

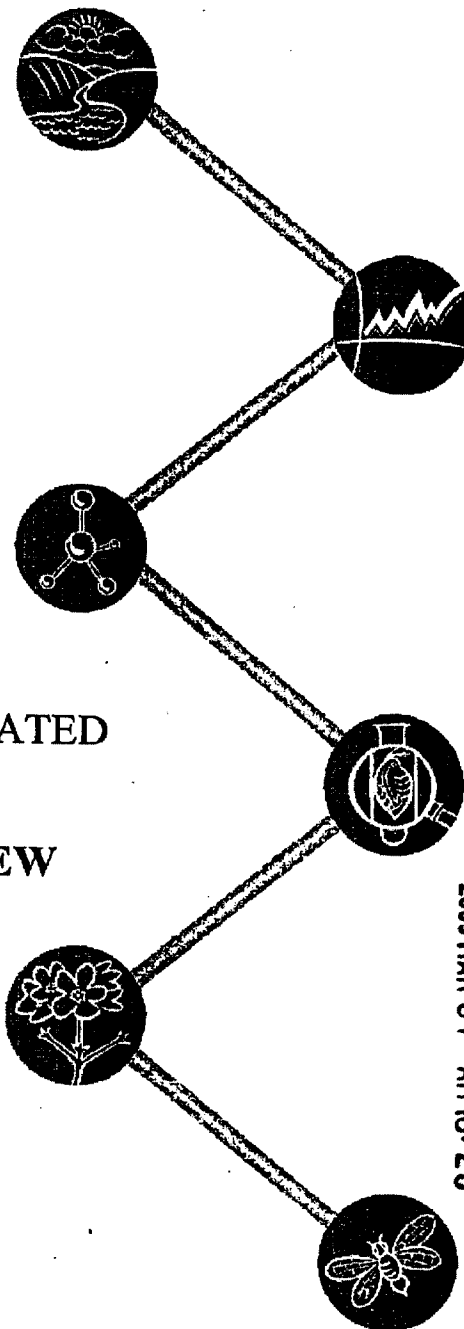
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**NATIONAL CENTRE
FOR
ECOTOXICOLOGY &
HAZARDOUS
SUBSTANCES**

**REVIEW OF OCCURRENCE AND
HAZARDS OF PERFLUOROALKYLATED
SUBSTANCES IN THE UK**

A NON-CONFIDENTIAL OVERVIEW

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PERFLUOROALKYLATED SUBSTANCES IN THE UK
A NON-CONFIDENTIAL OVERVIEW**

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1. EXECUTIVE SUMMARY

This study has been performed as a response to the decision of the 3M company to phase out some of its chemical products that contain fully-fluorinated alkyl groups from the market. Whilst severe effects of these substances on the environment have not been identified, the substances are very persistent, and therefore the potential exists for long-term effects to be caused. The Environment Agency needs to be informed about the properties of such substances, and of the possible responses of the market to 3M's decision. Whilst most attention has been focussed previously on perfluorooctanesulfonic acid and its salts (PFOS), this substance is one of a family of substances, and there are competitor products on the market which also include fluorinated alkyl groups; the present report takes a much broader view.

The approach to the research has been to gather data from regulatory authorities, companies and publicly available sources. The whole supply chain from importers and producers through to users of these substances has been covered. The scope of the project has had to be limited to some extent, because there are at least 100 000 substances with highly-fluorinated alkyl groups known in Chemical Abstracts. The main emphasis has been on the kinds of chemistry around the 3M type of product, and also a number of other important technologies; despite this limitation, at least 1000 substances can be identified within the scope. Regulatory authorities from other countries have listed around 200 substances.

The sector is characterised by applications of the PFOS type surfactants, with a very wide range of end uses, mostly of low tonnage. These cover many industries, some with high potential for environmental exposure. Therefore, any controls that might be required would need to focus on the importers and producers. There are trade associations in this sector, but none representing all producers. A particular cause for concern is that, apart from PFOS, there is almost no publicly available data for these substances, in respect of environmental fate and effects. Companies are developing new products, and others are trying to move into the gap 3M has left; 3M itself has not left the sector entirely. In the absence of significant amounts of data, estimates of environmental fate and effects properties have been calculated, although validation has been necessarily limited.

The project has developed an extensive framework in which future developments in this area can be understood. There is significant media interest in the area, and new data, as they emerge, will need to be interpreted carefully.

The project has stimulated considerable interest among relevant industries and organisations, and further responses are expected over forthcoming months, particularly after interested groups have had opportunity to read the report. It is necessary for the Environment Agency to seek further ways to encourage the industry to come forward with use data and property data, preferably through some new representational channels. At that stage it should be possible to establish how much new property data are required for a sufficient understanding of the fate and effects.

A full confidential Project Record has been produced to accompany this report.

2. INTRODUCTION

In May 2000, the US company 3M announced it was phasing out its production and marketing of perfluorooctanyl chemicals. The affected products of highest commercial significance are those based on the perfluorooctanyl sulfonyl group, of which the principal ultimate degradation products are perfluorooctanyl sulfonic acid and its salts (collectively termed PFOS). The PFOS ion or salts may also be present as an impurity in the commercial products. Perfluorinated substances are very persistent, and the phase-out decision was based on the finding of a widespread low level occurrence in biota and humans, and some questions over the mammalian toxicity. Certain fluorinated compounds have the potential to deplete ozone, though other environmental effects are of more concern in this work. PFOS-based substances are used in a variety of applications, including food contact materials and fire fighting foams. Consequently there is an international collaborative effort in place to produce a risk assessment of PFOS and its derivatives.

3M is not the only company with a commercial interest in this group of substances. In addition, there are a number of related commercial compounds with different carbon chain lengths. There are also various types of substance that can degrade to give a perfluorinated product. Whilst there is a limited number of raw material suppliers, perfluoroalkylated substances (PFAS) are used in a wide range of products covering a number of applications over several industry sectors. The unique properties of perfluorocarbons give them a place in a very diverse range of applications, and in some of these an effective non-fluorinated replacement would be very hard to find. The concern over the phase-out of perfluorooctanyl chemistry is that the substances might simply be replaced with other highly fluorinated substances exhibiting a similar hazard profile. It is also important to review what, if any, ecotoxicological effects these substances exert.

It is possible that perfluoroalkylated substances of different chain lengths should follow the pattern of the perfluorooctanyl substances and become priorities for assessment (and indeed some have been flagged during the OSPAR prioritisation process on the basis of QSARs). The Agency therefore requires a review of this whole group of substances, with an emphasis on those that are available on the UK market.

While the focus of this study is to be on perfluoroalkyls of the 'PFOS-type', some (limited) consideration will be given to other fluorinated organic chemicals to place the study in a broader context.

3. BACKGROUND AND SCOPE

3.1 Overview of Regulatory Activity

3.1.1 United States of America

The full background is given in Appendix 1.

The Toxic Substances Control Act (TSCA) Interagency Testing Committee (ITC) was initially interested in perfluorinated chemicals, because:

- The carbon-fluorine bond is highly stable and likely to persist.
- There is potential for long-range atmospheric transport, persistence, bioconcentration, and bioaccumulation.
- There are few publicly available data on ecological effects, health effects, wildlife exposures, or human exposures.

A list of 392 potentially persistent chemicals was identified (of which 50 could be grouped together as perfluorinated chemicals) for which the ITC needs

- (1) Measured bioconcentration data for 73 potentially persistent chemicals with estimated bioconcentration factors (BCFs) >1000,
- (2) Use and exposure data for 277 potentially persistent chemicals with no use and exposure data,
- (3) More specific use and exposure data for 14 potentially persistent chemicals,
- (4) TSCA use and exposure data for 29 potentially persistent pesticide chemicals, and
- (5) Use and exposure data for 58 potentially persistent dyes and pigments.

The 12 structurally related perfluorinated chemicals from TSCA section 8(e) submissions include chemicals that:

- i. Are present in human and animal blood.
- ii. Are pesticide active ingredients.
- iii. Cause tumours and developmental toxicity in animal studies.
- iv. Are metabolites of the 38 perfluorinated chemicals that satisfy the DEBITS criteria.

On May 17th 2000, following negotiations with the US Environmental Protection Agency (EPA) 3M announced that it would "voluntarily" phase out and find substitutes for the "so-called" perfluorooctanyl sulfonate (PFOS) chemistry used to produce a wide range of its products. However it is worth noting that the EPA had already singled out perfluorooctanesulfonic acid and its potassium, lithium and ammonium salts for in-depth evaluation.

On October 18 2000 the first phase of regulatory action with respect to PFOS was enacted when EPA proposed a significant new use rule (SNUR) under section 5(a)(2) of the Toxic Substances Control Act (TSCA) (5). Because the proposed rule would designate certain manufacturing and importing activities as significant new uses, persons that solely process the chemical substances that would be covered by this action would not be subject to the rule.

3.1.2 OECD

The OECD, with the US as the lead co-ordinators are carrying out a hazard assessment of PFOS and its salts, which will be followed by a risk assessment once the information is available. Decisions will then be taken on the need for international risk management to be made, although individual countries may take their own action.

3.1.3 Canada

On June 10 2000, using powers set down in the Canadian Environmental Protection Act 1999, the Canadian Government required industry to provide data on certain perfluoroalkyl and fluoroalkyl substances, their derivatives and polymers (4). This required any person manufacturing, importing or exporting more than 100 kg of such substances (whether alone or in a mixture) during the period 1997 to 2000 inclusive to notify the Minister of the Environment of such activity by July 11, 2000 and to provide data concerning use pattern and environmental effects by September 7 2000.

The list of substances of concern is set out in Schedule 1 to the notice. This list identified 182 substances embracing 22 classes of PFAS. It is thus far more extensive than the list published by the USEPA containing, for example, 19 compounds under the category perfluoroalkylsulfonates. The data request excludes certain classes of PFAS in particular chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), hydrofluoroethers (HFEs) and perfluoroalkene polymers (including polytetrafluoroethylene).

The details of the data call-in are set out in Schedule 2 to the notice. Information is required on the nature, level, source and destination of traded substances as well as data on the "fate and levels in, and effects on, humans, non-human organisms or the environment", including details of the persistence, bioaccumulation or inherent toxicity of the substances. This information is being used to assess whether the substances or the classes of substances are toxic or are capable of becoming toxic and whether and how to control these substances.

Discussions with the Canadian EPA indicate that of the 182 substances on the Canadian list, 159 are recognised as being in Canadian commerce. PFAS are not reported to be manufactured in Canada, but 16 companies are involved in importation. At the time of discussions (January 2001) the Canadian Government was unable to provide more information from the survey because of confidentiality issues and the fact that not all of the data had been compiled.

3.1.4 OSPAR

The OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic replaces the Oslo and Paris Conventions. Thirteen countries (Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, the Netherlands, Norway, Portugal, Spain, Sweden and the UK) and the European Union as a whole are party to the convention. The objective of the OSPAR Commission (OSPARCOM) is:

"to prevent pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances ... with the ultimate aim of achieving concentrations in the marine environment near background values

for naturally occurring substances and close to zero for man-made synthetic substances."

The Commission is guided by the precautionary principle, the 'polluter pays' principle, the use of best available techniques (BAT) and also the principle of substitution (i.e. hazardous substances should be substituted with less hazardous ones). Emissions of new hazardous substances should be prevented except where allowed for by the substitution principle. Risk assessment is also to be used as a tool for prioritising and developing action programmes.

The following is taken, with minor modifications, from a selection process undertaken for OSPAR by the Netherlands.

Possible candidates for the biomagnification safety net route

Candidates were selected from Danish QSAR database selection of substances with:

- *a calculated $\log K_{ow} > 6$*
- *a calculated persistence following Selection V**
- *a calculated $BCF < 500$*

An overview of the estimated PBT data was included.*

Substances that were not selected from that database are:

- *semi-volatile substances that have a calculated rapid rate of photo-oxidation ($t_{1/2} < 2$ days)*
- *substances that have free linear or branched alkyl chains, which are likely to be metabolised in higher organisms*
- *substances that have a large molecular diameter which may prevent passage of biological membranes*

Results:

92 substances were selected as possible candidates, including about 60 PFAS.

Remarks:

Many fluorinated substances appear on the list. Expert judgement predicts that fluorinated substances are more persistent than their hydrocarbon analogues with respect to aerobic biodegradation. Other abiotic degradation processes, such as photolysis in air or water or anaerobic degradation processes are also likely to be slow. Additional information on biodegradation of those substances is thus highly needed.

