

Uses of Perfluorinated Substances

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1 Introduction

Most organic molecules contain long carbon chains with most bonding sites occupied by hydrogen atoms. Though not exactly labile, the hydrogen atoms are available for reaction e.g combustion, breakdown to smaller molecules etc. Whilst a lack of polarity results in hydrophobic traits (an inability to dissolve in, and repulsion of, water) the molecules will dissolve in oils, fats, and other organic solvents. What was discovered (serendipitously) in the 1930s by DuPont workers was that if the hydrogen atoms in an organic molecule or polymer are replaced either entirely or substantially by fluorine atoms then a substance with remarkably different properties results.

Carbon - fluorine bonds are very strong and relatively short. Therefore saturation of bonding sites on an organic molecule with fluorine prevents chemical attack resulting in a very **inert** substance. As well as being **hydrophobic** fluorinated molecules are also generally **oelophobic** (oil and fat insoluble). This sets heavily fluorinated substances apart from heavily chlorinated or brominated substances such as polybrominated diphenyl ethers and polychlorinated biphenyls which dissolve in fats and oils. The unique properties are exploited in a wide range of discrete molecules, co-polymers and homopolymeric substances for a variety of applications.

For over 50 years the novel properties of perfluorinated substances have been utilised in a very wide range of products and applications. However in the late 1990s it was discovered that one widely used perfluorinated compound, PFOS, was becoming widespread in the environment, animals and humans, as a ubiquitous pollutant. This discovery heralded the recognition of a new kind of persistent organic pollutant (POP). Due to the unique chemical properties of perfluorinated compounds (PFCs), their environmental behaviour, bioaccumulation, and toxicological activity all occur via different routes to the more extensively studied POPs (eg organochlorine and organobromine compounds). Since 2000 there has been a great deal of activity by research laboratories, regulatory authorities and industry to classify, monitor and regulate these pollutants.

Two compounds in particular, perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), represent the final environmental degradation products of (and contaminants in) a wide range of other perfluorinated products and have been most extensively studied. PFOS is now subject to varying but (increasing) levels of control in a number of countries. Perfluorooctanyl sulphonic acid and its salts (PFOS) has been added to the OSPAR list of List of Chemicals for Priority Action (LoCfPA). The substance meets the criteria for inclusion to the Stockholm Convention on Persistent Organic Pollutants and a draft risk profile is in production. PFOA, also a widespread contaminant but with a far lower bioaccumulation potential is still under evaluation. The US EPA released a draft risk assessment of the potential human health effects of exposure to PFOA and its salts in January 2005. A subsequent review by the EPA Science Advisory Board (SAB) concluded that there is sufficient evidence to classify the compound as a "likely" human carcinogen, though this has yet to be adopted as the official opinion of the EPA.

We have previously published a review of the body of knowledge relating to the environmental distribution and (eco) toxicity of perfluorinated compounds:
Perfluorinated compounds: an emerging concern (Allsopp *et al* 2005).

The current document is intended to supplement this, providing a more detailed examination of:

