File No: PLC/126

September 1999

#### NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

#### **FULL PUBLIC REPORT**

## **Tersperse 2600**

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Director

Chemicals Notification and Assessment

# **FULL PUBLIC REPORT**

# **Tersperse 2600**

#### 1. APPLICANT

Huntsman Corporation Australia of Gate 2 Newsom St ASCOT VALE VIC 3032 has submitted a Polymer of Low Concern notification statement in support of their application for an assessment certificate for Tersperse 2600.

#### 2. IDENTITY OF THE CHEMICAL

The chemical name, CAS number, molecular and structural formulae, methods for detection, spectral data, details of the polymer composition, specific use and customer sites have been exempted from publication in the Full Public Report.

# Characterisation as a Synthetic Polymer of Low Concern

Marketing names/other names Tersperse 2600 (100% active polymer)

Tersperse 2650 (40% (w/w) aqueous polymer) Polysil TDA2650 (40% (w/w) aqueous polymer)

Number-Average Approximately 15 000

Molecular Weight (NAMW):

Weight-Average Approximately 45 000

Low Molecular Weight Species

Molecular Weight (WAMW):

**Molecular Weight < 500:** < 0.1% **Molecular Weight < 1 000:** < 0.1%

**Residual Monomers:** Below the concentration cut-off for classification of the

polymer as a hazardous substance

**Polymer Stability:** Unlikely to degrade or decompose

Reactivity: Functional group (carboxylic acid) in the low concern

category

Particle Size Distribution: > 20 μm; approx. 30% in range 20-30 μm

Charge Density: Anionic in the environmental pH range (4-9)

Water Solubility: 550 g/L

Method of Detection

and Determination:

Data claimed as exempt information; gel permeation chromatography (GPC) was used to derive the NAMW

Spectral Data: Spectral data used to characterise the polymer was

provided; specific details are claimed as exempt

information

The polymer meets the criteria for assessment as a synthetic polymer of low concern under Regulation 4A of the *Industrial Chemicals (Notification and Assessment) Act 1989*.

# **Comments on Chemical Identity**

The new polymer is an acrylic copolymer formed through free radical polymerisation of two monomers in roughly equimolar proportions. The polymerisation produces pendant carboxylic acid groups, which are then reacted with sodium hydroxide to form carboxylate. However, data in the notification indicated that approximately 50% of the stoichiometric requirement of base is added and so the final polymer contains approximately equimolar proportions of carboxylic acid and carboxylate groups. The Functional Group Equivalent Weight (FGEW) of the carboxylic acid groups in the parent polymer is approximately 117g/mol. However, in the notified polymer, the FGEW of both the carboxylic acid and (ionised) carboxylate groups is approximately 234 g/mol. The notified polymer is an anionic salt. The high charge density and absence of large aliphatic hydrocarbon moieties in the molecule confers very high water solubility on the material.

The molecular weight data were derived by GPC, with the notifier supplying traces and slice printouts for two samples of the new polymer. The data from both samples were similar, with the approximate NAMW and WAMW indicated above. In both cases, the weight percentage of low molecular weight species was low (< 0.1% less than MW 1000).

#### 3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C, 101.3 kPa: white-tan hygroscopic powder (solid)

viscous amber liquid (solution)

**Melting Point:** > 250°C (see comment below)

**Specific Gravity:** 725 kg/cm<sup>3</sup> (solid form of polymer);

1.15 x 10<sup>-3</sup> kg/cm<sup>3</sup> (liquid form of polymer)

Vapour Pressure: Not determined for liquid form

Water Solubility: 550 g/L

Flammability Limits: combustible but not flammable solid

**Autoignition Temperature:** > 300°C

**Explosive Properties:** lower limit of the explosive range: 20 g/m<sup>3</sup>

Reactivity/Stability: Stable

## **Comments on Physico-Chemical Properties**

Decomposition of the polymer at temperatures greater than 250°C prevented the establishment of a melting point value. This is characteristic of highly ionic solid polymers.

The very high water solubility is a consequence of the high anionic charge density (FGEW = 234 g/mol), and is necessary for polymers intended to act as dispersants in aqueous systems. However it is likely that the water solubility would depend strongly on the ambient pH. Due to the weakly acidic nature of the carboxylate groups, it is likely that the water solubility would be significantly reduced in conditions where pH is less than 5 because the anionic charge density would be substantially reduced due to protonation (see further comments below).

Data on the n-octanol/water partition coefficient and adsorption/desorption is not routinely required for the assessment of synthetic polymers of low concern. However, the high water solubility indicates that the polymer would have little affinity for the oil or organic phase. Consequently, it is expected to have a correspondingly low affinity for the organic component of soils or sediments, that is, a low value for log  $K_{oc}$ . However, some minerals have a positive surface charge due to incompletely neutralised di- and tri- valent ions near the surface of the crystal lattice (e.g. calcium, magnesium and iron), and the polymer could become adsorbed to the surfaces of these minerals through electrostatic interactions. Thus, while the polymer may become weakly associated with certain minerals in some soil types, it is likely that, overall, it would be mobile in the soil compartment.

The new polymer contains pendant carboxylate and carboxylic acid groups, which may be susceptible to hydrolytic cleavage. However, in the environmental pH region (pH 4-9), significant hydrolysis is considered to be unlikely.

As indicated above, the polymer as prepared contains both carboxylate groups together with un-dissociated carboxylic acid functionalities in approximately equimolar proportions. Carboxylic acid groups are weakly acidic with  $pK_a$  typically around 4.5. Consequently, in the environmental pH region (4-9), it is expected that the polymer would be primarily in the (charged) carboxylate form. In this form, the effective FGEW for the charged centres would be considerably less than the 234 g/mol mentioned above. However, under extremely acidic conditions (pH < 4), the polymer would become substantially protonated, which would lessen the effective electrical charge, that is, raise the FGEW for the charged centres. This may significantly reduce the water solubility.

