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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

POLYMER IN BETZ NOVUS POLYMER 2666

This Assessment has been compiled in accordance with the provisions of *the Industrial Chemicals (Notification and Assessment) Act 1989,* 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 Human Services and Health.

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

POLYMER IN BETZ NOVUS POLYMER 2666

1. APPLICANT

Betz Laboratories Pty Limited of 69-77 Williamson Road, Ingleburn, NSW 2565 have submitted a limited notification for assessment of Betz Novus Polymer 2666.

2. IDENTITY OF THE CHEMICAL

Betz Novus Polymer 2666 has been classed a type II hazard according to Worksafe Australia approved criteria for classifiying hazardous substances and National Model regulations. There is no requirement for chemical identity to be disclosed. For commercial reasons, the chemical identity and composition, identity of hazardous and non-hazardous impurities and manufacture/import volume have been granted exemption from publication in the Full Public Report and Summary Report.

2. IDENTITY OF THE CHEMICAL

Chemical Abstracts Service (CAS) Registry No.: not available

Trade name(s): Betz Novus Polymer 2666, Polymer 2666.

3. PHYSICAL AND CHEMICAL PROPERTIES OF FORMULATION

Appearance at 20°C and 101.3 kPa: White emulsion

Odour: Hydrocarbon

Boiling Point: Approximately 100°C

Glass-transition Temperature: Not provided

Density: 1.006 x 10^{-3} kg/m^3 at 21ºC

Vapour Pressure: Approximately 2.4 X 10^{-5} kPa at 25°C

Water Solubility: 5% (notified polymer, see below)

Fat Solubility:	Not provided
Partition Co-efficient (n-octanol/water) log P_{OW}:	see below
Hydrolysis as a function of pH:	see Environmental Effects
Adsorption/Desorption:	The notified substance is a charged cationic polymer and is expected to bind strongly to negatively charged surfaces and particles.
Dissociation Constant pKa**:**	see below.
Flash Point:	>93°C
Flammability Limits:	Not applicable since the polymer is not flammable and formulated into a water containing emulsion.
Combustion Products:	Not applicable
Pyrolysis Products:	Not provided
Decomposition Temperature:	Not provided
Decomposition Products:	Possible thermal decomposition products include elemental oxides.
Autoignition Temperature:	Not applicable since polymer is not flammable.
Explosive Properties:	Not applicable since polymer is not flammable.
Reactivity/Stability:	The chemical is stable but, contact with strong acids, bases or oxidants should be avoided.
Particle size distribution:	Not applicable . The notified substance is imported as an emulsion.

Comments on Physico-Chemical Properties
Water solubility was determined by the measurement, after shaking, of turbidity, clarity, viscosity, gel formation, and precipitation on a range of concentrations.

A partition co-efficient was not determined because the polymer is expected to be surface active due to the high proportion of charged groups.

Betz Novus Polymer 2666 is a cationic polymer which is expected to bind strongly to negatively charged surfaces and particles. Further, it contains salts of quaternary ammonium groups which will dissociate completely in water.

4. PURITY OF THE CHEMICAL

Degree of purity (of the notified chemical alone)**:** Polymer purity is >99%

5. INDUSTRIAL USE

The notified chemical will be supplied as a water purifying substance. It will be used as an open, non dispersive flocculant to treat industrial waste water streams. The notified polymer is intended to replace other emulsion-based polymers used in waste water clarification or sludge dewatering.

6. OCCUPATIONAL EXPOSURE

The notified polymer will be imported as a finished product (water in oil emulsion containing notified polymer) and will be distributed to industrial customers without any reformulation. Repackaging into intermediate bulk containers (IBC, referred to by Betz as Semi-Bulk Containers, SBC) or 205 L drums may occur depending on the needs of the specific application.

Waterside workers will unload Betz SBC (1500 L) or 205 L drums containing the polymer emulsion and load them onto trucks for road transport. The containers will be taken to a warehouse facility in Sydney where they will be stored in a purpose built containment area. Exposure from transport and handling should be 10 times/year; 2-3 hours/day.

