File No PLC/504

17 February 2006

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Fluoroacrylate Modified Urethane

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Director
NICNAS

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1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
3M Australia Pty Ltd (ABN 90 000 100 096)
2-74 Dunheved Circuit
St Marys NSW 2760

NOTIFICATION CATEGORY
Polymer of Low Concern

EXEMPT INFORMATION (SECTION 75 OF THE ACT)
Chemical Name
Other Name
CAS Number
Molecular and Structural Formula
Means of Identification
Number average molecular weight
Weight-average molecular weight
Weight percentage of polymer species with MW < 1000 and MW < 500
Charge Density
Polymer Constituents
Residual Monomers/Impurities
Reactive Functional Groups
Detailed Use
Import Volume
Site of Manufacture/Reformulation
Purity

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

Variation to the schedule of data requirements is claimed as follows:
Melting Point/Glass Transition Temperature
Water Solubility
Particle Size Distribution

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
None

NOTIFICATION IN OTHER COUNTRIES
United States (2004)

2. IDENTITY OF CHEMICAL

MARKETING NAME(S)
3M Brand Protective Material

3. COMPOSITION

PLC CRITERIA JUSTIFICATION

Criterion	*Criterion met (yes/no/not applicable)*
Molecular Weight Requirements	Yes
Functional Group Equivalent Weight (FGEW) Requirements	Yes
Low Charge Density	Yes
Approved Elements Only	Yes
Stable Under Normal Conditions of Use	Yes
Not Water Absorbing	Yes
Not a Hazard Substance or Dangerous Good	Yes

The notified polymer meets the PLC criteria.

4. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

The notified polymer will be imported in 200 L and 1000 L closed-head polypropylene drums as a liquid dispersion at a concentration of < 20%.

MAXIMUM INTRODUCTION VOLUME OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

Year	*1*	*2*	*3*	*4*	*5*
Tonnes	<20	<20	<20	<20	<20

USE

Fabric protector for use by industrial plants. The treated fabric to be used in the fabrication of furnishing and carpet wares.

5. PROCESS AND RELEASE INFORMATION

5.1. Operation Description

The notified polymer will not be manufactured in Australia. The notified polymer will be imported by sea as a component of a liquid dispersion (<20% notified polymer). The imported drums containing the notified polymer will be transported by road from the wharf to a bunded warehouse for storage prior to distribution to industrial end-users plants Australia-wide, as required.

The fabric protection process, which incorporates a curing/heat-setting step, is a highly automated continuous operation (as described below) that occurs after the textile fabric is woven and processed. The non-mist coating process is intended to give an even distribution of the coating (containing <1% notified polymer) across the textile substrate. The notified polymer will principally be used in carpet protection (80-95% import volume) with the remainder for coated textiles (5-20% import volume).

Importation, storage, transport and distribution

Following importation, warehouse or stores personnel will receive and store the imported product prior to consignment. The product will be typically handled in the warehouse by forklift handling of pallets or drums.

Carpet Application

The imported product will be mixed (as described below) at the plant(s) either manually or by means of an automated metered dosing system to produce a foam application (containing <1% notified polymer) for use in an airless spray method.

Manual mixing

At the application plant(s) ‘mix kitchen’ (a dedicated wet area), plant workers will manually decant the imported product from the drum into a pail typically by means of a bung and tap and assisted by mechanical drum lifters and trolleys. The decanted treatment dose is manually added to a blending container for dilution and mixing with a foaming agent via a mechanical stirrer. Plant workers will transfer via trolley the blending container containing the resulting solution (containing <1% notified polymer) to the foam applicator machine where dedicated transfer lines and pumps will be attached to charge and supply the foam applicator heads. Drum, pail, blending container and application machine rinsate is used to prepare succeeding applications.

Automated mixing

At the application plant(s), plant workers will transfer the imported product and a foaming agent by means of an automated metered dosing and dilution system directly to the foam applicator machine. Using the system's dedicated transfer lines and pumps, the resulting applicator foam (containing <1% notified polymer) is used to charge and supply the foam applicator heads. If washing is necessary, residual material left in the drums or transfer lines is flushed mechanically with water and the washing is used for subsequent applications.

PUDDLE foam process

At the application plant(s), reels of textile substrate for treatment are mechanically loaded onto the automated applicator machine. Under local exhaust ventilation and via means of rollers, the textile substrate is feed at a pre-determined feed rate thru a coating, curing and drying processes.

The applicator machine applies the foam (containing <1% notified polymer) typically to a moist textile substrate at a moisture add-on of 10% of yarn weight using either a line of spray or PUDDLE foam heads positioned above and close to (within inches of) the fabric surface. Due to the nature of the applicator process, no mist is used or formed nor air automisation of the spray occurs.

