



**Stockholm Convention  
on Persistent Organic  
Pollutants**

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**Persistent Organic Pollutants Review Committee**  
**Sixth meeting**  
Geneva, 11–15 October 2010

**Report of the Persistent Organic Pollutants Review Committee  
on the work of its sixth meeting**

**Addendum**

**Guidance on alternatives to perfluorooctane sulfonate and its  
derivatives**

At its sixth meeting, the Persistent Organic Pollutants Review Committee endorsed guidance on alternatives to perfluorooctane sulfonate and its derivatives, on the basis of the draft guidance contained in document UNEP/POPS/POPRC.6/INF/8 as amended during the meeting. The text of the guidance as endorsed is set out below.

## **Annex**

# **Guidance on alternatives to perfluorooctane sulfonate and its derivatives**

## **Disclaimer**

The present document is a status report based on available information on alternatives to perfluorooctane sulfonic acid (PFOS) and its derivatives. It is important to note that toxicological and ecotoxicological data gaps remain with regard to potential alternatives to PFOS and its derivatives. The data presented in the document are only suggestive, and it is important that research continue with the aim of yielding additional health and environmental data that will enable a better understanding of the toxicological and ecotoxicological effects of the alternatives presented. The document responds to specific issues relating to the Stockholm Convention and does not address issues unrelated to persistent organic pollutants.

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## List of abbreviations and acronyms

AFFF	aqueous film-forming foams
AR-AFFF	alcohol-resistant aqueous film-forming foams
AR-FFFP	alcohol-resistant film-forming fluoroprotein foams
BCF	bioconcentration factor
CAS	Chemical Abstract Service
CCD	charge-coupled device (technology for capturing digital images)
CEN	European Committee for Standardization
D4	octamethyl cyclotetrasiloxane
D5	decamethyl cyclopentasiloxane
D6	dodecamethyl cyclohexasiloxane
diPAPs	diesters of polyfluoroalkyl phosphonic acids and phosphoric acids
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ETFE	ethylene tetrafluoroethylene
EtFOSA	<i>N</i> -ethyl perfluorooctane sulfonamide (sulfluramid)
EtFOSE	<i>N</i> -ethyl perfluorooctane sulfonamidoethanol
EtFOSEA	<i>N</i> -ethyl perfluorooctane sulfonamidoethyl acrylate
EtFOSEP	di[ <i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate
EU	European Union
FC-53	potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate/perfluoro[hexyl ethyl ether sulfonate]
FC-53B	potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
FC-80	PFOS potassium salt
FC-98	potassium perfluoroethyl cyclohexyl sulfonate
FC-248	PFOS tetraethyl ammonium salt
FFFP	film-forming fluoroprotein foams
INCI	International Nomenclature of Cosmetic Ingredients
LD <sub>50</sub>	doses that killed 50%
MeFOSA	<i>N</i> -methyl perfluorooctane sulfonamide
MeFOSE	<i>N</i> -methyl perfluorooctane sulfonamidoethanol
MeFOSEA	<i>N</i> -methyl perfluorooctane sulfonamidoethyl acrylate OECD
MDM	octamethyl trisiloxane
MD2M	decamethyl tetrasiloxane
MD3M	dodecamethyl pentasiloxane
MM (or HMDS)	hexamethyl disiloxane
NGLF	Norsk Galvanoteknisk Landsforening,
NOAEC	No observable adverse effect concentration
NOAEL	No observable adverse effect level
OECD	the Organisation for Economic Co-operation and Development
PAPs	polyfluoroalkyl phosphonic acids and phosphoric acids
PFAAs	perfluoroalkanoic acids
PFAS	perfluorinated alkyl sulfonates
PFBS	perfluorobutane sulfonic acid/potassium perfluorobutane sulfonate
PFBSF	perfluorobutane sulfonyl fluoride
PFBSK	PFBS potassium salt
PFCs	polyfluorinated chemicals
PFCA	perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoic acid
PFDS	perfluorodecane sulfonic acid

PFHpA	perfluoroheptanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFOSA	perfluorooctane sulfonamide
PFOSF	perfluorooctane sulfonyl fluoride
PTFE	polytetrafluoroethylene
ZVO	German national metal plating association
QSAR	quantitative-structure-activity-relationships

Below is the decision taken by the Conference of the Parties of the Stockholm Convention at its fourth meeting on the listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. Acceptable purposes and specific exemptions are shown in the table.

### SC-4/17: Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride

*The Conference of the Parties,*

*Having considered* the risk profile, risk management evaluation and addendum to the risk management evaluation for perfluorooctane sulfonate transmitted by the Persistent Organic Pollutants Review Committee,<sup>1</sup>

*Taking note* of the recommendation by the Persistent Organic Pollutants Review Committee to list perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in Annex A or Annex B of the Convention,<sup>2</sup>

1. *Decides* to amend part I of Annex B of the Convention to list perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride therein by inserting the following row, with the acceptable purposes and specific exemptions specified in the row:

Chemical	Activity	Acceptable purpose or specific exemption
Perfluorooctane sulfonic acid (CAS No: 1763-23-1), its salts and perfluorooctane sulfonyl fluoride (CAS No: 307-35-7)	Production	<p><b>Acceptable purpose:</b> In accordance with part III of this Annex, production of other chemicals to be used solely for the uses below. Production for uses listed below.</p> <p><b>Specific exemption:</b> As allowed for Parties listed in the Register.</p>
	Use	<p><b>Acceptable purpose:</b> In accordance with part III of this Annex for the following acceptable purposes, or as an intermediate in the production of chemicals with the following acceptable purposes:</p> <ul style="list-style-type: none"> <li>• Photo-imaging</li> <li>• Photo-resist and anti-reflective coatings for semiconductors</li> <li>• Etching agent for compound semiconductors and ceramic filters</li> <li>• Aviation hydraulic fluids</li> <li>• Metal plating (hard metal plating) only in closed-loop systems</li> <li>• Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)</li> <li>• Fire-fighting foam</li> <li>• Insect baits for control of leaf-cutting ants from <i>Atta spp.</i> and <i>Acromyrmex spp.</i></li> </ul> <p><b>Specific exemption:</b> For the following specific uses, or as an intermediate in the production of chemicals with the following specific uses:</p> <ul style="list-style-type: none"> <li>• Photo masks in the semiconductor and liquid crystal display (LCD) industries</li> <li>• Metal plating (hard metal plating)</li> <li>• Metal plating (decorative plating)</li> <li>• Electrical and electronic parts for some colour printers and colour copy machines</li> <li>• Insecticides for control of red imported fire ants and termites</li> <li>• Chemically driven oil production</li> <li>• Carpets</li> <li>• Leather and apparel</li> <li>• Textiles and upholstery</li> <li>• Paper and packaging</li> <li>• Coatings and coating additives</li> <li>• Rubber and plastics</li> </ul>

2. *Also decides* to create a new part III in Annex B called “Perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride (PFOSF)”, which reads:

1. UNEP/POPRC.2/17/Add.5, UNEP/POPRC.3/20/Add.5 and UNEP/POPRC.4/15/Add.6.
2. UNEP/POPS/COP.4/17.

**Part III****Perfluorooctane sulfonic acid, its salts  
and perfluorooctane sulfonyl fluoride**

1. The production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) shall be eliminated by all Parties except as provided in part I of this Annex for Parties that have notified the Secretariat of their intention to produce and/or use them for acceptable purposes. A Register of Acceptable Purposes is hereby established and shall be available to the public. The Secretariat shall maintain the Register of Acceptable Purposes. In the event that a Party not listed in the Register determines that it requires the use of PFOS, its salts or PFOSF for the acceptable purposes listed in part I of this Annex it shall notify the Secretariat as soon as possible in order to have its name added forthwith to the Register.
2. Parties that produce and/or use these chemicals shall take into account, as appropriate, guidance such as that given in the relevant parts of the general guidance on best available techniques and best environmental practices given in part V of Annex C of the Convention.
3. Every four years, each Party that uses and/or produces these chemicals shall report on progress made to eliminate PFOS, its salts and PFOSF and submit information on such progress to the Conference of the Parties pursuant to and in the process of reporting under Article 15 of the Convention.
4. With the goal of reducing and ultimately eliminating the production and/or use of these chemicals, the Conference of the Parties shall encourage:
  - (a) Each Party using these chemicals to take action to phase out uses when suitable alternatives substances or methods are available;
  - (b) Each Party using and/or producing these chemicals to develop and implement an action plan as part of the implementation plan specified in Article 7 of the Convention;
  - (c) The Parties, within their capabilities, to promote research on and development of safe alternative chemical and non-chemical products and processes, methods and strategies for Parties using these chemicals, relevant to the conditions of those Parties. Factors to be promoted when considering alternatives or combinations of alternatives shall include the human health risks and environmental implications of such alternatives.
5. The Conference of the Parties shall evaluate the continued need for these chemicals for the various acceptable purposes and specific exemptions on the basis of available scientific, technical, environmental and economic information, including:
  - (a) Information provided in the reports described in paragraph 3;
  - (b) Information on the production and use of these chemicals;
  - (c) Information on the availability, suitability and implementation of alternatives to these chemicals;
  - (d) Information on progress in building the capacity of countries to transfer safely to reliance on such alternatives.
6. The evaluation referred to in the preceding paragraph shall take place no later than in 2015 and every four years thereafter, in conjunction with a regular meeting of the Conference of the Parties.
7. Due to the complexity of the use and the many sectors of society involved in the use of these chemicals, there might be other uses of these chemicals of which countries are not presently aware. Parties which become aware of other uses are encouraged to inform the Secretariat as soon as possible.
8. A Party may, at any time, withdraw its name from the Register of Acceptable Purposes upon written notification to the Secretariat. The withdrawal shall take effect on the date specified in the notification.
9. The provisions of note (iii) of part I of Annex B shall not apply to these chemicals.



## Executive summary

1. At its fourth meeting the Conference of the Parties to the Stockholm Convention decided that the production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) should be eliminated by all parties except for the use and production allowed as acceptable purposes and specific exemptions in accordance with Part III of Annex B to the Convention. While the PFOS-related chemicals used in practice are often precursors of PFOS and may not themselves be specifically listed in the Convention, their production and use is restricted by the listing of PFOS, its salts and PFOSF.
2. The objective of the present study is to summarize what is currently known about alternatives to PFOS, its salts and PFOSF, along with other substances produced where those substances are used as intermediates, and to enhance the capacity of developing countries and countries with economies in transition to phase out PFOS, its salts and PFOSF taking into account the need for longer phase-in schedules for alternatives for some uses and the fact that for certain uses no alternatives exist.
3. The present paper discusses the various uses of PFOS, its salts and PFOSF as a surfactant in impregnation, coating, metal plating, fire-fighting foams and the like and indicates where alternatives have been suggested, are available or have already been introduced to the market in some countries. Fluorinated or non-fluorinated alternatives exist for nearly all current uses. Available alternatives may not be ideal and are not necessarily economically and technically equivalent to PFOS; they may also pose environmental and health hazards at a certain level.
4. The key to the performance of fluorosurfactants is their extreme stability and low surface tension, which currently cannot be matched by other surfactants. The most optimal substance with regard to these properties is PFOS. Owing to environmental and health concerns regarding PFOS, however, other surfactants with or without fluorine could be used as alternatives in circumstances in which these properties are not needed to the degree that they are exhibited by PFOS. Given the relatively high prices of some fluorosurfactants, switching to alternatives can in some cases also have economic benefits.
5. The most common PFOS alternatives in use are fluorotelomers, which are precursors for perfluoroalkyl carboxylic acids (PFCA). Formerly the choice was often C<sub>8</sub>-fluorotelomers; those substances, however, have been shown to degrade into perfluorooctanoic acid (PFOA), whose hazardous properties are also cause for concern. For that reason the major global producers of fluorochemicals have agreed with the United States Environmental Protection Agency to phase out C<sub>8</sub>-fluorotelomers before 2015. As a result, there has been a shift to C<sub>6</sub>-, C<sub>4</sub>- and C<sub>3</sub>-perfluoroalkylated chemicals, which may be less hazardous.
6. For some uses non-fluorinated chemicals such as silicones, aliphatic alcohols and sulfosuccinates have been introduced as alternatives. In other cases particular uses or products are obsolete or could perhaps be changed so that they do not require PFOS; examples are digital techniques in the photographic industry and physical barriers in chrome plating.
7. A comparative assessment of PFOS and possible alternatives with regard to technical, social, economic, environmental, health and safety considerations is a very complex task requiring a large amount of data and other information – more than is normally available. Often the available information about PFOS is much more extensive than the available information about possible alternatives, which may be newly developed substances or formulations covered by trade secrets.
8. Furthermore, much of the information on a given alternative is often non-peer-reviewed and may be of relatively low scientific quality. A mechanism may be needed for continually updating information regarding the substitution properties and hazardousness of alternatives. Such a mechanism would be consistent with subparagraph 1 (b) of Article 9 of the Convention regarding the exchange of information on alternatives to persistent organic pollutants.
9. Available economic data may also be scarce and biased. The information received to date, however, suggests that alternatives are priced comparably to the PFOS-related compounds. Especially for coatings and paints, the non-fluorinated alternatives are cheaper.
10. PFOS and its derivatives are hazardous and, once released to the environment, will stay there forever since no degradation is foreseen; the final sink is likely to be the water bodies. As there is no possibility of recapturing emitted substances from the environment as a precaution all uses of PFOS globally should be limited, with a priority focus on uses resulting in high emissions.

11. Collecting and destroying existing stocks – for example, of PFOS-containing fire-fighting foams – instead of using them up, as is commonly done now, would prevent further contamination of areas (e.g. around airports). As long as PFOS is in a container it is likely that it will remain under control and cause no damage. Part III of Annex B of the Convention describes the goal of reducing and ultimately eliminating the production and use of the PFOS substances listed there.