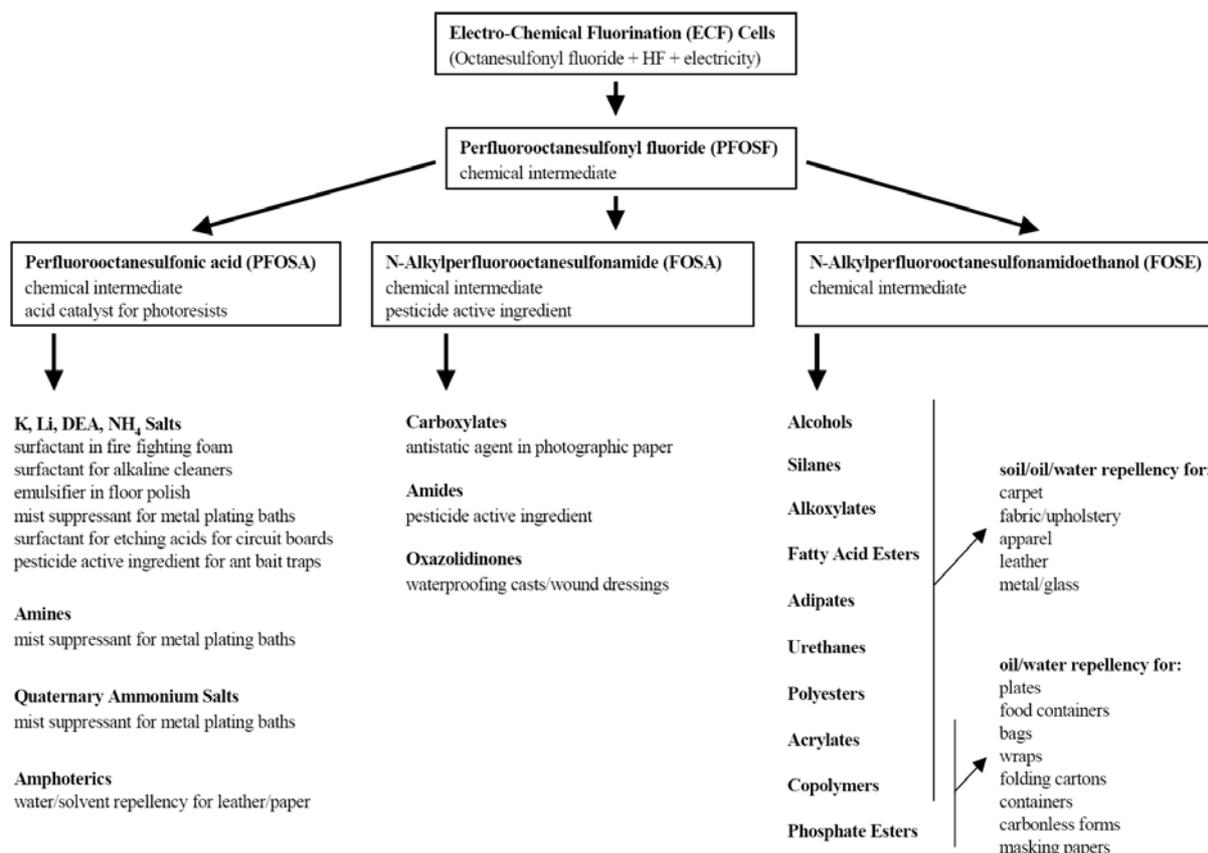
- i. Products containing perfluorinated compounds especially PFOS and related compounds
- ii. Sources of PFOA and the manner in which other PFCs may act as sources of PFOS and PFOA

2 Terminology

- Fluorochemical:** A term used to describe broadly all chemicals containing the element fluorine; Specifically, the term is used most commonly to describe small (1-8 carbon length) fluorinated molecules which are most used for refrigeration, fire suppression and as specialty solvents.
- Fluorinated chemical:** a term used synonymously with “fluorochemical”.
- Fluorotelomer:** a term used to describe an oligomer created by reaction of tetrafluoroethylene (TFE) with perfluoroethyl iodide $\text{CF}_3\text{CF}_2\text{I}$ to produce $\text{F}(\text{CF}_2\text{CF}_2)_n\text{I}$ [$n = 3-6$, avg. 4], the term “*telomer*” is often used synonymously with *fluorotelomer*.
- Fluoropolymer:** a term used to describe a polymer which has fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone. Common fluoropolymers are: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylenepropylene (FEP), etc.
- Fluorinated organic polymer:** a term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which a fluorinated carbon chain is attached.
- Perfluoro- /Perfluorinated:** describes a substance where *all* hydrogen atoms attached to carbon atoms are replaced with fluorine atoms – CF_n - where $n = 1 - 4$.
- Perfluoroalkylated substance:** a substance which bears a perfluorocarbon, also known as a perfluoroalkyl, functional group. $\text{F}(\text{CF}_2)_n\text{-R}$ where n is an integer and R is not a halogen, or hydrogen.
- Fluorinated organic surfactant:** a term to describe a surface active, low molecular weight, substance which contains fluorinated carbons; the term fluorosurfactant is used synonymously.
- Perfluorinated surfactant:** a term used to describe a surface active, low molecular weight, substance where *all* carbons bear fluorine in place of hydrogen; the term fluorosurfactant is used synonymously.

3 PFOS and related substances

PFOS is an environmentally persistent compound. Though not used extensively on its own it is an essential intermediate and breakdown product of a (once) diverse class of PFCs.



Perfluorooctyl sulphonates: Major product categories
OECD (2002)

Many of the substances shown above may potentially break down to PFOS. The compound has a much higher bioaccumulation factor (6300-125000) (Hekster *et al* 2003) than most other PFCs. Unlike other POPs, which accumulate in fatty tissues PFOS the substance binds to blood and accumulates in the liver.

A number of toxicological concerns surround this substance; these are reviewed extensively in *Perfluorinated Chemicals: an emerging concern* (Allsopp *et al* 2005). PFOS meets the criteria for a PBT (persistent, bioaccumulative, toxic) substance under REACH (Annex XII of the proposed legislation details the criteria).

