File No: NA/202

Date: 14 August 1995

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in ULTIMER 92LT174 and ULTIMER 92LT175

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

Polymer in ULTIMER 92LT174 and ULTIMER 92LT175

1. APPLICANT

Nalco Australia Pty Ltd of 2 Anderson Street, Botany NSW 2019 has submitted a limited notification for the assessment of the new polymer in ULTIMER 92LT174 and ULTIMER 92LT175.

2. IDENTITY OF THE CHEMICAL

The notified chemical is a cationic acrylamide terpolymer. The polymer contains a number of hazardous impurities. These are present at levels below the cut-off concentrations necessary to classify the polymer as a hazardous substance according the *Approved Criteria for Classifying Hazardous Substances* (1).

Based on the nature of the chemical and the data provided the notified polymer is considered to be non-hazardous. Therefore, the chemical name, CAS number, molecular weight, molecular formula and structural formula have been exempted from publication in the Full Public Report and the Summary Report.

Trade names: ULTIMER 92LT174, ULTIMER 92LT175

Number-average molecular weight: > 1000

3. PHYSICAL AND CHEMICAL PROPERTIES

The following data were submitted for the product ULTIMER 92LT175, containing the major constituents: notified polymer (10-30%), ammonium sulfate (10-30%) and water.

Appearance at 20°C and 101.3 kPa:	White liquid
Melting Point:	-10°C (water)
Boiling Point:	120°C (water)
Specific Gravity:	1.16
Vapour Pressure:	Expected to be that of water
Water Solubility:	Completely soluble in water
Partition Co-efficient (n-octanol/water) log P_{ow}:	Not provided
pH:	3.7 - 4.2
Hydrolysis as a function of pH:	The polymer is expected to hydrolyse under environmental conditions. This was supported by a report on the hydrolysis of a similar polymer.
Adsorption/Desorption:	Not provided

Dissociation Constant	No data provided. Polymer contains no acid protons or basic nitrogens.
Flash Point:	> 100°C
Flammability Limits:	Not flammable
Combustion Products:	Ammonia, oxides of sulphur, nitrogen and carbon
Explosive Properties:	None
Reactivity/Stability:	May react with strong oxidisers and strong alkalis

Comments on Physico-Chemical Properties

The partition coefficient is difficult to measure but is expected to be low due to the high solubility in water.

As cationic polymers are known to bind to humic acid in water (1), it is likely that the polymer will bind to the organic matter in soils and thus the adsorption is expected to be relatively strong.

The hydrolysis of the ester functions in the polymer is expect to occur under environmental conditions. The hydrolysis data presented for pH 7 shows 47.8, 58.9 and 65.6 % hydrolysis on days 1, 7 and 14 respectively (40°C). The first half-life is quick (approximately 1 day) and subsequent half-lives being much slower. Using the factor that the rate of reaction doubles every 5°C increase in temperature, then the first half life at 25°C is expected to be 8 days. Subsequent rates of hydrolysis is expected to slow down significantly.

4. PURITY OF THE CHEMICAL

Degree of purity: The polymer is manufactured as a 10-30% active aqueous polymer solution. The polymer itself is never isolated.

Hazardous residual monomers:

. **Chemical name:** Acrylamide
CAS No.: 79-06-1
Weight percentage: 0.15%
Toxic properties: Toxic by oral, dermal and inhalational route. Experimental carcinogen and neoplastogen, experimental reproductive effects, eye and skin irritant, mutagen (3).

Listed on *List of Designated Hazardous Substances* (4) with cut-off concentration of 3%.

WSA exposure standard (5): TWA 0.03 mg/m^3;
Sk - absorption through the skin may be a significant source of exposure.

Other hazardous impurities:

. **Generic name:** Aromatic alcohol
Weight percentage: 0.01%
Toxic properties: Toxic by oral route, moderately toxic by inhalation and skin contact, mild skin irritant, severe eye irritant (3).

Listed on *List of Designated Hazardous Substances* (4) with cut-off concentration of 25%.

Non-hazardous impurity/impurities (> 1% by weight):

. **Chemical name:** Water
CAS No.: 7732-18-5
Weight percentage: Balance

Maximum content of residual monomers: 0.9%

Additives/Adjuvants: None

5. INDUSTRIAL USE

The polymer will be imported as a white aqueous solution in 200 L steel drums. The polymer will be used for the flocculation of pollutants in waste water, emulsion breaking and sludge dewatering in industrial waste treatment.

The applicant will import > 1 tonne of polymer per annum.