12. There is a need for incentives for the development and application of safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for such development. The requirements of the Stockholm Convention that must be implemented in national legislation by all parties to the Convention can serve as an important tool for promoting such incentives.

13. Because of current restrictions governing PFOS, it is likely that closely related but unregulated chemicals could be manufactured commercially as alternatives. The risks posed by these substances, along with their socio-economic impacts, should be considered in deciding whether and how to regulate their use.

14. Increased efforts are needed to study the toxicological and environmental properties of alternatives and to make the resulting data and information trustworthy and public by subjecting it to peer review and publishing it in scientific journals.

15. PFOS and its alternatives are being studied and evaluated in parallel by authorities in many countries. Enhanced international cooperation will save resources and speed up these processes.

## I. Introduction, background and objectives

### A. History of the proposal to list PFOS in the Stockholm Convention

16. A letter of 14 July 2005 from the Swedish Ministry of the Environment proposed listing PFOS in Annex A to the Convention. A proposal to that end<sup>1</sup> was discussed at the first meeting of the Persistent Organic Pollutants Review Committee in November 2005. The Committee concluded (decision POPRC-1/7) that the information on PFOS presented met the screening criteria specified in Annex D to the Convention. A PFOS risk profile was adopted at the Committee's second meeting, in November 2006, and published on 21 November 2006.<sup>2</sup> A risk management evaluation for PFOS<sup>3</sup> was adopted at the Committee's third meeting, in November 2007, and published on 4 December 2007. Finally, an addendum to the risk management evaluation was adopted at the Committee's fourth meeting, in October 2008, and published on 30 October 2008.<sup>4</sup>

### B. Decision at the fourth meeting of the Conference of the Parties

17. At its fourth meeting the Conference of the Parties decided to amend Annex B to list PFOS, its salts and PFOSF.<sup>5</sup> Some acceptable purposes and specified exemptions were agreed upon because of a lack of alternatives for various uses, especially in developing countries and countries with economies in transition.

### C. Objective of the study

18. The objective of the present study is to summarize what is currently known about alternatives to PFOS, its salts and PFOSF and to enhance the capacity of developing countries and countries with economies in transition to phase out PFOS, taking into account the need for longer phase-in times for alternatives for some uses and the fact that there are no alternatives for certain uses.

## II. Characteristics of PFOS and its derivatives

### A. PFOS related substances

19. The chemical names and CAS numbers listed in Annex B as PFOS, its salts, and PFOSF are summarized in table 1.

**Table 1: Chemical names and CAS numbers listed in Annex B as PFOS, its salts, and PFOSF**

PFOS substance	CAS no.
Perfluorooctane sulfonic acid	1763-23-1
Potassium perfluorooctane sulfonate	2795-39-3
Lithium perfluorooctane sulfonate	29457-72-5
Ammonium perfluorooctane sulfonate	29081-56-9
Diethanolammonium perfluorooctane sulfonate	70225-14-8
Perfluorooctane sulfonyl fluoride	307-35-7
Tetraethylammonium perfluorooctane sulfonate	56773-42-3
Di(decyl)di(methyl)ammonium perfluorooctane sulfonate	2551099-16-8

20. Many more PFOS-related chemicals and PFOS precursors exist. The proposal by Sweden to list PFOS in the annexes to the Convention specified PFOS and 96 PFOS-related substances. The United Kingdom's report from 2004 contains a draft list of 98 compounds that have the potential to degrade to

1 UNEP/POPS/POPRC.1/9 and UNEP/POPS/POPRC.1/INF/9.

2 UNEP/POPS/POPRC.2/17/Add.5.

3 UNEP/POPS/POPRC.3/20/Add.5.

4 UNEP/POPS/POPRC.4/15/Add.6.

5 UNEP/POPS/COP.4/38.

PFOS in the environment. <sup>6</sup>A report from China indicates that 66 PFOS-related chemicals have been identified in a national inventory in China (2009). In 2007 in Denmark 92 polyfluorinated substances, including 13 PFOS-related ones, were registered as being used in products.<sup>7</sup> In the preliminary list of PFOS, perfluorinated alkyl sulfonates (PFAS), PFOA and related compounds and chemicals that may degrade to PFCA published by the Organization for Economic Cooperation and Development (OECD), many more PFOS-related chemicals were listed.<sup>8</sup> In Canada more than 60 PFOS chemicals have been listed.<sup>9</sup>

21. More complex PFOS derivatives not specified in Annex B are also widely used. These derivatives are covered through the listing of PFOSF, the basic material for their manufacture. PFOSF is an intermediate material for production of all C<sub>8</sub>-perfluorinated alkyl sulfo compounds. Production and use of PFOSF and consequently also of all other C<sub>8</sub>-perfluorinated alkyl sulfo-compounds is restricted to acceptable purposes and specific exemptions. Therefore the present document includes descriptions of alternatives to substances which are not directly listed in the Convention but which nevertheless are covered by it.

22. Some of the most important PFOS derivatives are listed in table 2.

**Table 2: Examples of PFOS derivatives not specified in Annex B<sup>10</sup>**

Chemical name	Abbreviation	CAS no.
Perfluorooctane sulfonamide	PFOSA	754-91-6
<i>N</i> -Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8
<i>N</i> -Methyl perfluorooctane sulfonamidoethanol	MeFOSE	2448-09-7
<i>N</i> -Methyl perfluorooctane sulfonamidoethyl acrylate	MeFOSEA	25268-77-3
Ammonium bis[2- <i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate <sup>1</sup>		30381-98-7
<i>N</i> -Ethyl perfluorooctane sulfonamide (sulfluramid)	EtFOSA	4151-50-2
<i>N</i> -Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2
<i>N</i> -Ethyl perfluorooctane sulfonamidoethyl acrylate	EtFOSEA	432-82-5
Di[ <i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate	EtFOSEP	67969-69-1
3-[[Heptadecafluorooctyl]-sulfonyl]amino]- <i>N,N,N</i> -trimethyl-1-propanaminium iodide/perfluorooctyl sulfonyl quaternary ammonium iodide	Fluorotenside-134	1652-63-7
Potassium <i>N</i> -ethyl- <i>N</i> -[(heptadecafluorooctyl) sulfonyl] glycinate		2991-51-7
<i>N</i> -Ethyl- <i>N</i> -[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide		61660-12-6

23. There are many other PFAS and derivatives thereof with shorter or longer alkyl chain lengths that are used for applications similar or related to those for which PFOS is used – in other words as PFOS alternatives. Some examples are shown in table 3.

6 Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

7 Jensen, A.A., Poulsen, P.B., Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, 99. Danish Environmental Protection Agency.

8 Document ENV/JM/MONO (2006) 15 (not available online).

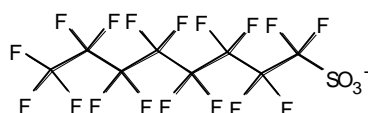
9 Government of Canada. Completed Assessments of Existing Substances: [www.chemicalsubstanceschimiques.gc.ca/about-apropos/assess-eval/caes-ecse/caes-pp-eng.php](http://www.chemicalsubstanceschimiques.gc.ca/about-apropos/assess-eval/caes-ecse/caes-pp-eng.php).

10 Alternative CAS name: 1-Octanesulfonamide, *N,N'*- [phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt.

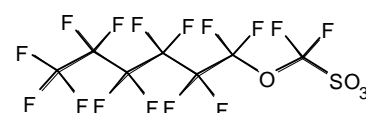
**Table 3: Examples of PFAS**

Chemical name	Abbreviation	CAS no.
Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	67584-42-3
Perfluorobutane sulfonic acid	PFBS	59933-66-3
Potassium perfluorobutane sulfonate		29420-49-3
Perfluorohexane sulfonic acid	PFHxS	432-50-7
Perfluorodecane sulfonic acid	PFDS	335-77-3
Perfluorodecane sulfonate		67906-42-7

24. Because of the restrictions on PFOS use it is expected that closely related but unregulated chemical structures, such as perfluoro[hexyl methyl ether sulfonate], could be commercialized. The similarity of these substances to PFOS is illustrated by the following structure formulas:



Perfluorooctane sulfonate



Perfluoro[hexyl methyl ether sulfonate]

25. The related perfluoro[hexyl ethyl ether sulfonate] (FC-53) is used as mist suppressant in Chinese chrome plating enterprises.

## B. Properties of PFOS related substances

26. The strong carbon-fluorine bond makes the perfluoroalkyl chain present in PFOS extremely stable and nonreactive. PFOS resists even strong acids and high temperatures and is not degradable in the environment. The basic PFOS structure is persistent, and the more complex PFOS-related chemicals listed in table 3 will during use or presence in the environment degrade to the basic PFOS structure, which is why they are called PFOS derivatives.

27. The surfactant properties of PFOS give extremely low surface tension. The perfluorocarbon chain is both oleophobic and hydrophobic; thus it repels water, oil and dirt and insulates electricity. These properties have been found useful in many applications.

28. PFOS as a salt is more hydrophilic and soluble in water. The non-dissociated acid and the sulfonamides are less hydrophilic but more volatile than the salts, and can therefore be transported long distances by air. More details may be found in the PFOS risk profile.<sup>11</sup>

## C. Production and consumption of PFOS related substances

29. The company 3M voluntarily phased out PFOS production in 2002 and changed to production of shorter-chain polyfluorinated chemicals (PFCs). Sporadic data on PFOS production exist from national information in Committee documents. For example, in 2003 production of PFOS and PFOSE was initiated in China after production was voluntarily suspended in the United States. In 2006 annual production of PFOSE in China exceeded 200 tonnes, of which about 100 tonnes was exported to other countries, including Brazil and member States of the European Union. In 2003 Germany and Italy produced less than 60 tonnes and less than 22 tonnes of PFOS respectively. The United States in 2006 estimated total use in that country to be less than 8 tonnes a year, and Ireland reported import and use of 10 kilograms of PFOS during 2006. Switzerland gave several estimates for relatively recent use (March 2007) of PFOS, ranging from 230 kilograms to 5 tonnes a year.

30. According to a recent estimate, global production of PFOSE, the basic chemical for production of PFOS derivatives, was 96,000 tonnes between 1970 and 2002.<sup>12</sup>

<sup>11</sup> UNEP/POPS/POPRC.2/17/Add.5.

<sup>12</sup> Paul, A.G., Jones, K.C., Sweetman, A.J. 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environmental Science and Technology* 43: 386–392.

### III. Alternatives to the use of PFOS

31. At the fourth meeting of the Conference of the Parties several countries asked for acceptable purposes and specific exemptions for various applications, which together reflect the entire historical use pattern of PFOS.
32. PFOS in articles remains, and may continue to be, an issue for all countries that import products containing PFOS, even if PFOS is not manufactured in or imported into that country.
33. The present chapter presents the range of currently available alternatives and describes various uses of PFOS for which alternative chemicals have been suggested, presented or introduced to the market in some countries.
34. These alternatives are not necessarily all technically as fit for use as PFOS or without potential risks. Sometimes, but not always, there is enough information to determine whether they are safe enough. In order to be commercialized, substitutes should be safer than PFOS.
35. A safer alternative is one that, when compared to PFOS, either reduces the potential for harm to human health or the environment or has not been shown to be a potential persistent organic pollutant itself.
36. It might also be that a particular use or product is obsolete and not essential or that a process could be changed so that it does not require the use of PFOS.
37. The major producers of fluorochemicals have agreed to phase out C8-perfluorotelomers – a group of possible alternatives that degrade into PFOA – before 2015. That, however, may not prevent other companies from starting or continuing to market these chemicals as alternatives to PFOS.<sup>13</sup>

#### A. Textile impregnation and surface protection

38. PFCs are used extensively by the textile industry and by consumers for the treatment of all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, leather, footwear, rugs, mats, carpets and the like to repel water, oil and dirt (stains).
39. The main PFOS derivatives (normally 2–3% of the fibre weight for textiles but 15% for carpets) previously used for textile and carpet surface treatment applications were the acrylate, methacrylate, adipate and urethane polymers of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE).
40. Examples of well-known trademarked soil and dirt repellents are:
- Scotchgard™ (3M)<sup>14</sup>
  - Zonyl® and Foraperle® (DuPont).<sup>15</sup>
41. Before 2000 these were the most important uses of PFOS derivatives. Since it was banned in many countries PFOS has been replaced mainly with shorter-chain analogues and fluorotelomers but also with non-fluorinated chemicals. The trade names have been retained.
42. Analyses of perfluorinated substances in textiles conducted by the Norwegian Institute for Air Research on behalf of the Norwegian Pollution Control Authority have shown very low concentrations or have failed to identify the presence of PFOS. The analyses indicate that perfluorinated acids and telomer alcohols are now used as alternatives to PFOS in impregnating agents.<sup>16</sup>
43. The alternative surfactants for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles are:
- Other polyfluorinated compounds with shorter alkyl chain length such as:
    - (i) Substances based on perfluorobutane sulfonate (PFBS)
    - (ii) fluorotelomer-based substances, including polymers
  - Silicone-based products

13 [www.epa.gov/oppt/pfoa/pubs/stewardship/index.html](http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html) and [www.epa.gov/oppt/existing\\_chemicals/pubs/actionsplans/pfcs.html](http://www.epa.gov/oppt/existing_chemicals/pubs/actionsplans/pfcs.html).

14 [http://solutions.3m.com/wps/portal/3M/en\\_US/Scotchgard/Home/](http://solutions.3m.com/wps/portal/3M/en_US/Scotchgard/Home/).

15 [www2.dupont.com/Zonyl\\_Foraperle/en\\_US/products/zonyl\\_pgs/zonyl.html](http://www2.dupont.com/Zonyl_Foraperle/en_US/products/zonyl_pgs/zonyl.html).