In 2000, the world largest producer of PFOS-related substances, 3M announced that it intended to cease production in recognition of increasing evidence and concern relating to its environmental distribution. Over the next couple of years the company reformulated its entire range of “Scotch” brand products with chemistry based around another PCF, perfluorobutane sulfonate (PFBS). This substance (like all PFCs) is

persistent but it appears that short chain sulfonates do not bioaccumulate (Martin *et al* 2003 a) and exhibit relatively low toxicity.

Usage data for Europe are conflicting. It is to be expected that since 3M withdrew from the market, household use of PFOS related substances ceased. Some specialist industrial use of PFOS substances still occurs in the UK (RPA 2004). All applications exploit the substances' unique surfactant properties and include:

- **Chromium Plating** (mist suppressant)
- **Aviation hydraulic fluid** (PFOS compounds are used as components of this)
- **Photolithography and Semiconductors** (surface active qualities are exploited)
- **Photographic industry** (anti-static and cleaning properties considered essential)
- **Fire-fighting Foams** (Since the 3M phase out this should have reduced)

Estimated current demand for PFOS-related substances in the EU

Industry Sector	Application	Quantity (kg/year)
Metal Plating	Chromium plating	10 000
	Anodising and Acid pickling	20-30
Photographic Industry	Paper products	<50
	Printing plates	<100
	Film products	>850
	Total	1000
Semiconductor Industry	Photoresists	46
	Edge bead removers	86
	Top antireflective coatings	136
	Bottom antireflective coatings	8
	Developers (surfactant)	195
	Total	471 (assumed 500)
Aviation	Industry Hydraulic fluids	730
Storage for Emergency Use (Note not annual usage)		
		EU Total Storage (kg)
Fire fighting foam storage for emergency use		122 000

OSPAR (2005)

The UK and Swedish governments, the OECD, US EPA and a number of other bodies have all adopted positions on PFOS and related substances. In the US, the use of these chemicals must be notified to the EPA. During 2005, the UK government prepared draft legislation for the phase out of PFOS by 2010, which it intended to implement from April 2006 unless the European Commission came forward with a draft measure in the meantime (DEFRA 2005). The proposed UK approach drew upon aspects of the REACH model in that any continued use after that date will be subject to specific authorisation.

In the latter part of 2005, the European Commission did propose controls, under the so-called (Restrictions on) Marketing and Use Directive (76/769/EEC), as laid out in paper COM (2005) 618 (EC 2005). However, the major part of the uses prohibited under this draft measure have already been discontinued within Europe, including use in carpets, upholstery and other textiles and in paper packaging products. Moreover, evidence exists that many of the remaining uses which would be permitted under the Commission's proposed amendment, such as use in semiconductor manufacture, industrial photographic applications, chrome-plating and in fire-fighting foams, could also be phased-out within the next five years. Indeed, proposals for

national measures in the UK and Sweden explicitly expressed the desirability and feasibility of such programmed phase-outs addressing all uses other than as components of hydraulic fluids used in aviation, setting out, in the case of the UK, a series of application-specific sunset dates ranging from 2007-2010.

The restrictions proposed by the Commission also fall short in other ways, such as the allowance for 0.1% by weight of PFOS in preparations and finished articles, which may ultimately result in continued or future use in a far broader range of product groups in which deliberate use at concentrations below 0.1% is feasible (OECD 2004).

A more detailed critique of the European Commission proposal, currently before the European Parliament, is provided in the Appendix to this document.

4 Perfluorocarboxylic Acids

PFOA (known as C8- ie 8 carbon atoms) is by far the most extensively studied perfluorocarboxylic acid (PFCA). Attention has focused primarily on PFOA due to the use of it and its ammonium salt as polymerisation aids in the manufacture of polytetrafluoroethylene (PTFE). This has resulted in major point source releases of the compound for 50 years (Paustenbach *et al* 2005). Issues relating to contamination caused by these compounds has led to class action lawsuits against DuPont in the United States. However, the longer chain acids (C9-C14) have bioconcentration factors orders of magnitude greater to that of PFOA (Martin *et al* 2003 a,b) and may exhibit similar modes of toxicity (Martin *et al* 2004). Martin *et al* 2004 report the presence of the longer chain acids in Canadian Arctic biota at higher concentrations than PFOA itself, combined with sparse toxicological information on these longer chain acids.