During spray application, any downward over-spray is wholly collected in an under-tray and the lees pumped by dedicated transfer lines back to the application heads for re-use. Any sideway-spread of the foam across the fabric substrate as a result of PUDDLE foam application is contained by foam guards (barriers) on either side of the fabric. Following application, top and bottom rollers press the foam into the textile substrate (without seepage to the under surface) prior to feeding the treated textile substrate into a heat-setting chamber/oven (110-120°C) to cure and dry the coated fabric.

A sample of the imported product and or applicator foam may be taken for quality testing prior to use. It is anticipated that industrial plant(s) may return empty import containers to the supplier for re-filling. Textile substrates coated will be characteristically trimmed and sized according to customer needs and be warehoused at the application plant(s) prior to distributed to industrial customers Australia-wide. Samples of the coated textile substrates are typically sent off-site for testing the performance of the coating.

All workers involved in handling the commercial product containing the notified polymer and the application solution will wear personal protective equipment including safety glasses, impervious gloves, protective clothing and respiratory protection, if necessary. All workers will have access to the Material Safety Data Sheet.

Textile Application

Mixing

While the notifier provides no specific details, it is expected that mixing operations will be similar to that described above.

Padder and Lick-roller process

A padder comprises of a trough contain a treatment solution comprising of the notified polymer with auxiliary chemicals. Textiles are 'dipped' via a continuous and automated roller process into the trough to collect the coating solution, followed by a roller-squeeze process (i.e., a dip>squeeze>dip>squeeze process) prior to drying the coated textile in a curing oven. The rollers assist in the penetration of the notified polymer into the textile substrate and reduce the wet-add-on to around 50-70%. Any excess coating solution is squeezed from the textile down into the trough and is filtered and stored for future application. As such, there is no anticipated release of excess coating solution to the sewer.

In the lick roller process, the notified polymer is applied by means of an injector slot and is distributed across the textile surface by a fixed doctor blade (similar to a wiper) or fixed roller. The coating solution is fed in a foam form, using low moisture (approximately 20% wet-add-on) to hasten the drying and curing process. Consequently, the foamed treatment solution stays on the textile surface during application. An optional air cushion may be used to support the fabric web during the application. The coating is fixed to the textile substrate in the drying oven (140-180°C). The remaining solution is stored or subsequent use.

End Use –Fabrication
Textile substrates coated with the notified polymer will be transported Australia-wide for use in a variety of furnishing and carpet wares.

6. EXPOSURE INFORMATION

6.1. Summary of Occupational Exposure

There is the potential for dermal and accidental ocular exposure to the notified polymer by fabric-treatment workers during the mixing and application operation as a result of inadvertent drips, splashes and spills during manual decanting and addition of the imported product to the blending container (<20% notified polymer) and when connecting and disconnecting pipelines and transfer hoses and operating valves and pumps on the applicator machine (<1% notified polymer).

Fabric-treatment workers are not expected, however, to have significant contact with the applicator foam during the automated application process unless manual intervention is required. The concentration of the notified polymer in the foam coating is low (<1%) and the design of the applicator machine is such that any inadvertent exposure to the notified polymer should be low.

Given the molecular weight of the notified polymer, absorption through intact skin is not expected. On the basis of the high molecular weight of the notified polymer and hence expected negligible vapour pressure, inhalation exposure is not expected. Mixing, application, curing and drying operations occur under local exhaust ventilation - with curing and drying occurring at temperatures slightly above the glass transition temperature. Such engineering controls further limit any potential for inhalation exposure. Due to the non-mist/airless spray method and close applicator process, inhalation exposure to the notified polymer via aerosol formation is not expected.

Waterside, warehouse and transport/distribution workers are unlikely to be exposed to the notified polymer (<20% notified polymer) unless the packaging is breached. End-use textile fabricators, retail workers on-selling treated textile/fabric wares and quality control personnel involved in testing coated samples are not expected to be exposed to the notified polymer. This is because after application and once dried, the notified polymer is bound into an inert matrix and hence unlikely to be bioavailable.

6.2. Summary of Public Exposure

The notified polymer is intended only for use in industry. The notified polymer will not be sold to the public except in the form of finished fabric wares. Members of the public may come into contact with fabric wares coated with the notified polymer.

6.3. Summary of Environmental Exposure

6.3.1. Environmental Release

The notified polymer will principally be used in carpet protection (80-95% import volume) with the remainder for coated textiles (5-20% import volume). The notified polymer applied to carpets or textiles would be required to be dried and cured at temperature in excess of 120ºC. At this temperature, the notified polymer will melt and fix to the fibre both by physical and chemical bonding via trans-amidation if fibres contain amide groups, or simply by hydrogen bonding via fluorine atoms.

The process for the use of notified polymer on textiles could be padding via nip-rolls and lick-rolling. A padder comprises of a trough containing the notified polymer. The rollers assist the notified polymer to penetrate the textile substrate and reduce wet-add-on to around 50-70%. Any excess from squeezing will run down to the trough, be filtered and stored for future application. Therefore, there is no anticipated release of the excess notified polymer to the sewage from its use on textile processing.

