

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION  
AND ASSESSMENT SCHEME**

**FULL PUBLIC REPORT**

**PERFLUOROALKYL SUBSTITUTED POLYURETHANE**

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 Arts, Sport, the Environment and Territories and the assessment of public health is conducted by the Department of Health, Housing and Community Services.

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Director

Chemicals Notification and Assessment

**FULL PUBLIC REPORT****PERFLUOROALKYL SUBSTITUTED POLYURETHANE****1. APPLICANT**

3M Australia Pty Ltd, 2 - 74 Dunheved Circuit, St Mary's NSW  
2760.

**2. IDENTITY OF THE CHEMICAL**

**Name:** Perfluoroalkyl substituted polyurethane

**Molecular weight:**

**Number-average molecular weight:** approx 3000

**Method of detection and determination:**

UV/visible spectral data may be used to detect and determine the notified chemical.

**3. PHYSICAL AND CHEMICAL PROPERTIES**

**Appearance at 20°C and 101.3 kPa:** hard, ivory coloured solid

**Melting Point/Boiling Point:** 40 - 44°C

**Specific Gravity/Density:** 1,370 kg/m<sup>3</sup>

**Water Solubility:** 1.5-4.7 g/L at 20°C

**Partition Co-efficient:**  $p_{ow}$  0.007  
(n-octanol/water)

**Hydrolysis as a function of pH:** Not provided

**Dissociation Constant:** estimated at approx  $pK_a$  = 5 on basis of similar compounds

**Flash Point:** >95°C

**Flammability Limits:** not flammable

**Pyrolysis products:** at temperatures above 350°C thermal decomposition products include toxic products such as oxides of nitrogen, carbon monoxide, sulphur dioxide, hydrogen cyanide and hydrogen fluoride.

**Autoignition Temperature:** not flammable and will not sustain combustion

**Explosive Properties:** not explosive

**Reactivity/Stability:** not reactive

**Particle size distribution:** range - 35% > 1µm  
median (of emulsion) ~.1µm

Vapour pressure measurement was considered not appropriate as the polymer is a hard, non volatile substance as indicated by a constant amount of solids at elevated temperature (>100°C).

No data were provided for hydrolysis on the grounds that it is difficult to measure for a mixture of polymers such as the notified substance. The polymer contains potentially hydrolysable linkages, for example, polyurethanes which are prone to attack by acids and bases (1). It is unlikely that the polymer would hydrolyse under environmental conditions such as are found in sewers where the pH of the water may range from 6 to 10 and it is unclear whether the product containing the polymer will be discharged to the sewers.

No data were provided for adsorption/desorption on the grounds that it is not appropriate for a polymer with a nAMW of 3000. The lowest nAMW polymer is estimated to be 1500 and less than 1% species are below molecular weight 500 as residual monomers. The permeability of the soil would be restricted by this type of polymeric material and no meaningful results could be obtained. The company also states that its experience with many similar fluorochemical polymers indicate that it is expected that this substance would not be absorbed onto soil.

No data were provided for the dissociation constant on the grounds that only a small portion of the material would be expected to dissociate in water. The company expects that the dissociation constant of this portion to be typical of other organic aliphatic carboxylic acids ( $pK_a \sim 5$ ).

#### **4. INDUSTRIAL USES**

The notified chemical will be imported into Australia as a component in a preparation for use in the treatment of polypropylene fibres in the carpet industry.

Products containing the notified chemical have been in use in the US for a period of six years without reports of adverse health effects.

#### **5. PURITY**

The purity of the polymer is >90%. The hazardous impurities are at <1% and at these levels can be considered non-hazardous.

#### **6. OCCUPATIONAL EXPOSURE**

The notified chemical will be imported in ready for use form. Exposure during transport and storage will be minimal under normal circumstances. The substance will be applied to polypropylene fibres prior to being stretched, texturized, cut and baled. Losses of <1% are expected during these processes and exposure is therefore expected to be low.

The bales are shipped to yarn manufacturers where the fibres are made into yarn, heat set at temperatures of 190-200°C and tufted into carpet.

#### **7. PUBLIC EXPOSURE**

The polymer will be part of a product to be used as a component of spin finish lubricants in the manufacture of polypropylene fibres to impart oil and water repellency properties to carpet fibres. It is stated that the material solids will make up approximately 2% of the spin finish lubricants or approximately 10% of the solids.

A worst case estimate of product waste is that 18kg polymer/year could be discharged to sewer but may also be recovered and disposed of through a waste disposal company. Carpets coated with the substance are likely to be eventually sent to landfill.

No special transport facility has been indicated.

