highest concentration of the notified polymer, 50-52% for 1-3 hours/day for 12 days/year. This reformulated product will then be used

by service engineers to dose cooling systems resulting in a concentration of the notified polymer of 2-25 ppm. They may be potentially exposed during dosing, maintenance and draining of the cooling systems.

The main route of occupational exposure will be via dermal and eye exposure through spillage and splashing. There is a possibility of further dermal and eye exposure as well as respiratory exposure through the formation of mists and aerosols during reformulation and use of the cooling system additive.

7. PUBLIC EXPOSURE

There is little potential for public exposure to Acumer 4161 during transport, reformulation or end use. The notified polymer will not be manufactured in Australia and is imported as the main component of (approximately 50% w/w) of an aqueous solution polymer. The aqueous solution polymer is expected to be transported to and within Australia in 205 L drums. Transport spills are to be diked with absorbent material and the spilt liquid and solid absorbent are to be disposed of for waste incineration or according to local regulations.

Reformulation is performed by various customers and not the notifier, hence specific information on release to the environment during this process was not provided. However, packaging spillages will be collected in inert materials, (e.g. sand, earth) for incineration according to local, state and federal legislation. The notified polymer vapour pressure is very low, and loss due to volatilisation is expected to be negligible.

The notified polymer will be added to cooling system water of large cooling towers by trickle feed or total water replacement at a presently unknown number of sites. The final concentration of the notified polymer is approximately 25 ppm maximum. There is potential for public exposure through spills, cooling tower malfunction and spray drift.

8. ENVIRONMENTAL EXPOSURE

. Release

The imported aqueous solution will be sold directly to customers for formulating into products suitable for use in cooling water systems for large scale plants. It is anticipated that reformulation in Australia will occur at 5 to 10 customer facilities, and from these facilities, the reformulated product will be transported to end use sites. As yet, it is not clear where these customers will be located.

At the reformulation sites, the aqueous solution polymer will be pumped into mixing vessels with a capacity of around 2 000 litres. Following high speed dispersing, the aqueous solution is mixed mechanically with other ingredients and is packed off into 20 and 205 litre containers. The notified polymer may be at a concentration of 10 - 25% in the reformulated product. Transport to end use sites will occur by road or

rail. Service engineers replace existing treatment fluids in cooling systems with the new formulated water treatment product. Losses may be up to 10% through this process and occur through drum/storage residues; transfer piping; blending tank residues; and samples. It is likely these residues will either be washed to sewer when cleaning occurs, or landfilled with empty containers.

The concentration of the formulated product in cooling towers is estimated to be about 20 - 100 ppm, of which the notified chemical is 10 - 25%. The maximum concentration of the notified polymer in the cooling towers is expected therefore to be around 25 ppm. Servicing may be done continuously by trickle feed, or conducted every 6 weeks or so, depending on the type of system used. In some instances the tanks may be fully drained during the service and the fluid replaced, but with more sophisticated systems, draining may not be required. Water drained from cooling towers will form part of the company's trade waste, and concentrated liquid and solid residues are expected to be disposed of by incineration and/or landfill.

Apart from leaking storage containers and accidental spills, release of the polymer to the environment might occur from cooling tower drift, short-term manual blowdown, or operational blowdown (i.e. release of excess water). The majority of the polymer is expected to be released via the latter two mechanisms.

Disposal of release water will be according to the relevant government regulations. Such disposal would include release to sewer, together with other process streams, and might involve secondary treatment.

Fate

The polymer is used to scavenge positively charged aqueous ions. It is therefore expected to share the fate of these ions and be disposed of to sewer. The notifier could not estimate the amount of treated water which is likely to enter the sewer. Servicing is done through continuous trickle feed, so any overflow (bleed) will be sent to the sewer, and any blowdown is likely to enter the sewer. The concentration upon entering will be a maximum of 25 ppm.

Losses from container residues, transfer piping, blending tank residues and samples through the reformulation process are expected to amount to around 10%. The concentrated liquid and solid residues are expected to be disposed of by incineration and/or landfill with empty containers. Other wastes through piping and samples are likely to be washed to sewer.

It is unlikely that the component of free polymer contained in landfill would biodegrade to a significant degree. Due to the ionisable nature of the polymer, it would be expected to bind to cations within the soil, and become immobilised.