#### 4. PURITY OF THE CHEMICAL

**Degree of Purity:** > 94.3 %

**Hazardous Impurities:** reaction product of one of the residual monomers with

alkali, 5.2%

risk phrases R36/37/38: irritating to eyes, respiratory

system and skin

**Non-hazardous Impurities** 

(> 1% by weight):

None

**Residual Monomers:** 5.7% (total residual content)

Additives/Adjuvants: None for Tersperse 2600

Water for Tersperse 2650 and Polysil TDA2650 (>

60%)

# 5. USE, VOLUME MANUFACTURE AND FORMULATION

The notified polymer will be used as a dispersant in chemical formulations. The polymer will be manufactured as a solid (Tersperse 2600) for use in manufacturing agricultural chemicals or as a 40% (w/w) aqueous solution for use in paint formulations (Tersperse 2650) or mineral processing in the mining industry (Polysil TDA2650). In the agricultural formulations the concentration will be 1 to 5% w/w, in paints 0.5% w/w and in mineral processing water 0.1% w/w. Most (80%) of the notified polymer manufactured in 5 tonne batches will be used for agricultural formulations with the remainder divided evenly between paint manufacture and mineral processing formulations. The notified polymer will be manufactured at the notifier's plant and will be used by a number of agricultural chemical formulators, paint manufacturers and mine-sites. Estimated manufacture volume during the first five years is as follows:

year	volume (tonne)
1	10
2	150
3	400
4	700
5	700

Transport and Storage

The notified polymer will be packaged and transported by road or rail as follows:

Tersperse 2600-25 kg plastic bags contained in cardboard boxes; and

Tersperse 2650 and Polysil TDA2650- 200 kg plastic lined (or polylined) steels drums.

Formulations containing the notified polymer will be packaged and transported by road as: Agricultural chemicals- typically in 5 or 20 kg plastic containers; and Industrial paints- 20 kg pails or 200 kg plastic lined steel drums; and Architectural paints- epoxy lined tin plate cans of 500 mL, 1 L, 4 L and 10 L capacity.

## 5.1 Polymer Manufacture

#### 5.1.1 Manufacture of Solid Form

Stage 1:	Raw material	s charging.	solvent and	cataly	ist addeo	to reactor.
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- Stage 2: Polymerisation: monomers fed concurrently into reactor at 120° C; polymerisation occurs;
- Stage 3: Solvent removal;
- Salt formation: water added to wet polymer, the mixture stirred, then liquid caustic soda is added. The mixture is reacted at 95° C for 6 hours at constant pH

to ensure complete hydrolysis;

- Stage 5: Drying of the polymer to form a brittle solid;
- Stage 6: Milling of the polymer to a uniform size ( $> 20 \mu m$ );
- Stage 7: Packaging and storing.

#### 5.1.2 Manufacture of Solution Form

Stages 1-4: As described above (5.1.1)

Stage 5: Adjustment to desired solids content with water; Stage 6: Cool, filter and drum for storage and distribution.

## **5.2** Application in Formulations

# 5.2.1 Formulation of Agricultural Chemicals- Water dispersal granules

- Stage 1: Tersperse 2600, active ingredient, other surfactants charged to blender;
- Stage 2: Dry blending;
- Stage 3: Hammer milling;
- Stage 4: Kneading. Water added to dry blend to agglomerate;
- Stage 5: Extrusion granulation;
- Stage 6: Drying;
- Stage 7: Packaging and storage.

#### 5.2.2 Paint Manufacture

- Stage 1: Tersperse 2650, pigment, solvents charged to mixer;
- Stage 2: High speed dispersion. Latex added to mixer and blended;
- Stage 3: Batch adjustment and testing;
- Stage 4: Filtration and filling into containers;
- Stage 5: Storage and distribution.

## 5.2.3 Industrial Paint Application

- Stage 1: Stir and dilute paint;
- Stage 2: Place diluted paint into spray gun;
- Stage 3: Paint applied in ventilated booth;
- Stage 4: Paint heat cured;
- Stage 5: Finished article.

## 5.3 Mineral Processing

- Stage 1: Crushed ore, plant water and Polysil TDA2650 loaded to rod mill;
- Stage 2: Milling (slurry preparation). Addition of flotation reagents;
- Stage 3: Froth flotation of slurry. This produces an underflow and overflow;
- Stage 4: Underflow sent to thickener to remove excess water;
- Stage 5: Thickened underflow sent to tailings pond. Water from thickened underflow
  - returned to Stage 1.

## 6. OCCUPATIONAL EXPOSURE

The notifier provided details for the different categories of workers expected to handle the notified polymer during manufacturing and/or application. The number of workers, nature of work carried out and duration of exposure for each category are summarised in the following tables.

## 6.1 Manufacture of the notified polymer

Nature of work	Number of workers exposed	Maximum duration of exposure (hr/day)	Days/year
Manufacture	4	8	80
QC testing	2	4	40
Packaging	2	2	40
Distribution and	50	1	40
storage			

The notified polymer will be manufactured in 5 tonne batches using existing routine. The notified polymer will be manufactured in two forms: a solid powder form (Tersperse 2600) and a liquid solution form (Tersperse 2650 and Polysil TDA2650). The polymer constituents are identified as hazardous substances.

Potential for worker exposure is expected to occur at stage 1 (sections 5.1.1 and 5.1.2), for manufacture of the notified polymer in both solution and solid form and during formulation/packaging, stages 5 and 6, and stage 7 for the solid form.

The method of charging raw materials to the reactor (stage 1) is not described in the submission. However, given the nature of the raw materials, potential for exposure to aerosols and vapour exists.

During manufacture of the polymer at 40% in solution form, dermal exposure to spillages may occur during liquid product transfer at stages 4, 5 and 6. Stage 6 packaging involves plant operators placing drums on filling lines and sealing them when filled.