Based on the high level life cycle estimates during carpet manufacture, the notifier indicates that 7% will be released using topical spray application of which 1% will go to air and 6% to the on site sewage treatment works. Another 3% will be landfilled as carpet trimmings. Carpet mills are required by law to have an in-house industrial waste treatment facility. The process involves flocculation, separation and drying and the solids disposed as per local regulation. The perfluorinated polymer is not water soluble once outside of the emulsified product, and it is predicted the notified polymer would partition to the sludge in a waste water treatment facility. The ultimate fate of the sludge containing the notified polymer would be landfilled.

The foam application method is used in the lick rolling for textile and on carpet, as it creates no waste due to the absence of misty spray. The foamed product is contained by guard plates and thus the entire product is deposited onto the carpet. The foam applicator is rinsed with water and the wash water is to be collected for preparing next chemical mix to minimise waste as the chemical is considered to be expensive.

The notifier estimates that the loss of fluorinated carpet treatments is 30% during typical steam cleaning. This is not because of water solubility of the polymer but rather the physical removal of the polymer during the cleaning process. The notifier indicates that over time the notified polymer may, through mechanical action, slowly wear off the carpet surface and be either vacuumed away or be walked-off onto surrounding ground. It is estimated that up to 67% of the polymer may be extracted from the carpet through steam cleaning, vacuum and walked off over a period of 12 years.

At the end of their useful life, carpets and textiles to which the notified polymer is bound will be disposed of in landfill or incinerated (where 18% will be left in carpet). Therefore, a majority of the notified polymer will be released into the environment during its use on carpet.

Similar estimates are not available for textile use but again releases from cleaning etc may be expected prior to landfill of discarded textiles.

6.3.2. Environmental Fate

If incinerated, the polymer would be rapidly destroyed and converted to water vapour and oxides of carbon, sulphur and nitrogen and hydrogen fluoride. On disposal to landfill, the hydrocarbon and nitrogen containing portions of the polymer are likely to be slowly degraded by biotic and abiotic processes. Any polymer entering receiving waters at a sewage treatment plant is likely to become associated with the sludge and sediment compartment given the expected low water solubility. In time, the hydrocarbon moiety may become assimilated with the organic phase, while the fluorinated moiety will remain.

The fluorocarbon moiety is unlikely to be susceptible to biodegradation (Remde and Debus, 1996). This is understandable, in view of the electronegativity of fluorine and the great strength of the carbon-fluorine bond. Perfluorocarbons are more thermally stable than their corresponding hydrocarbon analogues. In particular, perfluorocarboxylic acids and perfluoroalkane sulfonic acids are considered the most thermally stable fluorinated surfactants. In addition to thermal stability, perfluorinated hydrocarbons are stable against degradation by acids, bases, oxidants and reductants (Moody and Field, 2000). Fluorinated carboxylic acids can undergo hydrolytic defluorination, reductive defluorination, and decarboxylation. To date, however, significant defluorination has only been observed for hydrolytic attack of monofluorinated carboxylic acids, and compounds of more than one fluorine atom per carbon atom are generally recalcitrant.

The notifier has provided degradation studies on the US carpet urethane polymer but not on the urethane polymer being notified in Australia. The results show no degradation from hydrolysis or biodegradation under the conditions of studies. There are some significant differences in structure between the two polymers and the notifier indicates that the notified polymer will ultimately degrade with the ultimate degradation product as perfluorobutane sulfonate (PFBS), which has been shown not to bioaccumulate. Due to the importance of these results these tests are assessed in detail below.

7. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa	Milky white aqueous emulsion
Melting Point	Not applicable as only imported as a liquid dispersion. Boiling point is similar to water.

Glass Transition Temp	110°C
Specific gravity	1.1
Water Solubility	No result provided. The product is a water based emulsion which contains 10-20% of the fluorinated urethane. Therefore, the product is soluble because it is emulsified, but the fluorinated urethane is not water soluble outside the emulsion. While the notified polymer contains a small amount of hydrophilic functionality, the major hydrophobic portion would outweigh this. It is expected to have low water solubility.
Dissociation Constant	The notified polymer contains no dissociable functional groups.
Particle Size	Not applicable. The polymer will be imported only in a liquid dispersion.
Reactivity	Stable under normal environmental conditions
Degradation Products	None under normal conditions of use.

Hydrolysis as a Function of pH

METHOD OPPTS 835.2110 “Hydrolysis as a function of pH”

Compounds	*$t_{1/2}$ of formation (years at 25°C)*
N-MeFBSE Alcohol	≥32.2
N-MeFBSA	≥65.1
FBSA	≥62.2
PFBS	≥62.4
PFBA	≥44.5

Remarks The related urethane polymer was suspended into two sets of buffers of pHs 4, 7 and 9 at a concentration of 19.8 ppm. The first set was cooled to 0°C and the second set was allowed to react with the buffer solutions for 6 days at 50°C. Both buffer sets were analysed by HPLC/MS for perfluorobutanesulfonate (PFBS), perfluorobutyric acid (PFBA), 2-(N-methylperfluorobutanesulfonamido) ethyl alcohol (N-MeFBSE Alcohol), 2-N-methylperfluorobutanesulfonamide (N-MeFBSA) and perfluorobutanesulfonamide (FBSA). The results indicate that the related urethane polymer is unlikely to hydrolyse in the environmental pH range of 4-9, despite the presence of the hydrolysable functionalities.