Potentially ,waste treatment operators (1 or 2 per site) may be exposed (once per day for 0.5 to 1 hour/day) to the chemical. Site workers will be exposed to the notified chemical (as an emulsion) while handling the product containers, removing the bungs and connecting up pumping equipment to the storage containers. The polymer emulsion will be automatically pumped from the containers to a holding tank (day tank or continuous make down system). The make down tank will be dosed via an automatic metering system. The polymer emulsion will then be diluted with water, whilst being mechanically agitated, before the mixture is pumped into the waste water streams through a mechanical dosing system. The volume of chemical will depend on the volume of waste water to be treated and the unit operation, such as clarification, thickening or dewatering.

Local exhaust ventilation will be used to capture emissions during decanting. During pumping, personnel will be required to wear impermeable gloves, chemical goggles to prevent eye contact and protective overalls.

7. PUBLIC EXPOSURE

The notified chemical will be imported into Australia as a finished product, and will be distributed only to industrial customers, without any reformulation. At waste water treatment sites the notified chemical, as an emulsion, will be pumped from storage containers to a holding tank. The chemical will then be diluted with water and agitated, before being pumped into waste water streams through a mechanical dosing system. The amount of chemical used will depend on the volume of waste water to be treated, and the unit operation, such as clarification, thickening, or dewatering. Water treatment units will be dosed at 1 (clarification) to 1000 mg/L (dewatering) of the polymer.

The solids from the waste water treatment streams, containing the notified polymer, will be disposed to landfill. The amount of the notified chemical released to the environment with treated waste water is considered to be negligible. Empty product containers will be returned to Betz for appropriate disposal. It is unlikely that the public will be exposed to the chemical during any of these procedures.

8. ENVIRONMENTAL EXPOSURE

. Release

The polymer emulsion will be automatically pumped from the containers to a holding tank. It will then be diluted with water while being mechanically agitated, before the mixture is used in automatic dosing of the waste-water stream. No information was supplied by the notifier on the volume of chemical used. It is claimed that release of the notified substance to the environment will be minimal, while the majority released will be associated with the sludge produced by the waste-water treatment. The amount released will depend on the volume of waste-water treated and the process for which it will be used, such as clarification at a rate of 1 mg/L, or dewatering at a rate of 1000 mg/L.

Other possible releases of the polymer could occur during re-packing, 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 MSDS, should minimise the possibility of environmental release during these processes.

Any residual product or empty containers will be returned to Betz for appropriate disposal at the Lidcombe Aqueous Waste Treatment Plant operated by WRAPS.

## .	Fate

The polymer is used to scavenge negatively charged suspended solids, such as clays or humic substances. It is therefore expected to share the fate of these particles as dewatered sludge, and be disposed of to landfill.

Using OECD test guideline 301D (closed bottle test), Betz Novus Polymer 2666 can not be classified as readily biodegradable, with only 31% loss of dissolved oxygen in 28 d. However, using OECD test guideline 302B (Zahn-Wellens test), it can be classed as inherently biodegradable with 54% loss of dissolved organic carbon (DOC) over 28 d (accepted range for inherent biodegradability is 20-70% loss of DOC over this period).

Also, hydrolysis of the quaternized esterifying group is most likely to occur, yielding the co-polymer backbone (of acrylamide and acrylic acid) and choline chloride. The choline chloride is expected to undergo further degradation. The final fate of the backbone is unknown but it is likely to slowly degrade (hydrolyse) in the environment (3).

No bioaccumulation of the polymer is expected because its very large molecular size is likely to inhibit membrane permeability and prevent uptake during exposure (4,5).

## 9.	EVALUATION OF TOXICOLOGICAL DATA

### 9.1	Acute Toxicity

Toxicology studies were conducted with the polymer emulsion product, Betz Novus Polymer 2666. According to the material safety data sheet, Betz Novus Polymer 2666 also contains isoparaffinic petroleum distillate and C12-C14-secondary ethoxylated alcohols.