*Through the DYNAMEC (Dynamic selection and prioritisation Mechanism) process, hazardous substances have been prioritised for work according to the OSPAR Strategy agreed at the 1998 OSPAR ministerial meeting. Five sets of DYNAMEC criteria for persistence, potential to bioaccumulate, and toxicity (PBT), with varying levels of stringency (Selections I-V) were developed, Selection V being the most lenient and hence having the greatest catchment of substances. In the first selection phase Selection V criteria were used:

P: Not readily biodegradable and **B:** $\log K_{ow} \geq 4$ or $BCF \geq 500$ and **T_{aq}:** acute $L(E)C_{50} \leq 1$ mg/l, long term $NOEC \leq 0.1$ mg/l or **T_{mammalian}:** CMR or chronic toxicity.

Perfluorinated chemicals that are either included on the OSPAR list of chemicals of possible concern or are in the EU database of existing substances (IUCLID¹) as medium production volume substances (annual EU production/import tonnage of 10-100 tonnes) (or both) are:

CAS no.	Substance
307-34-6	Octane, octadecafluoro-
335-36-4	Furan, 2,2,3,3,4,4,5-heptafluorotetrahydro-5-(nonafluorobutyl)-
335-57-9	Heptane, hexadecafluoro-
335-67-1	Octanoic acid, pentadecafluoro-
355-42-0	Hexane, tetradecafluoro-
355-43-1	Hexane, -tridecafluoro-6-iodo-
375-72-4	1-Butanesulfonyl fluoride, -nonafluoro-
423-50-7	1-Hexanesulfonyl fluoride, -tridecafluoro-
507-63-1	Octane, -heptadecafluoro-8-iodo-
678-26-2	Pentane, dodecafluoro-
1691-99-2	1-Octanesulfonamide, N-ethyl-heptadecafluoro-N-(2-hydroxyethyl)-
2795-39-3	1-Octanesulfonic acid, -heptadecafluoro-, potassium salt
2991-51-7	Glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-, potassium salt
3825-26-1	Octanoic acid, pentadecafluoro-, ammonium salt
13417-01-1	1-Octanesulfonamide, N-[3-(dimethylamino)propyl]-heptadecafluoro-
25268-77-3	2-Propenoic acid, 2-[[[(heptadecafluorooctyl)sulfonyl]methylamino]ethyl ester
67969-69-1	1-Octanesulfonamide, N-ethyl-heptadecafluoro-N-[2-(phosphonoxy)ethyl]-diammonium salt

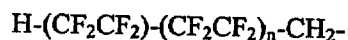
3.1.5 Other

Consultation with the Danish Environmental Protection indicates that a project concerning the use of PFOS in Denmark has just begun in the first quarter of 2001.

3.2 Chemistry overview

3.2.1 Scope of perfluoroalkylated substances of interest

In this report, perfluoroalkylated substances (PFAS) are individual chemical compounds that contain a perfluoroalkyl group, designated as C_nF_{2n+1} or mixtures or formulations that contain such compounds. The EPA selected substances containing C_4 - C_{10} perfluorinated chains for their investigations. No limit has been placed on the value of n for this study. There is also at least one important class of multifluorinated compounds, which although strictly speaking do not fall within the above definition, are potentially capable of presenting environmental problems, in terms of persistence. These compounds which contain the structural unit:



will be mentioned where their existence is relevant to the discussion.

¹ International Uniform Chemical Information Database - containing property and hazard information for 2604 EINECS-listed chemicals on the European market during the 1990s at a supply level of over 1000 t.p.a., submitted under the Existing Substances Regulation (ESR), EC 793/93.

As simple illustrations of the range of nomenclature that can be encountered, the following examples are cited:

$C_6F_{13}-$ may be referred to as 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl, or simply as perfluorohexyl

$C_6F_{13}CH_2CH_2-$ may be referred to simply as 1H,1H,2H,2H Perfluorooctyl, 3,3,4,4,5,5,6,6,7,7, 8,8,8-tridecafluorooctyl, or 2-(perfluorohexyl)ethyl-

The perfluorooctanesulfonyl group is a chemical group of formula $C_8F_{17}SO_2-$, being a specific example of a perfluoroalkane sulfonyl group of general formula $C_nF_{2n+1}SO_2-$.

There are several important types of products that contain a perfluoroalkyl group, which, although similar in structure have important structural differences attributable to the process of manufacture. These structural differences can be appreciated by reference to products of types A and B.

A	$C_7F_{15}SO_2NHC_2H_5$ $C_7F_{15}CO_2NH_4$
B	$C_6F_{13}CH_2CH_2SO_2NHC_2H_5$ - $C_4F_9CH_2CH_2CO_2NH_4$

Type A products possess a fully fluorinated alkyl chain, whereas Type B products possess a bridging two carbon moiety between the perfluoroalkyl group and the functional group.

Perfluoroalkanes of general structure:



are included in the scope of the report, because they contain the perfluoroalkyl group. However, such substances are already under scrutiny from an environmental perspective, because of their long atmospheric lifetimes and their high global warming potential.

Fluoropolymers containing perfluoroalkyl structural units are mainly confined to perfluoroalkyl acrylate and methacrylate copolymers.

3.2.2 Production processes

Commercially important perfluoroalkylated substances of the R_F-X type (where R_F is a perfluorinated alkyl group, and X is any substituent) are produced by one of two general approaches:

- Organic compounds with the carbon skeleton of the desired product are subjected to a perfluorination process to produce the target molecule.
- The perfluoroalkyl skeleton of the target molecule is constructed using a perfluorinated "building block" containing some potentially useful functional group as in the telomerisation technologies. The most important "building blocks" are the low molecular weight perfluoroolefins and their derived perfluoroalkyl iodides.

Perfluorination processes

The commercially operated perfluorination processes are:

- electrochemical fluorination, (ECF)
- cobalt trifluoride mediated fluorination (CTMF) with elemental fluorine
- direct fluorination with elemental fluorine

and all inherently lack selectivity in respect to the position of fluorination. The major perfluorination technologies mentioned above are described in the Project Record.

Telomerisation processes

There are two commercially operated telomerisation processes (preparation of linear polymer chains of limited and relatively short length) used for producing highly fluorinated compounds, referred to as:

A. Telomer iodide process

B. Telomer alcohol process

Telomer iodide technology, by far the most important, is based on pentafluoroethyl iodide as the telogen with a fluoroolefin, which is usually tetrafluoroethylene.

Telomer alcohol technology. The main products contain one $-CH_2$ group between the perfluoroalkyl group and hydroxyl group and carry a terminal hydrogen atom. These compounds are often described as polyfluorinated (partially perfluorinated) but do fall within the scope of the US EPA and Environment Canada studies.

3.3 Substance types of interest in this project

Because this project is concerned with the substances to which the environment is likely, ultimately, to be exposed, a very wide range of chemical structure types fall within the specification. The basic principle is that any substance that could degrade in the environment to a perfluoroalkylated substance was of interest in this project. For example, the EPA list includes acrylate copolymers including perfluorinated side chains. Substances with, for example, six fluorinated carbons and a series of CH_2 groups are also included, since the potential to break down in the environment releasing the fluorinated group, perhaps as a carboxylic acid, exists. Inorganic fluorides were not considered as part of this project.

The most evident potential environmental hazard attached to the perfluoroalkyl environmental chemistry is that it will be extremely resistant to degradation in the environment, and be able to exert long-term effects. Such effects on the environment may or may not exist, but it is not possible to be certain that there are no effects, particularly for substances that may bioaccumulate. Perfluorinated alkyl moieties in larger non-fully-perfluorinated molecules may be released as the rest of the molecule is degraded in the environment, e.g. by microbes.

The categories included therefore are:

- Perfluorinated alkanes, alkenes and alkynes and derivatives, including polymers, but excluding poly(tetrafluoroethylene) (PTFE) itself
- Hydrocarbon-based organics with perfluoroalkyl groups or side chains, i.e. PFOS-type chemistry – long perfluoroalkyl chain, functionalised at one end, strongly surface active.

Since the scope of the project is so broad, and hence the range of properties is so varied, the investigations carried out have uncovered a wide range of applications in industry.

The set of substances could potentially have been in the order of 100 000, including the various types of substance set out above. In order to limit the list to a manageable size, decisions had to be made regarding the extent of reasonable coverage. The OECD list of perfluoroalkyl substances, which the Agency provided at the start of the project, served to initiate the substance list. The Canadian list was also used. OSPAR priority lists of perfluoroalkyl substances, brought to our attention by the Agency partway through the project, added further substances to the list. Searching by relevant terms in various publicly available databases (e.g. the CIA Sourcerer, Chemfinder, ChemIndustry and HSDB Internet databases) gave many additional substances. The list was carefully studied in order to eliminate any duplicates, which could have arisen due to different styles of nomenclature in different sources.

It was necessary to limit the number of substances to follow up at the scale of this project. Substances which were available on a commercial scale were identified and these took priority over the low-production-level speciality substances, produced for research purposes, and those substances already identified as posing a particular hazard. Thus, only substances identified by Environment Canada or OSPAR, those produced by more than one company, and substances considered likely to be produced at any considerable scale, were retained. This process reduced the list of substances with which to approach industry and other data sources. 573 PFAS appear in the final database.

An important issue, which was raised in the development of the substance set and in the course of research, is that many commercially available PFAS are in fact complex reaction products and mixtures. These substances, relevant components of which are likely to be covered by the list for this project, should not be overlooked by other regulatory initiatives (See Recommendations). An example is a particular commercial family of fluorinated surfactants. The CAS numbers are not available through the company's public information. These can be obtained from the CAS Registry file, although so little data were available through this route besides the number itself, it was not pursued for this work.

4. METHODS

4.1 Overview

Information on supply tonnage, industrial use pattern and environmental fate and effects was gathered through literature review, Internet and database searches and consultation. Given the paucity of publicly available information, the main route for data gathering was direct contact with industry, in particular the producers of PFAS and trade associations representing PFAS users. As review material and initial scoping on the Internet and other resources indicated, the range of applications for PFAS is extremely wide. Many consultees were identified from relevant organisations (trade associations, companies, regulatory and other organisations, expert individuals and groups) to gain information on these applications.

The core of the approach adopted was to use personal contact (usually by telephone) to develop a dialogue with the consultee. This was followed by written correspondence, with e-mail increasing as the preferred mode of communication identified by consultees. In some cases, meetings and conference calls were also held. By explaining the goals of the project and its long-term implications for industry, the aim was that consultees would be encouraged to participate and take an active role in data provision. Unfortunately, in this case, the level of voluntary data supplied was very low owing to a number of factors. These varied by consultee but included a lack of available data, the time scale allowed for data gathering, the sensitivities associated with the substances and higher priorities.

During the course of the project contact was made with Peter Field, a consultant working in the fluorochemical area. Dr. Field was commissioned to assist by preparation of a review of relevant aspects of the fluorochemical sector, and his report has been provided to the Agency.

4.2 Industry Research

4.2.1 PFAS Producers

Contact was made with the five European producers of PFAS, as well as two of the three US producers, and one in Japan (see Section 5.3 for details of producers). This consultation has been of limited success. While initial contact with producers was in almost all instances very positive, offers of assistance have not resulted in the provision of data as hoped.

Detailed data on tonnages of PFAS sold onto the UK market has been provided by three producers, with one other providing data on one application area (see Section 1.1 in the Project Record). With respect to ecotoxicological information, comprehensive data on PFOS has been provided by 3M as compiled for the OECD assessment of that substance. Limited information has been provided by two other producers.

Given the small number of producers, the low level of response and the need to protect confidentiality, it is not possible to report in detail on the information provided or the reasons why information was not forthcoming (although a comprehensive summary is given in the confidential project record).

With respect to non-PFOS type chemistry, one reason cited for the paucity of data is the scope of this current study compared with the scope of work for the USEPA, with the activities and

requirements of the USEPA being major driving force for producers. In particular, a telomer producer has indicated that the USEPA is focussing on PFOS-type chemistry at present and will not focus on telomer-based chemistry for a couple of years.

Added to this is a desire amongst PFAS producers to draw a clear line between PFOS-based and other chemistries. In this regard the telomer producers have joined together to form the **Telomer Industry Research Panel (TIRP)**. The TIRP is an industry sponsored research programme, managed by a third party, and is focussing on data gathering common to all its members - DuPont, Asahi Glass, Clariant, Daikin and Atofina. The first step has been to identify a product common to all members (the telomer B alcohol) and the second to purify this so that a single substance can be tested. The telomer B alcohol covers a range of chain lengths, mostly C6 to C8, and it is the 8-2 telomer alcohol ($n\text{-C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$) that is being tested. Studies on environmental properties begun only in 2001, with Jan-Feb 2001 being the target to complete the methodology for the environmental fate and effects work. Studies are planned on environmental fate, acute aquatic toxicity, bioconcentration and biodegradation.

The substances containing non-fluorinated methylene groups might reasonably be expected to be degradable in part. A reasonable working hypothesis might be that $\text{R}_f\text{CH}_2\text{CH}_2\text{-X}$ would degrade to $\text{R}_f\text{CO}_2\text{H}$, therefore these substances are also of concern.