TEST FACILITY 3M Environmental Laboratory (2003)

8. HUMAN HEALTH IMPLICATIONS

8.1. Toxicology

No toxicological data were submitted.

The breakdown product of the notified polymer, perfluorobutane sulfonate (PFBS), has been assessed as the potassium salt by NICNAS (NICNAS 2005). PFBS is expected to be persistent.

PFBS is rapidly excreted in animals (monkeys) by the kidneys with up to 87% excreted in the urine within 24 hours post dosing. No difference is observed between male and female animals. The notifier is currently developing urinary data for PFBS in potentially exposed workers. This study has not been finalized and was not provided during this assessment. Studies show PFBS is highly bound to human albumin with indications of a saturated binding to albumin in serum and negligible binding to the other liver-manufactured proteins gamma globulin, alpha globulin, fibrinogen, alpha-2-macroglobulin, transferrin and beta lipoproteins.

The mammalian (animal) toxicology of potassium PFBS shows low acute oral and dermal toxicity. No information on acute inhalation toxicity is available. PFBS is not irritating to skin. Potassium PFBS is found to be an eye irritant with the potential to cause severe eye damage. There is no evidence of skin sensitisation.

A 90-day study in rats (0, 60, 200 and 600 mg/kg bw/day) indicates no serious damage to health by prolonged exposure to potassium PFBS at doses up to 200 mg/kg bw/day. The target organs in rats following repeated exposure are the kidney and stomach with treatment-related microscopic changes observed in the kidneys and stomach of the male and female rats. However, histopathological examination of the kidney by an independent expert reported that no consistent changes were seen in the kidneys and the renal effects were not secondary to treatment.

The results of two in vitro studies and a chromosomal aberration test show no evidence of mutagenicity due to potassium PFBS. Animal data to date does not indicate potassium PFBS is a developmental toxin nor a substance toxic to reproduction, fertility or lactation.

A pre-natal developmental toxicity in rats (0, 100, 300 and 1000 mg/kg bw), shows a No Observed Adverse Effect Level (NOAEL) of 300 mg/kg bw/day for maternal toxicity based on reduced body-weight gains and feed consumption at 1000 mg/kg bw/day and a NOAEL of 1000 mg/kg bw/day for developmental toxicity.

In accordance with the NOHSC Approved Criteria for Classifying Hazardous Substances (NOHSC, 2004), potassium PFBS is classified “Hazardous” with the following risk phrases: R36 – Irritating to Eyes.

Potassium PFBS does not meet all the criteria of the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP).

8.2. Human Health Hazard Assessment

The notified polymer meets the PLC criteria and can therefore be considered to be of low hazard.

9. ENVIRONMENTAL HAZARDS

9.1. Ecotoxicology

The following toxicological studies were submitted:

9.1.1. Ready biodegradability

TEST SUBSTANCE	Notified polymer
METHOD	OECD Closed Bottle Test 301 D (Modified)
Inoculum	Polyseed commercial mix
Exposure Period	28 days
Auxiliary Solvent	None
Analytical Monitoring	COD

Remarks - Method	The notified polymer was tested at concentrations of 133, 330, 670 and 1670 mg/L. Duplicate tests were performed on medium blank, seeded blank, reference standard (glucose/glutamic acid solution), toxicity checks and each test concentrations. Temperature, pH and dissolved oxygen were measured over a period of 28 days.

RESULTS

	*Test substance**
Day	*Mean % Degradation*
5	1
10	1
20	3
28	3

* Although the solubility of the test substance is expected to be low, it was found to be >100 g/L in the test media.

Remarks - Results	The test substance was considered not biodegradable with 3% degradation observed after 28 days of exposure. 5 and 10 days reference biodegradability tests with glucose/glutamic acid were conducted and found to be within the acceptable limits. The test substance was found not inhibitory to the micro-organisms based on the toxicity check.
CONCLUSION	The test substance is considered not biodegradable.
TEST FACILITY	Era Laboratories Inc. (2004)

9.2 Inherent biodegradability

TEST SUBSTANCE	Analogue polymer
METHOD	Aspects of the USEPA Zahn-Wellens/EMPA Test (OPPTS 835 3200) and USEPA Modified SCAS (OPPTS 835 3210) were used
Inoculum	Sludge
Exposure Period	28 days
Auxiliary Solvent	None
Analytical Monitoring	HPLC/MS
Remarks – Method	The test substance was suspended into three mediums: Medium A (mineral salts medium and sludge), Medium B (mineral salts medium, sludge and antimicrobial agent) and Medium C (mineral salts medium and antimicrobial agent) After incubating these cultures with shaking for increasing intervals, study samples were prepared using solid phase extraction (SPE) and analysed by HPLC/MS. The predicted degradation products were measured rather than the direct measurement of the loss of the test substance.