Perfluorocarboxylic acids are the final degradation products (under normal conditions) of a wide range of other perfluorinated compounds. Whilst levels in urban environments are likely to result from point sources, processing or producing perfluorinated substances (Stock *et al* 2004, Paustenbach *et al* 2005) or fugitive emissions of residual material present in fluoropolymers and perfluorinated products, the compounds' low atmospheric mobility (Simcik 2005) has led to the theory that the levels found in remote areas result from the degradation of more mobile precursors such as telomer alcohols and sulfonated perfluorocarbons (Martin *et al* 2004, Simcik 2005, Stock *et al* 2004). This theory remains to be confirmed but represents the most likely explanation to date for the widespread environmental presence of PFOA.

4.1 Product sources of perfluorocarboxylic acids

4.1.1 Fluoropolymers

The only direct use of PFOA (and its ammonium salt APFO) is as a non-reactive polymerisation aid in the production of fluoropolymers. PTFE, the first and probably most widely used fluoropolymer, has a number unique properties including:

- Extreme resistance to chemical attack
- Stability up to 250 °C
- Very high electrical resistance
- One of the lowest coefficients of friction of any substance
- UV resistance

Applications of PTFE include: electrical wire insulation, specialist circuit boards, plumbers tape, waterproof membranes for garments (such as Gore-Tex), surgical implants, dental floss, engine protector additives, non-stick coatings, moulded parts and coatings for use in a wide range of chemically hostile environments. Whilst manufacturers state that PFOA/APFO may be present in polymer pastes, membranes and mouldings the concentration in final products depends upon the processing techniques employed. Heat has been shown to volatilize PFOA leaving finished products relatively free of the contaminant.

4.1.2 Non-stick cookware

Manufacturers claim that PFOA present in pastes used for producing non stick pan coatings is entirely driven off in the curing process (conducted at >300 °C) (Washburn *et al* 2005).

It has been known since the 1950s that PTFE degrades at high temperatures to release toxins. At lower temperatures (still greater than 250 °C) particulate matter is released that is known to be fatally toxic to birds. Generally temperatures greater than 300 °C are required for chemical decomposition of PTFE to occur. DuPont state that their Teflon PTFE coating systems can withstand up to 260 °C safely. The only paper found in this search of the literature that directly analysed the toxic effects of particles and compounds evolved from a heated non-stick pan was published in 1975. The study (Waritz 1975) involved heating pans to various temperatures and passing the evolved products through a chamber containing live rats, parakeets or Japanese quails for 4 hours. The gases were subsequently chemically analysed. The PTFE pan evolved lethally toxic agents at high temperatures, a phenomena known as “polymer fume fever” (mortality was observed in parakeets at 280 °C, quails at 330 °C, and rats at 425-450 °C). It was suggested that particulate matter was the principle toxic agent in each case. At 450 °C, tetrafluoroethylene itself was the only identified compound produced, higher temperatures yielded heavier fluorinated compounds (hexafluoropropylene and perfluoroisobutylene). Interestingly if non-PTFE coated pans are left to heat containing either corn oil or butter lethal pyrolysis products are produced at much lower temperatures.

Ellis *et al* (2001) published an analysis of the temperature dependant thermolysis of PTFE polymer. The analysis methods employed allowed for a wider range of compounds to be identified. The main product identified-hexafluoropropylene- may react in the atmosphere to form trifluoroacetic acid. Other compounds isolated included perfluoroacids (eg PFOA). The paper also reports that the same range of compounds was found in tests with Teflon coated pans.

Overall there is clear evidence that a dry PTFE treated pan left on the heat to reach temperatures greater than those used for cooking will result in the release of harmful compounds and particles. However, PTFE can be expected to endure temperatures up to 260 °C more than 2 years without significant degradation (Dupont 2005). It is unlikely therefore that harmful substances derived from the pans will be detected in food cooked in non-stick pans. The temperatures required for this would ensure that the food itself constituted a greater health hazard.

4.1.3 Reported levels of PFOA from fluoropolymers

Washburn *et al* (2005) report levels of perfluorooctanoate (the anion of PFOA) extracted from finished fluoropolymer products:

Article Group	Extraction test result for finished consumer article (ng of PFO/cm ² article)	Extractant used
Membranes for apparel	0.008 - 0.07	Water
Nonstick cookware	Not detected (<0.1)	10% or 95% ethanol in water
Thread seal (plumbers) tape	0.02 - 0.08	Water, simulated perspiration

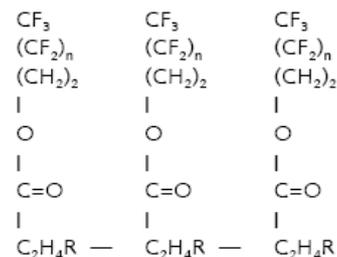
Interpretation of these data is difficult. Generated to form part of an exposure assessment and risk characterisation, it does not report levels of perfluorooctanoate per unit mass but only per unit area. This combined with the varying solvent system used, prevents any detailed comparative overview being gained on either the levels of total contamination for each article type or the relative levels of contamination in different article types.