It has been reported that the TIRP is keen to share the findings of its studies with all interested governments however little data are yet available. There is also believed to be a paucity of data amongst individual producers. While comprehensive data are available for PFOS, it has been suggested that few data are available for other chemistries at present – major research activities beginning only after the 3M decision to phase-out its PFOS-based chemistry.

Added to this is a degree of nervousness amongst PFAS producers which is also believed to have contributed to the lack of data provision. This has taken the form of concerns about data confidentiality and a need to involve legal departments with the information request, adding considerably to response times. A high workload and the need to meet statutory obligations have also been cited as reasons for the lack of data provision.

There is no trade association representing all PFAS producers. However, some are members of the **European Fluorocarbon Technical Bureau** (a CEFIC sector group), which represents major producers of pure perfluoroalkanes. While this organisation has been contacted on more than one occasion concerning the study, no information has been forthcoming. This may be owing to a desire on the part of the fluorine industry to draw clear lines between functionalised PFAS and other fluorinated chemicals – indeed initial discussions with the EFTB contact indicated that enquiries concerning PFAS should be directed to the Association of Plastics Manufacturers Europe (see Section 4.2.3). In the case of pure perfluoroalkanes, these are the subject of considerable attention, interest and international regulatory activity resulting from their global warming/ozone depleting potential.

Contact was also made with the **Fluorine Technology Bureau**. This is an informally constituted group, with companies, academics and consultants who meet to discuss items of mutual interest. They have a very wide range of contacts. The possibility of paying to use the services of consultants within this group was discussed with the project manager, but not taken further.

Other PFAS Suppliers

Contact was also made with a number of other UK companies involved in the supply chain, including formulators, distributors and laboratory and development chemical suppliers (see Section 1.1 in the Project Record). Only one of these companies (a formulator) was able to provide information for the study in the form of Material Safety Data Sheets (MSDSs).

4.2.2 User Trade Associations

Contact has been made with a number of user trade associations and some user companies in order to gather data on use pattern. The full list of contacts is given in the project record and the main trade associations are listed in Appendix 4. The aims, objectives and data requirements of the study were also publicised in key publications such as the Focus on Surfactants newsletter produced by the Royal Society of Chemistry.

The success of consultation depended on a number of key factors:

- whether the trade association was aware of the PFAS issue: as a result of the 3M decision to phase-out its PFOS-based chemistry a number of trade associations were aware of PFOS and related products. Some had already spoken to members about these issues and so were able to provide data directly for the study;
- whether the trade association was prepared to survey members: a number of trade associations surveyed members concerning PFAS use, providing useful information for the study;
- where there was a need for the study team to contact members direct, for example for reasons of confidentiality: it was not possible to contact a large number of user companies for the study given the wide range of industry sectors using PFAS – as a result, it was not possible to gather information for some industry sectors.

One trade association active in this area is the **Association of Plastics Manufacturers Europe (APME)**. APME, along with their sister trade association in the USA, is gathering data on ammonium perfluorooctanoate (APFO) used as a processing aid for some fluoropolymers (e.g. PTFE) and also in some polymer dispersions. The data gathering exercise includes a global mass balance of APFO, due to be completed at the end of the first quarter of 2001, plus data toxicological and ecotoxicological data – with the latter being passed onto the project team, tonnage data not being available at the time of asking. With respect to other PFAS, APME has also collated data on hexafluoropropylene (HFP) and tetrafluoroethylene (TFE), although this relates to human not environmental toxicology.

As many PFAS are used for their surfactancy properties, contact was made with the two key UK trade associations to elicit information concerning use:

- the organic surfactants group (GOSIP) of the Chemical Industries Association;
- the Speciality Surfactants Group of the British Association for Chemical Specialities.

In both instances the groups as a whole were unable to provide information, save for suggesting some companies to contact.

The most useful information was provided by two trade associations representing members for whom PFAS are key substances:

- the British Fire Protection Systems Association, representing the manufactures of fire fighting foams; and
- the British Surface Treatment and Suppliers Association, representing cadmium platers.

In contrast, a limited number of trade associations were unwilling to provide information or indeed enter into a dialogue concerning the study.

4.3 Substance data

Having set down the key properties to obtain, potential industry sources were contacted regarding the data needed. As the searches of publicly available sources confirmed, much of the information on both use pattern and properties is only available direct from industry. The expectation was that PFAS manufacturing companies might be willing to pass on their own data, possibly commercially sensitive, which we could then use. In practice very little was really useful in terms of substance properties, as most of the data made available by companies were for commercial mixtures, and could not be seen to be representative of the component(s) of interest.

Certain web sites were extremely useful, giving free access to product brochures and MSDSs. Manufacturers also sent a limited number of MSDSs for use in the project.

Commercial availability was determined through evidence from the producers' web sites. Many of the substances on the list are thought to be speciality fine chemicals, and not commercially produced on any considerable scale.

Publicly available property data

The following publicly available data sources were consulted in respect of each and every substance on the refined list:

- Hazardous substances data bank (HSDB)
- Elsevier Ecotox Database
- Syracuse Research Corporation PhysProp and ChemFate databases
- MSDSs (supplied by companies and via the Internet)

The IUCLID database (confidential version) was also accessed. Relevant, recent information from the literature (see *Documents List*) and the Internet (see *Web Sites*) was also sought.

In fact, so very few of the listed substances are present in any of these resources, the only available real data is that which industry has chosen to provide.

The substances listed under this project have been categorised based on the functional chemistry identified by Canada as the basis of their 22 groups. Since the UK project had a slightly different scope, there were substances on our list that could not be considered to conform to any of these. Therefore it was necessary to create additional categories to accommodate the remaining substances:

It should be noted that it has not been possible to undertake a detailed review of all of the chemical structures identified in the list. Rather, the groupings are based on key fragments,

identified in the chemical name, and can be considered only provisional. Hence not all substances identified in the database have been assigned to a category.

Table 4.1: Categories of PFAS assigned by the Canadian EPA and extended for the purposes of this project

Category	Substance type	Number listed
1	Perfluoroalkylsulfonates	18
2	Perfluoroalkylsulfonyl derivatives	10
3	Perfluoroalkylsulfonamides	60
4	Perfluoroalkylsulfonamide alcohol derivatives	12
5	Perfluoroalkylsulfonamide phosphate derivatives	6
6	Perfluoroalkylsulfonamide glycine derivatives	6
7	Perfluoroalkylsulfonamide polyethoxylate derivatives	7
8	Perfluoroalkylsulfonamide aminopropyl derivatives	28
9	Perfluoroalkylsulfonamide chromium complex derivatives	6
10	Perfluorocarboxylic acids	29
11	Fluorosulfonamides	1
12	Fluoroesters	5
13	Fluorothioethers	9
14	Fluorocarboxylates	3
15	Fluorourethanes	2
16	Fluoroalcohols	14
17	Fluoroacrylates	84
18	Fluorophosphates	8
19	Fluoroalcohol derivatives	5
20	Fluoroborates	0
21	Perfluorosulfonamide acrylate polymers	13
22	Fluoroacrylate polymers	10
23	Perfluoroalkanes	41
24	Perfluoroalkyl and -alkoxy silanes	6
25	Perfluoroalkenes	15
26	Perfluorophosphonics	4

5. USE PATTERN

5.1 Overview of Market

5.1.1 Introduction

The incorporation of one fluorine atom into an organic molecule has a significant effect on the compound's chemical and physical properties: the incorporation of a perfluorinated chain has a profound effect. The properties of perfluoroaliphatic structures lead to the development of materials with novel and practically valuable characteristics including: chemical inertness, low refractive index; high electric insulation; high thermal stability, good resistance to corrosion and weather; high volatility, sublimation, and gas solubility; and low surface energy.

The market for PFAS is extremely diverse and highly fragmented in end-product terms. A very high proportion of PFAS is used in proprietary formulations of performance chemicals. There are literally thousands of consumer and industrial products on the global market, ranging from shoe polishes to optometry aids, which rely on low concentrations of the highly fluorinated products, for their exceptional properties (see Appendix 3).

The UK market for PFAS in the year 2000 is estimated to be around 400 tonnes of fluorinated active ingredient, all of which is imported. It is considered that these figures can be broken down as follows (although these should be treated with caution):

Table 5.1: Proportional breakdown of PFAS applications

Application sector	Volume (tonnes)	Percentage
Carpet & Textile Treatment	195	48.8%
Paper & Board Treatment	60	15.0%
Speciality Surfactants	70	17.5%
Fire-Fighting Chemicals	65	16.3%
Chemical Intermediates	10	2.5%
Total	400	

Source: (1) PGF Associates, Exeter, England

Data provided by individual producers is presented in the Project Record (and cannot be reproduced here for reasons of commercial confidentiality).

5.1.2 Key Applications

While a very wide range of PFAS applications are identified (see Appendix 3), consultation indicates that not all the possible applications are available on the UK market. The two main applications for PFAS are as protective treatments (e.g. for carpets, textiles, paper and board) and surfactants (including fire fighting chemicals).

Generally speaking functionalised PFAS are employed as **surfactants**, i.e. for their ability to modify surfaces, frequently reduction of surface tension of both aqueous and non-aqueous systems. Fluorosurfactants can attain extremes in surface activity (detergency, wetting, foaming, emulsifying, dispersing) as well as possessing high stability against acidic, alkaline,

oxidising and reducing agents and to elevated temperatures.

These surfactants may be represented as $R_F X$, where the R_F portion is the stable fluorocarbon chain, and X represents a solubilising group. The fluorochemical chain is modified in length and structure to meet end use needs, providing the exceptional resistance to thermal and chemical attack. The perfluorocarbon chain confers low surface energy on the molecules and is basically responsible for its capability to dramatically reduce surface tension.

The solubilising group, X is commonly water soluble, but can be designed to be oil soluble for use in non-aqueous systems, where hydrocarbon surfactants are ineffective. The precise nature of X varies considerably, and many fluoro-surfactants have been prepared which are extremely surface active in hostile environments. Fluorosurfactants can attain extremes in surface activity (detergency, wetting, foaming, emulsifying, dispersing) as well as possessing high stability against acidic, alkaline, oxidising and reducing agents and to elevated temperatures.

The chemistry and functions of fluorosurfactants have been comprehensively reviewed by Kissa (13), and the Project Record includes some useful tabulations of physicochemical data taken from the book.

For **protective treatments**, the general approach consists of converting the reactive end-group in a fluorochemical surfactant to an acrylate or methacrylate moiety and then copolymerising it with a commercial resin suitable for fabric treatment. These treatments are frequently referred to as fluoropolymer coatings. For example, treatment of textiles, leather and carpets with fluorochemical acrylates followed by polymerisation (curing) provides a polymeric surface capable of repelling oil and water and having stain-release properties. Protective treatments are used for both soft-surface materials (e.g. domestic and apparel textiles, industrial textiles, carpets, leather and non-wovens) and hard-surface materials (e.g. construction products such as concrete, stone, porous brick, etc.)

PFAS are also used as **intermediates** in the high pressure emulsion polymerisation of tetrafluoroethylene (TFE). This employs water in which ammonium perfluorooctanoate and an initiator (usually diisopropylperoxydicarbonate) are suspended (dissolved). The perfluorooctanoate exists as micelles, providing it is present at a concentration greater than the critical micellar concentration, which is about 0.001%. The size of the micelles controls the amount of TFE in suspension, which in turn controls the PTFE particle size. Perfluorooctanoic acid can be used in copolymerisation of TFE with other fluorinated monomers. There is good experimental evidence that the ammonium perfluorooctanoate assists in the solubilisation of the TFE.

5.1.3 Review of uses

Key issues associated with the use pattern for PFAS are summarised in Section 5.1.4, with further information in Appendix 3. The main market areas have been recorded for the series of applications shown in table 5.2 overleaf.

Table 5.2: PFAS application areas and specific industrial applications within these

Application Area	No.	Specific Application Area
Carpet & Textile Treatment	1	carpets
	2	leather
	3	textiles
Paper & Board Treatment	4	paper
Speciality Surfactants	5	agriculture
	6	coatings
	7	construction
	8	metal extraction, refining and processing
	9	oil and fuel
	10	photography
	11	public domain
	12	fire fighting foams
Fire Fighting Chemicals	12	
Chemical Intermediates	13	intermediates

The summaries record the following information for each of these applications:

- use of perfluoroalkylated substances: describes the way in which perfluoroalkylated substances are used in this industrial sector;
- tonnages of PFAS: provides an indication of the tonnages of PFAS used for this particular application and puts this in the context of the total market for PFAS;
- trends in use: describes any trends in the use of PFAS in that industry sector and the factors influencing these trends;
- PFAS types: provides an indication of the types of PFAS used for this application;
- PFAS concentrations: indicates the concentration of PFAS present in formulated and end products;
- substitutability issues: gives details of the substitutability of PFOS-based chemistry with telomer-based chemistry and of PFAS with other chemistries. Discusses key issues;
- formulators and users: an indication of the number and nature of formulators and users;
- issues relating to exposure: describes factors affecting levels of exposure arising from this particular application;
- policy issues: identifies any policy issues identified during the consultation process;

Two of the use area reviews - fire fighting foams and metal extraction, refining and processing - have been developed in consultation with the user trade associations, and have been reviewed by them. The information contained in the other reviews makes a useful start towards understanding the use of PFAS within specific industries. Sharing this information with relevant trade associations would make a useful starting point for further consultation with industry, but the short time scale of the project has not allowed such an extensive review.