Table1 Summary of the acute toxicity of Betz Novus Polymer 2666

Test	Species	Outcome	Reference
oral toxicity	Sprague-Dawley rats	LD_{50}= >5000 mg/kg	6
skin irritation	NZW rabbits	moderate irritant	7
eye irritation	NZW rabbits	slight irritant	8

### 9.1.1	Oral Toxicity (6)

Sprague-Dawley rats (5/sex) were administered 5000 mg/kg weight of undiluted Betz Novus Polymer 2666 by oral gavage. There were no deaths, no clinical signs of toxicity, and no gross abnormalities observed in the 5 rats necropsied at the conclusion of the 14-day observation period. One rat lost body weight between days 7-14, but body weight gains were normal in all the other rats. The acute oral LD_{50} of Betz Novus Polymer 2666 was >5000 mg/kg body weight.

9.1.4 Skin Irritation (7)

A 0.5 mL amount of Betz Novus polymer 2666 was applied to about 6 cm^2 of shaved, intact backskin in each of 5 female and 1 male New Zealand White (NZW) rabbits. Adjacent untreated areas of skin served as controls. Treated and untreated skin were covered with gauze patches and tape, and a semi-occlusive dressing was secured around the trunk with tape. The wrapping was removed after 4 hours, and the test sites were wiped with deionised water. The observation period was extended to 28 days, due to persistent skin irritation.

Well defined/moderate to severe erythema occurred in all 6 rabbits at 4, 24, 48 and 72 hours. Very slight/slight oedema occurred in 4 rabbits at 4 hours, in all 6 rabbits at 24 hours, and in 5 rabbits at 48 and at 72 hours. Erythema and oedema was not observed at days 7, 14, 21 and 28, however dry, flaky skin was observed in all 6 rabbits on day 7, 3 rabbits on day 14, and 2 rabbits on day 21. No rabbits had skin irritation on day 28. Based on approved criteria (1) the notified chemical is classed as a skin irritant.

9.1.5 Eye Irritation (8)

Nine NZW rabbits were treated with 0.1 ml of Betz Novus Polymer 2666 by instillation into the conjunctival sac of one eye. The eyes of 3 rabbits were washed with 250 ml distilled water for one minute after 30 sec exposure.

The test chemical produced conjunctival irritation in all 6 unwashed eyes at 1 and 24 hours. Conjunctival irritation was also observed in 5 unwashed eyes at 48 hours, 2 eyes at 72 hours, and 1 eye at days 4, 7, 14 and 21. No conjunctival irritation was observed at day 28.

One unwashed eye, which did not show conjunctival irritation, exhibited a clear mucus discharge on days 3-14. No iritis or corneal opacity was noted during the 28-day observation period. Positive fluorescein readings were observed in all 6 unwashed eyes at 24 hours, in 5 eyes at 48 hours, in 3 eyes at 72 hours, in 2 eyes at 4 days, and in 1 eye at 7 days.

The test chemical produced conjunctival irritation in all 3 washed eyes at 1 hour, and in 2 eyes at 24 hours. No conjunctival irritation was observed at 48 hours, or beyond. A clear discharge was also observed in all 3 eyes at 1 hour, and in 1 eye at 24 and 48 hours, and 7 days. No iritis or corneal opacity was observed during the 14-day observation period. Positive fluorescein readings were observed in all 3 eyes at 24 hours, and in 1 eye at 48 hours.

In both unwashed and washed eyes, the positive fluorescein readings appeared to be due to damage to the corneal epithelium, although it was not sufficient to produce a visible opacity of the cornea. The average ocular irritation scores were 7.3, 4.7 and 5.3 in unwashed eyes, and 4, 1.3 and 0 in washed eyes, at 24, 48 and 72 hours, respectively. While the notified chemical exhibited some irritant properties, it does not meet the approved criteria for an eye irritant (1).