4.1.4 Fluorotelomer products

Fluorotelomer alcohols (FTOH) are used as surfactants and intermediates in the manufacture of a variety of products with a wide range of applications including polymers, paints, adhesives and cleaning agents. The link between fluorotelomer alcohols and prefluorocarboxylic acids occurs on two levels. Firstly, production of 2-perfluorodecylethanol (C₈F₁₇CH₂CH₂OH or 8:2 FTOH) causes unintended production of PFOA (C₈F₁₇CO₂H) (Washburn *et al* 2005). Though no substantiating information is readily available it may be assumed that production of other telomer alcohols also leads to perfluorocarboxylic acid contamination. Secondly, due to the stability of perfluorocarboxylic acids, these are the likely final environmental degradation products of telomer alcohols.

One application of particular relevance in terms of consumer exposure is the use of FTOH to produce polymers for use on fabrics and in paper. For textile applications FTOH derived polymers are used to impart water/grease repellence and anti-soiling properties to fabric, leather or carpets. These (commonly) acrylate/methacrylate polymers are sold under a variety of trade marks and may either be impregnated as part of finishing or sold as after-care products:

- Baygard – Lanxess formally part of Bayer
- Zonyl – DuPont
- Nuva – Clariant
- Unidyne – Daikin
- Stainmaster – DuPont



///// FIBER SURFACE\\\\\\

The diagram above illustrates how PFC (perfluorocarbon) chains form a flexible repelling barrier and prevent anything from interacting with the fibre surface.

Impregnation of paper/cardboard with either FTOH derived polymers or additives can provide both grease and water repellence. Products treated this way are used for both food contact (plates, food containers, bags, and wraps) and non food contact (folding cartons, carbonless forms, and masking papers) applications (Poulsen *et al* 2005). Common brand names include:

- Zonyl – DuPont
- Foraperle – Atofina/Dupont
- Baysize-S (some formulations) – Lanxess (formally Bayer)
- Cartafluor – Clariant
- Lodyne – Ciba

Exposure to PFOA from articles treated with these products may occur through a variety of routes. Industry sources (Boese *et al* 2005) state that FTOH derived polymers contain less than 0.1% unbound FTOH. However, 8:2 FTOH, a commonly used telomer alcohol building block of many products has been shown to breakdown to PFOA through oxidative radical mechanisms in the atmosphere (Ellis *et al* 2005), through microbial metabolism (Dinglasan *et al* 2004) and through the metabolic activity of isolated rat hepatocytes (chief functional cells of the liver) (Martin *et al* 2005).

Direct releases of contaminant perfluorocarboxylic acids present a quantifiable source of exposure (Barton *et al* 2005). The degradation of polymers and subsequent release of PFCA precursors cannot be eliminated as a further potential source. Given the types of chemical linkage attaching the perfluorinated moiety to the polymeric backbone, release is possible. A limited number of inconclusive industry studies, however, refute this hypothesis (Boese *et al* 2005, Berti *et al* 2005). Dinglasan-Panlilio & Mabury (2006) report that the commonly used monomer, 8:2 telomer methacrylate, may degrade in sewage sludge to metabolites similar to those of 8:2 FTOH.

A limited body of evidence is available reporting concentrations of the PFOA in consumer articles. Washburn *et al* (2005) report levels extracted from a number of articles treated with fluorotelomer based products. Limitations to interpretation and inter-comparison of those data have already been noted above.

Article Group	Extraction test result for finished consumer article (ng of PFO/cm ² article)	Extractant used
Mill-treated carpeting	ND(<0.2) – 23	Water, Simulated saliva, Simulated sweat
Treated upholstery	0.4 – 4	
Treated apparel	ND (<0.01) – 12	
Carpet-care solution-treated carpeting	28 – 50	Water

The data presented below, also from Washburn *et al* (2005) estimates concentrations in consumer product formulations based on assumptive dilutions of the FTOH ingredient.

Article group	Concentration in fluorotelomer product formulation (mg of PFO/kg of article)	Calculated total conc. in finished consumer article (mg of PFO/kg of article)
Industrial floor waxes and wax removers	5 – 120	0.0005 – 0.06
Latex paint	50 – 150	0.02 – 0.08
Home and office cleaners	50 – 150	0.005 – 0.05

No information is reported concerning the levels of unbound FTOH present in the articles.