With respect to descriptions of various industries, it appears that useful information is available from the Department of Trade and Industry. For example, their "Updated Strategic Analysis of the UK Carpet Industry" provides details of the UK carpet industry in terms of levels of production, imports and exports, number of manufacturers and retailers, etc.

5.1.4. Key Issues

PFAS tonnages and types

The estimates of PFAS tonnages associated with specific applications (see Section 5.1.1) have not been confirmed using producer data, as not all producers have provided tonnage data. Data provided by producers to date accounts for half of the market of 400 tpa.

With respect to users, only two industry groups (metal plating and intermediates) were able to estimate tonnages of PFAS used within their industry sectors. In some instances trade associations were prevented from making estimates of market size owing to members' concerns over commercial confidentiality. In the case of fire fighting foams this led to some members providing data on PFAS use direct to the project team.

In some cases trade associations had no information on PFAS use. This was the case for paper where, despite representing 15% of use, none of the trade associations contacted were able to identify current UK applications or possible users. In contrast, information provided by producers indicates that PFAS are used in the UK paper industry.

Other data provided by producers indicates that where trade associations are unable to identify PFAS use this may be because PFAS producers manufacture a number of products unique to specific customers.

With respect to PFAS types, in most instances trade associations and their members were not aware of the PFAS contained in their products. That said, a number of trade associations were keen to distinguish between PFOS-based products and the products used in their industries, reflecting the telomer producers' desire to differentiate between theirs and 3M-type chemistries.

Substitution of PFAS by other types of substance

In general terms it appears that PFOS-type chemistry is interchangeable with telomer-based chemistry – telomer-based products appearing to be available for all PFOS-type applications. Even for fire fighting foams where PFOS-type chemistry is reported to be the market leader, telomer-based chemistry is widely used by UK industry. That said, with respect to all industries, it might be difficult or very costly for individual users to switch from one type of PFAS to another owing to the need to reformulate large product ranges.

With respect to substitution with non-fluorinated alternatives, this may be problematic in some instances. For example, a number of consultees have mentioned the high price of fluorinated surfactants and that use is restricted to areas for which no effective alternatives are available. In this regard, fluorinated surfactants have a number of advantages over the other two classes of surfactants - hydrocarbons and silicones. In particular, they are generally more effective in water-based systems, they are able to reduce surface tensions to levels not attainable with hydrocarbon and silicone, and they are the only surfactants available for solvent or liquid-resin systems.

Issues relating to Exposure

Surface protectors can be applied by textile finishers but also at other stages in the chain of trade, particularly for upholstery, e.g. by the furniture manufacturer, by the retailer prior to delivery, at the time of delivery, or by commercial cleaners after cleaning. Similarly for carpets, surface protectors can also be applied: during fibre production; as part of the carpet manufacturer's process; by retailers prior to delivery; by the carpet fitter at the time of fitting; or in DIY applications by the householder.

As well as allowing for direct and immediate release into the environment, application of surface protectors after the manufacturing stage can lead to increased exposure in the longer term owing to wear. In this regard, fibre treatments for carpets are more durable to wear and cleaning than topical treatments, as the fluorochemical is distributed over the entire length of fibre.

With respect to surfactants, many applications are associated with diffuse release such as consumer care products. However, the concentration of PFAS in finished products is very low.

The longevity of PFAS means that releases at the end of the service life of the final product must also be considered, and the possibility of release from landfill sites has been identified in the literature.

A further issue is the lifetime of products already on the market. In this regard the shelf-life of all fluorosurfactant based fire fighting foams is 10 – 20 years.

Other policy issues

In some instances use of PFAS is reported to reduce human health risks. For example, PFAS-containing fire fighting foams are reported to be the most effective means of reducing burning flammable liquid fires and minimising the threat to life and property. In the metal plating industry, use of PFAS-containing mist suppressants in chromium plating reduce the emission of hazardous (potentially carcinogenic) gases. Thus if considering substitution, it is important to consider the change in health risks alongside reductions in environmental risk.

In this regard it has been reported that a number of "essential uses" have been put forward to the USEPA by PFAS users in response to its Significant New Use Rule. In addition, information provided by 3M to the USEPA to support its continued production of some PFOS-based substances for a limited number of applications until the end of 2002 identifies products under the following headings:

- those involved in a critical safety function;
- products for which there are not effective alternatives;
- those which help reduce polluting emissions; and
- products where time is required for regulatory approval for alternatives.

The existence of such applications in the UK should be taken into account in developing policy on PFAS. These include fire fighting foams and acid mist suppressants (as mentioned above), as well as APFO used in the production of PTFE (for which industry has indicated that there is no alternative).

5.2 Production of PFAS

5.2.1 Overview

The most significant global producers of primary perfluoroalkylated substances are listed in Table 5.3. All other suppliers of perfluoroalkylated substances are not primary producers and source their fluorochemical feed-stocks from the primary producers.

It is important to note that 3M have only phased-out a limited number of their PFAS substances from the market (i.e. those based on PFOS). More detail is given in the Project Record.

Table 5.3: Global Producers of Primary Perfluoroalkylated Substances

EUROPE	NORTH AMERICA	JAPAN	OTHERS
3M (BELGIUM)	DUPONT	ASAHI GLASS	KIROVO-CHEPETSK (CIS)
F ₂ CHEMICALS (UK)	3M	CENTRAL GLASS	GIPKh AT PERM (CIS)
ATOFINA (FRANCE)	AIR PRODUCTS & CHEMICALS	DAIKIN	CHENGUANG (CHINA)
CLARIANT (GERMANY)		F-TECH	
MITENI (ITALY)		TOHKEM	

Source: (1) PGF Associates, Exeter, England

The only primary source of chemicals containing the perfluoroalkyl group in the UK is F₂ Chemicals. However, these products are perfluoroalkanes (i.e. not functionalised).

5.2.2 Production by Perfluorination Process

Table 5.4 provides estimates of production of PFAS by the three most important production processes.

Table 5.4: Production Capacity

Electrochemical Fluorination		Cobalt Trifluoride Mediated Fluorination		Perfluoroethylidide Telomerisation	
COMPANIES	Estimated Capacity (t)	COMPANIES	Estimated Capacity (t)	COMPANIES	Estimated Capacity (t)
6	4650	3	1300	5	3000

Source: (1) PGF Associates, Exeter, England

With respect to other techniques which are also used:

- direct fluorination: despite continuously evolving technology this is currently of little commercial significance in the production of PFAS, although it could well play an increasingly important role in the future;
- telomer alcohol technology: there are believed to be three operators of this technology in the world;
- oligomerisation: only one company is believed to produce fluorinated surfactants by this route.

5.2.3 Chain of trade

The market for primary perfluoroalkyls containing >6 carbon atoms is predominantly captive to their producers, i.e. most products are either sold directly as performance products, or converted into performance products and sold, either directly or indirectly as consumer or industrial speciality products by the producer companies. Sales of the products to major accounts are handled directly by the primary producer, but because of the small volumes of products often required by the end-users, distributors are generally appointed by the producers.

Additionally there is a wide range of laboratory and development chemical suppliers, both in the UK and abroad that together supply virtually all the possible PFAS compounds. Some of these suppliers supply a few PFAS as part of an extremely diverse product list, while other companies specialise in the supply of fluorine chemicals. Certain of these are capable of producing their own products on a small scale, while others claim to have privileged relationships with small-scale contract manufacturers, with niche skills in organofluorine chemistry.

5.3 Highly fluorinated substances outside the main emphasis of this study

5.3.1 Perfluoroalkanes of low molecular weight

Several companies produce fluoroethers as chlorofluorocarbon replacements.

The European Fluorocarbon Technical Committee (EFCTC) has an interest in some perfluoroalkanes (straight-chain C_1-C_6 and perfluorocyclobutane). It lists the applications of these substances as:

- closed-systems dominant (dielectric inert coolant),
- inert formulation ingredients,
- microcell-forming additive for insulating foam production,

and considers the sources of these perfluorocarbons to be:

- Natural (~65% of total C_4 fraction),
- Aluminium production (C_2F_6 , CF_4),
- Semiconductor manufacturing,
- Electronics manufacturing and
- Speciality polymer formulations.

Fluorocarbon fluids for use in the electronics industry contain perfluoroalkanes such as:

Perfluoropentanes,
Perfluorohexanes,
Perfluoro(methyl cyclohexane),
Perfluoro(dimethyl cyclohexane),
Perfluoro(butyl tetrahydrofuran),
Perfluoro(Propyl tetrahydropyran),
Perfluoro(tributylamine).

5.3.2 Fluorinated polymers

While polymers having a fully fluorinated backbone (e.g. PTFE, poly(vinylidene fluoride)) are entirely outside the scope of the study, it is possible that some (e.g. perfluoropolyethers) could undergo slow decomposition in the environment.

PTFE

It is beyond the present scope to describe this area in detail. PTFE chemistry is fairly simple, but it appears that ways have been found to use it in many forms, presumably by chemical and physical modification. Application found include:

- normal domestic/engineering applications of PTFE (e.g. components of machinery, vessels),
- fabrics,
- aqueous dispersions, e.g. for inks.

Polymers other than PTFE

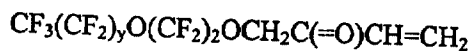
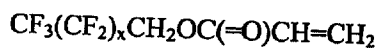
Perfluoropolyethers

Modified polyethers are important membrane and ion-exchange materials. They are derived from the important intermediate perfluoropropene oxide:



Poly(fluoroalkyl acrylates)

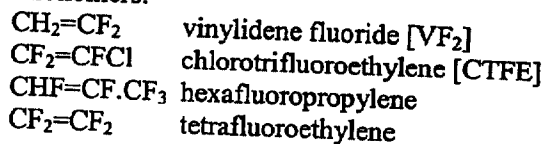
These are manufactured from the corresponding perfluoroacrylates.



are included within the scope of the study and have had uses as elastomers.

Vinylidene fluoride types

Many of the other fluoro-containing polymers are not fully fluorinated e.g. poly(vinylidene fluoride), and are likely to be very stable, and therefore are not within the present scope. Typical monomers:



6. PROPERTY DATA

The original aims of the project were centred on the expectation that a reasonable level of data would be available for review. In actuality, measured data proved so scarce overall that the level of review was limited. In order to make some kind of assessment possible, the Syracuse Research Corporation estimation software, based on established QSARs, were used to estimate properties. These data are summarised in this section also. However, due to the limited amount of measured data, validation of the estimates was not possible at the time of writing.

Trifluoroacetic acid is a substance which is within the scope of this study, but which has attracted interest for a different set of reasons. It is discussed as a special case in Appendix 2.

6.1 Physicochemical property data

These data are widely used in models of environmental fate and behaviour.

PFOS

Some data for PFOS are given in Table 6.1. These data have been reviewed by OECD.

Table 6.1: Physical-chemical data summary for PFOS (potassium salt)

	System	Protocol	Results
Melting point		OECD 102	>400°C
Boiling point			N/A
Density			No test
Vapour pressure	Spinning Rotor gauge	OECD 104	The reported value of 3.3E-04 Pa reflects the whole substance; that of the octyl component is more likely to be of the order of 1E-10 Pa.
n-Octanol-water partition coefficient	Shake-flask	Preliminary test only	Recent studies have shown that no reliable result can be obtained.
Water solubility	Shake-flask	OECD 105	519 mg/l
PH/pK _a			The sulfonic acid is a strong acid, and ionisation is complete at all relevant pH values.
Oxidation/reduction potential	No test		The sulfonate group is fully oxidised, stable in respect of reduction.

APFO adsorption-desorption screening studies

Indications are that APFO adsorbs strongly to soil; the Project Record gives more details.

Other substances

A very limited amount of data was found, and so estimates were necessary, as described above. The Project Record describes how all the data were obtained, and also contains a full set of the values.

As a generalisation, the main groups of PFAS can be categorised as:

- Low molecular weight, volatile liquids and gases, of moderate water solubility. These are the substances used as solvents, for example.
- Medium to high molecular weight, involatile, adsorbing, potentially bioaccumulative, low solubility in water. These are the substances identified by the US EPA.

6.2 Degradation data

Biodegradation

Data for PFOS and ammonium perfluorooctanoate (APFO) indicate low levels of biodegradability.