9.2 Overall Assessment of Toxicological Data

Based on the toxicity studies provided, Betz Novus Polymer 2666, had low acute oral toxicity in rats, but was a moderate skin and a slight eye irritant in rabbits. Washing eyes with water reduced the severity of the eye irritation, but did not completely eliminate it. The skin and eye irritancy may have been due to the petroleum distillate present in the final product, however, the notified chemical as a charged polymer is also likely. The notified chemical would appear to be a significant skin irritant as defined by approved criteria (1).

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The ecotoxicity studies were conducted using Betz Novus Polymer 2666 water treatment product. The results in Table 2 were provided by the notifier, using nominal concentrations only.

Results were provided from three screening algal tests that had inhibition of labelled metabolite uptake as an end-point. These preliminary results had no test details, which appeared to be non-standard and determined the extent of inhibition of uptake of a radio-labelled metabolite (HCO_3^-), as opposed to standard growth inhibition. Marked inhibition at 10 ppm was observed with lower concentrations not tested. Based on the comparison of LC_{50}s, cationic polymers have been shown to be about 6 times more toxic to algae than fish (9). In this instance, the fish LC_{50} for the polymer is 760 µg/L which would give an estimate of the lowest algal LC_{50} of about 127 µg/L.

Table 2. Ecotoxicity test results

Test	Species	Result (nominal concentrations of Betz Novus Polymer 2666)1
96 h acute	Fathead minnow (Pimephales promelas)	LC_{50} = 2 mg/L *(0.76 mg/L)*
48 h acute	Water Flea (Daphnia magna)	EC_{50} = 15 mg/L *(5.7 mg/L)*
% Inhibition of labelled metabolite uptake	Green Alga2 (Chlorella vulgaris)	100% inhibition at 100 mg/L 98% inhibition at 10 mg/L
% Inhibition of labelled metabolite uptake	Green Alga2 (Selenastrum capricornutum)	94% inhibition at 100 mg/L 88% inhibition at 10 mg/L
% Inhibition of labelled metabolite uptake	Green Alga2 (Scenedesmus obliqua)	89% inhibition at 100 mg/L 86% inhibition at 10 mg/L

1. Nominal concentrations of notified polymer given in italics
2. Results from screening tests which determined the extent of inhibition of uptake of radiolabelled HCO_3^-

The above information shows that these polymers are potentially highly toxic to algae and fish, and moderately toxic to water flea. However, as these polymers have >3.3% amine nitrogen, these effects are mitigated by binding to dissolved organic carbon in natural waters. The USEPA has calculated a mitigation factor of 94 times for such polymers when the measured TOC was 10 mg/L on adding humic acid to dilution water (9).

Initial hydrolysis of the polymer to give the backbone polymer (copolymer of acryl amide and acrylic acid) gives an anionic polymer which are normally toxic to algae due to chelation of key nutrients (9). The toxicity is within the range of 1-100 ppm, but in this instance, the hydrolytic product is of low concern because the free acids in the copolymer are not positioned correctly to easily chelate nutrients. The rate at which the hydrolytic product is formed is not clear also.

- Tests on other polymers

The applicant has provided data (10) for 4 cationic polyelectrolytes (see Table 3 for their toxicities in dilution/culture water). The tests study the ecotoxicity of polyelectrolytes below and above the optimum dosage. The optimum dosage will be specific for the polyelectrolyte, treatment type and treatment water combination (eg an epichlorohydrin-amine condensate used to clarify waste water from one food processing plant might have an optimum dosage of 1 ppm, while the same polyelectrolyte used for clarification of waste water from another food processing plant may have an optimum dosage of 10 ppm).
The test results indicate:

- When two polymers (A&B in Table 3) were used at the optimum dosage (ie the dose required to achieve required function but leaving little, if any, excess polyelectrolyte) for clarification of a synthetic river water containing kaolinite clay, humic acid, and salts (cf dilution/culture water without clay and humic acid), there is little free polymer left, if any.