RESULTS

Analyte	**Day 0 (%)***	**Day 7 (%)**	**Day 14 (%)**	**Day 28 (%)**
N-MeFBSE Alcohol	0.631	<0.0169	<0.0169	<0.0847
N-MeFBSA-Acetic acid	0.0212	0.663	0.541	0.43
N-MeFBSA	<0.0484	0.0270	<0.0194	<0.0194
FBSA	<0.0202	0.0359	0.0736	0.0948
PFBS	<0.0220	<0.022	<0.022	0.0422
PFBA	<0.0447	<0.0447	<0.0447	0.183

* The % biotransformation is calculated using a theoretical amount of fluorine available in the initial dose of the test substance.

Remarks – Results	The results indicate that the test substance did not biodegrade significantly

over a 28 days period of exposure. The % degradation from the test substance to the predicted reference substances range from <0.0194 to 0.63%. From the table there is a possible trend of formation of the predicted products that may be attributed to the biotransformation of the test substance, particularly the last 3 products. However, the report indicates the presence of 0.5% N-MeFBSE-OH which may be responsible and concludes that the test substance did not biodegrade under the conditions of the test.

CONCLUSION The test substance is considered to be not inherently biodegradable. Whether this (and the hydrolysis test) conclusions would apply to the notified polymer is unclear as there are some significant structural differences.

TEST FACILITY 3M Environmental Laboratory (2003)

9.3 Effects results

Endpoint	*Result and Conclusion*
Fish Toxicity (Fathead Minnow; OECD 203)*	96 h EC50 >100 mg/L. Thus the test substance is considered not toxic to fish.
Daphnia Toxicity (*Daphnia magna*; OECD 202)*	48 h EC50 >100 mg/L. Thus the test substance is considered not toxic to Daphnia.
Algal Toxicity (*Selenastrum capricornutum*, OECD 201)	96 h EC50 >100 mg/L. Thus the test substance is considered not toxic to alga.
Inhibition of Bacterial Respiration (Activated sludge; OECD 209)	3 h EC50 >1000 mg/L. Thus the test substance is considered not toxic to micro-organisms.

* Only one concentration was tested. It is noted that the test solutions appeared as a slightly cloudy white solution for the entire exposure period for fish and Daphnia

All results were indicative of low hazard.

9.3.1. Discussion of observed effects

No mortality was observed for test substance and control over the entire exposure period for fish and Daphnia. No inhibition was observed based on cell density and growth rate for alga over a period of 96 h. As the test solutions remain cloudy over the test period for fish and daphnia, it is not clear what is the actual concentration of the test solutions. Therefore, these results should be treated with caution, though no aquatic toxicity may be expected up to the limit of water solubility.

9.2. Environmental Hazard Assessment

The results indicate that the notified polymer is not toxic at the nominal test concentration of 100 mg/L to fish, Daphnia and alga, indicative of low toxicity to the aquatic compartment.

10. RISK ASSESSMENT

10.1. Environment

The notified polymer is expected to have a low water solubility and is considered not readily biodegradable. Based on the proposed use of the notified polymer on carpets and textile, the notified polymer is not expected to be significantly discharged to sewage after the fixation process. This is due to the use of the foam application method and the re-cycle of the waste from washing and ‘dipping’. The notified polymer will be fixed to the fibre by chemical bonding via trans-amidation, or simply by hydrogen bonding via fluorine atoms. Consequently the notified polymer is unlikely to be exposed to the aquatic compartment in significant amounts.

The main environmental exposure would be from the use of the notified polymer on carpet as usage on textile is expected to be 10%. Based on the life cycle estimates from a carpet manufacture, 7% of the notified polymer will be released during topical spray application, 6% of which will enter the on site sewage works. It is expected that the released notified polymer, due to its expected low water solubility, will be partitioned to the sludge in the waste water treatment and will ultimately be landfilled. Therefore, on the basis of its low toxicity to aquatic organisms and its expected partition to sludge during waste water treatment, the notified polymer is unlikely to pose an aquatic risk during carpet manufacture.

The notifier has estimated that the loss of fluorinated carpet treatments is 30% during typical steam cleaning and that up to 67% of the polymer may be extracted from the carpet through steam cleaning, vacuum and walking off over a period of 12 years. At the end of their useful life, treated carpets and textiles will be disposed of in landfill or be incinerated (where 18% will be left in carpet). Therefore, steam cleaning will be the major pathway for the release of the notified polymer into the environment and the majority of the notified polymer will be dispersed during the lifetime of the carpet. In the environment eventual degradation to PFBS is expected to occur.