During manufacture of the polymer in solid form, dermal exposure may occur at stages 4 to 6 during transfer of liquid product to drying belts and during transfer of dry, dusty product. Inhalation exposure may occur at stage 7 during packaging, which involves workers filling bags from a hopper, sealing them when filled and transferring the sealed bags to cardboard boxes for storage.

Once the manufacturing process is complete, worker exposure may also occur during clean up and waste disposal. Reaction vessels and piping are rinsed with water, and the drying belt, mill and solids packaging equipment are cleaned with an industrial vacuum cleaner. Further exposure via inhalation or direct skin contact may occur during sampling for quality control (QC) testing. There is little potential for aerosol formation from the liquid solution of the finished polymer because of its viscosity. However, potential for skin exposure to the polymer solution may occur as a result of drips or spills.

Exhaust ventilation is provided for charging of raw materials and discharging the final product. Manufacturing production vessels are sealed or vented into a scrubbing system to capture volatile emissions. Vapour and dust extraction will also be employed over the drying belts at the bag filling point and where drums are filled with liquid products. QC testing of products will be conducted in a fume cupboard with airflow. Laboratory technicians are required to wear flameproof cotton laboratory coats, safety glasses and safety shoes when performing QC testing.

The notifier stated that workers involved in the manufacturing and packaging stages of the

notified polymer solution wear flameproof cotton overalls, safety boots, hard hats, nitrile gloves and wide vision safety goggles with indirect ventilation. In addition, operators involved in Tersperse 2600 manufacture and packaging are required to wear Australian standard compliant air purifying dust respirators with a particulate filter. The notifier indicated that safety showers and eye wash stations are readily accessible during the manufacturing process.

The notifier stated that plant operators are trained in the aspects of using safety equipment and instructed on the safe handling of all new chemicals in the process using relevant MSDS and manufacturing procedure as a reference. In addition, a new starter training programmes and refresher courses are regularly conducted to update operator skills.

# 6.2 Formulations of agricultural chemicals

Nature of work	Number of workers exposed	Maximum duration of exposure (hr/day)	Days/year
Box handling (store to	)		
factory)			
Product transfer to	)		
blending vessel	50	4	90
QC testing			
Formulation packaging			

Tersperse 2600 will be used for the production of agricultural chemicals in granular form (section 5.2.1). Spillages may occur at all stages of production. Consequently, dust exposure to Tersperse 2600 exists. Exposure to the notified polymer may occur during charging of raw materials (active and other non active ingredients in the agricultural chemical product) into the blending vessel (Stage 1) and during formulation at 1-5% (Stages 2 to 5). Potential for exposure also exists at packaging.

Packaging is a semi-automated process, whereby granules are fed under gravity from a hopper into lined paper or plastic bags. Workers hold the bags under a hopper to load with granules then seal the bags. The notifier indicates that the granules are less dusty than the starting materials. Exposure to a dilute, aqueous suspension of the notified polymer is also possible during clean-up activities where mixers are washed out.

Dust extraction is maintained over all the vessels used in the granulation process and also over the packaging areas. QC testing is conducted in a manner similar to that described in section 6.1.

Operators involved in all stages of the process are required to wear flameproof cotton overalls, rubber boots, rubber gloves and helmets. Those handling raw materials are also required to wear rubber aprons and air hoods (upper body). QC technicians are required to wear protective equipment as described in section 6.1.

The notifier stated that workers involved in agricultural chemicals formulation and use are experienced in handling toxic chemicals. Formulation workers receive initial safety training involving safe handling of chemical, reinforced by regular training sessions throughout the year. MSDS are available for all chemicals in use, and are incorporated into the manufacturing instructions for formulation.

# 6.3 Application of agricultural chemical formulations

Nature of work	Number of workers exposed	Maximum duration of exposure (hr/day)	Days/year
Dilute formulation in water Spray crops with diluted formulation	1000s	8	60

Workers with potential exposure to the formulated agricultural chemical (granule) containing the notified polymer at 1-5% w/w include transport workers, agricultural trade suppliers, farmers and contract sprayers. Transport and trade suppliers would only be exposed to the polymer in the event of spill. Safety directions for end-use of agricultural products containing the notified polymer will be prescribed by a separate regulatory agency, the National Regulation Authority for Agricultural and Veterinary Chemicals. Farmers and spray contractors will prepare an aqueous spray formulation following the instructions on the product label.

# 6.4 Manufacture of paint formulations

Nature of work	Number of workers	Maximum duration of	Days/year
	exposed	exposure (hr/day)	
Drum handling:	50	1	30
(store to factory)			
Introduction to high	100	4	30
shear dispersion			
Paint make-up	100	2	30
QC testing	15	8	30
Packaging paint	100	8	30
formulations			

Exposure to the notified polymer in Tersperse 2650 during transport and storage is unlikely except in the event of a spill.

At the paint manufacture site, the polymer and solvents are automatically transferred to the blending vessels. Exposure to the notified polymer may occur in stage 1 (section 5.2.2) as the operator connects/disconnects the transfer hoses. Inhalation exposure from aerosols is unlikely as the polymer solution is viscous. Further exposure is expected during washing and cleaning of equipment.

Batch adjustment and QC testing (section 5.2.2) of the paint as it is manufactured will be conducted. Although not described in the submission, QC testing typically involves sampling of vessel contents during manufacture, for laboratory analysis and for applications. Exposure to the notified polymer is expected to be negligible as the polymer is compounded at 0.5% w/w into the paint mixture.

Exposure to low concentrations of the notified polymer may occur during packaging and

equipment clean up and maintenance.

Engineering controls include exhaust ventilation of the blending vessels, and packaging area. QC testing will be carried out in fume cupboards under conditions similar to those described previously. Testing of spray paints is to be conducted in a booth subject to regular maintenance procedures.

All workers are required to wear rubber gloves, flameproof cotton overalls, safety shoes and wide vision safety goggles with indirect ventilation. Those involved in spray painting testing will also be required to wear respirators compliant with the relevant Australian standards.