In another recent study, Buck *et al* (2005) report that, under simulated processing conditions, all of the residual 8:2 FTOH and 95% of the PFOA present in a product used to treat a polyester garment were emitted to air during subsequent drying at 190 °C representing a source of perfluorinated compounds in the atmosphere. This information, though useful, should be treated with caution as it seems to contradict the direct reported concentrations found in garments elsewhere (Washburn *et al* 2005).

The German Ökotest consumer magazine reports levels of PFOA in both waterproof Gore-Tex jackets and water repellent sprays (Ökotest 2005). The garments from brands Arc'teryx, Berghaus, Mammut, Millet and Salewa contained PFOA at concentrations between 0.08 and 0.6 mg/kg. These values appear to be higher than those reported by Washburn *et al* (2005). However the different reporting units and potentially different experimental methodologies prevent direct comparison.

Three Water repellent sprays produced by Granger's Ltd, Salzenbrodt, and Erdal Rex were tested for perfluorinated acids. The Grangers product was found to not contain any of the compounds tested for within the reporting range. The other two sprays contained levels of PFOA between 0.24 and 0.48 mg/kg and perfluorononanoic acid (PFNA) between 0.25 and 0.77 mg/kg.

One Danish study (Engelund and Sørensen 2005) report the presence of both perfluoroheptanoic acid (1.1 mg/kg) and PFOA (3.6 mg/kg) in one of four shoe care products analyzed probably indicating the presence of a FTOH based polymer in the product.

5 Substitutes

For some applications substitutes for fluorinated compounds/polymers are available (Poulsen & Jensen 2005). However many of these are either other fluorinated substances or novel chemistries for which there is a lack of toxicological information. It may be the case that in many cases substitution would involve significant product redesign or, even more fundamentally, questioning of the necessity of the particular technical performance feature imparted by fluorinated chemistry.

Alternative compound	Product trade name	Company	Used in / used for
Perfluorobutanesulfonate (PFBS) - C ₄ or based on different C ₄ -perfluorocompounds	Novec®	3M	Paint and coatings industry. As electronic coating. Industrial and commercial cleaning. Cleaner for solder flux residue. Degreasing applications.
Dodecafluoro-2-methylpentan-3-one (CF ₃ -CF ₂ -C(O)-CF(CF ₃) ₂)	Novec®	3M	Fire-fighting fluid
C ₆ fluorocompounds (predominantly ~80%)	FORAFAC®	DuPont	Fire-fighting foam
CF ₃ or C ₂ F ₅ pendant fluoroalkyl polyethers	PolyFox®	OMNOVA Solutions Inc.	Surfactant and flow, level, and wetting additive for coating formulations. Also used in floor polish.
Propylated aromatics (naphthalenes or biphenyls)	Ruetasolv®	Rütgers Kureha Solvents GmbH	Water repelling agents for rust protection systems, marine paints, coatings, etc.
Aliphatic alcohols (sulphosuccinate and fatty alcohol ethoxylates)	Emulphor®, Lutensit®	BASF	Levelling and wetting agents
Sulfosuccinate	(EDAPLAN®LA 451)	Münzing Chemie	Paint and coating industry: Wetting agents for water based applications – e.g. wood primers
Sulfosuccinate	(HYDROPALAT® 875)	Cognis	Paint and coating industry: Wetting and dispersing agents
Silicone polymers	WorléeAdd®	Worlée-Chemie	Wetting agents in the paint and ink industry

(Poulsen *et al* 2005)

6 Conclusions

No other published data regarding levels of PFOA (and precursors) in products was available at the time of writing. However as the limited information presented here shows there is reason to suspect that all PTFE (and possibly other fluoropolymers) may be contaminated with PFOA unless it has been subjected to a high temperature processing stage. The same applies to many fluorotelomer based and treated products currently available. In any case, manufacturing results in substantial releases to the environment.

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Appendix: Comments to “Proposal for a Directive of the European Parliament and of the Council relating to restrictions on the marketing and use of perfluorooctane sulfonates (amendment of Council Directive 76/769/EEC)”, COM(2005) 618 final, 5.12.2005

Prepared by Greenpeace International, January 2006

Given ever increasing recognition of the widespread environmental distribution of PFOS, arising from its use and use of other PFOS-related chemicals to date¹, coupled with its known properties as a toxic, persistent and bioaccumulative substance (PBT) and propensity to undergo long-range environmental transport², regulatory measures aimed at reducing the risks to health and the environment through restrictions on marketing and use are certainly welcome, though long overdue.