16 Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

- Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins
- Fluorotelomer silicones such as polyfluorooctyl triethoxy silane (1*H*,1*H*,2*H*,2*H*-perfluorooctyl triethoxy silane, a NanoCover™ product) used in a bathroom floor spray product. This and similar substances were banned in Denmark in April 2010 because of toxic effects on mouse lungs.<sup>17</sup>

44. Scotchgard™ Protector product produced by 3M (universal spray) containing 1–5% of a perfluorobutane sulfonyl urethane (the identity of the chemical is a trade secret) has also been suggested as an alternative for stain-repellent impregnation of textiles, leather and carpets.

45. DuPont has introduced a new brand name, Capstone™, for a series of alternative products for various applications based on short-chain fluorotelomers, mainly involving C6 chemistry.

46. Bluestar Silicones markets some silicone-based PFOS alternatives for textile applications under the trade name Advantex™. The technology offers long-lasting water repellence, quick drying, waterproofness and breathability.<sup>18</sup>

47. Rudolph Group, in partnership with Sympatex, has introduced BIONIC-FINISH®ECO as a fluorocarbon-free, water-repellent treatment for textiles. BIONIC-FINISH®ECO is composed of a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers.<sup>19</sup> The exact identity of the chemical is a trade secret.

## B. Impregnation of packaging (paper/cardboard)

48. Fluorinated chemicals are used in the paper industry to produce waterproof and greaseproof paper. A 1.0–1.5% concentration of fluorochemical, based on the dry weight of the fibres, is needed for paper protection. Following are the main suppliers of fluorochemicals in the paper industry, with their brand names:

- 3M                    Scotchban®
- Bayer                Baysize S®
- Ciba (BASF)        Lodyne®<sup>20</sup>
- Clariant             Cartafluor®<sup>21</sup>
- DuPont              Zonyl®

49. PFOS derivatives have been used both in food contact applications such as plates, food containers, popcorn bags, pizza boxes and wraps and in non-food contact applications such as folding cartons, containers, carbonless forms and masking papers. Paper protection by PFOS derivatives has been achieved by using one of the following:

- Mono-, di- or triphosphate esters of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE)
- *N*-Methyl perfluorooctane sulfonamidoethanol acrylate polymers

50. Before 2000 about 32% of the total use of PFOS in the European Union was for paper coating; the use of PFOS for this purpose is no longer allowed and PFOS has been replaced mainly by other fluorinated chemicals.

51. The known alternative surfactants for impregnation of paper and cardboard for use in packaging are short-chain telomer-based substances, polyfluoroalkyl phosphate, phosphonate-type compounds and poly(dimethyl siloxane).

52. Grease-proof paper did exist before PFOS technology was introduced to the market, and other technologies can do the work. In a survey conducted by the Norwegian Food Safety Authority in 2006, it was concluded that no fluorinated substances were used in fast-food packaging in Norway. The

17 [www.mst.dk/Nyheder/Pressemeddelelser/Nanospray.htm](http://www.mst.dk/Nyheder/Pressemeddelelser/Nanospray.htm).

18 [www.advantex-textiles.com/](http://www.advantex-textiles.com/).

19 [www.rudolf.de/innovations/hydrophobic-future/bionic-finish/self-organisation.htm](http://www.rudolf.de/innovations/hydrophobic-future/bionic-finish/self-organisation.htm).

20 [www.ciba.com/pf/default.asp?search=1&DApname=lodyne](http://www.ciba.com/pf/default.asp?search=1&DApname=lodyne).

21

[www.paper.clariant.com/businesses/paper/internet.nsf/vwWebPagesByID/65137D7B8419F6EDC12571E0003D5C16](http://www.paper.clariant.com/businesses/paper/internet.nsf/vwWebPagesByID/65137D7B8419F6EDC12571E0003D5C16).

Norwegian paper producer Nordic Paper is using mechanical processes to produce, without using any persistent chemical, extra-dense paper that inhibits leakage of fat through the paper.<sup>22</sup>

### C. Cleaning agents, waxes and polishes for cars and floors

53. PFOS derivatives have historically been used as surfactants to lower surface tension and improve wetting and rinse-off in a variety of industrial and household cleaning products such as automobile waxes, alkaline cleaners, denture cleaners and shampoos, floor polish, dishwashing liquids and car wash products. PFOS derivatives have also been used in carpet spot cleaners.

54. A PFOS derivative that was often used in cleaning agents, floor polishes and auto polishes is potassium N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] glycinate (CAS no. 2991-51-7). The concentration of that PFOS derivative in the final product was generally between 0.005% and 0.01% but might have been ten times as high.

55. The possible alternative chemicals identified for use in cleaning agents, waxes and floor polishes are:

- Telomer-based surfactants and polymers
- Various C<sub>4</sub>-perfluorinated compounds: Novec™ (3M), for commercial and industrial cleaning, contains methyl nonafluorobutyl ether (CAS no. 163702-07-6) and methyl nonafluoroisobutyl ether (CAS no. 163702-08-7)
- Fluorinated polyethers: PolyFox™ (OMNOVA Solutions Inc.), a line of fluorosurfactants that are polymers with a molecular weight greater than 1,000 based on ether links and with C<sub>2</sub>F<sub>5</sub> or CF<sub>3</sub> as the starting material.

56. A shift to softer waxes that are more biodegradable or entirely biodegradable may completely eliminate the need for persistent polyfluorinated compounds. In these products, the fluorinated surfactants are replaced with non-ionic or anionic surfactants, which have good wetting properties.

### D. Surface coating, paint and varnish

57. PFOS derivatives have had several uses in coating, paint and varnishes to reduce surface tension – for example, for substrate wetting, for levelling, as dispersing agents and for improving gloss and antistatic properties. PFOS derivatives can be used as additives in dyes and ink, as pigment grinding aids and as agents to combat pigment flotation problems. The concentrations used were below 0.01% (w/w).

58. The possible alternatives identified for use in paints and varnishes are surfactants based on the following:

- Fluorotelomer-based surfactants (e.g. Capstone™ products)
- C<sub>4</sub>-compounds based on perfluorobutane sulfonate, especially in the area of electronic coating
- Fluorinated polyethers (PolyFox™)
- Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water, which is used as an alternative in wood primers and printing inks
- Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd®)
- Propylated naphthalenes and propylated biphenyls, which can be used as water repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications
- Fatty alcohol polyglycol ether sulfate, sometimes together with a sulfosuccinate.

59. Information from suppliers in the paint and varnish industry suggests that fluorosurfactants are in general much more expensive than other alternative surfactants.<sup>23</sup> They are therefore used in paint and varnishes only in situations where very low surface tension is needed and no other

22 Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

23 Poulsen, P.B., Jensen, A.A., Wallström, E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project no. 1013. Danish Environmental Protection Agency. [www2.mst.dk/Udgiv/publications/2005/87-7614-668-5/pdf/87-7614-669-3.pdf](http://www2.mst.dk/Udgiv/publications/2005/87-7614-668-5/pdf/87-7614-669-3.pdf).



(non-fluorinated) alternatives can achieve it (e.g., in products where an extremely smooth surface is necessary).

## E. Oil production and mining

60. PFOS derivatives may be used as surfactants in the oil and mining industry to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, as jet fuel and hydrocarbon solvents and to enhance the amount of recovery of metals from the ores in copper and gold mines. According to information submitted by China at the fourth meeting of the Conference of the Parties, at the time PFOS was still used as a surfactant in old oil fields in China to recover oil trapped in small pores between rock particles. At the meeting, several representatives of other countries questioned this use of PFOS, saying that oil production and mining took place in their countries without the use of PFOS, which indicated that there were alternative processes that did not require PFOS.

61. According to information from the 2006 OECD survey<sup>24</sup> tetraethylammonium perfluorooctane sulfonate and potassium perfluorooctane sulfonate were used in the mining industry in member countries as suppressing agents in an annual combined volume of up to 50 tonnes.

62. Current information about alternatives in the oil and mining industries is scarce. 3M has, according to OECD, introduced PFBS as an alternative, and DuPont markets the telomer-based fluorosurfactants Zonyl® and Capstone™ for applications in the oil industry.<sup>25</sup> Other perfluoro-compounds patented (United States patent 20030153780) for uses in oil recovery are perfluoroalkyl-substituted amines, acids, amino acids and thioether acids.<sup>26</sup>

## F. Photographic industry

63. In the photographic industry PFOS-related substances (tetraethylammonium perfluorooctane sulfonate and perfluorooctyl sulfonamidopropyl quaternary ammonium iodide) have been used in manufacturing film, paper and plates. These PFOS-related compounds function as dirt rejecters and friction control agents and to reduce surface tension and static electricity. Imaging materials that are very sensitive to light (e.g., high-speed films) benefit particularly from the properties of PFOS-based materials. The concentration of PFOS-related substances in coatings in films, paper and plates is in the range of 0.1–0.8 µg/cm<sup>2</sup>.

64. As the spread of digital cameras has reduced film use, the use of PFOS in this area is not expected to grow. World consumption of PFOS for colour film production fell from 23 tonnes in 2000 to 8 tonnes in 2004. Current annual consumption in the European Union's photographic industry is 1 tonne. According to the industry, the estimated annual cost of this 83% reduction has been €20million to €40 million.

65. According to the 2006 OECD survey<sup>27</sup> up to 20 tonnes of lithium perfluorooctane sulfonate and perfluorooctane sulfonic acid were, at the time of the survey, used annually in the photographic industry as anti-reflective agents.

66. PFOS is still used (probably in small quantities) in X-ray film for photo imaging for medical and industrial uses (inspection by non-destructive testing). It is also used in film for other industries, such as the movie industry, as alternatives are claimed not to be of comparably high quality. Use of PFOS in industrial photographic coatings is exempt from the PFOS ban in the European Union and Canada.

67. PFOS-related compounds have also been used in developers for photographic film. According to EU Directive 2006/122/EC this application is now banned. Japan's photographic industry has reported that PFOS is no longer used for photographic processing in Europe, Japan, North America or elsewhere. Since photographic processing solutions using PFOS were highly sophisticated products, they were produced and supplied by a limited number of manufacturers, which have stopped using PFOS for their photographic processing products.

68. The possible alternatives identified for the photographic industry are:

24 Organization for Economic Cooperation and Development. 2006. Results of the 2006 OECD Survey on Production and Use of PFOS, PFAS, PFOA, PFCA, Their Related Substances and Products/Mixtures Containing These Substances. ENV/JM/MONO(2006)36. Available at [www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO\(2006\)36&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en).

25 [www2.dupont.com/Capstone/en\\_US/uses\\_apps/Fluorosurfactants/oil\\_field\\_services.html](http://www2.dupont.com/Capstone/en_US/uses_apps/Fluorosurfactants/oil_field_services.html).

26 Information from the United States Environmental Protection Agency, 2009.

27

[www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO\(2006\)36&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en).

- Digital techniques
- Telomer-based products of various perfluoroalkyl chain length
- C<sub>3</sub>- and C<sub>4</sub>-perfluorinated compounds
- Hydrocarbon surfactants
- Silicone products.

69. Properties that alternatives must have in order to match the quality of PFOS compounds include dynamic surface tension capability, static inhibition, solubility, photo-inactivity and stability when subjected to heat and chemicals.

## **G. Electrical and electronic parts**

70. Electrical and electronic equipment often requires hundreds of parts and thousands of processes. PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, radar systems and the like. The PFOS-related compounds are used as process chemicals, and the final products are mostly PFOS-free. No information about effects on the environment or human health, or about the level of PFOS in electronic waste, is available.

71. Intermediate transfer belts of colour copiers and printers contain up to 100 ppm of PFOS, while an additive used in producing PFA rollers contains  $8 \times 10^{-4}$  ppm PFOS. Industry groups reported that alternatives are not available for those applications.

## **H. Semiconductor industry**

72. PFOS reduces the surface tension and reflectivity of etching solutions, properties that are important for precise photolithography in the semiconductor industry (photo resists and photo masks).<sup>28</sup> Small amounts of PFOS-based compounds are required during the following critical photolithography applications in manufacturing semiconductor chips:<sup>29</sup>

- Ultra-fine patterning/photo resists as photo-acid generators and surfactants
- Anti-reflective coatings as uniquely performing surfactants.

73. The exact PFOS derivative used is not publicly known.

74. These applications are crucial for achieving the accuracy and precision required to manufacture miniaturized high-performance semiconductor chips. The annual use of PFOS in the European Union's semiconductor industry before 2000 was 470 kilograms, with emissions of 54 kilograms.

75. According to the industry no alternatives are available that would allow for the comprehensive substitution of PFOS in these critical applications, which have been exempted from restrictions on PFOS use. The World Semiconductor Council, an industry body, was committed to ending other uses of PFOS in member countries of the United Nations Economic Commission for Europe by May 2007 and globally in May 2009; the semiconductor industry, however, has persuaded the Council to change its position.

76. The Japanese semiconductor industry has been using less than 5 kilograms of PFOS annually for the etching of high-frequency compound semiconductors and piezoelectric ceramic filters. Alternative methods yielding comparable quality are not currently available, and more research and development are needed to achieve that quality. According to a submission from Japan, alternative methods are expected to be available in 2014.<sup>30</sup>

77. According to information submitted by the Chinese delegation to the fourth meeting of the Conference of the Parties, the semiconductor industry in China uses 30–40 kilograms of PFOS yearly for photo resists, as an anti-reflective coating, as a de-glueing agent and as a developing agent, and in 2007 industry sales were ¥100 billion.

78. New photolithography technologies use less photo resist per wafer than older technologies, and the new photo-resist formulations contain much lower concentrations of PFOS. Thus, the total use of PFOS is decreasing, lowering the total amount of releases. In 2002, effluent releases for these critical uses for the whole of Europe totalled an estimated 43 kilograms of PFOS.

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28 Photo masks are optically transparent fused quartz blanks imprinted with a pattern defined with chrome metal and are the templates used to inscribe the circuit pattern into the photo resist.