The notifier states that MSDS are available for all chemicals used in the manufacture of paint, and that workers who handle chemicals attend internal training sessions held at the commencement of employment and regular intervals during the year.

#### 6.5 Industrial Paint application

Nature of work	Number of workers exposed	Maximum duration of exposure (hr/day)	Days/year
Industrial paints: thinning of paint & addition to spray painting equipment;	10	8	200
spray painting operations;	10	8	200
equipment cleaning.	10	1	200
Professional painters; Apply paint by brush, roller or spray.	1000s	8	100

The notified polymer is formulated into industrial paints and architectural paints at a maximum concentration of 0.5% w/w. Exposure to the notified polymer during transport and storage and at retail outlets should only occur during spillages.

Potential for workers exposure to the notified polymer exists during preparation of paint for spraying, its application and during clean up after use. Inhalation exposure from aerosols/volatiles is possible as is skin exposure from handling contaminated spray equipment and spills and drips.

Industrial paint application utilises spray-coating equipment in an enclosed ventilation booth with a filtered exhaust system. Industrial users are required to wear safety clothing similar to that used in paint production (see section 6.4), with the addition of a cartridge type respirator during spraying. Industrial paint users instruct their workers on the safe handling of the formulated paint by reference to the MSDS.

Skin contact with low concentrations of notified polymer (0.5% w/w) may occur during spray painting activities and professional paint applications. Once the paint is dry the polymer will be immobilised within the matrix and no longer separately available. Exposure to aerosols in

spray painting is minimised by the recommended control measures.

The notifier indicated that professional painters will be provided with paint label recommendations; that is, to use in well-ventilated areas and wear safety glasses and overalls.

# 6.6 Mineral processing

Nature of work	Number of workers exposed	Maximum duration of exposure (hr/day)	Days/month
Drum handling: (store to work area)			
Product introduction to mineral dispersion	100	1	200
QC testing			

The aqueous solution Polysil TDA2650 containing 40% w/w of the notified will be used in mineral processing. Exposure to the notified polymer during transport and storage is unlikely except in the event of a spill.

The notified polymer will be automatically added to a final concentration of 0.1% w/w in rod mills with crushed ore and plant recycle water. Occupational exposure would mainly occur during stage 1 while connecting and disconnecting delivery/transfer hoses of pumps (see section 5.2.4). Inhalation exposure to aerosols is unlikely given the viscosity of the notified polymer solution. The operation is carried out under natural ventilation. Exposure by skin contact is the main route of exposure to the notified polymer from handling transfer hoses, contaminated equipment and from drips and spills.

The slurry passes through a froth flotation cell, where the overflow containing the minerals is collected for further extraction, and the underflow, containing most of the polymer, is re-used in the mine.

Further exposure to a more dilute form of the notified polymer (50 ppm) is expected during sampling of the process by QC technicians.

Production workers and QC technicians are required to wear a hard hat, safety shoes, wide vision safety goggles or safety glasses, flame-proof cotton overalls and nitrile gloves in plant areas. In QC laboratories, safety shoes, rubber gloves, safety glasses and flame-proof cotton laboratory coats are the minimum safety clothing requirements.

The notifier states that MSDS are available for all chemicals used in the mineral processing operations, and that workers handling chemicals attend internal training sessions held at the commencement of employment and regular intervals during the year.

## 7. PUBLIC EXPOSURE

The potential for public exposure to the notified polymer from its industrial, architectural

paint or mining use or from its subsequent disposal is assessed as being negligible. However, the public may be exposed to residues of the notified polymer if used in food crops in agriculture. The amount of notified polymer remaining as residues in food crops has not been established.

## 8. ENVIRONMENTAL EXPOSURE

#### Release

# Polymer Manufacture

The company has indicated that approximately 10 kg of polymer may be released during production of each 5 tonne batch (i.e. approximately 0.2% of production). Around half of this will result from the cleaning of residual solutions left in pipes, and this is likely to be released into the local sewerage catchment. The remainder is solid material removed by vacuum from conveyor belts and other dry handling equipment. This would be combined with other solid waste and disposed of to landfill. Assuming annual production of 700 tonnes, it is estimated approximately 700 kg of polymer will be discharged to sewer, while a further 700 kg will be placed into landfill.

# Herbicide Manufacture and Use

Preparation of the herbicide granules containing the polymer will take place in purpose constructed facilities operated by recognised agricultural chemical companies. It is expected that most of this processing will be performed under automatic control, and that fugitive dusts from the process would be collected using vacuum extraction techniques, and that the waste dust from the filters would be either incinerated or placed into landfill. No information of the quantity of dry solid polymer left in the packaging was supplied by the notifier, but this is unlikely to exceed 1% of the total. Assuming 560 tonnes of polymer are used annually in production of the herbicides, a maximum release of approximately 5.6 tonnes could remain in the emptied packaging. This is expected to be either incinerated or placed into landfill with the discarded packaging.

All of the 560 tonnes of polymer used in agricultural formulations, is expected to be released to the soil compartment with the herbicide spray. Typically, triazine herbicides are applied to crop land at approximately 3 kg active ingredient per hectare, and assuming that the ratio of dispersant (i.e. new polymer) to active ingredient in the formulation is approximately 6:90, the polymer would typically be released at a rate of 200 g per hectare. Triazine herbicides are applied to several million acres of land in Australia although, due to non uniform agricultural patterns, this application is not uniform across the nation. The major crop land to which triazine herbicides are applied include lands used for sugar cane, sorghum, maize, beans, peas and citrus fruit.

However, once released to the soil compartment the polymer is expected to be only weakly bound to soil minerals, and will be mobile in this phase. Consequently, all the material used in agricultural applications would eventually be released to the

# water compartment.

# Paint Manufacture and Use

The notifier indicated that up to 1% of the polymer (i.e. annually up to 700 kg) may be released from rinsing and cleaning the processing equipment during formulation and preparation of industrial paints. Those residues are to be combined with other aqueous wastes and disposed of by licensed waste contractors. Although no description of the waste treatment processes were supplied, it is presumed that waste solids including the new polymer would be recovered into sludge and placed into landfill.