Thermal degradation of the polymer takes place above 290°C. Combustion products are expected to include oxides of phosphorous, carbon and hydrogen. If combustion is incomplete, acrylic monomers could be produced.

No bioaccumulation of the polymer is expected because of its high water solubility and its high molecular weight which is likely to inhibit membrane permeability and prevent uptake during exposure.

9. EVALUATION OF TOXICOLOGICAL DATA

The Act does not require the provision of toxicological data for polymers of number-average molecular weight (NAMW) greater than 1 000. No data are available for the notified chemical. However, a summary of data for related polymers is described below (3).

In range finding studies a similar polymeric acid neutralised with NaOH was found to have an acute oral $LD_{50} > 5\,000$ mg/kg in rats, an acute dermal $LD_{50} > 5\,000$ mg/kg in rabbits, was not a skin irritant in rabbits and was a very slight eye irritant in rabbits.

A similar polymeric salt was found to have an acute oral $LD_{50} > 5\,000$ mg/kg in rats, an acute dermal $LD_{50} > 5\,000$ mg/kg in rabbits, was a very slight skin irritant in rabbits and was not an eye irritant in rabbits.

A similar polymeric acid in range finding studies was found to have an acute oral $LD_{50} > 5\,000$ mg/kg in rats, an acute dermal $LD_{50} > 5\,000$ mg/kg in rabbits, was not a skin irritant in rabbits and was a slight eye irritant in rabbits.

A similar polymer (40% solids) in range finding studies was found to have an acute oral $LD_{50} > 5\,000$ mg/kg in rats, an acute dermal $LD_{50} > 5\,000$ mg/kg in rabbits, was a slight skin irritant in rabbits and was a slight eye irritant in rabbits.

A 13 week inhalation study in rats on a broadly similar polycarboxylate material (4) was inconclusive as to effects on the lung at concentrations of 5 mg/m³ for 6 hours/day, 5 days/week. These effects were a mobilisation of alveolar macrophages primarily in the alveoli adjacent to the terminal airways, thickening of the alveolar wall, scattered areas of focal alveolitis, an increase in the number of polymorphonuclear granulocytes and pneumonocyte hyperplasia in the lungs. However as these effects were not clearly dose related and were also observed in the controls it would be incorrect to state that the broadly similar carboxylate material causes inhalational toxicity. The no observed effect level (NOEL) for this response was judged to be 1 mg/m³, by the reports authors. On the basis of this, a cautionary exposure limit of 0.1 mg/m³ (respirable fraction) has been stated on the Material Safety Data Sheet (MSDS) for the aqueous solution polymer, Acumer 4161. A chemical is considered as toxic if in an inhalation study using rats "major functional changes in lung" occur at ≤ 0.025 mg/L (≤ 25 mg/m³) 6hr/day (5). On this basis the broadly similar polycarboxylate material would not be classified as toxic. The applicability of this is limited as the notified polymer only has a broad similarity to the

polycarboxylate material in the inhalation study. Further tests on the irritant and toxic effect of the notified polymer would be necessary to confirm or refute the potential for the notified polymer to cause damage to the respiratory tract.

It can be concluded from the above studies that the notified polymer is likely to exhibit low oral toxicity in rats, low dermal toxicity in rabbits and may be a slight skin and eye irritant in rabbits. It is not classified as respiratory toxicant based on a study of another polycarboxylate material. The low pH of the formulation containing the notified polymer may be indicative of an irritant potential.

With no evidence to the contrary the notified polymer and the aqueous solution formulation containing the notified polymer should be considered as a possible eye and skin irritant.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided for the product Acumer 4161, which is acceptable for polymers of NAMW > 1 000 according to the Act.

However data on ecotoxicity for polymers of a claimed similar structure and function were provided in a previous application for the same notified chemical (NA/213), and are summarised below. All show low toxicity to aquatic species. The notifier was unable to provide the exact identities of these polymers.