10.1.1 Current levels of PFBS in the environment

Perfluorooctane sulfonate (PFOS) has now been found in environmental samples all over the world and was formerly present in Scotchguard. The notified polymer will replace the PFOS component and contains the perfluorobutane sulfonate (PFBS) moiety. Compared to the higher homologues (C6 and greater), there has been very limited detection of PFBS in the environment, partly due to previous insensitive detection limits, and also probably due to low levels of use to date. The published data are summarised in the following table.

Levels of PFBS detected in the environment

Location	Result	Reference:
Japanese lakes and bays etc	Not detected in water, fish, birds and humans (insensitive detection limits, <7.6 to <151 ng/g in liver or ng/mL in blood)	Taniyasu et al. (2003)
Tokyo Bay, South China Sea and Sulu Sea	Apparently not detected (much more sensitive detection limits, = 3.8 ng/g)	Yamashita et al. (2004)
Mid Atlantic Ocean, Western, Central and Eastern Pacific Ocean	As above	Yamashita et al. (2004)
Canada, Toronto International Airport	0.0090 and 0.0077 µg/g (both close to the detection limit of 0.0038 µg/g = 3.8 ng/g,) in fish livers taken from 2 sites of a creek contaminated following an AFFF spill. Also detected in water samples collected separately, but not quantified	Moody et al. (2002)
United States		Schultz et al. (2004)
Naval Air Station Fallon, Nevada	Groundwater, ≤LOQ – 210 µg/L	
Tyndall Air Force Base, Florida	Groundwater, 10 – 144 µg/L	
Dutch Wadden Sea, situated in the Northern part of Netherlands	Although levels were low, PFBS could be detected in spleen samples of Harbor seals (other tissues analysed were kidney, liver, blubber, muscle with levels below the LOD of 1.49 ng/g wet weight). Concentrations varied between 1.7 and 3.3 ng/g w wt, with a mean concentration of 2.34 ng/g wet weight	Van De Vijver et al. (2005)
Selected homes in the city of Ottawa, Canada	Dust samples from 67 houses. PFBS was not detected in any of the samples.	Kubwabo et al. (2005)

In a recent publication (Taniyasu et al., 2003) PFBS was tested for in water, fish, birds and humans obtained from a number of locations in Japan, but it was not detected. However, the HPLC/MS/MS detection limits, ranging from <7.5 to <151 (ng/g in liver, wet wt or ng/mL in blood) seem rather insensitive compared with those for perfluorohexane sulfonate (PFHxS), which was either detected in about 33% of fish blood samples (maximum concentrations in blood and liver were 121 ng/mL and 19 ng/g wet wt) or had much lower detection limits (<7.6 ng/g in liver, wet wt or ng/mL in blood). It is unclear whether this reflects a much lower use level in the past.

The same authors (Yamashita et al., 2004) developed a much more sensitive assay using liquid chromatography-tandem mass spectrometry, which is able to analyse perfluorinated acids, including PFBS, PFOS and PFHxS down to the parts per quadrillion level. Marine water samples collected from a range of ocean environments (see Table above) were analysed for PFBS, but as opposed to the higher homologues, no detections were reported.

Moody et al. (2002) detected PFBS by LC/MS/MS only in two samples at concentrations of 0.0090 and 0.0077 µg/g (both close to the detection limit of 0.0038 µg/g = 3.8 ng/g, and therefore more sensitive than above) of fish livers taken from 2 sites (of the 6 tested) in a creek running beside an airport. By contrast PFHxS was detected in all samples, ranging from 0.011 to 0.29 µg/g. PFBS was not detectable either upstream or downstream of the site where an aqueous film forming foam (AFFF) had been spilt at this airport, in contrast to PFHxS where the levels were 0.046 and 0.29 µg/g respectively. Perfluoropentanesulfonate (PFPeS) was also detected at 4 of the 6 sites, though again levels were relatively low (range 0.0046 to 0.013 µg/g).

Perfluoroalkanesulfonates and perfluorocarboxylates are known to be present in AFFFs, as typified by PFOS levels being much higher (range 2.00 to 72.9 µg/g) at the eight sampling sites at this airport. Higher homologs and perfluorooctanoic acid were also detected.

Water samples were also analysed for perfluoroalkanesulfonates and perfluorocarboxylates by LC/MS/MS, but only levels of PFOS, PFOA and PFHxS were reported, with the latter at a maximum concentration of 134 µg/L. The paper notes other homologs were observed in water samples, including PFBS, but were not quantified.

Schultz et al. (2004) also used a direct injection, liquid chromatography tandem mass spectrometry (LC MS/MS) assay to quantify a suite of perfluoralkyl sulfonates (PFAS) and fluorotelomer sulfonate (FtS) surfactants in groundwater collected from two US military bases where fire-training activities using AFFF had been conducted. Levels of PFBS in ground water at the Naval Air Station Fallon, Nevada were $\leq$LOQ–210 µg/L, while they were 10–144 µg/L at Tyndall Air Force Base, Florida. These were in the same order or somewhat lower than the higher homologues. Total PFAS ranged from 0-1680 µg/L at the former and 273-3500 µg/L at the latter, which also had a total FtS content of 1100-14600 µg/L compared with none detected at Fallon (probably not used at this site). Total perfluorocarboxylic acids (PFCAs) were 0-7090 µg/L at Fallon and 0-298 µg/L at Tyndall.