Paints containing the new polymer would be used in both industrial situations, where application would be performed using spray techniques and in architectural applications, where application would be by brush and roller. No indication of the relative proportion of paint used in each application was provided. In spray booths, typically up to 50% of the paint may be released as overspray, while release resulting from waste paint used in architectural applications is expected to be modest. However, as a worst case scenario, assuming that all paint is used applied using spray techniques with 50% overspray, approximately 35 tonnes of polymer could be released each year. The notifier indicated that overspray would be collected in exhaust ventilation filters, or in aqueous waste streams where spray booths are fitted with "wet floors". Waste paint collected through exhaust extractors could be expected to be either incinerated or placed into landfill. Aqueous waste streams from industrial facilities are usually given some level of treatment to remove solid material prior to discharge to sewer systems. The new polymer is highly water soluble. However, in paint it is expected to be adsorbed to the surface of solid pigment particles where most would become assimilated into the waste sludge and placed into landfill or incinerated.

#### Use in Mineral Flotation

Mineral flotation circuits at mining sites are typically closed systems, in that all waste tailings and process water is retained within the precincts of the mining/milling operation. The new polymer when used as a depressant for naturally hydrophobic minerals is expected to become associated with particles of gangue material, and will be released with waste materials to the tailings dams. Any polymer that remains in the process water would be recirculated, then reused in the process. Tailings dams at modern mine sites are constructed with impermeable geotextile liners, and utilise other construction techniques to eliminate leakage and other non-evaporative losses. Consequently, while all the polymer used in mining operations will be released to the tailings dams, wider release to the general environment is unlikely. Widespread release from mining operations would occur only in the case of tailings dam failure.

# Summary of Release Scenarios

The major release of the polymer is to the soil compartment through association with herbicides. Further release to the soil is expected from disposal of unused paint and other residues into landfill. However, the polymer is highly water soluble, and as it is not expected

to have a strong affinity for the organic component of soils and sediments, it will be mobile in these media. Consequently, it is likely that most of the polymer will ultimately be released to the water compartment. This release is unlikely to be uniform, but would be concentrated in areas of intensive crop production.

#### **Fate**

It is expected that the majority of the polymer will eventually be released to the water compartment. The polymer is highly water soluble, and could be expected to persist in solution. However, under normal environmental conditions where the pH is 4-9, the material contains a high content of carboxylate functionalities, which have a high affinity for calcium and magnesium ions, both ubiquitous in natural waters and soils. Consequently, it is likely that the polymer charge would be partially neutralised through complex formation with these ions, and the polymer solubility would be reduced (lower effective electrical charge). The partially neutralised polymer may then become associated with aquatic sediments.

The new polymer is not readily biodegradable, and duplicate tests on the material indicated only 16% degradation after 28 days incubation with sewage sludge bacteria. This test was performed in accordance with OECD TG 302 B (Modified Zahn-Wellens Method), where the concentration of dissolved organic carbon in the test media is monitored over 28 days. Under the reporting protocols of this test, the polymer may be regarded as neither readily nor inherently biodegradable. However, it did exhibit some degradation over the 28 day test period, and could therefore be expected to be slowly decomposed in aerobic environments through bacterial action. Biodegradation will lead to formation of water and carbon dioxide, while the sodium ion component will remain unaffected.

Under most conditions abiotic degradation of released material through hydrolysis is unlikely since the polymer is expected to be stable at pH 4-9. However, some of the polymer will be used in mineral flotation activities, and will be released to the tailings dams with gangue minerals. In many mine tailings dams the pH is very low (possibly as low as 2 to 2.5) due to oxidation of sulfide minerals to sulfuric acid, and under these conditions, hydrolytic degradation may be possible. When released to creeks, rivers and other water bodies (as runoff from agricultural land), polymer near the water surface may undergo some photolytic degradation. However, the UV-visible spectrum of the polymer indicates significant absorption only below wavelengths of 280 nm, i.e. in the UV region of the spectrum. Since solar radiation intensity in this region of the spectrum is only a small percentage of the total, degradation by this mechanism is expected to be slow.

Although a large proportion of the material is expected to be released to the water compartment (at least 560 tonnes per annum from agricultural applications), and while not readily biodegradable, the polymer has a low potential for bioaccumulation because of the high molecular weight and high water solubility.

Some of the polymer is likely to be incinerated with paint residues and other

production and processing wastes, and would decompose to water and oxides of carbon.

## 9. EVALUATION OF TOXICOLOGICAL DATA

Data has been provided for assessment on acute oral toxicity and acute dermal irritation/corrosion of the notified polymer.

# 9.1 Acute Toxicity

# **Summary of the acute toxicity of Tersperse 2600**

Test	Species	Outcome	Reference
acute oral toxicity	rat	$LD_{50} > 2~000 \text{ mg/kg}$	Brook, 1999
skin irritation	rabbit	non-irritant	Shen, 1999

# **9.1.1** Oral Toxicity (Brook, 1999)

Species/strain: rat/Sprague-Dawley

*Number/sex of animals:* 5/sex

Observation period: 14 days

Method of administration: 2 000 mg/kg bw as a 30% (w/w) aqueous solution

by oral gavage

Clinical observations: hunched posture and reduced somatomotor activity

in 2 animals on the day of dosing

Mortality: none

Morphological findings: No gross abnormalities detected

Test method: Limit test, similar to OECD TG 401

 $LD_{50}$ : > 2~000~mg/kg

Result: the notified polymer was of very low acute oral

toxicity in rats

# **9.1.2** Skin Irritation (Shen, 1999)

Species/strain: rabbit/New Zealand White

*Number/sex of animals:* 3 females

Observation period: 72 hours

Method of administration: 0.5 g solid sample onto the moistened test site, for

4 hours under a semi-occlusive dressing

Test method: OECD TG 404

Draize scores: no erythema or oedema was noted in any animal at

any time observation; all scores were zero

Result: the notified polymer was not irritating to the skin

of rabbits

# 9.2 Overall Assessment of Toxicological Data

The notified polymer was of very low acute oral toxicity ( $LD_{50} > 2~000~mg/kg$ ) in rats and was not a skin irritant in rabbits. It is not determined to be a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC 1999b) in relation to these endpoints.