Product Name	Form	<i>Daphnia</i> <i>magna</i> 48 hr LC ₅₀ mg/L	Rainbow trout 96 hr LC ₅₀ mg/L	Bluegill sunfish 96 hr LC ₅₀ mg/L
QR-809A (LMW-45NX)	Na ⁺ Salt	> 1 000	700	> 1 000
QR-931 (LMW-10NX)	Na ⁺ Salt	> 1 000	> 1 000	> 1 000

Polymers similar to the notified polymer are moderately toxic to green algae, inhibiting growth through overchelation of nutrients. Similar polymeric acids have an ability to chelate nutrient elements and may exhibit toxic effects at concentrations greater than 1 ppm (6). However, toxicity is known to be mitigated by salt formation and humic acid.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

A predicted environmental concentration (PEC) through dilution as a result of liquid in cooling towers being lost as drift, or by being "bled off" to waste has been calculated below. The notifier could not estimate the amount of treated water which could enter the sewer. Annually however, > 1 tonne of the notified chemical will be used. After losses due to reformulation, > 1 tonne will be used in cooling towers

country wide. Much of this will be in water discarded from towers in company liquid waste, and will be disposed of by contractors. However, assuming it all enters the sewer through overflow, the following calculations show the concentrations in receiving waters will not pose an environmental threat.

Annual import volume: > 1 tonne
Loss through reformulation: (10%)
Annual amount used in cooling towers: > 1 tonne

	City	Country
Annual amount used in each case (assumed)	90%	10%
Amount of polymer entering sewer (per day)	> 10 kg	> 1 kg
Concentration after sewer dilution	0.09 ppm (250 ML)	0.5 ppm (5 ML)
Concentration in receiving waters dilution)	9 ppb (10:1 dilution)	0.25 ppm (2:1

Receiving waters from the city sewers will generally include oceans, so a further dilution factor of 10:1 is used. Receiving waters from country sewers will usually include rivers, so a further dilution factor of 2:1 is used.

Polymers similar to the notified polymer are moderately toxic to green algae, and may exhibit toxic effects at concentrations greater than 1 ppm (6). This shows the PEC in country receiving waters could be of concern. However, toxicity is known to be mitigated by salt formation and humic acid, and within these calculations, there has been no account of polymer being lost through adsorbing to cations in waste water sludge, and removal through liquid waste disposal. These two processes would account for removal of a large proportion of the polymer from the aquatic system. Even if 10% remained, the concentration in receiving waters in country areas would be reduced to around 25 ppb.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified polymer has a NAMW > 1 000 and should not, therefore, be able to cross biological membranes and cause adverse health effects. The levels of residual monomers and low molecular weight species also are unlikely to render the polymer hazardous (2). This is supported by the results of acute toxicity tests on a number of similar polymers which suggest that the notified polymer is likely to exhibit low acute oral and dermal toxicity. However it may be a slight skin and eye irritant. Inhalation of vapour or mist may result in irritation of the respiratory tract and may cause nausea and headache. Chronic inhalationary studies on a broadly similar polymer gave a no observed effect level of 1 mg/m³, a cautionary exposure limit has been recommended by the notifier of 0.1 mg/m³ TWA. This is stated on the MSDS for the aqueous solution polymer, Acumer 4161. On the basis of studies on similar materials the notified polymer should be considered as a possible eye and skin irritant until specific tests on the notified polymer are undertaken to confirm or refute this view.

It can be concluded that there is a low risk of exposure to workers during transport and storage. There is a low risk of adverse health effects during occupational exposure during reformulation and use unless dermal or eye contact occurs for extended periods. The acidic pH of the formulation will result in possible irritation effects through dermal or eye exposure. Inhalation of the polymer will be limited due to it's low volatility, this should limit occupational exposure if spilt or when mixed in an open system. A cautionary exposure limit, listed on the MSDS, of TWA 0.1 mg/m³ have been applied to the aqueous solution polymer by the notifier. This exposure limit is unlikely to be reached in well ventilated or open areas however, it may reached in badly ventilated and confined spaces.

There appears to be a small potential for public exposure to the notified chemical during the operation of large cooling towers. This would arise through tower malfunction or spray drift, but such airborne levels are expected to be low. At high temperatures (e.g. during burning of industrial waste) the polymer will degrade to oxides of nitrogen, carbon, hydrogen and phosphorous.

In the case of accidental spillage during transport, the public may be exposed to the notified polymer. The potential contact will be minimised by the recommended practices for storage and transportation. Emergency procedures for the containment and clean up of accidental spills are available and should be followed.