6. OCCUPATIONAL EXPOSURE

The notified polymer will constitute 10-30% of an imported liquid product. Product will arrive in sealed 200L steel drums and be transported by road to Nalco's plant in NSW. Transport workers (6 truck drivers) will handle packaged product only, and should therefore only be exposed to the chemical in the event of accidental spills. The product will be onsold to approximately 50 customers Australia-wide for addition to their treatment systems. In some cases repacking into returnable bulk shipping containers may occur at the Botany plant prior to selling.

Activities conducted at Nalco's plant will include storage, sampling for quality control and decanting imported product into alternate containers. Decanting procedures will be either direct or via a decanting vessel. Receiving clerks (two) and forklift drivers (four) will handle sealed drums only and should therefore only be exposed to the chemical in the event of accidental spills. Laboratory chemists (three) will be exposed for approximately 4-5 hours per annum during analysis of imported product and repacked products. Chemical operators (four) will be exposed for approximately 30-50 hours per annum during sampling for QC (10 minutes per sampling) and repacking/decanting (2-4 hours per batch). Maintenance workers at the Nalco plant are not expected to be exposed to the chemical under normal situations, as the vessels and equipment are flushed with water before maintenance work is commenced.

At the customer sites, product will be diluted (to a concentration of of 0.1-1.5% of product) and fed directly into the treatment systems using continuous feed dosing. For some treatment applications, undiluted product will be used. Approximately 100 personnel (2 per site) are expected to be involved in dosing, testing and calibrating feed equipment. The applicant states that exposure during these operations will be for a few minutes at a

time only. Nalco salespeople (fifteen) may be exposed to the chemical when visiting customer sites and verifying dose levels.

Maintenance personnel and workers involved in spill recovery will be exposed for longer periods. Maintenance personnel will be potentially exposed to residual chemical in the feed equipment (10-30%) as well as in the application system (< 0.45%) - exposure time will depend on the repairs required. Clean-up personnel will be potentially exposed for > 1 hour.

Exposure to chemical liquid, aerosols, mists or vapours will be limited by the use of engineering controls and automated equipment. Decanting vessels at the Nalco plant will be linked to a negative pressure extraction system. At the customer sites, worker exposure should be minimal as the chemical "will be dosed by continuous feed dosing equipment directly into the treatment system".

Workers will be instructed to wear chemical goggles or safety glasses and impermeable gloves during decanting operations, while setting up feeding equipment and during laboratory analysis. During maintenance and emergency clean-ups respirators will be worn if aerosols, mists, vapours etc are generated. If personnel are required to enter tanks, vessels or enclosed spaces with limited ventilation, workers will be required to use self-contained breathing apparatus. Safety footwear will be worn when handling containers.

7. PUBLIC EXPOSURE

At the customer sites, the product containing the notified polymer will be used neat for emulsion breaking applications or diluted to approximately 0.1-1.5% for water clarification. The notifier has indicated that the polymer is expected to be completely retained by the waste water sludge, which is typically landfilled. A worse case scenario would be 5% of the product remaining in the waste water phase. This concentration would enter the receiving water, invariably municipal sewerage treatment plants and undergo further dilution of many orders of magnitude. The treatment water is not intended for human consumption, as the polymer is not approved for the treatment of potable water. The notifier has stated that the likelihood of public exposure to the treated water would be the same as for treated municipal sewerage water.

Disposal is via landfill, incineration or aqueous water treatment in accordance with local regulations. The applicant states that the liquid product should be solidified with stabilising agents so that no free liquid remains before disposal to an industrial waste landfill.

8. ENVIRONMENTAL EXPOSURE

. Release

The polymer is expected to be released to the environment via treatment works. The polymer is used to treat effluent water from industrial sites etc., with the supernatant discharged to the sewer. The majority of the polymer will be in the solids, which are dewatered before disposal by either incineration or landfill.

Other possible releases of the polymer could occur during repacking, sampling or during dosing. These operations are done on industrial sites using appropriate equipment designed to reduce possible spills etc. This together with the instructions on the clean up of spills in the Material Safety Data Sheet (MSDS) should limit the possibility of environmental release to a minimum.

. Fate

The polymer is expected to undergo hydrolysis under environmental conditions to yield the polymer backbone (copolymer of acrylamide and acrylic acid) and other hydrolysis products. These other hydrolysis products released are expected to undergo further degradation (6).

The final fate of the water soluble backbone polymer is unknown but it is likely to slowly degrade (hydrolyse) in the environment.

9. EVALUATION OF TOXICOLOGICAL DATA

Toxicological data are not required for polymers of number-average molecular weight (NAMW) > 1000 according to the *Industrial Chemicals (Notification and Assessment) Act, 1989*. However, an acute oral toxicity test and a skin irritation test were submitted for the product ULTIMER 92LT175, containing the major constituents: notified polymer (10-30%), ammonium sulfate (10-30%) and water.