Public exposure to the substance is primarily limited to its presence in finished carpet.

## **8. ENVIRONMENTAL EXPOSURE**

### **8.1 Release**

When the fibres are treated with the product to impart water repellency, the main source of product waste will be generated from the cleaning of equipment at the yarn spinners. The company states that the worst case estimate would be 18 kg polymer/year on an anticipated annual usage of 9000 kg product per year in Australia. The polymer constitutes 20% of the product. The company also states the customer who will be using this product recovers this waste and disposes of it through a reputable waste disposal company according to EPA requirements. It is unclear whether any will be discharged to sewer, either before or after treatment.

No significant losses are expected to occur in other phases of carpet manufacture although some of the chemical will be disposed of on carpet and fibre scrap. The concentration of the polymer on the fibre will be 500 ppm.

### **8.2 Fate and Exposure Level**

A 20 day biological oxygen demand (BOD) determination gave a BOD value of "nil". This result indicates the polymer is not readily biodegradable.

The notifier states that under normal environmental conditions the substance would be expected to remain intact for a long period of time. Fragmentation of the polymer into smaller units would take place eventually but the chemical structure of the smaller units and the time required for fragmentation are not known. After fragmentation has occurred, those fragments made of

alkyl hydrocarbon of amide groups are likely to be degraded by microorganisms rather quickly.

The notifier also states that the loss of monomers from this polymer is highly unlikely as it is a very stable and not readily biodegradable polymer. The temperature (190-200°C) at which the product is applied is below the temperature at which normal thermal degradation might be anticipated. At 370-530°C the polymer degrades to CO, H<sub>2</sub>O, NO<sub>x</sub>, SO<sub>2</sub>, HCN and HF.

The major entry of the notified substance to the environment is when cleaning of equipment at the yarn spinners may result in wastewater containing the polymer entering the sewers of Melbourne. The frequency of cleaning and the amount of polymer entering the sewer after a cleaning event is not clear. However, the amount of polymer that could enter a sewer per annum is low (18 kg in a worst-case situation). It would appear unlikely the polymer would undergo significant microbial or chemical degradation in the sewerage system. The structure of the polymer suggests it may undergo hydrolysis but it is unclear whether this would occur under environmental conditions. Three treatment systems are combined throughout the course of a year at the Werribee treatment complex: land filtration in summer and grass filtration and lagoon treatment in winter (2). Its most likely fate would appear to be settling out over the land where it is likely to undergo microbial degradation as the polymer contains linkages such as the ester and amide which would be expected to be vulnerable to microbial cleavage in the soil.

The polymer is unlikely to bioaccumulate in biological systems due to its high molecular weight, relatively high water solubility and low  $p_{ow}$ .

Based on the characteristics to polyurethane polymers applied to carpet fibres, once the polymer has bonded to the carpet fibres it is unlikely to move off the surface. Little to none of the chemical is expected to be removed in the normal life time of the carpet.

The notifier states that the substance, which may eventually be sent to a landfill with the carpet material on which it was coated, is expected to remain in the landfill for long periods. Based on its structure, hydrolysis or biodegradation of this material is expected to be very low or negligible.

## **9. EVALUATION OF TOXICOLOGICAL DATA**

### **9.1 Acute Toxicity**

Toxicity test data was submitted on a formulation containing the notified chemical.

<b>Test</b>	<b>Species</b>	<b>Outcome</b>	<b>Ref</b>
Oral	Rat	LD <sub>50</sub> >5000 mg/kg (M&F )	(5)
Skin irritation	Rabbit	slightly irritant	(6)
Eye irritation	Rabbit	non irritant	(7)
Skin sensitisation	Guinea Pig	non-sensitising	(8)

#### **9.1.1 Oral Toxicity**

Five male and five female Sprague Dawley rats received 5000mg/kg of a product containing approx 20% of the notified chemical by gavage (5). No control group was used. Animals were observed for signs and symptoms at 1, 2.5 and 4 hours and daily for fourteen days. Body weights were recorded before dosing on day 7 and at the end of the study. After termination, a gross necropsy examination was carried out on all animals.

All animals appeared normal during the observation period. At necropsy all animals were normal except for one male which had diffusely red lungs with multiple white foci.

The oral LD<sub>50</sub> of the formulation was > 5000 mg/kg.

#### **9.1.2 Skin Irritation**

Approx 24 hours before treatment the hair was clipped from the backs and flanks of three male and three female New Zealand white rabbits (6). One application site was abraded immediately prior to the application of 0.5 ml of a formulation containing approx 20% of the notified chemical to that site and an unabraded site and the area covered by an occlusive bandage for 24 hours. At the end of the exposure time, the area was washed and dried and the skin examined for erythema and oedema 30 minutes and 48 hours after removal of the test substance.