29 Information provided by the European Semiconductor Industry Association.

30 UNEP/POPS/POPRC.4/INF/17.

79. The cost of developing a new photo-resist system is estimated to be US\$700 million (0.3 % of annual sales) for an industry which had global sales of US\$248 billion in 2006.
80. PFOS is also used to produce developers and edge bead removers. Substitutes do exist for these non-critical uses, and the semiconductor industry is committed to phasing out the use of PFOS. Substitution requires varying lengths of time. According to the industry, smooth substitution often requires more than 10 years, and substitution without approval from customers tends to halt the latter's production lines. Customers expect alternatives to perform comparably to PFOS-containing items.
81. There may be one additional specialized application for which, according to industry sources, there is currently no substitute for PFOS: use in liquid etchant in the photo mask rendering process. For photo mask etching with strong acids non-fluorosurfactants are not stable enough, and shorter-chain fluorosurfactants do not have sufficiently low surface tensions. While in some instances a dry etching process without surfactants can be used, such a process is not suitable for LCD panels measuring more than 1 m × 1 m.

## I. Aviation hydraulic fluids

82. Hydraulic oils with a potassium perfluorooctane sulfonate content of about 0.1% have been used in civil and military airplanes since the 1970s (United States patent 3679587 dates from 1972) to prevent evaporation, fires and corrosion. The total global market for fluorinated compounds in aircraft hydraulic fluids is about 2 tonnes per year. Annual PFOS consumption in the European Union for this use was about 730 kilograms/year.
83. There is uncertainty about alternative substances in this area. Aviation hydraulic fluids without fluorinated chemicals but based on, for example, phosphate esters exist,<sup>31</sup> and fluorinated chemicals other than PFOS can be used. A search for alternatives is said to have been under way for 30 years (starting before PFOS was considered a problematic substance). While about 2,500 different compounds are said to have been tested, neither the fluorotelomers nor the non-fluorinated chemicals tested have met the performance requirements or the high safety standards of this industry.<sup>32</sup>
84. The industry statements cited in the previous paragraph are probably obsolete. The potassium salt of perfluoroethylcyclohexyl sulfonate (CAS no. 67584-42-3) is not a PFOS related substance, and it has been used in hydraulic oils instead of PFOS. However, 3M, which formerly produced this chemical, has ceased to do so, probably because of lack of demand.

## J. Pesticides

85. *N*-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2) is both a surfactant and a pesticide used in tropical areas such as Brazil against termites, cockroaches and other insects..
86. According to information from the 2006 OECD survey sulfluamid was used in insecticides at a concentration of 0.01-0.1% at an annual volume of up to 17 tonnes.
87. Fluorosurfactants may also be used as "inert" surfactants (enhancers) in pesticide products. The two PFOS-related substances potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS no. 2991-51-7) and 3-[[heptadecafluorooctyl)sulfonyl]amino]-*N,N,N*-trimethyl 1-propanaminium iodide (CAS no. 1652-63-7) have been approved in pesticide formulations in the United States.<sup>33</sup> Both chemicals have other uses, for example as cleaning agents. PFOS derivatives were used in pesticides because they were considered rather inert and non-toxic.
88. PFOS is no longer used to manufacture ant bait or insecticides against beetles and ants in the European Union, and the United States Environmental Protection Agency cancelled the registration of sulfluramid in May 2008.<sup>34</sup> According to information submitted to the secretariat of the Stockholm Convention, sulfluramid had been used for pest control (to control cockroaches, white ants and fire ants) in China, and sulfluramid is used in Brazil in more than 95% of baits for the control of leaf-cutting ants, although the amount of PFOS used was not reported.

31 [www.freepatentsonline.com/6319423.html](http://www.freepatentsonline.com/6319423.html) and [www.freepatentsonline.com/WO2006138081.html](http://www.freepatentsonline.com/WO2006138081.html).

32 Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

33 [www.fluoridealert.org/pesticides/pfos.pfoas-page.htm](http://www.fluoridealert.org/pesticides/pfos.pfoas-page.htm).

34 [www.epa.gov/fedrgstr/EPA-PEST/2008/May/Day-16/p10919.htm](http://www.epa.gov/fedrgstr/EPA-PEST/2008/May/Day-16/p10919.htm).

89. According to the Brazilian delegation, the use of sulfluramid in Brazil prevents damage corresponding to losses of up to 14.5 % of trees per hectare. The cost of an attack by leaf-cutting ants is estimated at US\$6.7 billion. Other agricultural products likely to suffer costly losses are soybean and maize. Also, the per-hectare capacity to support livestock is likely to decrease if forage for grazing is reduced by ants.

90. Currently, the active ingredients registered in Brazil for producing bait to control leaf-cutting ants are sulfluramid, fipronil and chlorpyrifos. The latter two, however, are considered more acutely toxic to humans and the environment than sulfluramid. Furthermore, the effectiveness of these substances has been questioned; thus new alternatives are being studied in Brazil. According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose.<sup>35</sup> Sulfluramid is the only active ingredient with all the properties necessary for effective functioning as ant bait, which is the only effective option for controlling leaf-cutting ants.<sup>36</sup>

91. There are many differences between leaf-cutting ants and exotic ants (urban ants), including in alimentary behaviour. Such differences explain why certain active ingredients are effective for controlling urban ants and not for controlling leaf-cutting ants. Fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone and methoprene had been tested for leaf-cutting ants, but they were not effective.<sup>37</sup> An adequate insecticide used to formulate bait for the control of leaf-cutting ants should be lethal at low concentrations, act by ingestion and present a delayed toxic action. Additionally, it should be odorless and non-repellent, so as to be dispersed by trophallaxis to most workers in the colony.<sup>38</sup> Since 1958, over 7,500 chemical compounds for ant control have been studied in many countries. Fewer than 1% of those 7,500 compounds have shown promise.<sup>39</sup>

## **K. Medical devices**

92. Video endoscopes are used to examine and treat patients at hospitals. Around 70% of the video endoscopes used worldwide, or about 200,000 endoscopes, contain a CCD<sup>40</sup> colour filter that contains a small amount (150 ng) of PFOS. According to a submission from the Japanese delegation, repairing such video endoscopes requires a CCD colour filter containing PFOS.

93. It is technically possible to produce PFOS-free CCD filters for use in new equipment. There are, however, 200,000 existing endoscopes that use PFOS-containing filters. Gradual phase-out of existing endoscopes will permit the use of PFOS-free equipment.

94. PFOS is also used as an effective dispersant when contrast agents are incorporated into an ethylene tetrafluoroethylene (ETFE) copolymer layer. PFOS plays an essential role in radio-opaque ETFE production, allowing the achievement of the levels of accuracy and precision required in medical devices (e.g., radio-opaque catheters, such as catheters for angiography and in-dwelling needle catheters).

95. Since about 2000, when the harmful environmental effects of PFOS were identified, manufacturers of radio-opaque ETFE have been working with chemical materials suppliers to find alternatives. The 2006 OECD survey identified the use of PFBS as a surfactant in coating products. In some cases this substance can be used as a dispersant for inorganic contrast agent when it is mixed into ETFE.

## **L. Metal plating**

96. PFOS is useful as a surfactant, wetting agent and mist suppressing agent for chrome plating to decrease aerosol emission and improve the work environment. It was previously used for both decorative chrome plating and hard chrome plating processes, but new technology using chromium-III instead of chromium-VI has made PFOS use in decorative chrome plating obsolete. Chromium-III does not work for hard chrome plating, however. The use of PFOS as a wetting agent for hard chromium plating is therefore considered essential and is listed as an acceptable purpose and specific exemption.

35 UNEP/POPS/POPRC.3/20/Add.5.

36 Cameron 1990; Forti et al. 2007; Nagamoto et al. 2007.

37 Forti et al. 1998; Nagamoto et al. 2004.

38 Forti et al. 1998.

39 Forti et al. 1998.

40 Charge-coupled device (technology for capturing digital images).

97. In hard chrome plating PFOS works by lowering surface tension and forming a single foamy film barrier of a thickness of about 6 nanometres on the surface of the chromic acid bath, which maintains its aerosol (fog) formation, thus reducing airborne loss of chromium-VI from the bath and decreasing exposure of workers to this carcinogenic agent.
98. The PFOS derivative most frequently used in hard chrome plating is the quaternary ammonium salt tetraethylammonium perfluorooctane sulfonate (sold under trade names such as Fluorotenside-248 and SurTec 960), typically in a 5–10% solution. The potassium, lithium, diethanolamine and ammonium salts of perfluorooctane sulfonic acid may also be used.
99. In Denmark, ATOTECH markets Fumetrol® 140 with PFOS and Fumetrol® 21 without PFOS but with the fluorotelomer derivatives 1H,1H,2H,2H-perfluorooctane sulfonic acid (CAS no. 27619-97-2). The annual consumption of PFOS in the Danish hard chrome plating industry is about 28 kg. The price of products with 2-7% PFOS is 100-200 DKK/liter or about 30 US\$/liter. Some alternatives are cheaper and others are more expensive.<sup>41</sup>
100. A Danish hard chrome plating manufacturer has used a fluorinated but not PFOS-related product (probably a fluortelomer) for two years without any technical problems. Non-fluorinated alternatives for non-decorative hard chromium are available on the European market but are very new, and some are still being tested. These alternatives (whose chemical description and CAS are confidential) seem to work, but require continually adding to and stirring the chromium bath and require some technical changes before substitutes can be used.
101. During the electroplating process PFOS is broken down, and after about 7 months only about 1% of the original content is left. Thus, the bath must be refilled with PFOS once the foam layer is insufficient to withhold the Cr-VI aerosols.<sup>42</sup> Alternatives to the PFOS derivative are considered to be less stable and durable in the bath.
102. Discussions with stakeholders in the chrome plating industry in Denmark has revealed that they have not received information about the content of PFOS and the hazards of fluorotensides, which have been marketed as safe products.<sup>43</sup> Thus the incentive to introduce alternative substances and processes has been low. Because fluorotensides are not classified as dangerous, this use in Denmark is not reported to the National Product Registry, and its extent is not known to the authorities.<sup>44</sup>
103. When the chrome bath is burned out, the liquid must be disposed of. In Denmark it is sent to a chemical waste plant, where the chromium is precipitated and disposed of at a landfill. The PFC residues follow the waste water and end up in sewage sludge, which is sometimes used as fertilizer for agricultural soil. A great part of the PFC used in this industry therefore probably ends up in the environment. That would seem to be confirmed by the recent discovery of high levels of PFOS in agricultural soils in the United States and Germany.<sup>45</sup> On the other hand, the German national metal plating association (ZVO) states that in Germany only 20% of PFC is lost.<sup>46</sup>
104. In the European Union the annual PFOS use for chrome plating was about 10 tonnes in 2003 but has declined recently. According to data from the European Commission (2010)<sup>47</sup> the total use in the European Union today is estimated to be around 4 tonnes.
105. China reported that its chrome plating industry uses 25 tonnes of PFOS a year. The PFOS-containing mist suppressants used in China are FC-80 (CAS no. 2795-39-3 – PFOS potassium salt) and FC-248 (CAS no. 56773-42-3 – PFOS tetraethyl ammonium salt). The industry turnover is ¥30 billion. A phase-out without an effective alternative could worsen the health of 100,000 Chinese workers through exposure to Cr-VI, according to Chinese authorities. In China the available PFOS alternatives used for chrome plating are FC-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate), FC-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-

41 Personal communication from Pia B. Poulsen, FORCE Technology, August 2010.

42 Personal communication from Carsten Ree Jørgensen, CEO, Nichro, 2009.

43 Personal communication from Per Møller, Technical University of Denmark, 16 March 2009.

44 Personal communication from Frank Jensen, Danish Environmental Protection Agency, 17 March 2009.

45 Renner R. 2009. EPA finds record PFOS, PFOA levels in Alabama grazing fields. *Environmental Science and Technology* 43: 1246–1247.

46 Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

47 European Commission. 29 January 2010. Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks.

dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) and Fumetrol® 21(1H,1H, 2H,2H-perfluorooctane sulfonic acid).<sup>48</sup>

106. Canada reports having imported an estimated 3 metric tonnes of PFOS from the United States in 2004 for use in metal plating. France reports having used 200 kilograms for metal plating in 2006. All these figures are for all chrome plating, including decorative plating. A comprehensive report by the United States Environmental Protection Agency on the electroplating industry is available.<sup>49</sup>

107. The German national metal plating association (ZVO) describes the availability of PFOS-free alternative products from 10 German suppliers.<sup>50</sup> While information is lacking about the exact identity of these chemical compounds, three of them were fluorinated chemicals and seven were fluorine-free. The non-fluorinated alternatives were not stable enough in the hard chrome bath. It is stated that all 10 products could be used for decorative chrome plating, for which alternative Cr-III processes seem to exist already. Alternative surfactants for this process are being studied at the University of Wuppertal, Germany.<sup>51</sup> One possible non-fluorinated surfactant alternative for decorative plating may be Enthone® (ethoxylated oleyl amine, CAS no. 26635-93-8).

108. The Norwegian association of electroplaters (Norsk Galvanoteknisk Landsforening, or NGLF) has reported that its suppliers no longer provide PFOS wetting/anti-mist agent for chrome plating but instead provide PFOS-free tensides. NGLF considers the performance of those alternatives to be insufficient, however, and is developing better alternatives to PFOS and alternative technologies to solve the problem of airborne loss of hexavalent chromium from baths. NGLF has estimated the cost of replacing Cr-VI in plating baths with Cr-III to be approximately NKR100,000 (US\$15,000–16,000) per bath. NGLF, however, reports that the industry has already started to phase out the use of PFOS-containing wetting/anti-mist agent by using the Cr-III process instead of the Cr-VI process where possible.<sup>52</sup>

109. In Japan the use of PFOS in hard chrome plating has also been discontinued.<sup>53</sup>

110. Larger closed tanks and increased ventilation combined with extraction of chromium-VI from filters have been suggested as alternative solutions for applications where use of chromium-III is not yet possible. Increased ventilation will, however, result in increased energy consumption and therefore increased CO<sub>2</sub> emission and loss of chromium from baths. Increased ventilation is therefore not considered to be a workable solution, and other solutions, such as using physical covers (netting, balls) for baths to diminish hydrogen burst and catch aerosols, should be investigated. A Danish project at FORCE Technology and the Institute of Product Development to explore such possibilities was initiated in 2009 with financing from the Danish Environmental Protection Agency.