9.1 Acute Toxicity

Table 1 Summary of the acute toxicity of ULTIMER 92LT175

Test	Species	Outcome	Reference
Acute oral toxicity	Mouse	LD_{50} = 7518 mg/kg	(7)
Skin Irritation	Rabbit	Non-irritating	(8)

9.1.1 Oral Toxicity (7)

ULTIMER 92LT175 in distilled water was administered by gavage to mice at doses of 5951, 6557, 7213, 7934, 8727 or 9600 mg/kg (10 mice/sex/dose).

Clinical observations were made over 7 days. Necropsies were conducted at the end of the study or at time of death.

No low dose animals died during the study. All high dose animals died by either 5 hours (male) or 15 hours (female). Clinical symptoms included suppression of spontaneous movements and diarrhoea. All surviving animals recovered completely by 24 hours.

Gross pathology of dead animals showed swelling of the stomach and small intestine as well as red colouration of the intestine. Surviving animals given > 7934 mg/kg showed discoloured kidneys. Organ effects were limited to animals which received > 7213 mg/kg.

LD_{50} values estimated by Probit analysis were 7641 mg/kg for male and 7396 mg/kg for female mice. These values were not statistically different to each other.

The results of this study indicate that ULTIMER 92LT175 has an acute oral LD_{50} = 7518 mg/kg in mice.

9.1.2 Skin Irritation (8)

ULTIMER 92LT175 was applied to the shaved backs of 6 Japanese White rabbits. Two applications of 0.5g test substance were made to each animal, one on an abraded test site and the other on an intact test site. All test sites were 4 cm x 4 cm. The treated area was covered with lint fixed by adhesive plaster. The dressings were left in place for four

hours, then removed, and the application sites wiped with warm water. Skin responses were observed at 4, 24, 48, 72 and 96 hours.

In all animals, no oedema or erythema was observed on the intact or abraded sites at 4, 24 and 48 hours. Skin reactions at the other observation times were not reported.

The results of the study indicate that ULTIMER 92LT175 is a not a skin irritant in rabbits.

9.4 Overall Assessment of Toxicological Data

ULTIMER 92LT175 has very low acute oral toxicity (oral LD_{50} = 7518 mg/kg in mice) and is not a skin irritant in rabbits.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The ecotoxicity of the polymer was calculated using US EPA methods for cationic polymers (9) based on clean water.

Species	ULTIMER 92LT175*	ULTIMER 92LT174**
96 hr Fish LC_{50}	0.27 ppm	0.27 ppm
48 hr Daphnia LC_{50}	0.45 ppm	0.37 ppm
96 hr Algal EC_{50}	0.05 ppm	0.05 ppm

* ULTIMER 92LT175 contains the major constituents: notified polymer (10-30%), ammonium sulfate (10-30%) and water.

** ULTIMER 92LT174 contains the major constituents: notified polymer (10-30%), ammonium sulfate (10-30%), ammonium chloride (<5%) and water.

An ecotoxicity test for fish using ULTIMER 92LT175 is also available.

LC_{50} (freshwater) 48 hr	3.8 ppm
LC_{50} (seawater) 48 hr	2,000 ppm

The above information shows that the polymers are potentially highly toxic to algae and daphnia and moderately toxic to freshwater fish. As these polymers have >3.3% amine nitrogen, these effects are mitigated by binding to dissolved organic carbon in natural waters. The US EPA has calculated a mitigation factor of 94 times for such polymers (2).

Anionic polymers are normally toxic to algae due to chelation of nutrient elements (2), with the toxicity [EC_{50}] in the range of 1-100 ppm. However, initial hydrolysis of the polymer to give the backbone polymer (copolymer of acrylamide and acrylic acid) gives an anionic polymer that is of lower concern because the free acids in the copolymer are not positioned correctly to readily chelate nutrient elements.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Most of the polymer is disposed of with the solids (sludge) by landfill or incineration. The rest of the polymer in the supernatant will normally be disposed of in the municipal sewer.

Incineration of the polymer will produce water together with the oxides of carbon and nitrogen and is unlikely to present an environmental hazard. The polymer disposed of in landfills is expected to undergo hydrolysis to give the backbone polymer and other

hydrolysis products. The backbone polymer is expected to remain in the landfill, while the other products should further degrade and/or strongly absorb to organic matter within the landfill. The environmental hazard from disposal of the polymer by incineration or landfill is expected to be low.

It is not possible to determine the concentration in the supernatant for all cases as this will vary with the different sludges involved. The applicant states that typically >95% of the applied product remains with the sludge. At the maximum dose rate <2.5 ppm of the polymer will be in the supernatant.