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

While not routinely required for synthetic polymers of low concern, the notifier provided ecotoxicity tests on fish, daphnia and freshwater algae because of the expected significant release to waterways. The ecotoxicity tests were performed according to OECD test guidelines.

Test	Species	Results
Acute toxicity OECD TG 203	Rainbow trout  Oncorhynchus mykiss	LC <sub>50</sub> (96 h) 134 mg/L 95% confidence interval 100-180 mg/L NOEC (96 h) 100 mg/L

Acute immobilisation Water flea EC<sub>50</sub> (48 h) 54 mg/L

OECD TG 202 Daphnia carinata 95% confidence interval 32-56

mg/L

NOEC (48 h) 32 mg/L

Growth inhibition Algae ECr<sub>50</sub> (72 h) 548 mg/L

OECD TG 201 Scenedesmus capricornutum 95% confidence interval 506-593

mg/L

NOEC (72 h) 125 mg/L

The tests on fish were performed using a semi static methodology with 80% renewal at 24, 48 and 72 hours. The tests were conducted using solutions of the test substance made up at nominal concentrations of 32, 56, 100, 180 and 320 mg/L, together with controls containing no test substance. The tests were performed in duplicate using five fish per replicate at 19.4 ± 0.6 °C, and pH 6.9-9.3. Continuous aeration was applied to the test vessels, which maintained the dissolved oxygen levels between 9.2 and 9.9 mg/L. After 24 hours exposure to the 180 mg/L solution, all test fish in both replicate tests had died, while no mortality was observed after 96 hours exposure to solutions containing nominally 100 mg/L of polymer. The dose response curve is very sharp, and Trimmed Spearman-Karber analysis (US EPA) furnished the results tabulated above. The report mentioned that the fish exposed to 100 mg/L exhibited some signs of distress, and were dark in colour, and that dead fish from exposure to the higher concentrations were bloated. Despite these effects, the results indicate that the new polymer is practically non toxic to this species of fish.

The immobilisation tests with daphnia were performed under static conditions using solutions prepared with nominal concentrations of the test substance of 10, 18, 32, 56 and 100 mg/L, together with controls containing no test material. The temperature, pH and dissolved oxygen levels during the tests were respectively  $22.4 \pm 0.1$ °C,  $7.4 \pm 0.2$  and  $9.2 \pm 0.1$  mg/L. The tests were performed with four replicates at each test concentration, using five daphnia in each test vessel. After 24 hours exposure to the solution containing (nominally) 156 mg/L of test substance, 30 % (i.e. six out of 20 animals) immobilisation of the daphnia had occurred, while after 48 hours exposure at this concentration 70% immobilisation was observed. There was no immobilisation after 48 hours for the daphnia exposed to lower test concentrations. As with the fish test, the dose/response curve is very steep and Trimmed Spearman-Karber analysis (US EPA) gave the results tabulated above. The results indicate that the polymer is slightly toxic to daphnia.

Tests on algal growth inhibition were also performed over a 72 hour period with seven nominal concentrations of the polymer (10, 65, 125, 250, 500, 750 and 1000 mg/L) and controls. Each test was conducted in triplicate, and the temperature was maintained at  $24 \pm 2$ °C, the light intensity maintained around 4000 lux, and the pH of the test media was always between 6.7and 7.2. The cell density was observed daily and the data used to calculate the effect of the polymer on the rate of algal cell multiplication by Dunnett's Multiple Comparison Test (US EPA). The results indicate that the new chemical is practically non toxic to this species of algae.

#### 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

<sup>\*</sup> NOEC - no observable effect concentration

The major use of the new polymer is as a non-active constituent in granulated herbicide formulations at 1-5% w/w. Approximately 560 tonnes per annum are likely to be used in agriculture, and since the polymer is highly water soluble with little affinity for soils or sediments, all of this is expected to be eventually released to the water compartment. It is difficult to calculate an accurate Predicted Environmental Concentration (PEC), however, if it is assumed that the herbicide is applied at a rate of 3 kg per hectare, and that the new polymer comprises 7% of the herbicide, then each hectare could contain around 200 g of the material after spray application. The distribution is expected to be uniform across sprayed areas, and if it is also assumed that the polymer penetrates 10 cm below the soil surface, then the predicted mean concentration within the soil is 240 mg/m³, or 170 ppb w/w assuming a soil density of 1.4 kg/m³.

The polymer is expected to be mobile in soils, and most could be expected to eventually reach water courses. However, due to the many factors which may effect the release from the soil (e.g. weather and soil type), it is difficult to estimate realistic PECs for the water compartment caused by runoff. However, if as a worst case scenario, it is assumed that the polymer is applied directly to water at 200 g per hectare, and that the water body is 15 cm deep, the resultant PEC is 0.14 mg/L. This PEC is at least two orders of magnitude below the level that is toxic to daphnia (54 mg/L). Direct application to water is considered to be a rare accidental event, and the more likely scenario of 10% spray drift offers an additional order of magnitude in the safety factor.

When released to natural water bodies with agricultural spray drift or run off, the polymer is expected to be slowly degraded through biological processes. Some degradation through photolysis may also occur.

A further 70 tonnes per annum of the new polymer will be used as a dispersant for pigments in paint, and it is possible that up to 50% (35 tonne per annum) could be released to landfill with residual overspray. However, this could also be incinerated with waste sludge from industrial facilities using the paint, and produce water vapour and oxides of carbon.