111. Besides chrome plating, fluorinated surfactants (including PFOS) are also used in other metal plating applications as, for example:

- Agents to prevent haziness of plated copper by regulating foam and improving its stability
- Non-foaming surfactants in nickel-plating baths to reduce surface tension
- Agents added to tin-plating baths to ensure that plating has uniform thickness
- Agents to impart a positive charge to fluoropolymer particles and to aid electroplating of polymers (e.g. PTFE) onto steel for surface protection

112. No assessments or reports have been made regarding alternatives to uses listed above.

## M. Fire-fighting foams

113. Fire-fighting foams with fluorosurfactants are very effective for extinguishing liquid fuel fires at airports and oil refineries and storage facilities. They include:

- Fluoro-protein foams used for hydrocarbon storage tank protection and marine applications

48 Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

49 [www.epa.gov/r5water/npdestek/pdf/pfoschromeplaterstudypdf\\_final.pdf](http://www.epa.gov/r5water/npdestek/pdf/pfoschromeplaterstudypdf_final.pdf).

50 Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

51 Personal communication from Jutta Hildenbrand, University of Wuppertal, 15 October 2009.

52 Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

53 Personal communication from Roland Weber, March 2010.

- Aqueous film-forming foams (AFFF) developed in the 1960s and used for aviation, marine and shallow spill fires;
- Film-forming fluoroprotein foams (FFFP) used for aviation and shallow spill fires
- Alcohol-resistant aqueous film-forming foams (AR-AFFF), which are multi-purpose foams
- Alcohol-resistant film-forming fluoroprotein foams (AR-FFFP), which also are multi-purpose foams; developed in the 1970s

114. Normally, a mixture of fluorinated surfactant and a hydrocarbon-based surfactant is used in AFFF, as this combination is more cost-effective and performs better than either surfactant separately. The concentration of perfluorinated compounds in fire-fighting foams is about 0.9–1.5%.<sup>54</sup>

115. The fluorinated surfactant used in AFFF forms an aqueous film covering the surface of oil and is used for stopping fires at chemical plants, fuel storage facilities, airports, underground parking facilities and tunnels. A PFOS-related compound used in the past was 3-[[[(Heptadecafluorooctyl)-sulfonyl]amino]-N,N,N-trimethyl-1-propanaminium iodide.

116. Today most fire-fighting foams are manufactured not with PFOS but with fluorochemicals/telomers based on a perfluorohexane (C6) chain. However, more than 50 enterprises in China that produce AFFF still consume more than 100 tonnes of PFOS per year. AFFF was phased-in in China in the 1990s as an alternative to halons, which are ozone-depleting substances, with support from the international community.

117. As fire-fighting foams have a long shelf life (10–20 years or longer), PFOS-containing fire-fighting foams (FC-600) may still be used around the world in accidental oil fires. In 2004 European Union stocks of fire-fighting foams with PFOS totalled 122 tonnes. In Norway in 2005 the stocks of fire-fighting foams containing PFOS were estimated to be 21 tonnes, with their main use in the off-shore oil industry.<sup>55</sup> In Switzerland stocks of PFOS in 2007 were estimated to be 13 tonnes, with consumption of 15–20% annually.<sup>56</sup> Canada reports an estimated 300 tonnes of stockpiles of PFOS-containing fire-fighting foams, which represents approximately 3 tonnes of PFOS. In Japan stocks of AFFF amount to 19,000 tonnes (50% of which are stored in 23,000 underground parking areas), and the maximum annual production capacity for alternative fire-fighting foams without PFOS is 2,100 tonnes.

118. Collecting and destroying these stocks of PFOS instead of using them will avoid considerable pollution from this persistent organic pollutant (for example, around airports). The cost of replacement and destruction of the PFOS currently found in fire-fighting foam stores in the European Union has been estimated at €6,000 per tonne, or about €700,000 in total. Replacing PFOS throughout Japan with alternatives in an environmentally appropriate way (including collection, refilling, transportation, storage and incineration) would cost ¥1.7 million (€13,000) per tonne, or ¥22 billion (€170 million) in total. In Canada, in 2006, disposal and replacement costs for PFOS-based fire-fighting foams were estimated to be Can\$ 700,000 (€500,000).

119. Manufacturers, distributors and users of AFFF fire-fighting agents and their chemical components have formed a not-for-profit trade association, the Fire Fighting Foam Coalition (FFFC), whose stated aim is to ensure that accurate industry information about PFOS alternatives, including telomer-based products, is disseminated to appropriate audiences.<sup>57</sup> The industry position was published in the June 2008 issue of *Asia Pacific Fire Magazine*.<sup>58</sup>

120. The alternatives to the use of PFOS fluorosurfactants in fire-fighting foams are:

- Non-PFOS-based fluorosurfactants with shorter chain length such as:
  - C<sub>6</sub>-fluorotelomers such as perfluorohexane ethyl sulfonyl betaine, often used in combination with hydrocarbons such as FORAFAC<sup>TM</sup> products (DuPont)
  - Dodecafluoro-2-methylpentan-3-one (3M)

54 Pabon M, Corpart JM. 2002. Fluorinated surfactants: synthesis, properties, effluent treatment. *Journal of Fluorine Chemistry* 114: 149–156.

55 Climate and Pollution Agency (former SFT), Norwegian Ministry of the Environment. 2005. Kartlegging av PFOS i brannskum [Survey of PFOS use in fire-fighting foam]. TA-2139.

56 Buser, A., Morf, L. 2009. Substance flow analysis of PFOS and PFOA in Switzerland. *Environmental Studies* 0922. Federal Office for the Environment, Bern.

57 [www.ffc.org/](http://www.ffc.org/).

58 *Asia Pacific Fire Magazine* 26: 2008.

- A return to the previously used technology, which employed fluorine-free fire-fighting foams. Examples include:
  - Silicone-based surfactants, often used in combination with fluorosurfactants
  - Hydrocarbon-based surfactants, often used in combination with fluorosurfactants
  - Synthetic detergent foams, often used for forestry and high-expansion applications and for training (“Trainol”); new products with glycols (Hi Combat A™ from AngusFire)<sup>59</sup>
  - Protein-based foams (e.g. Sthamex F-15), which are less effective for flammable liquid fuel fires and are mainly used for training but also have some marine uses.

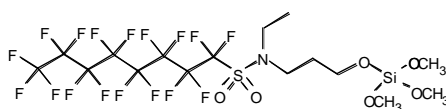
121. FFFC has claimed that fire-fighting foams made from fluorinated surfactants have been shown to be the only technology that can quickly and effectively extinguish fires resulting from highly combustible and flammable materials. Fluorine-free fire-fighting foams can provide an alternative in some applications but cannot provide the same level of fire suppression (capability, durability, etc.).

122. In Norway, the offshore oil industry voluntarily and systematically phased out the use of PFOS before the ban in 2007. PFOS containing fire-fighting foam has also been phased out by other users in Norway. While the most used alternatives in Norway are now PFOS-free telomer-based fluorosurfactants, there are also fluorine-free alternatives on the market, such as Arctic Re-Healing Foam™ RF, developed by 3M Australia. The Norwegian producer Solberg Scandinavian AS states that this fluorine-free alternative is not as effective as AFFF and will not be an alternative at offshore installations or for the petroleum industry, but that its fire-fighting performance is close to that of AFFF and that it is a good alternative for other uses. It has been approved for the control and extinguishing of class B flammable liquid hydrocarbon and polar fuel fires. Arctic Re-healing Foam RF meets the requirements of parts 3 and 4 of the European Committee for Standardization (CEN) EN 1568 specifications.<sup>60</sup>

123. A British survey states that the fluorine-free alternatives to fire-fighting foams in the United Kingdom are approximately 5–10% more expensive than fluorosurfactant-based foams.<sup>61</sup> According to a manufacturer of fluorine-free alternatives, the price would fall if the market size increased. A more deliberate shift towards fluorine-free fire-fighting foam alternatives would probably eliminate the difference in cost.

## N. Other uses

124. According to information from the 2006 OECD survey less than 1 tonne of *N*-ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide (CAS no. 61660-12-6) had been used as an additive in toner and printing inks. Low volumes of PFOS-related substances were also used in sealants and adhesive products.



*N*-Ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide

## O. Summary of the information on alternatives to the use of PFOS

125. The information on alternatives to the use of PFOS is summarized in table 4.

**Table 4: Summary of the information on alternatives to the use of PFOS**

Use	Use status	Alternatives used
Impregnation of textiles, leather and carpets	PFOS-related substances have been phased out in most OECD countries.	Other fluorinated compounds, like C <sub>6</sub> -fluorotelomers and PFBS, silicone-based products, stearamidomethyl pyridine chloride

<sup>59</sup> [www.kiddecanada.com/utcfs/Templates/Pages/Template-50/0,8061,pageld%3D2587&siteId%3D463,00.html](http://www.kiddecanada.com/utcfs/Templates/Pages/Template-50/0,8061,pageld%3D2587&siteId%3D463,00.html).

<sup>60</sup> Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

<sup>61</sup> Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.



Use	Use status	Alternatives used
Impregnation of paper and cardboard	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances and phosphates, mechanical processes
Cleaning agents, waxes and polishes for cars and floors	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances, fluorinated polyethers, C <sub>4</sub> -perfluorinated compounds
Surface coatings, paint and varnish	PFOS-related substances have been phased out in most OECD countries.	Telomer-based compounds, fluorinated polyethers, PFBS, propylated aromatics, silicone surfactants, sulfosuccinates, polypropylene glycol ethers
Oil production and mining	PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.	PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether acids
Photographic industry	A shift to digital techniques has reduced the use drastically.	Telomer-based surfactant products, hydrocarbon surfactants, silicone products, C <sub>3</sub> -C <sub>4</sub> -fluorinated chemicals
Electrical and electronic parts	PFOS-based chemicals are or have been used in the manufacture of digital cameras, mobile phones, printers, scanners, satellite communication, radar systems, etc.	For most of these uses, alternatives are available or are being developed.
Semiconductor industry	PFOS is still used but in lower concentrations.	No substitutes with comparable effectiveness have been identified, and doing so may take up to 5 years, according to the industry. It should be possible to use PFBS, fluorinated polyethers or telomers.
Aviation hydraulic oils	PFOS-related compounds may still be used.	Other fluorinated substances and phosphate compounds could be used.
Pesticides	Sulfluramid is used in some countries as an active substance and surfactant in pesticide products for termites, cockroaches and other insects. Other fluorosurfactants may be used as inert surfactants in other pesticide products.	Synthetic piperonyl compounds such as S-Methoprene, Pyriproxyfen, Fipronil and Chlorpyrifos are alternative active substances, sometimes used in combination. Alternative surfactants may exist.
Medical devices	Old video endoscopes at hospitals contain a CCD colour filter that contains a small amount of PFOS. PFOS is also used as an effective dispersant for contrast agents in radio-opaque catheters.	Repairing such video endoscopes requires a CCD colour filter containing PFOS. New CCD filters are PFOS-free. For radio-opaque ethylene tetrafluoroethylene, PFBS can replace PFOS.
Metal plating	PFOS-compounds are still used in hard chrome plating. Cr-III has replaced Cr-VI in decorative chrome plating.	Some non-fluorinated alternatives are marketed but they are not considered equally effective in hard chrome plating. A C <sub>6</sub> -fluorotelomer is used as a substitute and may be effective. PFBS derivatives may also be used. Physical barriers may also be used.
Fire-fighting foams	The use of PFOS-related substances in new products has been phased out in most OECD countries. Stocks are still being used up.	C <sub>6</sub> - fluorotelomers are used as substitutes in new products; fluorine-free alternatives are used for training exercises and possibly in other settings than offshore.

## IV. Properties of alternative substances and hazard assessment

### A. Overview

126. This chapter contains a brief description of the environmental, safety and health properties of PFOS alternatives. For some of these alternatives, a general discussion of properties might be all that is possible owing to a lack of specific information. For each of the chemical groups discussed, a more comprehensive compilation of information would have been possible but was beyond the scope of the present study.

127. The key to the performance of fluorosurfactants is extremely low surface tension. Currently, no other surfactant can match the low surface tension of PFOS. Because of environmental and health concerns and the often high prices of fluorosurfactants, however, other surfactants should be used as alternatives where very low surface tension levels are not needed.

128. When production of PFOS ceased in the United States in 2002, other chemicals took their place. They were mainly derivatives of perfluoroalkyl sulfonates with a shorter alkyl chain and C<sub>8</sub>-based fluorotelomers. Since 2006, the major manufacturers of C<sub>8</sub>-based telomers have been working towards the elimination of C<sub>8</sub>-based and longer-chain-based PFCs by 2015, in accordance with the United States Environmental Protection Agency's 2010/2015 PFOA Stewardship Program.<sup>62</sup> Thus, C<sub>6</sub>-fluorotelomers now dominate the trade. Thus far it has been difficult for non-fluorinated alternatives to gain a firm foothold in the market, partly because of established supplier relationships.

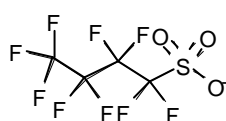
129. Table 5 gives a brief overview of groups of alternatives to PFOS.