Assuming an industrial site produces 10 tonnes of liquid waste on a given day at 1% solids, ie 100 kg of solid waste, then after flocculation/dewatering there will be approximately 10,000 L of supernatant (9.9 tonne of water) discharged to the sewer. Assuming the treatment works do not remove any of the polymer, then:

Concentration of polymer entering sewer (worst case)	2.5 ppm
Dilution in city sewer, 250 ML	0.1 ppb
Concentration in receiving waters (ocean, 10:1 dilution)	0.01 ppb
For a regional based site, Dilution in country sewer, 5 ML	5 ppb
Concentration in receiving waters (river, 2:1 dilution)	2.5 ppb

The calculations above show that the concentration in the regional receiving waters is 20 times less than calculated EC_{50} of the most sensitive organisms, algae. The US EPA has determined that highly charged cationic polymers (greater than 3.3% amine nitrogen) combining with organic matter in water to form a precipitate, result in an estimated 94 fold mitigation of the aquatic toxicity (2). As the notified polymer has greater than 3.3% amine nitrogens, the risk to aquatic organisms is further reduced. Hydrolysis in the alkaline sewage environment would further reduce levels.

The only other sources of environmental contamination is from accidental spills etc. during transport. The MSDS is adequate to limit the environmental exposure and therefore limit the environmental hazard.

Overall the environmental hazard can be rated as negligible.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified chemical is a high molecular weight polymer (NAMW >1000), therefore, it is unlikely to pass biological membranes and cause systemic effects. The polymer contains a number of hazardous impurities. These are present at levels well below the cut-off concentrations necessary to classify the polymer as hazardous (1) and are therefore not expected to cause any significant toxicological concerns.

The product ULTIMER 92LT175, containing 10-30% notified polymer, ammonium sulfate (10-30%) and water, has very low acute oral toxicity (oral LD_{50} = 7518 mg/kg in mice) and is not a skin irritant in rabbits. Although these results do not suggest any specific toxicological concerns for the polymer, skin exposure should be avoided as a precautionary measure.

The notified chemical will arrive in Australia as a 10-30% aqueous solution. The imported product is stable, non-flammable and has a vapour pressure equal to that of water. As the product is non-volatile, exposure to the notified chemical via the inhalational route should be unlikely during normal use.

The major sources of worker exposure will be during direct decanting methods at the Nalco plant, during maintenance of dosing equipment and treatment systems at the customer sites, as well as during emergency clean-ups. During direct decanting processes splashing and spillages may result in skin and eye contact. The use of personal protective equipment, such as goggles, impervious gloves and protective clothing, will minimise contact during these operations. During maintenance work and emergency clean-up operations, aerosols or mists may form, and inhalational exposure may result. The use of an approved respirator, in addition to eye and skin protection, should reduce exposure during these operations.

Personnel entering poorly ventilated enclosed spaces will be required to use self-contained breathing apparatus. With the appropriate personal protective equipment exposure to the notified chemical will be minimal.

In the case of accidental spillage during transport, the public may be exposed to the notified polymer. This is 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. Public exposure to the notified chemical is therefore expected to be very low.

13. RECOMMENDATIONS

To minimise occupational exposure to the polymer in ULTIMER 92LT174 and ULTIMER 92LT175 the following guidelines and precautions should be observed:

- when using the notified chemical the following protective equipment should be worn:
  - impervious gloves conforming to Australian Standards (AS) AS 2161 (10),
  - protective eye goggles conforming to AS 1336 (11),
  - protective clothing conforming to AS 3765.2 (12), and
  - protective footwear conforming to AS/NZS 2210 (13).
- if mist, vapour or aerosols are generated, and engineering controls are not sufficient to control exposure, the following protective equipment should also be worn:
  - respiratory protection conforming to AS/NZS 1715 (14).
- the NOHSC exposure standard for acrylamide should be observed:
  - TWA 0.03 mg/m^3 (5).
- when entering poorly ventilated enclosed spaces, tanks or vessels the following protective equipment should be worn:
  - self-contained breathing apparatus conforming to AS/NZS 1715 (14).
- good work practices should be implemented to prevent splashing and spillages.

- good personal hygiene practices should be observed.
- a copy of the MSDS should be easily accessible to employees.

14. MATERIAL SAFETY DATA SHEET

The MSDS for ULTIMER 92LT174 and ULTIMER 92LT175 (containing 10-30% notified polymer) were provided in Worksafe Australia format (15).

This MSDS were provided by Nalco Australia Pty Ltd as part of their notification statement. The accuracy of this information remains the responsibility of Nalco Australia Pty Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989*, secondary notification of the polymer in ULTIMER 92LT174 and ULTIMER 92LT175 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

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