The polymer will also be used in mineral flotation. Approximately 70 tonnes per annum are likely to be released with talc and other unwanted minerals to mine tailings dams. Here it is likely to be slowly degraded through hydrolysis resulting from the high acidity in most tailings dams, or through slow photolytic degradation. Release to the wider environment in leakage from tailings dams is unlikely.

When used as a dispersant for agricultural formulations, in paint or as a mineral flotation reagent the new polymer presents is expected to present a low hazard to the environment.

# 12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified polymer was of very low acute oral toxicity and was not a skin irritant. Data are not available on the effects of repeated or prolonged exposure. The acute dermal toxicity of the notified polymer is not known, but is expected to be low given the high molecular weight, small percentage of low molecular weight species, and low acute oral toxicity. Whilst no ocular irritation studies were conducted, the MSDS for the polymer indicates that because of the particulate nature of the polymer some eye and respiratory irritation is likely. The particle

size of the powder, > 20µm, indicates its non-respirable, therefore unlikely to be toxic by the inhalation route. Vapours of the polymer in aqueous solution may also give rise to eye and respiratory irritation. The notified polymer, Tersperse 2600, is not classified as a hazardous substance according to NOHSC Approved Criteria for Classifying Hazardous Substances (NOHSC, 1999b) in terms of the available data.

The constituent monomers of the polymer are hazardous substances (NOHSC, 1999a) and have national exposure standards (NOHSC, 1995). The health effects of concern identified for the monomers are skin and eye burns, skin irritancy and respiratory sensitisation.

The notified polymer will be formulated into water dispersible granules containing herbicides such as simazine and triazine. These chemicals are hazardous substances and carry the risk phrases simazine, Carcinogen Category 3, R40- possible risk of irreversible effects, and atrazine, Carcinogen Category 3, R40- possible risk of irreversible effects, Mutagen Category 3, R40- possible risk of irreversible effects, R20/22- harmful by inhalation and if swallowed, R36- irritating to eyes, R43- may cause sensitisation by skin contact. The NOHSC exposure standard for atrazine is 5 mg/m³ Time-Weighted Average (TWA) (NOHSC, 1995).

# **Occupational Health and Safety**

The notified polymer will be manufactured in Australia in two forms, a solid powder and an aqueous solution. It will be formulated into agricultural chemicals and paints, and used in mineral processing.

# Transport and Storage

Exposure to the notified polymer is not expected during transport or storage as long as the packaging remains intact. The notified polymer in solid or aqueous form is combustible; dusts of the notified polymer have a lower explosive limit of 20 g/m³. Storage of the notified polymer when not in use, in closed containers, in a well ventilated area is required to avoid the potential for dust explosions. Exposure after a spill would be controlled by use of the recommended practices for spillage clean-up given in the MSDS supplied by the notifier. The risk of adverse health effects for transport and storage workers is considered low.

## Occupational Exposure

Manufacture of the notified polymer in its solid powder form (Tersperse 2600) and its formulation into agricultural chemical granules employs processes where herbicides and hazardous substances are already used. Dust exposure is of greatest concern during the drying and packaging of Tersperse 2600, when it is mixed with herbicides and other non-active constituents to produce granular agricultural formulations, and at disposal. There exists potential for exposure by inhalation and/or through skin contact with dust particles and granules.

Exhaust ventilation, sealed/vented production vessels and dust/vapour extraction needs to be maintained over production and packaging areas to capture volatiles and dust at source, and minimise exposure to airborne particulates generated from the polymer and other ingredients. Other control measures employed throughout these operations include the use of personal protective equipment, such as flame proof cotton overalls, safety boots, hard hats, nitrile gloves and wide vision safety goggles with indirect ventilation as well as air purifying dust respirators with particulate filters meeting Australian standards. Where workers handle raw materials in agricultural chemical formulations, rubber aprons and upper body air hoods are additional requirements. Workers exposure to dust is thus further minimised, and therefore

the risk of adverse health effects is minimised.

Exposure to dusts/vapours and high temperatures during quality control testing is also minimised through the use of appropriate control measures and automated systems of operation.

End-users of agricultural chemicals containing the notified polymer will be expected to follow the safety directions on product labels.

The NOHSC exposure standard for atrazine and inspirable dust will need to be adhered to in the workplace.

The strict control measures needed for the hazardous substances used in association with the notified polymer are sufficient to adequately control exposure to the polymer itself.

Exposure to the aqueous formulations of the notified polymer (Tersperse 2650 and Polysil TDA2650) is controlled through the use of automated dosage equipment and engineering control measures, such as exhaust ventilation to capture volatiles/vapours and spray painting booths. In addition, personal protective equipment including rubber gloves, flame proof cotton overalls, safety shoes and wide vision safety goggles with indirect ventilation are a requirement in the workplace. Cartridge type respirators are recommended for use in industrial spray painting. The above control measures are sufficient to adequately control exposure to the polymer in solution. Accordingly, the risk to the health of workers involved in handling the aqueous polymer in paint formulation, industrial application and mineral processing is negligible.

Overall, the controls employed in the workplace minimise inhalation and dermal exposure and therefore reduce the risk of and protect against respiratory and dermal irritation that may arise.

According to the notifier, workers involved in the manufacture and formulation processes and in industrial paint applications are trained in health and safety practices and instructed on the safe handling of chemicals. In addition, manufacturing processes undergo a rigorous hazard assessment involving external consultants, plant management and operators prior to implementation on the plant; critical safety issues are also addressed. These practices will need to continue to ensure that hazards in the workplace are appropriately controlled and measures are updated to minimise the risk of adverse effects to the health of workers.

Measures should also be implemented in the disposal of the notified polymer and its formulated products containing hazardous substances to ensure that exposure is avoided.

#### Public exposure

The potential for public exposure to the notified polymer during transport, coating operations, disposal and in the finished product in its industrial and domestic paint, and mineral processing applications are assessed as negligible. However, there is potential for public exposure from agricultural application since it is likely that at least some polymer will remain as residue and therefore enter the human food chain.