- Toxicity tests were also performed with the treated synthetic water using fathead minnows in a 96 h acute test, or *Daphnia magna* in a 48 h acute toxicity test, which indicated no mortality occurred at this optimum dosage.

- At concentrations 2-3 times the optimum dosage, 80-100% mortality of the fish was observed, depending on the polymer used.

- At concentrations 4 times the optimum dosage, there was 100% mortality of *Daphnia magna* for both polymers.

- The increase in free polyelectrolyte concentration past the optimum dosage, corresponded with restabilisation of the substrate water's colloidal properties.

- This led to an increase in suspended solid concentrations and release of additional free polyelectrolyte, due to polyelectrolyte in excess of the available binding sites on the added clay and humic acid.

A similar pattern in toxicity was found for two different waste water streams (food processing industry and pharmaceutical industry), each using a different cationic polymer (C&D in Table 3, respectively), dosed at above and below the optimum concentration for clarification. In each case, the toxicity of the waste water to *Daphnia magna* was reduced on addition of the polymer up to and including the optimum dosage. Once the optimum dosage was exceeded, free polyelectrolyte was available and toxicity increased markedly because of the very low LC_{50}s for each polymer.

Table 3. Toxicities of cationic polyelectrolytes determined in dilution/culture water

Code	Polyelectrolyte	Molecular Weight	EC_{50} Daphnia (µg/L)	EC_{50} Minnow (µg/L)
A	epichlorohydrin-amine condensate	2×10^4	0.07	0.23
B	homopoly(diallyl-dimethylammonium chloride)	3×10^5	0.23	0.20
C	epichlorohydrin-amine condensate	4×10^5	0.29	0.22
D	acrylamide, vinyl quaternary amine copolymer	3×10^6	<1.0	<0.5

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The notifier expects most of the polymer will be disposed of with the solids (sludge) by landfill, with some slow degradation as it was shown to be inherently biodegradable. The remaining polymer in the supernatant is likely to be disposed of in the municipal sewer.

The concentration of the polymer in supernatant will vary according to the type of sludge and process that it will be used for.

Additional information provided by the notifier gave results of a Modified Free Drainage test to determine the optimum dosage with a sample of sludge using Betz Novus Polymer 2666. This indicated that the detection limit for determination of the residual polymer levels using potassium polyvinylsulfate titrated with Toluidine Blue (PVSK test method) was 3 ppm. The results showed that the optimum dose was 300 ppm, with <1% (ie below the detection limit) of the polymer remaining in the aqueous filtrate at this dose.

The worst case therefore would be an optimum dose rate of 1000 ppm of the polymer, where 1% of the polyelectrolyte was left in the aqueous filtrate, ie 10 ppm. Assuming an industrial site produces 10000 L of Liquid waste on a given day at 1% solids, ie 100 kg of solid waste, then after flocculation/dewatering there will be approximately 10000 L of supernatant discharged to the sewer. If further, down-stream, treatment works do not remove any of the polymer, then:

Concentration of polymer entering sewer	10 ppm
Dilution in city sewer, 250 mL	0.4 ppb
Concentration in receiving waters (ocean, 10:1 dilution)	0.04 ppb
For a regional based site, Dilution in country sewer, 5 mL	20 ppb
Concentration in receiving waters (river, 2:1 dilution)	10 ppb

The calculations show that the concentration in the regional receiving waters is an order of magnitude above the estimated lowest effect concentration for algae. The US EPA has shown that highly charged cationic polymers (>3.3% amine nitrogen) in dilution water with a total organic carbon concentration of 10 mg/L, reduced acute fish toxicity by 94 times (10). As the notified polymer has greater than 3.3% amine nitrogens, the risk to aquatic organisms may be further reduced to a factor of <3 orders of magnitude. Hydrolysis in the alkaline sewage environment would further reduce levels.