Van De Vijver et al (2005) has reported for the first time on levels of longer chain PFCAs, together with some short chains PFAs, PFBS and PFBA in liver, kidney, blubber, muscle and spleen tissues of Harbor seals from the Dutch Wadden Sea. The Wadden Sea is a nursery and a feeding zone of prime importance for the seal population in the North Sea, and lies at the edge of the Northwest Europe and is an important pollution sink by atmospheric deposition or water in flow from highly industrialised countries in Northwest and Central Europe. It is claimed that this is the first time that PFBS could be found at detectable concentrations (2.3 ± 0.7 ng/g wet wt) in environmental samples. PFBS was only detected in spleen tissue. PFBS has not been shown to accumulate in biota and until present, no PFBS traces were confirmed in biota samples yet (see however, table above). The reason for this observation is unknown, but the low contamination level might be a result of the minor use of this compound in industrial applications so far.

In order to better understand the human exposure routes of perfluorinated compounds, levels of PFOS, PFOA, PFBS, PFHS and PFOSA in house dust samples were investigated from houses in Ottawa, Canada (Kubwabo *et al* 2005). The data revealed a correlation between the concentrations of PFCs and the percentage of carpeting in the house. The results indicate that older houses tended to have less carpeting, hence lower levels of these perfluorinated compounds in their dust. Among the samples from 67 houses PFOA, PFHS and PFOS had a much higher detection frequency (63, 85 and 67%, respectively) than PFOSA, which was detected in only 10% of the samples, while PFBS was not detected in any of the samples. The authors note the absence of PFBS may be explained by the fact that the perflurobutyl chemical component has only been recently introduced on the market as a building block molecule for surfactants.

10.1.2 Sources of perfluoralkyl substances in the environment

As noted above, levels of PFBS in the global environment currently appear to be very low, reported as at or below the limits of detection, except through contamination by fire-training activities using Aqueous Film Forming Foam (AFFF). Whether this situation will remain so if PFBS use increases, for example by its wide substitution in products that currently include perfluorooctane sulfonate (PFOS) or related higher homologues, is unclear.

The current information/hypotheses on how the higher homologues have become widely disseminated through the environment is briefly summarised below, followed by comments on possible implications for PFBS. Information is currently only available for these higher homologues since such chemicals have been the most widely used to date.

The vapour pressure and Henry's law constant of PFOS indicates it has very low volatility and therefore unlikely to enter directly into the atmosphere (Stock et al., 2004). It has been hypothesized that PFOS must therefore be globally distributed via more volatile, neutral airborne contaminants that undergo long-range transport and then degrade to yield the free acids.

Polyfluorinated sulfonamides are widely distributed throughout the North American troposphere with mean concentrations ranging from 22 to 403 pg/m^3. The dominant polyfluorinated contaminant is dependent on the sampling location (Stock et al., 2004).

For example, high mean concentrations of the polyfluorinated sulfonamide chemical N-methyl perfluorooctane sulfonamidoethanol (NMeFOSE) of 359 pg/m^3 were identified in the air of Griffin, Georgia which is located in the main carpet manufacturing and treatment area of the US. The authors hypothesise that the polyfluorinated sulfonamide probably enters the environment from carpet treatment products, many of which consist of fluorinated molecules linked to polymeric materials. It is possible that free chemical may be left in the carpet fibres. An alternative hypothesis is that the chemically-bound chemical NMeFOSE-is released from carpets due to chemical, physical, and/or biological degradation processes. Paper products were also suggested by Stock et al., (2004) as a possible source of polyfluorinated sulfonamides in air.

Support for the hypothesis of release from carpets comes from Shoeib et al., (2004) who measured NMeFOSE and the related polyfluorinated sulfonamide chemical N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE) in indoor and outdoor air. Mean indoor air concentrations for these were 2590 and 770 pg/m^3, respectively, and the ratios between indoor and outdoor air were 110 and 85, respectively. Shoeib et al., (2005) have recently published additional information confirming these results.

These findings have major implications for the substitution of PFOS containing compounds/polymers with PFBS containing chemicals/polymers in Australia. The lower molecular weight PFBS precursors would be expected to be more volatile and therefore more readily subject to long-range transport, before they break down to PFBS. While not bioaccumulative, PFBS is persistent, and levels would build up in environment, staying mostly in the water column due to the much higher water solubility compared with higher homologues.