Two animals showed minimal erythema at the abraded site 30 minutes after removal of the test substance. One of these also had minimal erythema at the application site with non-abraded skin. No signs of skin irritation were reported 48 hours after removal of the test substance.

The formulation is slightly irritating to the skin.

### **9.1.3 Eye Irritation**

Three male and three female New Zealand White rabbits received 0.1 ml of a preparation containing approx 20% of the notified chemical into one eye (7). The chemical was not rinsed out. The other eye served as an untreated control. Treated eyes were observed 24, 48 and 72 hours after treatment. Fluorescein was instilled at 72 hours to enhance the examination for corneal damage. No signs of redness, swelling or corneal damage were reported at any time interval. The chemical was judged to be nonirritating to the eye.

### **9.1.4 Skin sensitisation**

The sensitisation potential of the notified chemical was tested in a maximisation test in guinea pigs (8). Initial induction was carried out in ten guinea pigs by injection into a trio of clipped sites of:

Freund's adjuvant ;

test article 5% in saline, and

test compound 5% in Freund's adjuvant.

Topical induction using undiluted test compound occurred seven days later. A positive control group of five animals received 0.1% 2,4-dinitrochlorobenzene (DCNB).

At challenge, two weeks after the topical induction phase, a bandage which contained undiluted test compound (or 0.01% positive control) was applied to the induction site

After challenge all animals receiving the positive control showed erythema and were assessed as sensitised. No erythema or oedema



was noted at the induction site in any of the animals exposed to the test compound which was considered non sensitising.

## 9.2 Genotoxicity

### 9.2.1 Effect on *Salmonella typhimurium*

Compound T-3547 was tested (9) against the TA1535, TA1537, TA1538, TA98 and TA100 strains of *Salmonella typhimurium* at concentrations of 10, 50, 100, 500, 1000 and 5000 ug/plate with and without metabolic activation.

Dimethylsulfoxide (DMSO), 50 ul/plate, was used as negative control. the following positive controls were used:

TA1535	sodium azide	1 ug/plate	2-anthramine 2.5 ug/plate with and without metabolic activation
TA1537	9-aminoacridine	50 ug/plate	2-anthramine 2.5 ug/plate with and without metabolic activation
TA1538	a	5 ug/plate	2-anthramine 1 ug/plate with and without metabolic activation
TA98	a	5 ug/plate	2-anthramine 1 ug/plate with and without metabolic activation
TA100	sodium azide	1 ug/plate	2-anthramine 1 ug/plate with and without metabolic activation

Sodium azide, 9-aminoacridine, and all produced increased numbers of revertant colonies as did 2-anthramine after metabolic activation. Concentrations of up to 5000 ug/plate of the test substance did not increase colony counts.

The test substance/notified chemical was not mutagenic to *Salmonella typhimurium* in this test.

#### **9.2.2 Mitotic recombination in *Saccharomyces cerevisiae***

A preparation containing approx 20% of the notified chemical was tested (9) for activity in producing mitotic recombination in *Saccharomyces cerevisiae*, strain D3. Cultures were incubated at 30°C for 4 hours in concentrations of 0.05, 0.1, 0.5, 1 and 5% (w/v). DMSO served as the negative control with and without metabolic activation.

Other controls were sterigmatocystin 0.005% (w/v), with and without metabolic activation, and 1,2,3,4-diepoxybutane, 0.025% (w/v).

1,2,3,4-diepoxybutane and sterigmatocystin with metabolic activation produced greatly increased numbers of mitotic recombinants. The test compound did not produce any increase in mitotic recombinants with or without metabolic activation. The test compound containing the notified chemical was not recombinogenic in *Saccharomyces cerevisiae*.

#### **9.4 Overall Assessment of Toxicological Data**

The polymer has an average number molecular weight >1000. Under the *Industrial Chemicals (Notification and Assessment) Act 1989*, toxicology data is not required. Some toxicology studies were submitted on a formulation containing the notified chemical. The formulation had an oral LD<sub>50</sub> >5000 mg/kg. It was very slightly irritating to the skin, nonirritant to the eye and did not cause skin sensitisation in guinea pigs. It was not mutagenic towards *Salmonella typhimurium* or recombinogenic in *Saccharomyces cerevisiae*.

## **10. ASSESSMENT OF ENVIRONMENTAL EFFECTS**

The notifier has provided results of a study on the acute toxicity (96 hour) of the product containing 21% polymer to Fathead Minnows. The product was not miscible with water. The study recorded a result of a LC50 greater than 1000 mg.L<sup>-1</sup>. This result indicates that the product and the polymer is not toxic to fish.