**Table 5: Overview of main alternatives to PFOS compounds**

Alternative compound	Product trade name	Company	Uses
Perfluorobutane sulfonate (PFBS) derivatives or other alternatives based on various C <sub>4</sub> -perfluoro compounds	Novec™ Scotchgard™	3M	Paint and coatings industry, electronic coatings, industrial and commercial cleaning, stain protectors for carpets and leather, furniture, automotive uses, hard surfaces and other apparels, catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression, rubber moulding defoamers in electroplating, etc.
Perfluorobutyl methyl ethers	Novec™	3M	Industrial cleaning
Dodecafluoro-2-methylpentan-3-one	Novec™ 1230	3M	Fire-fighting foams
Polyfluorodialkyl ether sulfonates	FC-53	-	Mist suppressant hard chrome plating
Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	3M	Hydraulic fluids
Fluorotelomer alcohols and esters	Zonyl® Capstone®	DuPont	Surfactants, coatings, printing, textile and chemical industries, chrome plating
C <sub>6</sub> fluorotelomer sulfonamide compounds	Forafac™ 1157, 1183	DuPont	Fire-fighting foams
Fluorinated co-polymers	Foraperle® 225, etc.	DuPont	Impregnation of leather and indoor car upholstery
CF <sub>3</sub> or C <sub>2</sub> F <sub>5</sub> fluoroalkyl polyethers	PolyFox™	OMNOVA Solutions Inc.	Surfactant and wetting additives for coating formulations and floor polish
Propylated naphthalenes or biphenyls	Ruetasolv™	Rütgers Kureha Solvents	Water-repelling agents for rust protection systems, marine paints, coatings, etc.
Sulfosuccinate	Lutensit™	BASF	Levelling and wetting agents
	Edaplan™ LA 451	Münzing Chemie	Paint and coating industry: wetting and dispersing agents for water-based applications such as wood primers
	Hydropalat™ 875	Cognis	
Siloxanes and silicone polymers	WorléeAdd™	Worlée-Chemie	Wetting agents in the paint and ink industry
	Advantex™	Bluestar Silicones	Impregnation of all-weather textiles. Also related products for car polish, cleaners, anti-foaming agents, car waxes
Polypropylene glycol ethers	Emulphor™	BASF	Levelling and wetting agents
	Enthone	Cookson Electronics	Decorative chrome plating, etc.

## B. Shorter-chain perfluoroalkyl sulfonates

130. After the phase-out of PFOS, 3M introduced a new generation of polymeric anionic fluorinated surfactants (Scotchgard™ and Novac™ products), which are based on perfluorobutane sulfonates (PFBS; C<sub>4</sub>-chemistry):



62 [www.epa.gov/oppt/pfoa/pubs/stewardship/index.html](http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html).

131. These compounds are claimed to have a low dynamic surface tension or rather a rapid surface migration, which is important in high-speed coating processes and low-viscosity systems. Generally these surfactants have a lower surface tension than hydrocarbon and silicone surfactants. They can also be used in smaller amounts than hydrocarbon surfactants. The compounds are said to influence the adhesion of the second-layer coating less than silicon or conventional fluorinated surfactants.

132. These short-chain alternatives should be useful as surfactants in the paint and coatings industry; for stain-repellent impregnation of textiles, leather and carpets; in electronic coating; in industrial commercial cleaning; and in cleaners for solder flux residue.

133. According to information from the 2006 OECD survey, 50–160 tonnes of potassium perfluorobutane sulfonate and 40–60 tonnes of perfluorobutane sulfonyl fluoride were produced in 2005 as intermediates for the production of catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression systems, rubber molding defoamers for electroplating and the like.

#### **Health effects of shorter-chain perfluoroalkyl sulfonates**

134. No information is available about the specific chemicals in use; only information about PFBS and its potassium salt (PFBSK) from unpublished laboratory test reports is available. In the Australian assessment those reports are reviewed and evaluated. The following is based on that review.

135. The body half-life of PFBSK in intravenously exposed monkeys is 4 days. No degradation was detected and urinary excretion of the chemical by the monkeys was a major route of elimination. High levels of binding of perfluorobutane sulfonate to human albumin occurred in the blood. The acute toxicity was low; in rats the oral and skin LD<sub>50</sub> (doses that killed 50%) were more than 2,000 milligrams per kilogram of body weight. The test material was irritating to the eyes and fulfilled the criteria for classification as irritating to eyes (R36). The chemical did not, however, cause skin irritation or sensitization. In oral rat studies NOAEL (no observed adverse effects level) values of 100–300 milligrams per kilogram of body weight per day were detected. The test material was not mutagenic in the applied bacteria tests.

136. It has been claimed that PFBS does not have the particularly serious toxic effects associated with PFOS and other long-chain analogues but data published in peer-reviewed literature are lacking.

#### **Environmental effects of shorter-chain perfluoroalkyl sulfonates**

137. PFBS is a strongly acidic and highly water-soluble substance which has a low vapour pressure and is poorly adsorbed to soils and sediments, and is therefore expected to remain in the water compartment on release into the environment. PFBS is as persistent in the environment as other perfluorinated compounds and is being detected in increasing concentrations in some water bodies, including the North Sea; bioaccumulation in wildlife and humans, however, seems to be much lower than for PFOS. PFBS stays mostly in the water column as its water solubility is much higher than that of higher homologues. In a laboratory fish test the bioaccumulation potential for PFBS was low.

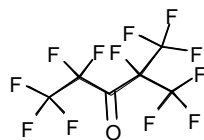
138. The Australian report mentioned earlier concludes that as use of PFBS – for example, as a substitute for PFOS – increases, levels of PFBS may build up and be distributed widely in the environment, given that its precursors are likely to be more volatile, yet structurally very similar, to PFOS.

139. A range of unpublished tests show that PFBS has low toxicity for birds, algae, aquatic invertebrates, fishes or sewage micro-organisms. In a quail reproduction study the dietary NOAEC (no observed adverse effects concentration) was 900 milligrams of PFBS per kilogram of wet weight feed.<sup>63</sup> However, PFBS was not tested in the chironomid *Chironomus tentans*, which has been shown to be two to three orders of magnitude more sensitive to the effects of PFOS than other aquatic organisms. Whether *Chironomus tentans* would be similarly sensitive to PFBS is unclear.

### **C. Shorter-chain perfluoroalkyl ketones and ethers**

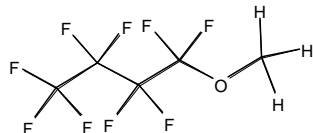
140. According to 3M's website, a C<sub>6</sub>-fluorinated compound, Novec™ 1230, is used in a fire protection fluid produced by that company. The compound is dodecafluoro-2-methylpentan-3-one (CAS no. 756-13-8):

63 Newsted JL, Beach SA, Gallagher SP, Giesy JP. 2008. Acute and chronic effects of perfluorobutane sulfonate (PFBS) on the Mallard and Northern Bobwhite quail. *Archives of Environmental Contamination and Toxicology* 54: 535–545.



Dodecafluoro-2-methylpentan-3-one

141. 3M also markets some C<sub>4</sub>-perfluorinated compounds for commercial and industrial cleaning under the trademark Novec™, such as methyl nonafluorobutyl ether (CAS no. 163702-07-6) and methyl nonafluoroisobutyl ether (CAS no. 163702-08-7). Here the methyl group is not fluorinated.



Methyl nonafluorobutyl ether

#### Health effects of shorter-chain perfluoroalkyl ketones and ethers

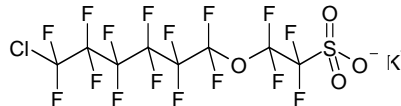
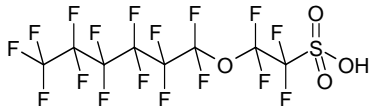
142. Published peer-reviewed data are lacking.

#### Environmental effects of shorter-chain perfluoroalkyl ketones and ethers

143. Published peer-reviewed data are lacking.

### D. Polyfluorodialkyl ether sulfonates

144. In China FC-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate) and FC-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) are available as PFOS alternatives for chrome plating.<sup>64</sup> The structure formulas of FC-53 and FC-53B are, respectively:



#### Health effects of polyfluorodialkyl ether sulfonates

145. No data are available.

#### Environmental effects of polyfluorodialkyl ether sulfonates

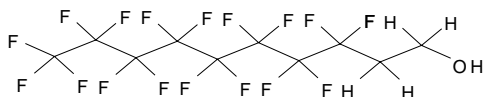
146. No data exist other than Chinese QSAR model results for persistence (half-lives) in water, sediment, soil and air, bioconcentration factors (BCFs) and toxicity to fish showing less hazardous potential than PFOS.

### E. Fluorotelomers and fluorophosphates

147. In general, fluorotelomers have been the most common alternatives to PFOS compounds. They are not fully fluorinated but contain more reactive hydrocarbon parts and functional groups. The perfluorinated tail, however, is similar to the tail of PFOS and is as persistent, and these chemicals are precursors of perfluorinated carboxylic acids (PFCAs). According to information from the 2006 OECD survey, more than 5,000 tonnes of PFCA precursors were produced and used in 2005.

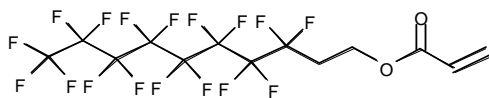
148. One of the basic structures is 8:2 fluorotelomer alcohol (8:2 FTOH), also named 1*H*,1*H*,2*H*,2*H*-perfluorodecanol; it has a C<sub>8</sub>-perfluorinated tail:

<sup>64</sup> Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.



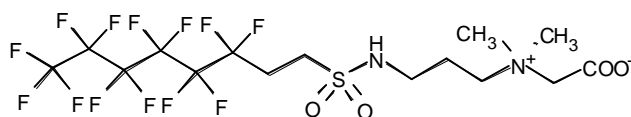
149. DuPont specializes in fluorotelomers and markets a wide range of Zonyl<sup>®</sup> products, generally associated with 8-2 alcohol-based products, and Capstone<sup>™</sup> products, generally associated with 6:2-fluorotelomer-based products.

150. An acrylate of fluorotelomer with the name of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (CAS no. 27905-45-9) has been marketed by DuPont as a telomer intermediate under the trade name of Zonyl<sup>®</sup> TA-N:



151. These fluorotelomers are covered by the United States Environmental Protection Agency's 2015 phase-out. While the shorter- and longer-chain telomers are not subject to the phase-out, they are covered by the recent United States Environmental Protection Agency action plan for long-chain PFCs.<sup>65</sup>

152. DuPont manufactures a range of fluorotelomers called DuPont<sup>™</sup> Forafac<sup>®</sup> products, with 65–95% C<sub>6</sub>-fluorinated amphoteric telomers based on perfluorohexyl ethyl sulfonamide, which are used in fire-fighting foam formulations.<sup>66</sup> A possible structure formula for an amphoteric compound 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctane sulfonamidopropyl carboxybetaine, which now replaces the analogous fully fluorinated perfluorooctane compound, is:

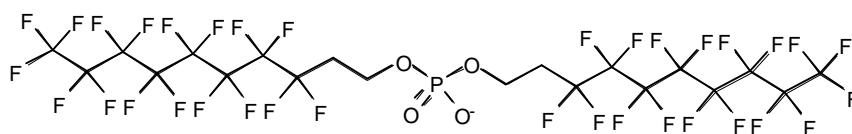


153. The polyfluoroalkyl phosphonic acids and phosphoric acids and their diesters (PAPs and diPAPs), used mainly in food packaging, have recently been discovered in the environment and in people.<sup>67</sup> Here are examples of structure formulas:



Perfluorooctyl phosphonate

8:2 PAP



8:2 diPAP

154. DuPont markets more Zonyl products in this group, such as Zonyl<sup>®</sup> 9027, a spot and dirt repellent, which is a telomer B phosphate diethanolamine (CAS no. 65530-63-4). Again, these chemicals are based on C8-fluorine chemistry and are to be phased out based on a global agreement with most producing companies by December 31, 2015. Similar chemicals with shorter chain lengths may still be used.

65 [www.epa.gov/oppt/existingchemicals/pubs/pfcs\\_action\\_plan1230\\_09.pdf](http://www.epa.gov/oppt/existingchemicals/pubs/pfcs_action_plan1230_09.pdf).

66 [www2.dupont.com/Forafac/en\\_US/index.html](http://www2.dupont.com/Forafac/en_US/index.html).

67 D'eon JC, Crozier PW, Furdui VI, Reiner EJ, Libelo EL, Mabury SA. 2009. Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers. *Environmental Science and Technology* 43: 4589–4594.

155. The C<sub>8</sub>-telomer-based materials are disappearing in favour of C<sub>6</sub>-based materials. C<sub>6</sub>-based materials are inherently more expensive (by a substantial amount) than C<sub>8</sub>- or telomer-based materials.<sup>68</sup>

#### Health effects of fluorotelomers and fluorophosphates

156. There is a lack of health data for the many specific and complex chemicals fluorotelomers and fluorophosphates used in practice. Some data exist on adverse effects seen in experimental animals and laboratory tests of precursors and the final degradation products: perfluorocarboxylic acids/salts (PFCAs) such as perfluorooctanoate (PFOA). Some PFCAs have well-known adverse health impacts. For example, PFOA has been shown to be tumorigenic and immunotoxic in laboratory animals. Little toxicological or ecotoxicological information is available for the other PFCAs, however, although they have been regularly detected in human blood, umbilical cord blood and breast milk. The toxicity of the degradation products increases with fluorinated chain length.

#### Environmental effects of fluorotelomers and fluorophosphates

157. There is also a lack of environmental data on the fluorotelomers and fluorophosphates used in practice. Some are volatile and may undergo long-range air transportation. They degrade to perfluorinated carboxylic acids, such as perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA), in organisms and in nature. These perfluorinated acids have been widely detected in the environment and wildlife. The environmental hazard, including tendency to bioaccumulation, increases with chain length, and all perfluorinated alkyl chains are completely persistent in nature.