10.1.3 Aquatic risk assessment

Of the PFBS-containing substitution products so far introduced into Australia, the proposed use on carpets for the notified polymer appears to be the most dispersive given the losses estimated during the carpet's life. Based on a 30% of the notified polymer released into sewage during steam cleaning, the PEC can be calculated based on the maximum usage volume of 20 tonnes with 90% of its usage on carpet. A calculated worst-case scenario daily PEC in the sewer effluent is 3.6 μg/L. In calculating the PEC, the following were assumed: (1) usage of the maximum import volume of 20 tonnes (0.3 X 0.9 X 20 tonnes) is evenly distributed over a 365 day period; (2) usage is nationwide, with a population of 20 million contributing 200 L of water per person per day to the sewer, (3) there is no adsorption or degradation in the sewer prior to release. Based on the aquatic toxicity end point (PNEC = >100 mg/L/100) of >1 mg/L, the Q value is calculated to be 3.6/>1000 = <<1. Therefore, there is unlikely to be an environmental risk in the aquatic compartment.

10.2. Occupational Health and Safety

On the basis of engineering controls such as the automated non-mist/airless foam spray and heat-curing process used, personal protective equipment worn by workers, low health hazard of the notified polymer, and low concentration of the notified polymer in the foam (<1% notified polymer), the OHS risk presented by the notified polymer is expected to be low. Furthermore, once the foam is dried and cured, the notified polymer is expected to be bound into an inert matrix and hence not expected to cross biological membranes and be absorbed.

The notified polymer may be present in formulations containing hazardous ingredients. If these formulations are classified as hazardous to health in accordance with the NOHSC Approved Criteria for Classifying Hazardous Substances, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

10.3. Public Health

The product containing the notified polymer is intended for use by industrial fabric treatment plants only and will not be sold to the public. Members of the public may make dermal contact with fabric treated with the notified polymer. However, the risk to public health will be low because the notified polymer the notified polymer is present at a low concentration (<1%) in the applied coatings and is cured and bound in an insoluble polymeric matrix coating and as such unlikely to be bioavailable.

Members of the public may be exposed to perfluorobutane sulfonate (PFBS) by means of secondary exposure via the environment as a result of degradation of the notified polymer. However, the risk to public health as a result of PFBS exposure is assessed as low based on the low toxicity of the breakdown product and the low predicted concentration of the notified polymer in the environment (See Section 10.1.3).

11. CONCLUSIONS – ASSESSMENT LEVEL OF CONCERN FOR THE ENVIRONMENT AND HUMANS

11.1. Environmental Risk Assessment

The polymer is not considered to pose a risk to the environment based on its reported use pattern and current levels of use.

11.2. Human Health Risk Assessment

11.2.1. Occupational health and safety

There is Low Concern to occupational health and safety under the conditions of the occupational settings described.

11.2.2. Public health

There is No Significant Concern to public health when used in the proposed manner.

12. MATERIAL SAFETY DATA SHEET

12.1. Material Safety Data Sheet

The notifier has provided MSDS as part of the notification statement. The accuracy of the information on the MSDS remains the responsibility of the applicant.

13. RECOMMENDATIONS

CONTROL MEASURES
Occupational Health and Safety

- No specific engineering controls, work practices or personal protective equipment are required for the safe use of the notified polymer itself, however, these should be selected on the basis of all ingredients in the formulation.

    - Guidance in selection of personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

- The following guidelines and precautions should be observed for use of the notified polymer as introduced as [Fluoroacrylate Modified Urethane]:

    - adequate induction and training programs for fabric-treatment personnel in the appropriate application techniques and methods be undertaken;

- A copy of the MSDS should be easily accessible to employees.

- If products and mixtures containing the notified polymer are classified as hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

Environment

- adequate induction and training programs for fabric-treatment personnel in the appropriate application techniques and methods be undertaken;

Disposal

- The notified polymer should be disposed of by landfill or incineration

Emergency procedures

- For larger spills, cover drains and bulk dikes to prevent entry into sewer systems or bodies of water. Working from around the edges of the spill inward, cover with commercially available absorbent material until it appears dry. Collect as much of the spilled material as possible. Clean up residues with detergent and water. Collect the resulting residue containing solution. Place residue in a closed container. Disposed of collected material as soon as possible.

Annotation of the Australian Inventory of Chemicals Substances

- Dispersive uses are required to be notified for assessment prior to approval. For use by industrial fabric-treatment plants for application on textile and carpet wares via an automated, contained and heat cured foam /airless spray process.

13.1. Secondary Notification

The Director of Chemicals Notification and Assessment must be notified in writing within 28 days by the notifier, other importer or manufacturer:

(1) Under subsection 64(1) of the Act; if

- further information becomes available on the release of perfluorinated substances from the proposed use on carpet and textile, or to indicate that PFBS and/or related substances are accumulating in environmental media such as biota, consideration should be given to a secondary notification. Any additional data should include more detailed information on the release of perfluorinated substances from the notified polymer, for example a higher tier biodegradation test.
- other uses and application techniques and or methods are proposed
- further information becomes available regarding transformations and degradation of the notified polymer including any adverse health and environmental effects of

the breakdown products. This information is to be provided to NICNAS as soon as practicable in order to determine if additional recommendations, if relevant, are required.

(2) Under subsection 64(2) of the Act:
- if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

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