PFOS – Data are given in Table 6.2

Table 6.2: SIDS Environmental fate and pathways summary for PFOS (potassium salt)

Endpoint	System	Protocol	Results
Photo- degradation	Aqueous solution, with solar simulation.	No standard available	Non-reactive.
Stability in water			Non-reactive, on the basis of no observed degradation in many studies using aqueous media.
Transport and distribution		N/A	The reported K_{oc} of 66 is of very low reliability. Fugacity modelling shows typically 80% in water, 20% in soil/sediment. No reliable bioconcentration data.
Biodegradation	Various, non-standard study designs, using	Non-standard	Non-biodegradable.

PFOS has been found widely in humans and other biota.

APFO

Biodegradation: 13% at Day 28. There is a suggestion that the substance may be inhibitory to sewage treatment micro-organisms. The likely products of biodegradation are not known.

Other substances

No other measured data were available, therefore the BIOWIN program was used to give an indication of the biodegradability. Table 6.3 indicates the way the outputs were categorised. These results were then combined with the log K_{ow} predictions and are displayed graphically in Figure 6.1. This graph simply shows that a majority of the substances have possible persistence coupled with high bioaccumulation potential, although partial degradation has been ignored at this stage.

Table 6.3: Assignment of biodegradation class from the BIOWIN predictions

	Primary degradation class					
	Days	Days-weeks	Weeks	Weeks-months	Months	Recalcitrant
Weeks	1	2				
Week-months		3				
Months		4	6			
Recalcitrant		5	7	8	9	10

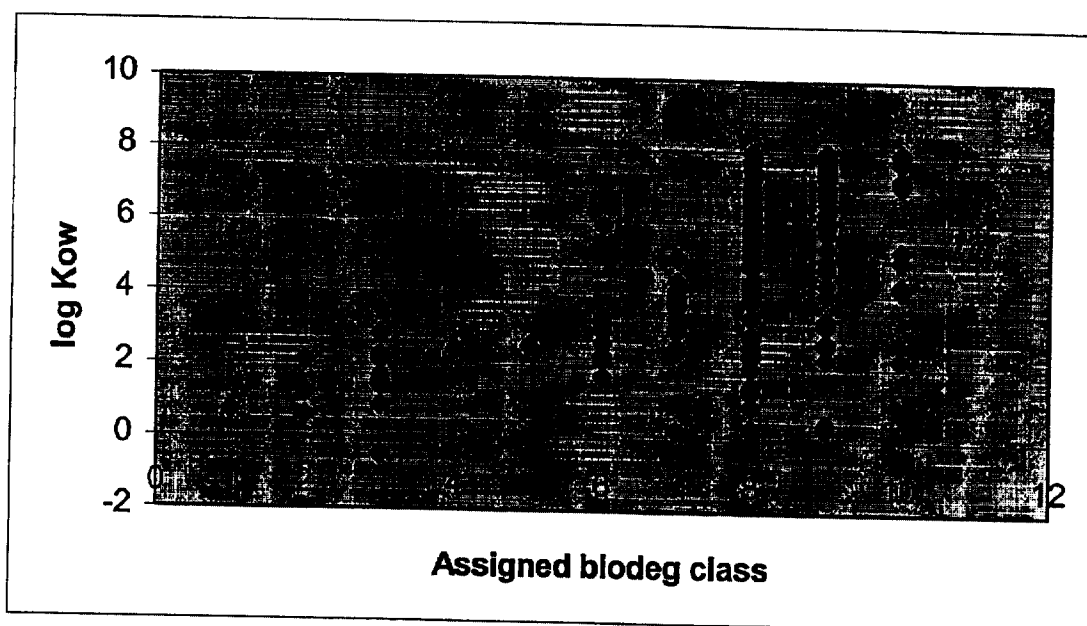


Figure 6.1: Representation of the persistence and bioaccumulation properties of the PFAS based on estimates using the SRC software

Photo-oxidation

Photo-oxidation is an important removal mechanism for substances that are persistent in other respects. The results for predicted rate of oxidation by photochemically generated hydroxyl radicals are given in the Project Record; not surprisingly for a large data set, a wide range of rates is exhibited. The rates do not imply total breakdown, but apply to the overall rate of hydrogen abstraction. As an indication, a rate of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule/s}$ is equivalent to a half-life in air of about 5 days. The database contains seventy substances with a predicted rate constant of zero, and these are of particular concern. The substances in question are not listed here.

6.3 Ecotoxicology data

Literature searching was carried out and potential Environment Agency and industry sources were contacted with a view to accessing ecotoxicity test results for perfluoroalkylated substances. Results obtained by testing could only be accessed for perfluorooctanesulfonate (PFOS - CAS Number 1763-23-1), ammonium perfluorooctanoate (CAS Number 3825-26-1) and a limited number of proprietary formulations. The latter have been excluded from the database and are not considered further in this report. Literature data for trifluoroacetic acid have also been obtained, and are discussed in Appendix 2.

PFOS and immediate analogues

A substantial number of PFOS test reports were made available for review by the 3M Company in the United States. The reports covered acute and chronic tests with aquatic organisms (fish, invertebrates, algae and sewage treatment micro-organisms) and dietary tests with birds. The tests were carried out on PFOS salts - potassium, lithium, ammonium and diethanolamine (DEA). Sufficient acute toxicity is exhibited to suggest that the classification N; R51/53 applies. Results are presented in Table 6.4 overleaf. Further data on PFOS salts are being generated by 3M and will be made available in due course.

Other analogues of PFOS have been studied and the data reviewed, but the results are not useful because they are not expressed in terms of the actual exposure concentration of the PFOS analogues in the tests.

Table 6.4: Ecotoxicological data summary for PFOS (test data expressed in units of mg/l unless noted otherwise)

Fish - freshwater			
Acute	<i>Pimephales promelas</i> (Fathead minnow)	96-hour LC ₅₀ = 9.5 96-hour NOEC = 3.3	Test substance: PFOS potassium salt
	<i>Lepomis macrochirus</i> (Bluegill sunfish)	96-hour LC ₅₀ = 7.8 96-hour NOEC = 4.5	Test substance: PFOS diethanolamine (DEA) salt
Chronic	<i>Pimephales promelas</i> (Fathead minnow)	42-day NOEC _{survival} = 0.30	Test substance: PFOS potassium salt
Invertebrates - freshwater			
Acute	<i>Daphnia magna</i> (Water flea)	48-hour EC ₅₀ = 27	Test substance: PFOS potassium salt
	<i>Unio complanatus</i> (Freshwater mussel)	96-hour LC ₅₀ = 59 96-hour NOEC = 20	Test substance: PFOS potassium salt
Chronic	<i>Daphnia magna</i> (Water flea)	28-day NOEC _{reproduction} = 7	Test substance: PFOS potassium salt
Invertebrates - salt water			
Acute	<i>Mysidopsis bahia</i> (Mysid shrimp)	96-hour LC ₅₀ = 3.6 96-hour NOEC = 1.1	Test substance: PFOS potassium salt
	<i>Crassostrea virginica</i> (Eastern oyster)	96-hour EC ₅₀ = >3.0 96-hour NOEC = 1.9	Test substance: PFOS potassium salt.
Sub-chronic/chronic	<i>Mysidopsis bahia</i> (Mysid shrimp)	35-day NOEC _{reproduction/growth} = 0.25	Test substance: PFOS potassium salt.
Algae - freshwater			
<i>Selenastrum capricornutum</i>		96-hour E ₅₀ (biomass) = 71 96-hour E ₅₀ (growth rate) = 126 96-hour NOEC _{biomass/growth rate} = 44	Test substance: PFOS potassium salt.
Micro-organisms			
Activated Sludge		3-hour IC ₅₀ = >905	Test substance: PFOS potassium salt.
Birds			
<i>Anas platyrhynchos</i> (Mallard duck)		LC ₅₀ = 628 ppm in diet NOEC _{mortality} = 146 ppm in diet NOEC _{body weight} = 37 ppm in diet	Test substance: PFOS potassium salt.
<i>Cotinus virginianus</i> (Northern Bobwhite quail)		LC ₅₀ = 220 ppm in diet NOEC _{mortality} = 73 ppm in diet NOEC _{body weight} = 73 ppm in diet	Test substance: PFOS potassium salt.

APFO

Results of acute (96-h) tests carried out on APFO with two species of freshwater fish (*Lepomis macrochirus* (Bluegill sunfish) and *Oncorhynchus mykiss* (Rainbow trout)) were provided for review by DuPont Haskell. The results were supported by analysis of exposure concentrations and are therefore considered to be valid. The lowest 96-h LC₅₀ of 634 mg/l was obtained in the test with *L. macrochirus*. The corresponding 96-h NOEC obtained in the same test was <262 mg/l. The results indicate that APFO has a low order of acute toxicity to freshwater fish.

Other substances

Ecotoxic concentrations for the remainder of the substances contained in the database were estimated by prediction using the ECOSAR software – a self-contained package allowing estimation of acute and chronic toxic concentrations for fish, invertebrates and algae. Further details of how this was done are given in the Project Record; the approach for known surfactants was to find a method which gave a reasonable prediction for PFOS and ammonium perfluorooctanoate, and then apply the same technique to their analogues.

The lowest acute EC₅₀, or LC₅₀ values determined for each of the substances by testing or prediction were used as the basis for categorising the substances in terms of their ecotoxic hazard according to the following criteria:

Table 6.5: Ecotoxicity categories, and criteria by which PFAS have been categorised

Category	Lowest acute EC ₅₀ , or LC ₅₀ (mg/l)
1	<1
1a	<1 but toxicity may not be expressed because of limited water solubility
2	1-10
2a	1-10 but toxicity may not be expressed because of limited water solubility
3	10-100
3a	10-100 but toxicity may not be expressed because of limited water solubility
4	100-1000
4a	100-1000 but toxicity may not be expressed because of limited water solubility
5	>1000
5a	>1000 but toxicity may not be expressed because of limited water solubility
?	Not possible to assign category – no acute data available

Categories 1a, 2a, 3a, 4a and 5a apply to those substances for which the lowest predicted acute EC₅₀, or LC₅₀ value was likely to be greater than the estimated water solubility. It is assumed that a substance placed in this category would not exert a toxic effect because of the limitations imposed on its bioavailability by its solubility in the test medium. If the solubility and ecotoxicity data were more robust and reliable (i.e. measured values) then there would be sufficient evidence for the assignment of the 'category a' substances to a separate group for which no toxicity would be expected below the limit of solubility. However, since in this case

the EC₅₀ and LC₅₀ values and also the solubilities are very largely estimates, it is more useful to keep the groups separate as in the table. This makes it easier to maintain a clear focus on the spread of toxicity levels against solubilities, and hence the possible implications of any subsequent validation exercise.

The substances were distributed across the categories with the highest frequencies in categories 1 (33.9%) and 1a (32.4%) - see table 6.6 overleaf. The comprehensive set of test results for PFOS places it in category 2. The limited set of test results for ammonium perfluorooctanoate place it in category 4.

Table 6.6: Breakdown of PFAS by ecotoxicity category

Category	Proportion of substances by category (%)
1	33.9
1a	32.4
2	9.8
2a	1.2
3	6.8
3a	2.1
4	6.5
4a	1.8
5	4.8
5a	0.3
?	0.3

Significant amounts of experimentally-derived data were available for a few substances and substance families – notably PFOS.

The UK Department of Environment, Transport and the Regions (DETR) has established a Chemicals Stakeholder Forum (SHF) to provide advice to government on chemicals issues. The SHF has recently set out PBT criteria (i.e. for persistence, potential to bioaccumulate and toxicity) with the intention that data can be compared against these criteria as part of a prioritisation procedure. In the present case it is not useful to attempt to apply the criteria, for the following reasons:

1. While bioaccumulation can be estimated by QSAR, the models are not valid for surface active substances, which many of these substances are.
2. With such a low level of available measured data, it is impossible to properly validate the models and therefore it would be difficult to justify applying watershed criteria, such as the SHF have developed, to the estimates in this case. However, relative comparisons, especially within a chemical class, may well be useful for prioritisation.

It can be assumed that the substances are persistent, and table 6.6 above shows that the vast majority of the substances are predicted to be toxic, although sufficient solubility to exert an effect may be in doubt.

7. PROJECT EVALUATION

7.1 General evaluation

Whilst the major objectives of the project have been addressed, it may be observed that:

- It would have been useful to give a more thorough review of substance types i.e. accurate categorisations according to the Canadian criteria, but the number of substances was too large.
- It was not ideal to present non-validated estimates of physicochemical and ecotoxicity properties, but the extent of validation was limited by the lack of data.
- Industry is aware at the supplier level of the OECD interest in these substances; at the user end, they are aware of issues, but many do not understand them. The team was therefore sometimes met with caution, which, over a longer time scale, could have been dispelled. It is our understanding that some companies have more data, but because they see this as part of wider discussions at the level of OECD, some are waiting for developments there before offering it up for consideration.
- It seems very likely that there are data which industry have chosen not to make available to us. In a longer project backed by a regulatory requirement these data could have become available.