Since only about 0.1% of the notified polymer has a molecular weight less than 1000 and is therefore unlikely to traverse biological membranes, it could be anticipated that the oral

toxicity and dermal irritation potential would be very low. This prediction was confirmed in toxicity and irritation studies. Hence, compounds with large molecular weights (> 1000) are not likely to pose a significant hazard to public health when ingested in the quantities anticipated to be present as residues in food.

Paint for architectural use has been available to the public for many years and the introduction of the notified polymer into paint formulations at the specified concentration is unlikely to change the existing hazard.

Based on the above information, it is considered that Tersperse 2600 will not pose a significant hazard to public health when used in the proposed manner.

#### 13. RECOMMENDATIONS

To minimise occupational exposure to Tersperse 2600, Tersperse 2650 and Polysil TDA2650 during manufacture and use the following guidelines and precautions should be observed:

- Avoid generation and breathing of dust when handling the notified polymer in powder form;
- Provide local exhaust ventilation when handling the notified polymer in powder form (Standards Australia 1994);
- Dust levels in the workplace should be maintained below the NOHSC exposure standard for non-hazardous dusts, 10 mg/m³ (TWA) measured as inspirable fraction (NOHSC, 1995). Employers are responsible for ensuring the exposure standard is not exceeded:
- Respiratory protection should conform to AS/NZS 1715 (Standards Australia/Standards New Zealand 1994), and AS 1716 (Standards Australia/Standards New Zealand 1994);
- Safety goggles should be selected and fitted in accordance with Australian Standard (AS) 1336 (Standards Australia 1994) to comply with Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand 1992);
- Industrial clothing should conform to the specifications detailed in AS 2919 (Standards Australia 1987) and AS 3765.2 (Standards Australia 1990);
- Impermeable gloves or mittens should conform to AS 2161 (Standards Australia/Standards New Zealand 1998);
- All occupational footwear should conform to AS/NZS 2210 (Standards Australia/Standards New Zealand 1994);
- Spray painting booth should conform to AS/NZS 4114.1 (Standards Australia/Standards New Zealand, 1995a) and AS/NZS 4114.2 (Standards Australia/Standards New Zealand, 1995b);

- Spillage of the notified polymer should be avoided. Spillages should be cleaned up promptly with absorbents which should then be put into containers for disposal;
- Good personal hygiene should be practised to minimise the potential for ingestion;
- A copy of the MSDS should be easily accessible to employees;
- Exposure to hazardous substances in the manufacture of the polymer, during paint manufacture and formulation of agricultural preparations should be maintained below the relevant NOHSC exposure standards (NOHSC, 1995); and
- Spray painting should be conducted under the guidance of NOHSC Draft National Reference Document for Spray Painting (NOHSC, 1999c).

If the conditions of use are varied, then greater exposure to the public may occur. In such circumstances, further information may be required to assess the hazards to public health.

#### 14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified polymer (solid and aqueous forms) were provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC 1994).

These MSDS were provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

# 15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Secondary notification under section 64 of the Act will be required if

- i) the polymer characteristics cease to satisfy the criteria under which it has been accepted as a Synthetic Polymer of Low Concern, or
- ii) the method of use changes in such a way as to greatly increase the environmental exposure of the notified polymer, or
- iii) if additional information becomes available on adverse environmental effects of the polymer, or
- iv) the polymer is to be used in herbicide formulations intended for direct application to water, or
- v) any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

#### 16. REFERENCES

NOHSC (1991). Draft National Code of Practice for Spray Painting. Canberra, Australian Government Publishing Service.

NOHSC (1994). National Code of Practice for the Preparation of Material Safety Data Sheets [NOHSC:2011(1994)]. Canberra, Australian Government Publishing Service.

NOHSC (1999a). List of Designated Hazardous Substances [NOHSC:10005 (1999)]. Canberra, Australian Government Publishing Service.

NOHSC (1999b). Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(1999)]. Canberra, Australian Government Publishing Service.

NOHSC (1999c). National Reference Document for Spray Painting. Canberra, Australian Government Publishing Service.

NOHSC (1995). Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment, [NOHSC:1003(1995)]. Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards. Canberra, Australian Government Publishing Service.

Standards Australia (1987). Australian Standard 2919-1987, Industrial Clothing. Sydney, Standards Association of Australia.

Standards Australia (1990). Australian Standard 3765.2-1990, Clothing for Protection against Hazardous Chemicals Part 2 Limited protection against specific chemicals. Sydney, Standards Association of Australia.

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Standards Australia (1994). Australian Standard 1668.2, Mechanical Ventilation and Air Conditioning Code Part 2 - Ventilation Requirements. Sydney, Standards Australia.

Standards Australia/Standards New Zealand (1992). Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994). Australian/New Zealand Standard 1715-1994, Selection, Use and Maintenance of Respiratory Protective Devices. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

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Standards Australia/Standards New Zealand (1994). Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1995a). Australian/New Zealand Standard 4114.1-1995, Spray painting booths - Design, construction and testing. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1995b). Australian/New Zealand Standard 4114.2-1995, Spray painting booths - Selection, installation and maintenance. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1998). Australian/New Zealand Standard 2161.2-1998, Occupational protective gloves, Part 2: General requirements. Sydney, Standards Association of Australia.

# **Attachment 1**

The Draize Scale for evaluation of skin reactions is as follows:

Erythema Formation	Rating	Oedema Formation	Rating
No erythema	0	No oedema	0
Very slight erythema (barely perceptible)	1	Very slight oedema (barely perceptible)	1
Well-defined erythema	2	Slight oedema (edges of area well-defined by definite raising	2
Moderate to severe erythema	3	Moderate oedema (raised approx. 1 mm)	3
Severe erythema (beet redness)	4	Severe oedema (raised more than 1 mm and extending beyond area of exposure)	4

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

# **CORNEA**

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

## **CONJUNCTIVAE**

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

# IRIS

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