Therefore, the use of a cationic polyelectrolyte will cause minimal impact so long as it is used at, or slightly below, its optimal dosage for treatment of the particular waste-water treatment system. The operational need for achieving optimum dosage to prevent restabilisation of the substrate's water colloidal properties to prevent an increase in suspended concentrations, would partly ensure that this condition would be met. The notifier has indicated trained personnel will provide on-going on-site assistance to determine the optimum dosing. It is also strongly recommends that the notifier determines the optimum dosage for each use application to account for site, process, and function specificity.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Betz Novus Polymer 2666 is expected to exhibit low oral toxicity but may be a skin and eye irritant. The mean average molecular weight of Betz Novus Polymer 2666 is greater than 1000, therefore it cannot cross biological membranes, it has low residual monomers and low levels of low molecular weight species.

Exposure to workers can occur at a number of stages. During the transport and handling of the notified polymer it is estimated that between 10-20 dockside/ transport/ warehouse workers may be exposed. It is during the transfer of the notified polymer from the drums to the holding tank via connecting pumping mechanisms appears to be the stage at which the greatest risk of exposure will occur. The number of people this may effect has not been established as the number of customer sites is not known. The volume of chemical they will be exposed to is also unknown as the usage of the notified polymer will depend on the volume of waste water to be treated and the unit operation. The amount of exposure to waste treatment operators should be low (30-60 minutes a day), this being restricted to exposure due to handling the product containers, removing the bungs and connecting up the pumping equipment. No exposure should occur during pumping as it is an automatic system. However, as the chemical is an irritant workers should be adequately protected with impermeable gloves, chemical goggles, protective overalls and protective shoes. The notifier has stated that engineering controls such as exhaust ventilation will be in operation to capture emissions during decanting.

The public will not be exposed to the notified chemical during its importation, use in industrial waste water treatment, and disposal.

13. RECOMMENDATIONS

To minimise occupational exposure and environmental exposure to Betz Novus 2666 the following guidelines and precautions should be observed:

- personal protective devices should be used which conform to and are used in accordance with Australian Standards (AS) for eye protection (AS 1336, AS 1337) (11,12), impermeable gloves (AS 2161) (13), protective clothing (AS 2919)(14) and protective shoes (AS 2210) (15) should be worn;

- good personal hygiene should be practiced to minimise the potential for ingestion

- good work practices should be implemented to avoid spillages and splashing; and

- a copy of the Material Safety Data Sheet should be easily accessible to employees.

The notified polymer is unlikely to present hazard to the environment when it is used at, or slightly below, the optimum rate. However, because of its potentially varied use, there is a strong possibility of it being used above the optimum rate. This, together with inadequate dilution on discharge, may present an unacceptable hazard to aquatic life. Therefore it is recommended that the notifier determines the optimum dosage for each use application to account for site, process, and function specificity.

The notifier has submitted a Material Safety and Data Sheet (MSDS) for Betz Novus Polymer 2666. This details the methods to use for waste disposal. Where appropriate, it refers the user to conform to local regulations. The label has a caution on preventing the entry of the notified substance to drains, streams, rivers, or waterways. However, the label, and the MSDS, should clearly state that:

The chemical is dangerous to aquatic plants (algae). To avoid environmental impact, the product must be used at, or just below, the established optimum rate. Please consult the company prior to use.

14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for Betz Novus Polymer 2666 was provided in Worksafe Australia format (16).

This MSDS was provided by Betz Laboratories Pty Ltd as part of their notification statement. The accuracy of this information remains the responsibility of Betz Laboratories Pty Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification of Betz Novus Polymer 2666 shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. Should any additional algal toxicity data arise which contradicts the present data a secondary notification of Betz Novus 2666 will be necessary. No other specific conditions are prescribed.

16. REFERENCES

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16. Worksafe Australia, 1994, 'National Code of Practice For The Preparation Of Material Safety Data Sheets [NOHSC:2011(1994)]', AGPS, Canberra.