7.2 Any aspects of the specification not fulfilled, and why

The Exchem database was not found to contribute usefully to the project so, whilst it was foreseen as being a potentially useful source at the time of tender, a full search using it was not carried out.

The major aspect of the specification which we have not been able to meet (other than for PFOS) is the assessment of data in terms of quality. At the beginning of the project the amount of publicly available data was not expected to be so low, and the project team had hoped to receive more assistance from industry with data provision. The balance of the team's resources was as a result slightly different than that foreseen at the outset.

8. RECOMMENDATIONS

INDUSTRIAL USE PATTERN

The international activity and interest in these substances is growing and co-ordinated research is vital in order to avoid unnecessary duplication. The initial impression of the OECD exposure summary information is that it is narrower in scope than has been identified in this work. It is necessary for the UK to share information with the other regulators.

RECOMMENDATION 1:

The findings of this study should be input to the wider regulatory discussions about the environmental exposure of PFAS. The number of substances may make it essential to share responsibilities between industry and regulatory authorities.

It has not been practicable to investigate the use of fluorochemical solvents and fluids in detail.

RECOMMENDATION 2:

Further study of low molecular weight solvents and gases is necessary to obtain a fuller view of the significance of fluorinated substances.

Given the relatively short time scale of this project, there is a need to allow for some organisations to complete their responses to the requests from the project team, and for some trade associations to be followed up.

RECOMMENDATION 3:

Allocate some time to additional work to seek and receive further information, and to monitor developments.

ECOTOXICITY, DEGRADATION, FATE AND BEHAVIOUR DATA

Apart from for PFOS, very little ecotoxicity data relating to this group of substances has been found or voluntarily submitted from any source. Given the high frequency of substances falling within toxicity category 1 and 1a on the basis of predicted toxicity, it is clear that there is an urgent need to obtain confirmatory test data for these substances as part of an in-depth evaluation. The category 1 and 1a substances are listed in Appendix 6.

Predictions indicate that little degradation of these substances can be anticipated in the environment, and that as a consequence persistence and the associated risk of effects arising from long-term exposure are a real concern. The reasons for setting up the current programme of work have thus been validated.

There is good reason to believe that further data are held confidentially by some companies, and some of these data are still being forwarded. In the event that future regulatory authority projects require the acquisition of commercial data for substances of this type, it is important to consider the findings of this study with respect to scope and response. Various commercial products that contain perfluorinated components are not readily assessed using publicly available data sources. It would be vital that any data call-in described the scope of work

appropriately. This would prevent the accidental overlooking of substances that could be relevant. Such a substance set would be extremely large.

This sector of the chemical industry is diverse and widespread. Controls based on use pattern would therefore be impractical if not impossible to achieve and producers/importers should be the primary focus.

RECOMMENDATION 4:

In view of the potential environmental hazards associated with these substances, it is recommended that measured data be obtained where it exists, and a strategy developed for the measurement of new data. A regulatory mechanism that would require producers/importers to submit data should be considered.

RECOMMENDATION 5:

The data now being forwarded by industry will allow the validity of estimated properties to be checked, and because fluorine compounds are unusual in behaviour, this is essential if estimates are to be used.

UK REGULATORY CONCERNS

Interest was expressed in the outcome of the study by Agency staff at both regional and national level. There was particular interest in PFOS because of recent highlighted concerns over its toxicity and persistence and its occurrence in the environment as a result of releases arising from its use in fire-fighting foams.

RECOMMENDATION 6:

It is important that the findings of the study are disseminated widely within the Agency so that the most comprehensive database available for this and other substances is available to those involved in developing policy, with some central resource being made available to regional and local officers. Co-ordination of activities is essential.

RECOMMENDATION 7:

PFAS are not high tonnage substances, and they have properties that make them uniquely valuable in various applications. It is recommended that the Environment Agency collaborate with DETR and other government bodies in developing an understanding of the risk-benefit analysis of these substances. It should be noted that there are so many substances in this class that a substance-specific risk assessment approach might not be the best model.

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APPENDIX 1: U.S. REGULATORY ACTIVITY

SUMMARY OF CURRENT REGULATORY ACTION ON PERFLUORINATED CHEMICALS

The Toxic Substances Control Act (TSCA) Interagency Testing Committee (ITC) submitted its 45th Report to the Administrator of the U.S. Environmental Protection Agency (USEPA) in November 1999. In this report, Degradation Effects Bioconcentration Information Testing Strategies (DEBITS) as strategies to test for the availability of degradation, ecological or human health effects, and bioconcentration information for wide range of chemicals were described.

In addition the report described the ITC's ongoing strategies to identify chemicals that are predicted to persist, bioconcentrate and cause ecological and human health effects.

The ITC implemented DEBITS to identify three classes of structurally related chemicals that have potential to persist and bioconcentrate. One of these classes was perfluorinated chemicals.

The ITC was initially interested in perfluorinated chemicals, because:

- The carbon-fluorine bond is highly stable and likely to persist.
- There is potential for long-range atmospheric transport, persistence, bioconcentration, and bioaccumulation.
- There are few publicly available data on ecological effects, health effects, wildlife exposures, or human exposures.

The 45th Report mentioned that the ITC would post lists of chemicals on its web site for which it was soliciting voluntary data submissions through the Voluntary Information Solicitation Innovative Online Network (VISION). The ITC also mentioned that if the ITC did not receive the voluntary data submissions by 29 February 2000, that it would consider asking EPA to promulgate TSCA section 8(a) and 8(d) rules to require the submission of these data. Since it took longer than anticipated to post these lists of chemicals on its web site, the ITC changed the submission date to 15 April 2000.

List 6, which was published contained 392 potentially persistent chemicals for which the ITC needs

- (1) measured bioconcentration data for 73 potentially persistent chemicals with estimated bioconcentration factors (BCFs) >1000,
- (2) use and exposure data for 277 potentially persistent chemicals with no use and exposure data,
- (3) more specific use and exposure data for 14 potentially persistent chemicals,
- (4) TSCA use and exposure data for 29 potentially persistent pesticide chemicals, and
- (5) use and exposure data for 58 potentially persistent dyes and pigments.

The list of 392 potentially persistent chemicals included 50 entities that could be grouped together as perfluorinated chemicals.

Forty-eight perfluorinated chemicals were assigned to 10 structural classes while two did not fit any structural class. (See APPENDIX 2). Thirty-eight perfluorinated chemicals satisfied the DEBITS persistence (ultimate biodegradation >2-3 months) and bioconcentration potential (log octanol-water partition coefficient 3-6) and production/importation criteria described by the ITC in its 45th Report. An additional 12 were selected from TSCA section 8(e) submissions because they were structurally related to the 38 perfluorinated chemicals and may be useful in developing Structure Activity Relationships (SARs). The 12 structurally related perfluorinated chemicals from TSCA section 8(e) submissions include chemicals that:

- i. Are present in human and animal blood.
- ii. Are pesticide active ingredients.
- iii. Cause tumours and developmental toxicity in animal studies.
- iv. Are metabolites of the 38 perfluorinated chemicals that satisfy the DEBITS criteria.

Estimated BCFs and Henry's Law Constants (HLCs) for perfluorinated chemicals were based on associated or non-hydrolysed chemical structures. Estimated BCFs for the 50 perfluorinated chemicals range from 3 to 26,000. HLCs ranged from 10^3 to 10^{-10} atm m³/mole. Approximately half of the perfluorinated chemicals had estimated HLCs $> 10^{-2}$ atm m³/mole, suggesting they could evaporate and be susceptible to long-range transport. The perfluoroalkyl iodides are likely to undergo rapid photolysis in the atmosphere, leading to possibly long-lived degradation products. The ITC is continuing to evaluate information on uses, exposures, environmental fate, ecological effects, and health effects of perfluorinated chemicals.

On May 17 2000, following negotiations with the US Environmental Agency (EPA) 3M announced that it would "voluntarily" phase out and find substitutes for the "so-called" perfluorooctanyl sulfonate (PFOS) chemistry used to produce a wide range of its products. **However it is worth noting that the EPA had already singled out perfluorooctane sulfonic acid and its potassium, lithium and ammonium salts for in-depth evaluation.**

3M says new testing techniques showed that PFOS is present at low levels in tissue samples, although there are no known adverse health or environmental effects. Data supplied to EPA by 3M indicated that chemicals based on PFOS are very persistent in the environment, have a strong tendency to accumulate in human and animal tissues and could potentially pose a risk to human health and the environment over the long term. EPA supported the company's plans to phase out and develop substitutes by the end of 2000, for the PFOS-derived products.

The announcement by 3M was intended to ensure that future exposure to the chemicals would be eliminated, and public health and the environment protected. The EPA Administrator Carol M. Browner was reported as saying that "EPA would work with 3M on the development of environmentally safe substitutes".

PFOS-based substances are used to produce a range of products from fire fighting foams, coatings for fabrics, leather, and some paper products, to industrial uses such as mist suppressants in acid baths. 3M is continuing a major research effort to enhance the understanding of any potential risks that may be associated with this class of substances. EPA is evaluating the substances to determine how individuals and the environment are exposed and what potential adverse effects may exist.

On October 18 2000 the first phase of regulatory action with respect to PFOS was enacted when EPA proposed a significant new use rule (SNUR) under section 5(a)(2) of the Toxic

Substances Control Act (TSCA) for the following substances:

- Perfluorooctanesulfonic acid (PFOSA) and certain of its salts (PFOSS),
- perfluorooctanesulfonyl fluoride (PFOSF), certain higher and lower homologues of PFOSA and PFOSF,
- certain other chemical substances, including polymers, that contain PFOSA and its homologues as substructures.

The complete list of perfluorinated substances, classified as PFOS, falling within the scope of the SNUR of the Toxic Substances Control Act (TSCA) is reproduced in Appendix 3 of the report.

This listing is not intended to be exhaustive, but provides a guide to entities likely to be affected by this action. Entities not listed in Table 1 of this unit could also be affected. Because the proposed rule would designate certain manufacturing and importing activities as significant new uses, persons that solely process the chemical substances that would be covered by this action would not be subject to the rule.

All of these chemical substances are referred to collectively in this proposed rule as perfluorooctyl sulfonates, or PFOS. This proposed rule would require manufacturers and importers to notify EPA at least 90 days before commencing the manufacture or import of these chemical substances for the significant new uses described. EPA believed that this action was necessary because the substances included in this proposed rule may be hazardous to human health and the environment. The required notice would provide EPA with the opportunity to evaluate an intended new use and associated activities and, if necessary, to prohibit or limit that activity before it occurs.

EPA is contacting foreign governments and other chemical manufacturers, both domestically and internationally, to seek their support for a voluntary phase-out of PFOS and related substances.

APPENDIX 2: TRIFLUOROACETIC ACID

Trifluoroacetic acid (TFA) is widely used in the fine chemicals industry and as a laboratory reagent. Five generic sources of TFA in the environment can be identified (7, 8, 9 and 10):

- Direct production: annual tonnage is approximately 1000 t but very little of this is expected to be released to the atmosphere.
- By-product: TFA is produced as a by-product of some chemical processing operations. Very little TFA from this source is expected to be released to the atmosphere.
- Atmospheric oxidation of organofluorine compounds: TFA is produced during the oxidation of several organofluorine compounds released to the atmosphere by human activities.
- Use of halothane and isoflurane anaesthetics. These anaesthetics yield trifluoroacetate when degraded. The global deposition of TFA from this source is estimated to be 800 tonnes per year.
- Decomposition of alternatives to CFCs: Some fluorocarbon alternatives to CFCs decompose in the atmosphere to form trifluoroacetate. Currently this source contributes about 2000 tonnes of TFA to environmental levels. This is expected to rise to about 160,000 tonnes by the year 2020.

It has also been suggested that incineration of fluorinated chemicals such as pesticides and surfactants may also result in the production of TFA but no data are available. Several commercially important pesticides contain the trifluoromethyl group attached to a carbon atom, therefore it is possible that TFA could be a terminal metabolite of degradation in the environment.

These sources do not account fully for the concentrations of TFA measured in the environment and some other, as yet unidentified, natural sources may exist.

Environmental fate properties

These properties, listed in the Project Record, suggest that TFA will not be retained in the atmosphere or soil but will preferentially partition to the water compartment where it has the potential to accumulate because of its persistence.

Toxicity to environmental species

The following results have been obtained in tests with environmental species (9 and 10):

- No effects on fish and invertebrates have been found at concentrations ≥ 100 mg/l. EC_{50} values for algae are generally >100 mg/l.
- A no effect concentration of 0.12 mg/l has been reported for one species of algae (*Raphidocelis subcapitata*), although the effect is algistatic rather than algicidal.
- TFA has been shown to have no effects on the biodegradation of organic carbon by activated sludge.
- No effects on plants seed germination have been observed.
- Effects on plant growth under hydroponic conditions have been observed at a concentration of 1 mg/l.