The amendments proposed by the Commission in paper COM(2005) 618 recognise that PFOS and many chemically-related substances which may give rise to equivalent concerns have received a diversity of uses, some of which have recently been phased-out through voluntary action by manufacturers but others of which continue. It is therefore right that the proposed restrictions address not only PFOS but also what are commonly termed PFOS-related substances. The proposed restrictions also appear to demonstrate an intent by the Commission to take more seriously the complex and potentially irreversible risks presented by PBT substances.

Nevertheless, the restrictions as proposed in paper COM(2005) 618 are not sufficient to address the full extent of the known and potential risks of PFOS and related chemicals, or of perfluorinated substances more generally. Key concerns can be summarised as follows:-

1. uses to be prohibited have already been phased-out

Although the intention of the proposed restrictions is to “cover the great part of the exposure risks”, almost all the uses which it will prohibit have already been phased-out (as acknowledged in the explanatory memorandum to the proposal itself), while current ongoing uses will remain largely unaffected. Therefore, although the restrictions should be effective in preventing future re-introduction for uses in carpets, textiles, upholstery, etc., the immediate impact of the amendments on current use patterns seems likely to be minimal at best. The proposals as they stand therefore have the characteristics of action which is “too little and too late” to address the full scale of the problem.

2. most uses which will be permitted to continue indefinitely could be phased-out within five years

¹Allsopp, M., Santillo, D., Walters, A. & Johnston, P. (2005). Perfluorinated Chemicals: an emerging concern. Greenpeace Research Laboratories Technical Note 04/2005: 45 pp.

http://www.greenpeace.to/publications_pdf/perfluorinated_chemicals_2005.pdf

² KemI (2005) Proposal for listing Perfluorooctane sulfonate (PFOS) in Annex A of the Stockholm Convention on Persistent Organic Pollutants, Prepared by the Swedish Chemicals Inspectorate (KemI), Sweden, June 2005: 4 pp. http://www.pops.int/documents/meetings/poprc/meeting_docs/en/POPRC1-INF9-b.pdf

At the same time, those uses which will be permitted by way of derogation from the general restriction on marketing and use may, in many cases, be amenable to substitution given sufficient time and incentives to develop and/or implement alternatives.

As the Commission proposals stand, uses in the semiconductor and photographic industries, chromium plating operations, aviation hydraulics, fire-fighting foams and any number of unspecified “controlled closed systems” will be permitted to continue indefinitely, with no apparent requirement for such uses to be justified, reviewed or targeted for phase-out in the future. Instead, all that is noted in the preamble is the recommendations from the Commission’s own Scientific Committee on Health and Environmental Risks (SCHER)³ for further assessment in relation to use in two of these categories, namely fire-fighting foams and chromium plating, with no specified timeline for such assessments to be completed and no formal process for any outcomes to be considered and, as necessary, addressed through further amendments.

In contrast, national proposals for restrictions on PFOS and related substances developed by Sweden⁴ and the UK⁵ recognise the desirability and feasibility of phase-out of most of these ongoing uses (with the exception of hydraulic fluids used in aviation) through a series of application-specific deadlines from 2007 through to the end of 2010. For example, in the UK government’s proposed Environmental Protection (Controls on Perfluorooctane Sulphonate) Regulations [2005]:-

- a) use in chrome plating is permitted only until the end of 2007
- b) use for specified applications in the photographic and semiconductor industries is permitted only until the end of 2010

Thereafter, any continued use (other than in aviation hydraulics) will be permitted only on the basis of justified case-by-case derogation, supported by evidence that efforts have been made to find alternatives and that emissions from the process in question have been eliminated.

It would appear, therefore, that the restrictions proposed by the Commission could go much further than those set out in COM(2005) 618, through the application of similar deadlines for these applications, after which continued use would require case-specific justified derogation, similar to the Authorisation procedure being developed for “substances of very high concern” under REACH.

3. maximum limits of 0.1% by mass in preparations and articles may not be stringent enough to prevent more widespread uses now or in the future

³ SCHER (2005) Opinion on “RPA’s report “Perfluorooctane Sulfonates Risk Reduction Strategy and analysis of advantages and drawbacks”, final report – August 2004”, Scientific Committee on Health and Environmental Risks, adopted during the 4th plenary of 18th March 2005: 16 pp.

http://www.eu.int/comm/health/ph_risk/committees/04_scher/docs/scher_o_014.pdf

⁴ G/TBT Notification (2005) PFOS and substances that could degrade to PFOS (perfluorooctyl sulphonic derivative), G/TBT Notification Number: G/TBT/N/SWE/51, 06/07/2005: 11 pp. [in Swedish]

⁵ DEFRA (2005) Consultation on proposed national action to restrict the use of perfluorooctane sulphonate (PFOS) and substances that degrade to PFOS, Annex A – Draft Regulations: 5 pp.