### F. Fluorinated co-polymers

158. DuPont markets many Zonyl<sup>®</sup> co-polymers for various purposes, such as Zonyl<sup>®</sup> G Fabric Protector for textiles, which consists of 2-methyl-2-propenoic acid dodecyl ester polymer with 10-15%  $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl poly(difluoromethylene) (CAS no. 65605-58-5).

159. Foraperle<sup>®</sup> 225 (DuPont) is an acrylic fluorinated co-polymer (25%) in a solvent medium (75% butyl acetate) used for finishing and protection of leathers and car upholstery through water and oil repellence. It contains the compound 2-propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate,  $\gamma$ - $\omega$ -perfluoro-C<sub>10</sub>-C<sub>16</sub>-alkyl acrylate and stearyl methacrylate (CAS no. 203743-03-7). Another acrylic fluorinated co-polymer is dodecyl methacrylate polymer with  $\alpha$ -fluoro- $\omega$ -[2-[(1-oxooctadecyl)oxy]ethyl]-poly(difluoromethylene) (CAS no. 65530-65-6), which is used in a concentration of 0.085–0.45%.

160. The substance 2-propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate,  $\gamma$ - $\omega$ -perfluoro-C<sub>10</sub>-C<sub>16</sub>-alkyl acrylate and stearyl methacrylate (CAS no. 203743-03-7) has been prohibited for manufacture, use, import, sale or offer for sale in Canada as it is a precursor to long-chain PFCAs. The following substances are also prohibited:

- Hexane, 1,6-diisocyanato-, homopolymer, reaction products with  $\alpha$ -fluoro- $\omega$ -2-hydroxyethyl-poly(difluoromethylene), C<sub>16-20</sub>-branched alcohols and 1-octadecanol
- 2-propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with butyl 2-propenoate and 2,5-furandione,  $\gamma$ - $\omega$ -perfluoro-C<sub>8-14</sub>-alkyl esters, tert-Butyl benzenecarboperoxoate-initiated
- 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylene tetramine.

161. In most instances the exact composition of the products and their active substances are trade secrets and have not been disclosed by the suppliers.

#### Health effects of fluorinated co-polymers

162. There is a lack of specific health data on the active fluorinated substance, but the marketed formulation, which includes solvents and non-fluorinated copolymers, is often tested and results may be traced on the Internet.<sup>69</sup> Polymers are generally of low availability/uptake and have low toxicity.

<sup>68</sup> Personal communication from Richard Thomas, January 2010.

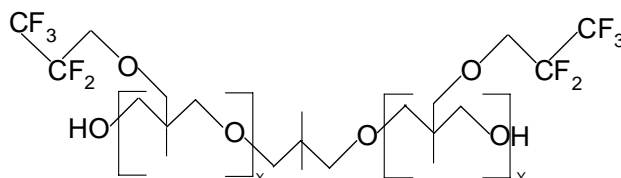
### Environmental effects of fluorinated co-polymers

163. There is a lack of data. Probably only the solvent and degradation products of polymers are hazardous. The ultimate degradation products may be perfluoroalkanoic acids (PFAAs), including PFOA.

## G. Fluorinated polyethers

164. OMNOVA Solutions Inc. produces under the trade name PolyFox™ a family of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C<sub>2</sub>F<sub>5</sub> or CF<sub>3</sub> perfluoroalkyl side chain structures. The PolyFox™ product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols.

165. The basic structure of PolyFox™ 656 compounds is illustrated in the following figures (x + y equals about 6):



166. It seems that these surfactants have a moderate surface tension that is not quite as low as that of conventional fluorinated surfactants. The new surfactants are claimed to have a broad processing window, with less interference with other compounds. Coating quality is improved as foaming is reduced. The latter is an important factor in producing and processing water-borne coatings.

167. PolyFox™ fluorosurfactants have been used in aqueous and solvent-borne semiconductor coating formulations. In a number of examples excellent wetting, flow and levelling properties have been achieved for semiconductor coatings.

168. In addition, the poly(alkylene oxide) chain of all PolyFox™ materials has an inherently low refractive index compared to other commercial polymers such as acrylics. The presence of even very short (-CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>) side chains further reduces the refractive index, and PolyFox™ materials have been used as antireflection layers in photo-resist and LCD screen applications. The PolyFox™ formulation is currently being used as a surfactant in floor polish products in the United States, Europe and Asia.

169. PolyFox™ products are priced competitively in comparison with any new C<sub>6</sub>-based materials but are more expensive than the C<sub>8</sub>-based materials, which is being phased out.<sup>70</sup>

### Health effects of fluorinated polyethers

170. The acute toxicity of fluorinated polyethers is low (LD<sub>50</sub> > 2 g/kg bw) but they may irritate skin and the respiratory system. Generally, data are lacking.

### Environmental effects of fluorinated polyethers

171. Fluorinated polyethers have a high molecular weight that makes them less available for transport across biomembranes and therefore less biologically available. Furthermore, the polymer backbone linkage of the PolyFox™ molecules is an ether link, which is more environmentally stable than, for example, the ester/amide links of PFOS and telomer-based fluorosurfactants. This makes the PolyFox™ molecule more resistant to degradation to lower molecular weight carboxylic acids. PolyFox™ has low acute toxicity with regard to aquatic organisms and is not known to bioaccumulate.

172. PolyFox™ products seem to have reduced environmental impacts in comparison with all other fluorosurfactants on the market. This is because PolyFox™ materials use a C<sub>1</sub>- or C<sub>2</sub>-based platform rather than a C<sub>8</sub>- or C<sub>6</sub>-telomer-based platform. Since they are made with shorter fluorinated alkyl chain lengths (C<sub>2</sub>F<sub>5</sub> or CF<sub>3</sub> structures), they cannot produce the longer perfluorinated acids such as PFOA.

69 [www.nicnas.gov.au/publications/CAR/new/NA/NAFULLR/NA0600FR/NA651FR.pdf](http://www.nicnas.gov.au/publications/CAR/new/NA/NAFULLR/NA0600FR/NA651FR.pdf);  
[www.epa.gov/r5water/npdestek/pdf/pfoschromeplaterstudyfinal.pdf](http://www.epa.gov/r5water/npdestek/pdf/pfoschromeplaterstudyfinal.pdf).

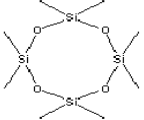
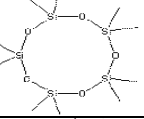

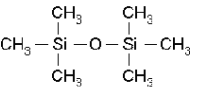
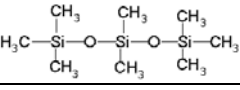
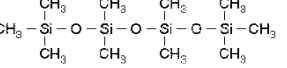
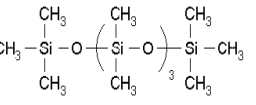
70 Personal communication from Richard Thomas, OMNOVA, January 2010.

## H. Siloxanes and silicone polymers

173. Siloxanes are chemical substances containing units with the general formula  $R_2SiO$ , where "R" represents either hydrogen or a hydrocarbon group. They may be straight-chain or cyclic compounds and vary in molecular weight from a few hundred to several hundred thousand g/mol for the polymers. Siloxanes are building blocks for silicone products.

174. The principal siloxanes of interest from an environmental perspective are the volatile methyl siloxanes with short SiO backbones, in particular the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes MM (or HMDS), MDM, MD2M and MD3M. They are shown in table 6.

**Table 6: Siloxanes of recent interest<sup>71</sup>**

Abbreviation	Name	CAS no.	Structure
D4	Octamethyl cyclotetrasiloxane	556-67-2	
D5	Decamethyl cyclopentasiloxane	541-02-6	
D6	Dodecamethyl cyclohexasiloxane	540-97-6	
MM (or HMDS)	Hexamethyl disiloxane	107-46-0	
MDM	Octamethyl trisiloxane	107-51-7	
MD2M	Decamethyl tetrasiloxane	141-62-8	
MD3M	Dodecamethyl pentasiloxane	141-63-9	

175. Out of these commercially used siloxanes, D4, D5, and MM are chemicals produced in high volumes in the European Union. The first two are the most commonly used siloxanes in the Nordic countries.<sup>72</sup>

176. Recent activities in the Nordic area have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as sealants, fuels, car polishes, cleaners, anti-foaming agents, car waxes and personal care and biomedical products.<sup>73</sup> The widespread use of siloxanes and their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they are widespread in the environment.

177. Silicone polyethers are another class of silicone derivatives that have special surfactant properties. The leading manufacturers are Bluestar, Dow Corning, Evonik-Goldschmidt, Momentive and Wacker. Other companies sell specially formulated mixtures for specific applications.

71 Cousins AP, Kaj L, Broström-Lundén E. 2009. Siloxanes in the Nordic environment. *Norman Bulletin* no. 1. [www.norman-network.net](http://www.norman-network.net).

72 Kaj L, Schlabach M, Andersson J, Cousins AP, Schmidbauer N, Brorström-Lundén E. 2005. Siloxanes in the Nordic Environment. *TemaNord* 2005:593.

73 Lassen C, Hansen CL, Mikkelsen SH, Maag J. 2005. Siloxanes – consumption, toxicity and alternatives. Environmental Project no. 1031. Danish Environmental Protection Agency.

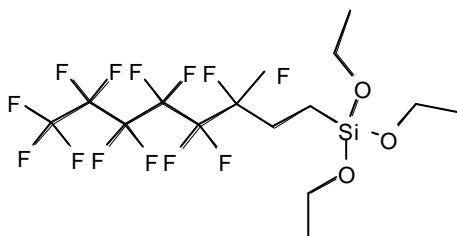


178. Bluestar Silicones markets some PFOS alternatives based on silicone for textile applications under the trade name Advantex™.

179. Worlée-Chemie produces silicone polymers, which in the paint and ink industry can in several cases be used as alternatives to fluorosurfactants as wetting agents. WorléeAdd® 340 is a low-viscous non-ionic special modified silicone polyether (containing 3-(polyoxyethylene) propylheptamethyl trisiloxane, CAS no. 67674-67-3) that can improve surface wetting of aqueous systems on difficult substrates like polyethylene and polypropylene or contaminated substrates. It has a low surface tension and is claimed to be highly effective in improving wetting, spreading and levelling of water-borne coatings and eliminating surface defects without foam stabilizing. It is further claimed that the compound normally has no negative effect on recoating.

180. Another product, WorléeAdd® 345, is a mixture of a silicone polyether (10–15%) and a dioctyl sulfosuccinate (50–55%) in ethanol and water. This surfactant can be used to improve wetting properties of aqueous coatings for different substrates, where penetration into absorbing surfaces also is improved.

181. Perfluoroalkyl derivatives of siloxanes also exist; they include 1H,1H,2H,2H-perfluoroalkyl triethoxysilane, which is effective for glass and surface treatment.<sup>74</sup> One compound, polyfluorooctyl triethoxysilane (1H,1H,2H,2H-perfluorooctyl triethoxysilane), has been banned in Denmark. The formula is:



#### Health effects of siloxanes and silicone polymers

182. A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air. Toxic effects of D3, D4, D5, D6 and HMDS were studied using a “read-across” method, which is based on structural similarity and its relation to toxicity. The linear siloxane HMDS appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also observed. An ambient quality criterion of 0.01 mg/m<sup>3</sup> was derived, based on lung toxicity, including a safety factor of 250.<sup>75</sup> The silicone industry disagrees with the conclusions of this study.<sup>76</sup>

183. Some years ago polysiloxanes or silicone polymers were evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC).<sup>77</sup>

184. Low-molecular-weight polydimethylsiloxanes have been studied extensively by industry to define their safety profile. These studies have demonstrated that the polydimethylsiloxanes studied all possess a very low potential for toxicity.

185. The Scientific Committee on Consumer Products in the European Union has published an Opinion on D4 in which the safety of D4’s use as a cosmetic ingredient has not been questioned.<sup>78</sup> In the United States, the Cosmetic Ingredient Review panel is about to publish its final assessment of the

74 ABCR 2006–2007 catalogue: Fluorochemicals. Karlsruhe, Germany.

75 Greve K, Nielsen E, Ladefoged O. 2008. Toxic effects of siloxanes: group evaluation of D3, D4, D5, D6 and HMDS in order to set a health-based quality criterion in ambient air. *Toxicology Letters* 180: S67.

76 Personal communication from Pascal-Louis Caillaud, Bluestar Silicones, 11 February 2010.

77 European Centre for Ecotoxicology and Toxicology of Chemicals. 1994. Joint Assessment of Commodity Chemicals 026 - Linear Polydimethylsiloxanes (CAS no. 63148-62-9) available at [www.ecetoc.org/index.php?mact=MCSOap,cntnt01,details,0&cntnt01by\\_category=3&cntnt01order\\_by=Reference%20Desc&cntnt01template=display\\_list\\_v2&cntnt01display\\_template=display\\_details\\_v2&cntnt01document\\_id=96&cntnt01returnid=91](http://www.ecetoc.org/index.php?mact=MCSOap,cntnt01,details,0&cntnt01by_category=3&cntnt01order_by=Reference%20Desc&cntnt01template=display_list_v2&cntnt01display_template=display_details_v2&cntnt01document_id=96&cntnt01returnid=91); updating of this report is in progress.

78 [http://ec.europa.eu/health/ph\\_risk/committees/04\\_sccp/docs/sccp\\_o\\_035.pdf](http://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_035.pdf).

safety of cyclomethicone, D3, D4, D5, D6 and D7.<sup>79</sup> The panel has concluded that D4, D5, D6 and D7 are safe for use in cosmetics. D3 will be taken off the International Nomenclature of Cosmetic Ingredients (INCI) list because it is not a commercial product.

186. Other studies of siloxanes, however, indicate that they seem to be harmful when inhaled and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact with WorléeAdd® 340 may cause skin irritation. In short, knowledge of the toxicity of siloxanes is still incomplete.