The notifier also provided results (full report not provided) of an activated sludge respiration inhibition test of the product. At 30 minutes and at 3 hours the EC50 was greater than 1000 mg.L<sup>-1</sup>. The results indicate that the product and the polymer is not toxic to microorganisms found in sewage sludge.

The polymers high molecular weight (nAMW > 1000) indicates that it is unlikely to cross biological membranes. As no ecotoxicological data is required for polymers of nAMW > 1000, the toxicity data provided are adequate.

## **11. ASSESSMENT OF ENVIRONMENTAL HAZARD**

The environmental hazard of the polymer is likely to be low as the wastewater from the yarn spinning factory sites containing the polymer will be discharged into metropolitan sewerage systems. As a worst case situation 18 kg of the polymer could enter the sewerage system of Melbourne each year. The concentration of the polymer in the sewer stream is unknown but is expected to be low (in the order of ppm). Based on an average daily flow rate of 500 ML at Werribee treatment complex (2) the concentration of the polymer will be further diluted (in the order of ppb) when it passes through Werribee.

The disposal of carpet containing the polymer is unlikely to present a hazard to the environment as the polymer is likely to remain with the carpet fibres.

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

The compound appears to be of low oral toxicity, to be minimally irritating to the skin, nonirritating to the eye and a nonsensitiser. It was nonmutagenic *in vitro*. It is stable. Vapour pressure is low. Industrial use is at temperatures of approximately 200°C, well below that at which thermal

decomposition occurs (350°C). Thus, the intrinsic hazard of the polymer is low and both public and occupational exposure is expected to be low as a result of which risks of adverse health effects are expected to be minimal.

There are possible hazards from decomposition products in a fire. Emergency services should wear appropriate protective equipment.

### **13. RECOMMENDATIONS FOR THE CONTROL OF PUBLIC AND WORKER EXPOSURE**

To minimise public and worker exposure to perfluoroalkyl substituted polyurethane the following guidelines and precautions should be observed:

- . precautions in the use of products containing perfluoroalkyl substituted polyurethane should be dictated by other ingredients present in the formulation.
- . areas where perfluoroalkyl substituted polyurethane or products containing it are being used should have good general ventilation or local exhaust ventilation.
- . in case of fire, emergency services should wear protective clothing conforming to Australian standards (10, 11, 12)
- . those working with perfluoroalkyl substituted polyurethane or products containing it should have access to MSDS.

### **14. MATERIAL SAFETY DATA SHEET(S)**

The Material Safety Data Sheet (MSDS) for perfluoroalkyl substituted polyurethane was provided in Worksafe Australia format. (13)

### **15. REQUIREMENTS FOR SECONDARY NOTIFICATION**

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification of perfluoroalkyl substituted polyurethane shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

## 16. REFERENCES

- (1) Schnabel W., (1981) in Polymer Degradation, Principles and Practical Applications pp 179-183.
- (2) Annual Report of the Board of Works (1990), Victoria.
- (3) RTECS: Registry of Toxic effects of Chemical Substances: US National Institute of Occupational Health and Safety (NIOSH).
- (4) Exposure Standards for Atmospheric Contaminants in the Occupational Environment. Guidance Note [NOHSC: 3008 (1991)]; National Exposure Standards [NOHSC: 1003 (1991)], 3rd Edition, October 1991.
- (5) Acute Oral Toxicity - Method , Summary, Pathology. Data on File, 3M, St Paul, Minnesota, USA.
- (6) Primary Dermal Irritation Method, Summary. Data on File, 3M, St Paul, Minnesota, USA.
- (7) Primary Eye Irritation -Method, Summary. Data on File, 3M, St Paul, Minnesota, USA.
- (8) Sensitisation study with T-2547 in albino guinea pigs. Data on File, 3M, St Paul, Minnesota, USA.
- (9) In vitro microbiologies assays of 3M Company's compound T-3547. Data on File, 3M, St Paul, Minnesota, USA.
- (10) Australian Standard 1337-1984 *Eye Protectors for Industrial Applications*, Standards Association of Australia Publ, Sydney 1984.
- (11) Australian Standard 2161-1978 *Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves)*, Standards Association of Australia Publ, Sydney 1978.
- (12) Australian Standard 1715-1991 *Respiratory Protective Devices*, Standards Association of Australia Publ, Sydney 1978.
- (13) Guidance Note for Completion of a Material Safety Data Sheet. [NOHSC : 3001 (1991)], 3rd Edition, October 1991.