Environmental concentrations

The following concentrations of TFA have been determined in environmental compartments:

- Atmospheric concentrations in the order of 10-1000 pg/m³ have been measured along with concentrations of <10-100 pg/g for rainwater.
- Surface water concentrations in Europe and the US are in the order of 100-300 ng/l.
- There are no data for concentrations in soils.

Concentrations of TFA in the atmosphere, in precipitation and in surface waters are several orders of magnitude higher than would be predicted by releases from the known direct sources. (10)

APPENDIX 3: APPLICATIONS OF PFAS

Expanded versions of these summaries are given in the Project Record.

A.3.1 Agriculture and forestry

This area has not been studied in detail.

- Wetting agent for herbicides, fungicides, weed killers, hormone growth regulators, parasiticides, insecticides, germicides, bactericides, nematocides, microbiocides, defoliants and fertilizers
- As an ingredient in chemosterilents, insect repellents and toxicants
- For wettable powder pesticides and chemical powders
- Corrosion inhibitor for chemical applicators
- Wetting agent for foliage
- Wetting additive for live stock dips, or to wet sheep skins during desalination
- Wetting adjuvant for manufacture of plywood veneer
- Penetrant for preservative impregnation
- Pulping aid
- For cleaning tubes in paper making, dyeing
- Grease/oil repellents for paper

Trends

Over the past decade or so, there has been an increasing interest on the part of the pharmaceutical and agrochemical industry in the incorporation of perfluoroalkyl or functionalised perfluoroalkyl groups into drugs and agrochemicals. Although, at first these substituents were mainly trifluoromethyl, trifluoromethoxy etc the range of groups under consideration has expanded greatly and now many companies routinely screen perfluoroalkyl analogues of their target molecules.

A.3.2 Carpets

A trade association was consulted to a limited extent.

A.3.2.1 Use of perfluoroalkylated substances in the carpet industry

Carpet fibres are treated with fluorochemicals so that oil and grit does not adhere to the surface and can be vacuumed away. The treatment also prevents staining from spills of liquids containing acid dyestuffs that bind to the amino groups in nylon carpets.

A.3.2.2 Tonnes of PFAS

The UK market for fluorinated active ingredients in textile, leather and carpet treatment is estimated to be 195 tpa. The breakdown between the three sectors is not known.

A.3.2.3 Trends in Use

The 3M corporate decision affected a number of carpet manufacturers who offer to the public this type of protection. Individual companies have undertaken individual checks on chemicals used and have made their own decisions.

As polypropylene carpets gain market share at the expense of nylon, perfluoroalkyls added during the extrusion process will become more prevalent. Perfluoroalkyls can be incorporated into polypropylene during fibre extrusion to produce durable hydrophilic spunbond and melt-blown microfibre webs. The additive is effective at low concentration and its hydrophilic performance properties compare favourably with those of hydrocarbon additives.

Some companies offering stain protectors indicate their products do not contain the chemicals of concern (therefore alternatives are available).

Treatments that contain no fluorochemicals at all are available.

A.3.2.4 The Carpet Industry

The chain of trade includes producers of carpet treatments, fibre manufacturers and UK carpet manufacturers, wholesalers and retailers.

- There are <150 carpet manufacturers in the UK, with UK carpet production of 141.3 million square meters (msm) in 1997;
- UK carpet imports were 156.0 msm in 1997 (57% of total market consumption) and UK exports 25.9 msm;

With respect to retail, there are 8,200 floor covering retailers in the UK, including 5,200 independent stores and around 1,000 stores in 5 major buying groups. In terms of sales, independent specialists have 45%, carpet chains 30%, furniture chains 11%, department stores 8%, DIY sheds 2%, Others 4%.

A.3.2.5 Issues relating to Exposure

Surface protectors can also be applied at various stages in the chain of trade:

- during fibre production;
- as part of the carpet manufacturer's process;
- by retailers prior to delivery;
- by the carpet fitter at the time of fitting; or
- in DIY applications by the householder.

The application of fluorochemicals during fibre manufacture allows the carpet manufacturer to purchase treated fibre and makes topical treatment of carpets unnecessary. Quite a number of retailers offer stain protectors which are added after the manufacturing. In such instances treatments are applied by specialist contractors and are sprayed or rolled on.

(11 and 12)

A.3.3 Coatings (Including Paints, Inks and Adhesives)

Two trade associations were consulted and others have been identified.

A.3.3.1 Use of perfluoroalkylated substances in paints and adhesives

Fluorosurfactants are included in water-borne paints to minimise cratering and peeling. They are used in some water-based adhesive compositions to improve levelling, and to impart release characteristics. Similarly, water-borne coatings applied to difficult to wet surfaces can show greatly improved leveling with the addition of small quantities of fluorosurfactants.

Responses to a survey by the British Coatings Federation (BCF) indicate that PFAS are used as wetting, flow and levelling agents in a limited number of uses and applications. Details of the end products are not given save in one instance where PFAS are used in fluoropolymer systems for non-stick and high temperature resistant coatings. Discussions with the BCF indicate that PFAS are not necessarily used in water-borne systems but may also be present in solvent-based ones.

The full range of uses for PFAS in the paint, pigment and finishing industries could include:

- Leveling, anti-cratering adjuvant for finishes and paints
- Agent to control differential evaporation of solvents
- Leveling agent for floor waxes
- Adjuvant for waxes to improve oil and water repellency
- Adhesion improver for oily or greasy surfaces
- To combat pigment flotation problems
- Improver for automotive finishes, based on water-based coatings in which the pigments are rendered non-reactive
- Pigment grinding aid to promote wetting, dispersion, color development
- Foam generator substance for the application of dyes, inks
- Electrolytic conversion coatings

A.3.3.2 Use of PFAS in Inks

Reduced surface tensions result in the ability to improve the wetting of a variety of materials, including such hard to wet surfaces as plastics and oily metals. Many printing ink formulations contain fluorosurfactants to enhance ink flow and levelling to improve cylinder life, and to eliminate snowflaking or non-uniform printing.

The survey by the BCF included manufacturers of printing inks but no responses were received.

A.3.3.3 Tonnes of PFAS

The UK market for fluorinated active ingredients in coatings is not known. This application is associated for surfactants, the market for which is estimated to be 70 tpa.

A.3.3.4 Trends in Use

Responses to a survey by the British Coatings Federation indicated that the high cost of PFAS significantly restricts their use to high added value/high performance products and/or use as the very last option.

A.3.3.5 PFAS Concentrations

Fluorosurfactants are included in floor polishes and latex paints at concentrations of 50 to 150 ppm, following reformulation of products containing 50% to 98.5% active.

A.3.3.6 Substitutability Issues

Fluorosurfactants are used together with hydrocarbon and silicone-based surfactants in coatings formulations. The general view is that hydrocarbon or silicone systems are less effective.

(11)

A.3.4 Construction

No consultation with trade associations took place since this was considered to be a low priority area.

Use of Perfluoroalkylated Substances

Protective treatments based on PFAS are used for construction products such as concrete, stone, porous brick. Fluorinated surfactants reduce the shrinkage of cement and can improve weather resistance. Fluorochemicals can also be used as air entrainment additives for low density concrete. Fluorochemical treated nonwovens are used as roofing substrates; the finish prevents asphalt migration. Similarly treated nonwoven constructions are used for cable insulation, tapes and protective wrappings.

PFAS Types

Acrylate copolymers are used to impart water repellency, with the specific products frequently being the same as in the paper and board sector.

Substitutability Issues

New products are anticipated.

(11,13)

A.3.5 Fire-Fighting Foams

Reviewed by

- *Foam Sub-Group, British Fire Protection Systems Association (BFPSA)*
- *EA Area Emergencies Co-ordinator with experience of foam issues.*

Fire fighting foams have unique features and benefits in fighting flammable liquid fires. The foam solution is aerated at the discharge nozzle into air filled bubbles, which float on the surface of the fuel. The properties of the constituents of the foams give them resistance to heat. The bubbles form a blanket which:

- prevents the release of flammable and toxic vapours
- separates air from the flames, and therefore:
- suffocates and extinguishes the fire
- cools the fuel to reduce vapour release and the danger of re-ignition.

Use of Perfluoroalkylated Substances in Fire Fighting Foams

Fire fighting foams containing PFAS are used on fires involving flammable liquids (hydrocarbon and polar solvent). They can be applied via fixed systems and/or manually to safeguard the following:

- spills and bunds
- tanks and tankers
- process areas both indoor and outdoor
- aircraft and aircraft maintenance facilities
- flammable liquid storage

Fire fighting foams are 'mechanical' foams produced by diluting a foam concentrate with water prior to delivery via a nozzle. The "foam solution" is fed under pressure to the discharge nozzles, which aerate the solution, so a blanket of foam bubbles forms over flammable liquids. After a period of time, the bubbles break down (and as such the foam blanket would need replenishing if protection were to be required over an extended period) and foam solution remains. Foams have evolved since the 1940s and fall under the following generic types:

- Protein (P)
- Fluoroprotein (FP)
- Film Forming Fluoroprotein (FFFP)
- Aqueous Film Forming Foam (AFFF)
- Alcohol Resistant (AR) AR-AFFF and AR-FFFP
- Synthetic (S)

Class A foam concentrates are used on fires involving wood, paper and rubber. These rely mainly on inorganic mixtures of anionic surfactants, ammonium sulphate and or phosphates, clay thickeners and stabilisers with other solvents and colourants. Class A foams are designed primarily to lower the surface tension of the water and so allow better penetration of the solution into the mass of burning material. Class B foam concentrates are used on fires involving flammable liquids, oils or grease. These usually contain synthetic fluorochemical surfactants together with additives.

It is reported that fluorosurfactants are used extensively in formulating Class B foam concentrates and some Class A agents. Fluorinated surfactants are used because of their excellent physical and chemical stability. Because fluorinated chains repel oil as well as water it is an effective surfactant for fighting flammable liquid fires.

PFAS are also reported to be used in other fire fighting products.

Tonnages of PFAS in fire fighting foams

The UK market for perfluoroalkylated substances used in fire fighting foam manufacture is estimated to be 65 tpa (16.25% of the estimated total UK market of 400 tpa).

The relative quantity of foam used is set out in the table below. These are various industry rankings (1 – highest) for emissive users (non emergency discharges i.e. training, testing and commissioning) and non-emissive users (emergency discharges only).

Market Area	Emissive	Non-Emissive
Aviation	1	4
Off-shore	4	5
Oil refining	5	1
Petrochemical industry	5	5
Power generation	6	7
Government	3	2
Local Authority (fire services)	2	3
Fire extinguishers	7	6
* Order of importance in terms of volumes of fluorosurfactants used – 1 highest		

The shelf life of fluorosurfactant containing foams is 10 – 20 years.

Trends in Use

Fluorosurfactant-based systems are the foams of choice and no move away from them is occurring.

PFAS Concentrations

All fire fighting foams are supplied as a concentrate. The concentrate is used in dilute solutions of between 1% and 6% concentrate in water. The BFPSA reports that many UK foam manufacturers have formulated their products by using selected blends of hydrocarbon – fluorocarbon surfactants thereby minimising the amount of fluorine in the product. In general, for a 3% type AFFF product the amount of fluorine used in the concentrate would be approximately 0.5 to 0.8%. At 3% concentration in water the level of fluorine is reduced down to 0.015 – 0.024%. In fluoroprotein systems concentrations are somewhat less, at 5% to 10% of the figures for AFFF. the BFPSA also reports that fire fighting foam concentrates containing fluorinated surfactants produced by PFAS from telomerisation use much smaller amounts of these surfactants than for those produced by electrochemical fluorination, i.e. approximately 0.5 to 0.8% as opposed to 1.5% - 1.8% (approximately) for a 3% foam.

Substitutability

Only fluorosurfactants give the low surface tensions necessary for the film-forming vapour suppression properties of both AFFF and FFFP foam systems. A variety of surfactant systems have been tested, but the preferred performance is provided by perfluorinated, straight-chain aliphatic anionic surfactants with a chain-length of about C₈-C₁₀.

It is reported by the industry that fire fighting foams containing fluorosurfactants are the only effective means of extinguishing flammable liquid fires using current application techniques and minimising the threat to life and property. Fluorosurfactant based foams also reduce the amounts of potentially harmful fire effluents (air and water borne). Thus, when considering substitution, it is appropriate to consider the change in risks associated with fires as well as

with the foams themselves. Foams without fluorosurfactants are considerably less effective and also require special – gentle means of application.

Issues relating to exposure

Foams are held in storage until required. They are only used in emergency situations for fighting flammable liquid fires and in associated training exercises. This training takes place in designated and controlled areas and is of limited scale and duration.