On the basis of available information for similar polymers the notified polymer would not be classified as hazardous according to the criteria of Worksafe Australia (5).

13. RECOMMENDATIONS

To minimise occupational exposure to Polymer in Acumer 4161 the following guidelines and precautions should be observed:

- If engineering controls and work practices are insufficient to reduce exposure to a safe level, then personal protective devices which conform to and are used in accordance with Australian Standards (AS) for eye protection (AS 1336, AS 1337) (7,8), impermeable gloves (AS 2161) (9), protective clothing conforming to AS 2919 (10) and used in accordance with AS 3765 (11), protective footwear conforming to Australian/New Zealand Standard (AS/NZS) 2210 (12) should also be worn. In addition respiratory protection conforming to AS/NZS 1715 (13) and AS/NZS 1716 (14) should be used.
- Ensure that good general exhaust ventilation is installed in areas where formulation is used and that drift is minimised.
- Good personal hygiene should be practised.
- Work practices and training should be implemented to avoid spills which should be cleaned up promptly and disposed of in accordance with the recommendations contained in the MSDS.
- If there is a possibility of spills occurring then the personal protective devices listed above should be used.
- A copy of the MSDS should be easily accessible to employees.

14. MATERIAL SAFETY DATA SHEET

The attached MSDS for Acumer 4161 was provided in a format similar to the Worksafe Australia format (15).

This MSDS was provided by Rohm and Haas Australia Pty Ltd as part of the notification statement. The accuracy of this information remains the responsibility of Rohm and Haas Australia Pty Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, secondary notification of Polymer in Acumer 4161 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

- 1. Sax and Lewis 1989, *Dangerous properties of hazardous materials*, Van Nostrand Reinhold, New York
- 2. National Occupational Health and Safety Commission, 1994, *List of designated hazardous substances* [NOHSC:10005(1994)], AGPS, Canberra, 1994
- 3. National Industrial Chemicals and Notification Scheme (1994), *Full public report, Acumer 9400 polymer*. Worksafe Australia, 1994.
- 4. Busey W B,1988, 91-day Inhalation Study in Rats Using Maleic/Acrylic Acid Copolymer, Polyacrylate and Heavy Duty Granular Laundry Detergent, Report No. 87RN-1045, Experimental Pathology Laboratories Ltd.
- 5. National Occupational Health and Safety Commission, *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008], AGPS, Canberra, 1994.
- 6. Nabholz J V, Miller P, Zeeman M 1993. Environmental Risk Assessment of New Chemicals Under the Toxic Substances Control Act (TSCA) Section Five. In "Environmental Toxicology and Risk Assessment." ASTM STP 1179. G Landis, J S Hughes, M A Lewis (eds). American Society for Testing and Minerals, Philadelphia. pp 40-45.
- 7. Australian Standard 1336-1982, Recommended Practices for Eye Protection in the Industrial Environment, Standards Association of Australia Publ., Sydney, 1982.
- 8. Australian Standard 1337-1984, *Eye Protectors for Industrial Applications*, Standards Association of Australia Publ., Sydney, 1984.
- 9. Australian Standard 2161-1978, *Industrial Safety Gloves and Mittens* (excluding Electrical and Medical Gloves), Standards Association of Australia Publ., Sydney, 1978.
- 10. Standards Australia 1987, *Australian Standard 2919-1987, Industrial Clothing,* Standards Association of Australian Publ., Sydney.
- 11. Standards Australia 1990, Australian Standard 3765.1-1990, Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals, Standards Association of Australia Publ., Sydney.
- 12. Standards Australia/Standards New Zealand 1994, *Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear,* Standards Association of Australia Publ., Sydney, Standards Association of New Zealand Publ, Wellington.
- 13. Standards Australia, Standards New Zealand, 1994. *Australian/New Zealand Standard 1715 1994 Selection, Use and Maintenance of Respiratory Protective Devices*, Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ., Wellington, New Zealand.

- 14. Standards Australia, Standards New Zealand, 1991. *Australian/ New Zealand Standard 1716 1991 Respiratory Protective Devices,* Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ., Wellington, New Zealand.
- 15. National Occupational Health and Safety Commission, *National Code of Practice for the Preparation of Material Safety Data Sheets*, [NOHSC:2011(1994)], AGPS, Canberra, 1990.