<http://www.defra.gov.uk/corporate/consult/pfos/regulation.pdf>

Allowing 0.1% PFOS or related substance by mass in preparations or finished articles, presumably set with the intention of preventing widespread use in consumer products, may be too high to achieve a general prohibition on all uses other than those industrial uses specified in the derogation. Although many uses in treatment of textiles, leather, paper and packaging materials may require higher concentrations, recent OECD figures⁶ suggest that PFOS may be present in products at levels below 0.1% by mass. It will be essential to verify:-

- a) whether PFOS and/or related chemicals at levels below this 0.1% limit would arise exclusively from contamination or could possibly be serving some functional purpose, the latter implying a deliberate use and
- b) what types and levels of use such a limit would permit, especially in the form of surface coatings of bulk materials, and how significant these might be in terms of exposure to humans and overall inputs to the environment.

4. derogation for use in “controlled closed systems” is too generic and too lenient

Given that no examples are given, the applications intended to be covered by the general derogation for use in “controlled closed systems” are not clear and the need for such a derogation questionable. Moreover, permitting such a system to release up to 0.1% by mass of the PFOS or related compounds it employs during normal operations implies that such a system cannot be considered to be closed. Indeed, to associate this scale of permitted release with the concept of closed systems could set a dangerous precedent for future measures relating to other substances.

The scale of permitted releases in this case, and their likely contribution to human exposure and environmental contamination, would depend entirely on the quantities which would be used in these unspecified systems. Likewise, the 1µg/kg concentration limit placed on waste discharges from such processes is not likely to provide adequate protection as the total quantities of PFOS released will depend on the volume of waste generated and degree of dilution achievable prior to discharge.

widespread uses of other perfluorinated chemicals will continue unabated

While regulatory concerns to date have focused understandably on PFOS and PFOS-related substances, scientific concerns relating to the widespread use of perfluorinated chemicals and their potential environmental and health hazards extend well beyond this group, supported by an increasing body of evidence on distribution and effects^{7,8,9,10}. Concerns relating to PFOA

⁶ OECD (2004) Results of survey on production and use of PFOS, PFAS and PFOA, related substances and products/ mixtures containing these substances. OECD Environment, Health and Safety Publications Series on Risk Management No. 19, JT00176885, Paris 2004: 59 pp.
[http://www.oelis.oecd.org/olis/2005doc.nsf/LinkTo/env-jm-mono\(2005\)1](http://www.oelis.oecd.org/olis/2005doc.nsf/LinkTo/env-jm-mono(2005)1)

⁷ Martin JW, Smithwick MM, Braune BM, Hoekstra PF, Muir DCG, and Mabury SA (2004). Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environmental Science and Technology* 38 : 373-380

⁸ Stock NI, Lau FK, Ellis DA, Martin J W, Muir DCG, Mabury SC (2004) Perfluorinated telomer alcohols in the North American troposphere *Environmental Science and Technology* 38: 991-996

⁹ Simcik M (2005) Global Transport and Fate of Perfluorocemicals *Journal of Environmental Monitoring* 7:759-763

and related substances, and to products manufactured using PFOA (including the very widespread fluorotelomer alcohols which are suspected, in turn, of acting as a source of PFOA to the global environment), will ultimately also need to be addressed through timely action.

For example, a very recent study conducted by the Norwegian Institute for Air Research, and funded by the Swedish Society for Nature Conservation and the Norwegian Society for the Conservation of Nature, documents the presence of perfluorinated chemicals in all-weather clothing designed for children¹¹, providing an illustration of just how common these chemicals can be in consumer goods.

Therefore, although measures to address PFOS and related substances are welcome, providing they are effective in eliminating all uses for which alternatives are available (the principle of substitution), the Commission will ultimately also need to address a much wider range of substances if it is effectively to protect the environment and peoples of Europe from the threat of perfluorinated chemicals.

¹⁰ Prevedouros, K., Cousins, I.T., Buck, R.C. & Korzeniowski, S.H. (2006) Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology* 40(1): 32-44

¹¹ SSNC FoEN (2006) Fluorinated pollutants in all-weather clothing. Norwegian Society for the Conservation of Nature/Friends of the Earth Norway and Swedish Society for Nature Conservation, January 2005, ISBN 91 558 0721 6: 43 pp. <http://www.snf.se/pdf/rap-hmv-allvadersklader-eng.pdf>