The BFPSA recommends that the unnecessary discharge of foam should always be avoided but that where discharge is necessary to establish performance, foam amounts should be minimised. Releases must not threaten:

- conservation areas (i.e. Sites of Special Scientific Interest [SSSI])
- drinking water intake
- controlled waters (i.e. areas where rivers, lakes or ponds are present)

The BFPSA recommends that foam concentrate and/or foam solution, as well as fire effluents, should be collected and disposed of in a controlled and responsible manner as appropriate to local circumstances. Prior to the release/discharge of foam in any form, the Health & Safety Officer of the facility should be contacted to ascertain the disposal procedures. The waste water treatment authority receiving the foam should also be contacted to advise them of the intention. Foam solution or small spills of foam concentrate, can be diluted with water to 250 ppm (i.e. 120 litres per litre of foam solution or 4,000 litres per litre of foam concentrate) and then released to waste water treatment facilities in consultation with the receiving authorities. Larger volumes of foam concentrate must be disposed of through licensed disposal companies.

The Environment Agency and the Fire Services have a joint protocol (November 1999) which addresses the use of fire fighting foams amongst other things. The protocol indicates:

- the Fire Service should liaise with the Agency on a local basis to ensure that the use of fire fighting foam in training exercises does not cause pollution;
- advice will be exchanged on specific subjects such as fire fighting foams, fire water run-off decontamination procedures and waste management; and
- the Fire Services should inform the Agency of all incidents involving foam (car fires excluded) and all exercises involving foam (except in a designated test area).

(1, 14 – 22)

A.3.6 Intermediates

Consultation in this area has concentrated on additives used in polymer processes.

Use of Perfluoroalkylated Substances

PLASTICS AND RUBBER INDUSTRY

- Emulsifying agent for polymerization, particularly fluoro-monomers
- As a latex stabilizer
- To aid in the preparation of agglomerates of powdered fluorocarbon polymers

- In synergistic mixtures with hydrocarbon surfactants to wet low energy surfaces including natural and synthetic rubbers, resins, plastics
- Adjuvant for foaming agents for leak detection of cracks
- Foam additive to control spreading, crawling, edge buildup
- As a mould release agent for silicones
- In refractory processes
- As an antimist film former
- Additive for elimination of trapped air in plastic laminates
- Wetting agent for resin molds for definition, strength
- Hot-melt additive for oil and grease repellency
- Resin additive for improved wetting/bonding with fillers
- Flow modifier for extruding hot melts: spreading, uniformity, anti-cratering
- Adjuvant for resin etchant
- Mold release agent, demoulding agent
- Retarder for plasticiser migration or evaporation
- Internal anti-static agent for polyolefins
- Anti-blocking agent for polyolefins

PTFE production

The high pressure emulsion polymerisation of TFE employs water in which ammonium perfluorooctanoate and an initiator (usually diisopropylperoxydicarbonate) are suspended (dissolved). The perfluorooctanoate exists as micelles, providing it is present at a concentration greater than the critical micellar concentration, which is about 0.001%. The size of the micelles controls the amount of TFE in suspension, which in turn controls the PTFE particle size.

Perfluorooctanoic acid can be used in copolymerisation of TFE with other fluorinated monomers. There is good experimental evidence that the ammonium perfluorooctanoate assists in the solubilisation of the TFE. However its use is subject to considerable proprietary know-how in the production of the much higher value melt-processable TFE co-polymers.

A.3.7 Leather

One trade association was consulted and others have been identified.

Use of Perfluoroalkylated Substances in the leather industry

Treatments are applied to leather and suede to provide oil/water/stain repellence. Tanning treatments react with the leather in the tanning drum and on subsequent drying. On losing water they release hydrochloric acid and react with the proteins in the leather. This treatment is normally used on hide that requires very high levels of oil and water repellence throughout the thickness of the leather (for instance in upholstery grades), but can present problems if further treatments are required as the surface is rendered almost unwettable.

Fluorinated surfactants are also used in various leather manufacturing processes to improve the efficiency of the process, reduce processing time and increase the quality of the product. They can also improve the levelling of acrylic brightener emulsions on leather.

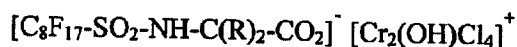
Tonnages of PFAS

The UK market for fluorinated active ingredients in textile, leather and carpet treatment is estimated to be 195 tpa. The breakdown between the three sectors is not known.

While the British Leather Confederation is aware that people are using PFAS, the extent of use is not known.

PFAS Types

Tanning treatments are usually based on chromium complexes containing a long perfluorocarbon chain. A typical structure might be:



Fluorinated surfactants can affect the rate at which chrome tanning agents and dyes are exhausted.

Substitutability Issues

The recent 3M decision has meant that some users in the leather industry have found alternatives (BLC).

The Leather Industry

In 1997 there were 126 tanners in the UK, 8% of the 1550 in the EU as a whole. Of these, 58% were classified as small (< 50 employees), 36% as medium (50 to 250 employees) and 6% as large (> 250 employees) (1).

Issues relating to Exposure

As protectors, fluorochemicals can be applied either at the tanning stage or as a topical treatment in the finishing of the leather.

Fluorinated surfactants have been used in hydrating, bating, pickling, degreasing and tanning processes. The techniques suitable for applying fluorinated surfactants after tanning are:

- tumbling in a drum, in which the leather soaks the fluorinated surfactant form an emulsion, suspension or solution;
- spraying
- cast coating

(13, 23)

A.3.8 Metal Extraction, Refining and Processing

Consultation with a supplier and a trade association took place.

Use of Perfluoroalkylated Substances

A wide range of possible applications for PFAS has been suggested:

- In cleaning agents for property improvement
- Additive for solvent cleaning
- Additive for metal pickling baths to increase bath life and acid runoff
- Additive for chrome electroplating: surface tension reduction, foaming
- Additive for soldering flux, especially for electronic circuitry
- Protective agent for coatings (tarnish resistance, grease repellency)
- Corrosion inhibitor
- Additive for etchant solution for improved definition
- To form antimist films and anticondensation surfaces
- Plastic preplate and silicon etchant technology
- In soldering flux for microelectronics to reduce foaming
- In chemical roughing agent solutions, prior to galvanization
- As a colloidal dispersion aid for magnetic solids
- Protective coatings for aluminum and as an antiblocking agent
- Wetting agent for leaching copper ores and as a froth flotation agent
- To promote ore wetting and quicker breaking of the protective oxide layer

With respect to metal treatment, the main use for PFAS is in mist suppressants. Fluorinated surfactants prevent mist formed by gas bubbles evolving at electrodes during electroplating. These surfactants reduce the size of gas bubbles by lowering the surface tension of the electrolyte solution.

Some PFAS are stable in hostile environments such as hot chromic acid, anhydrous hydrazine, hot concentrated sulfuric acid, hot concentrated hydrofluoric acid and sodium hydroxide solutions, permitting the production of stable foams in these media. The formation of a foam blanket on the surface of the treatment bath prevents the release of acid mists, by acting as a barrier and retarding the entrainment of the electrolyte.

Not all chromium platers use PFAS, only those producing decorative chromium plating – the “bright, shiny” plating for domestic use. PFAS is not used in hard chromium plating used for engineering purposes.

Tonnages of PFAS and Trends in Use

The chromium plating industry uses less than 2 tonnes per annum of PFAS.

PFAS Types

With respect to the products of electrochemical fluorination, mist suppressants for metal plating baths can be based on:

- K, Li, diethanolamine, NH_4 salts
- quaternary ammonium salts
- amines.

PFAS Concentrations

In the mist suppressant PFAS are present at a few ppm.

Substitutability Issues

Owing to their chemical stability, fluorinated surfactants can be used in electroplating baths where hydrocarbon-type surfactants would not survive, and the metal treatment industry is concerned about the possible loss of PFAS, as such substances are reported to be the most effective surfactants for the prevention of acid mists during chromium plating.

Formulators

The BSTSA indicates that there are three, maybe four, companies supplying acid mist suppressants for hexavalent chromium systems (these are believed to be taken from the group of main PFAS suppliers).

Around 100 chromium platers in the UK are estimated to be using these products.

Issues relating to Exposure

A large user in the UK may use a few hundred kilograms of these materials each year. The treatments in which PFAS are used are dragged out of the process tank to only a very limited extent. The rest remains on the material and oxidises. The dragout goes to waste water treatment, at a wastage rate of about 0.5%.

Policy Issues

PFAS are extremely useful as these help to protect the health of workers in chromium plating facilities. The plating solution, chromic acid, has a long list of health effects including carcinogenicity (while only a small number of cases have been reported, there is sufficient evidence in humans to show it is carcinogenic). A more common effect is chromium ulcers, where the dividing section in the middle of the nose is eaten away. Owing to these effects chromic acid is under pressure from the Health and Safety Executive. Thus if considering substitution, it is appropriate to consider the change in health risks associated with increased release of chromic acid mists alongside reductions in environmental risk.

(1, 13, 24)

A.3.9 Mineral Oil and Fuel

Consultation took place with several trade associations and expert groups.

Use of Perfluoroalkylated Substances

- Wetting assistant for oil well treatments, drilling muds
- As a film evaporation inhibitor for gasoline, jet fuel, solvents, hydrocarbons
- Lubricating, cutting oil improver, to improve penetration times
- In extreme pressure lubricants
- Oil spill collecting agent
- Additive to improve tertiary oil well recovery

Water-soluble fluorochemical surfactants have been used in the oilfield since the early 1970s, as surface tension depressants in a variety of aqueous stimulation fluids for low-permeability

oil and gas wells.

A.3.10 Paper

Five trade associations were consulted.

Use of Perfluoroalkylated Substances

- Fluorochemicals are used to provide oil, stain and grease barriers for paper and paperboard and moulded products. Products are mainly used in food, fast food and pet food packaging. Food packaging is one of the major applications and fluorochemical phosphate esters are approved for this use world-wide.
- In pigmented coatings on the outside of boxes or bags, fluorinated surfactants are used to prevent soiling and maintain the appearance of the package.
- PFAS may be used in association with plastic coated paper. A repellent treatment with a fluorinated surfactant prevents fat and grease from seeping into the edges of stamped out polyethylene or polypropylene lined cartons.

Materials treated with fluorinated surfactants for protective purposes include (2):

- liner board: for packaging machine parts, rope, twine, meat;
- folding cartons: for snack foods, fast food, cake mixes, margarine, confectionery and bakery products, and pet foods
- multiwall bags: snack foods, cake mixes, pet food
- flexible packaging; fast food, confectionery wrappings.
- duplicator and reproduction paper
- support cards: confectionery and bakery products.

Emulsions containing a fluorinated surfactant and waxes and/or paraffins are release agents for paper coating compositions used to produce high gloss paper for example. Fluorinated surfactants are also used in the manufacture of heat sensitive paper and ink jet printing paper (2).

Other reported PFAS applications include:

- for cleaning tubes in paper making, dyeing
- as a pulping aid

Tonnages of PFAS

The UK market for fluorinated active ingredients in paper treatment is estimated to be 60 tpa.

Trends in Use

Fluorochemical phosphate esters have gradually displaced chrome complexes for products directly in contact with food.

PFAS Types

Monomeric fluorinated surfactants, their chromium or zirconium complexes, and polymeric

fluorochemicals are used for repellent treatments. Two types of fluorochemical product are approved for use in food packaging; phosphate esters and polymeric acrylates.

PFAS Concentrations

One product is sold as a 20% aqueous solution in water/isopropanol.

For internal application about 1.0% to 1.5% (based on the weight of the dry fibre) of a fluoroalkyl phosphate, is needed for good oil repellency (2).

Issues relating to Exposure

Fluorinated surfactants can be added to the pulp slurry, applied to the paper surface, or included in pigmented coatings. The surface treatment process is the most efficient mode of application and is easier to control than the internal application process (2).

Most fluorinated compounds currently available are anionic compounds which can only be used in the wet end of paper production in the presence of a cationic retention aid. They are not water-repellent, so the application process requires the addition of a sizing agent to impart water-repellency.

Some products can also be applied by size press treatment on the paper surface.

Studies by DuPont have revealed that very low amounts of fluorinated surfactants are extracted from paperboard into solvents simulating food (2).

(1, 11, 13)

A.3.11 Personal and Domestic Use

Three trade associations were consulted.

Use of Perfluoroalkylated Substances

PFAS can be used in skin protection creams, as surfactants in shampoos and shaving foams and for their oil and water repellent properties in cosmetic powders. Fluorosurfactants are included in floor polishes to minimise cratering and peeling.

In dry cleaning formulations fluorinated surfactants improve soil suspension in perchloroethylene and reduce redeposition (1).

HOUSEHOLD

- Rinse-aid for dishwashing
- Liquid polishing compositions
- Floor polish levelling agent
- Additive for alkaline oven cleaners
- Synergistic improver for disinfectants
- Carpet cleaners
- Synergistic wetting agent in detergent formulations