187. The polyfluoroalkyl siloxane discussed above was banned in Denmark because of lung damage in experimental mice.<sup>80</sup>

### Environmental effects of siloxanes and silicone polymers

188. Siloxanes are widely distributed in the Nordic environment. In general, siloxanes are very stable and persistent compounds that do not degrade in the environment. The cyclic- and short-chain linear siloxanes bioconcentrate in aquatic organisms. These siloxanes may be toxic to aquatic organisms and are bioaccumulative; there are, however, still gaps in our knowledge.

189. According to the material safety datasheet for WorléeAdd® 340, the silicone polymer in that product is classified as environmentally dangerous with the R-phrases R51 (“Toxic to aquatic organisms”) and R53 (“May cause long-term adverse effects in the aquatic environment”). The R-phrase R53 indicates that the substance is bioaccumulative.

190. Canada has identified decamethyl cyclopentasiloxane (D5) and octamethylcyclotetrasiloxane (D4) as “inherently toxic to wildlife”.<sup>81</sup>

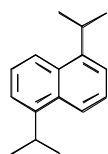
191. The cyclic siloxanes D4, D5 and D6 have been subjected to an environmental risk assessment by the United Kingdom Environment Agency applying European Union Technical Guidance. A review of the environmental properties of cyclic siloxanes is available on the Internet.<sup>82</sup>

## I. Propylated aromatics

192. Rütgers Kureha Solvents produces various aromatic surfactants with the trade name Ruetasolv®; based on propylated naphthalenes and biphenyls, these products can be used as water-repelling agents for different applications such as corrosion protection systems, marine paints, resins, printing inks, coatings and electrical, electronic and mechanical applications.

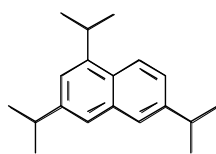
193. They may also be used as plasticizers and film-forming aids in emulsion paints and adhesives. The various isopropyl naphthalenes and isopropyl biphenyls are very hydrophobic substances that are compatible with almost all raw materials such as epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate co-polymers, mineral oils and bitumen.

194. Propylated aromatic products are all colourless liquids with a boiling point of about 300°C and have very low solubility in water.



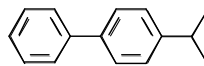
Ruetasolv DI

CAS no. 38640-62-9



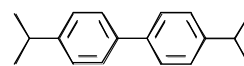
Ruetasolv TTPN

CAS no. 35860-37-8



Ruetasolv BP 4201

CAS no. 69009-90-1



Ruetasolv BP 4103

CAS no. 25640-78-2

<sup>79</sup> The draft amended final safety assessment can be accessed at [www.cir-safety.org/staff\\_files/blue.pdf](http://www.cir-safety.org/staff_files/blue.pdf).

<sup>80</sup> Nørgaard AW, Larsen ST, Hammer M, Poulsen SS, Jensen KA, Nielsen GD, Wolkoff P. 2010. Lung damage in mice after inhalation of nanofilm spray products: the role of perfluorination and free hydroxyl groups. *Toxicological Sciences* 116 (1): 216–224.

<sup>81</sup> [www.chemicalsubstanceschimiques.gc.ca](http://www.chemicalsubstanceschimiques.gc.ca).

<sup>82</sup> [www.cyclosiloxanes.eu](http://www.cyclosiloxanes.eu).

### Health effects of propylated aromatics

195. The substances *p*-isopropyl-1,1'-biphenyl (Ruetasolv BP 4103) and *p,p'*-diisopropyl-1,1'-biphenyl (Ruetasolv BP 4201) can cause skin sensitization or dermatitis upon repeated contact with skin, and long-term exposure causes irritation of the eyes, nose, throat, mucous membranes and respiratory tract. *p*-Isopropyl-1,1'-biphenyl has a very low acute toxicity with oral LD<sub>50</sub> values for rats of > 4 g/kg. Central nervous system, liver and kidney damage have, however, been reported as chronic effects of that chemical in animals.

196. Isopropylated naphthalenes are also irritating substances. The acute toxicity of diisopropyl-naphthalene (Ruetasolv DI) is very low, with an oral LD<sub>50</sub> value for rats of 3,900 mg/kg.

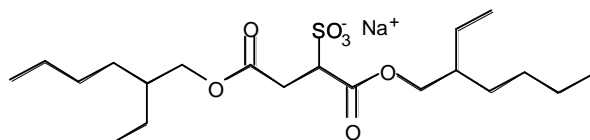
### Environmental effects of propylated aromatics

197. The biphenyls and the naphthalenes have high octanol/water partition coefficients (log K<sub>OW</sub>), and the bioconcentration factor (BCF) for the substances is greater than 100. These chemicals are therefore potentially bioaccumulative. The biphenyl moiety seems to be easily biodegradable, whereas the naphthalene moiety biodegrades slowly. The sparse available information suggests that the biphenyls are acutely toxic to aquatic organisms, whereas naphthalene appears to have no acute toxic effects on the investigated fish species.

## J. Sulfosuccinates

198. Several companies produce surfactants based on 50–75% of the sodium salt of di(2-ethylhexyl) sulfosuccinate, which can be used as a wetting agent for aqueous systems of detergents, cleaners, paints and coatings. It is also used in pesticides.

199. Following is the chemical structure of the sodium salt of di(2-ethylhexyl) sulfosuccinate (CAS no. 577-11-7):



200. In a product from BASF (Lutensit® A-BO) the sulfosuccinate is mixed with water and ethanol, and in a product from Cognis (Hydropalat® 875) the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol.

201. The product from Cognis can be used as a wetting agent in aqueous coating systems and is particularly suitable for difficult-to-wet substrates like plastics, metal, cellulose film, silicone-treated papers and glass. This surfactant may also be used as an emulsifier for emulsion polymerization. Another area where it can be used as an alternative to fluorinated surfactants is in optimizing the colour acceptance of aqueous pigment concentrates in different coatings. The product has medium foam formation.

202. Münzing Chemie also produces a surfactant (Edaplan® LA 451) based on a sulfosuccinate derivative in ethanol and water, which also can be used as a wetting agent for aqueous paints and coatings. The identity of the sulfosuccinate has not been disclosed. The product is claimed to have good wetting properties, no increase in foam and good recoatability. The surface tension is moderate. Application areas are decorative paints, wood and furniture coatings, automotive and repair coatings, industrial coatings, printing inks and overprint varnishes.

### Health effects of sulfosuccinates

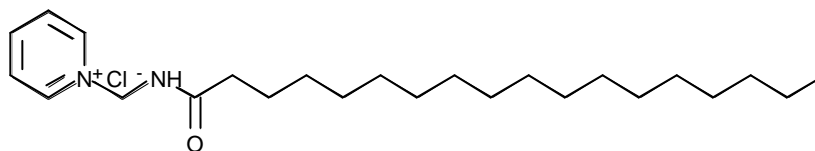
203. Toxicological information is scarce. Sulfosuccinates are irritants to eyes, skin and the respiratory system, especially upon prolonged or repeated contact. Dermatitis has been observed as a long-term effect, as have central nervous system depression and injury to the heart, the liver and blood-forming organs. The substance di(2-ethylhexyl) sulfosuccinate has low acute toxicity if swallowed (LD<sub>50</sub> (oral, rat) = 1.9 g/kg). Information found in the United States Government's Hazardous Substances Data Bank suggests that di(2-ethylhexyl) sulfosuccinate is mildly toxic (upon ingestion) to humans, with a probable oral lethal dose (in humans) of 0.5–5 g/kg. A possible metabolite is the branched 2-ethylhexanol, which may have reproductive effects.

**Environmental effects of sulfosuccinates**

204. Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate; however, a  $^{96}hLC_{50}$  value of 10–100 mg/l for *Leuciscus idus* (a small fresh-water cyprinoid fish) shows that the sulfosuccinate is harmful to aquatic organisms. More information is needed in order to make an accurate assessment.

**K. Stearamidomethyl pyridine chloride**

205. A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, which was previously marketed by ICI as Velan PF:



206. The substance reacted with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibres and that the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction had an unpleasant odour and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s, when government regulation of such substances increased. Pyridine might be evaluated differently now. Further information about its properties is lacking.

**Health effects of stearamidomethyl pyridine chloride**

207. Published data on this chemical are lacking.

**Environmental effects of stearamidomethyl pyridine chloride**

208. Published data on this chemical are lacking.

**L. Polypropylene glycol ether, amines and sulfates**

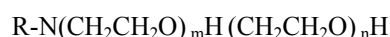
209. Possible replacements for fluorosurfactants in some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor<sup>®</sup> FAS 30 is the sodium salt of fatty alcohol polyglycol ether sulfates, which are preferentially used in the emulsion polymerization of acrylate and methacrylate esters, styrene and vinyl esters. These anionic emulsifiers are also combined with non-ionic Emulan<sup>®</sup> grades in order to achieve desired properties such as a particular particle size or emulsion stability. Because of their “foaming” properties, fatty alcohol polyglycol ether sulfates are also used in cosmetics and fire-fighting foams.

210. A fatty alcohol polyglycol ether sulfate has the following general formula:



in which  $R^1$  represents a linear or branched alkyl and/or alkenyl group having, for example, 12 to 16 carbon atoms,  $n$  represents a number mainly from 2 to 4 and  $X$  represents a cation selected from the group consisting of sodium, ammonium or substituted ammonium.

211. A related non-fluorosurfactant is Enthone<sup>®</sup> (ethoxylated oleyl amine, CAS no. 26635-93-8), used in decorative chrome plating and in many other applications.<sup>83</sup> Its general formula is as follows:

**Health effects of polypropylene glycol ether, amines and sulfates**

212. Emulphor FAS 30 has low acute toxicity by ingestion (oral  $LD_{50} > 2$  g/kg b.w.) and is not considered to be irritating. There is a lack of data on this chemical. Enthone and other polyethylene glycol amines are non-toxic and non-irritating non-ionic emulsifiers.

83 [www.enthone.com/pwb/index.aspx](http://www.enthone.com/pwb/index.aspx).

**Environmental effects of polypropylene glycol ether, amines and sulfates**

213. Emulphor FAS 30 is readily biodegradable (> 70% elimination according to the OECD biodegradation screening test (301E)) and does not seem to be acutely toxic to aquatic organisms, as the reported  $96^{\text{h}}$ LC<sub>50</sub> value for fish (*Leuciscus idus*) is > 100 mg/L. Enthone is readily degradable, with low toxicity. There is, however, a lack of data on these chemicals.

**V. Comparative assessment of PFOS and possible alternatives**

214. Comparative assessment of PFOS and its possible alternatives with regard to technical, socioeconomic, environmental, health and safety considerations is a very complex task requiring much more data and other information than are normally available. Often much more information is available about PFOS than about possible alternatives, which may be newly developed substances covered by patents and trade secrets. For this reason rigid selection criteria are not useful; information on the alternatives will be scarcer, and it will be of lower scientific quality because much of it will be non-peer-reviewed.

215. In addition, if sufficient information is available then one may have to subjectively weigh price and fitness for use against hazard. None of the alternatives will be perfect and without hazards, but at least they should be less hazardous than PFOS. That is the case, for example, with fluorinated alternatives with fluorinated alkyl chains shorter than C8. They are less toxic and bioaccumulative but still persistent indefinitely in the environment.

216. It might be that the C6-chemistry is not sufficiently safe. This is illustrated by the similar half-life of perfluorohexane sulfonate compared to PFOS in human blood. Furthermore, chemicals with fluorinated chains longer than C8 seem to be more toxic and bioaccumulative than PFOS.

217. Further, in evaluating the technical properties, fitness for use and durability of the alternatives for each separate application, it is necessary to evaluate socio-economic considerations; differences between branches, enterprises (including size), countries and regions; product importance; economic constraints; and social costs. The availability of alternatives seems to be the same worldwide, because the providers are mainly large international companies.

218. Economically useful data will probably also be scarce. In general, very little information about the prices of alternatives was found in the Danish survey 84 even though the producers of alternative products were asked specifically about such information. The information received, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. One company mentioned that the price of alternatives was intentionally kept at the same level as that of PFOS-related compounds. While it was impossible to obtain exact prices, in the coatings and paints area the non-fluorinated alternatives were found to be cheaper.

219. More recent information indicates that some alternatives may be priced comparably to one other but be more expensive than PFOS derivatives. For instance, PFOS seems to be less expensive than PFBS. Some price examples for laboratory chemicals are shown in table 7. The purity and prices of bulk materials may be lower.

**Table 7: Prices of selected basic polyfluorinated laboratory chemicals<sup>85</sup>**

Chemical	CAS no.	Molecular weight	Price in € per 100 g
Perfluorobutane sulfonyl fluoride (PFBSF)	375-72-4	303.09	136
Perfluorobutane sulfonic acid (PFBS)	59933-66-3	300.10	1,800
Perfluorooctane sulfonic acid (PFOS)	1763-23-1	500.13	1,122
Perfluorooctane sulfonyl fluoride (PFOSF)	307-35-7	502.12	92
Fluorotelomer 6:2 alcohol	647-42-7	364.10	130
Fluorotelomer 8:2 alcohol	678-39-7	464.12	187
Fluorotelomer 10:2 alcohol	865-86-1	564.14	1,440
Methyl nonafluorobutyl ether	163702-07-6	250.06	745

220. Although the table shows the opposite, C<sub>6</sub>-fluorochemistry alternatives may often be more expensive than C<sub>8</sub>-fluorochemistry alternatives, which are subject to a phase-out and therefore obsolete.

84 Poulsen PB, Jensen AA, Wallström E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project 1013. Danish Environmental Protection Agency. [www.mst.dk/Udgivelser/Publications/2005/06/87-7614-668-5.htm](http://www.mst.dk/Udgivelser/Publications/2005/06/87-7614-668-5.htm).

85 ABCR 2006–2007 catalogue: Fluorochemicals. Karlsruhe, Germany.

221. Especially at the beginning, alternatives might be more expensive to purchase or use; however, this increased cost could be an acceptable side effect of eliminating a very hazardous chemical. The prices of substitutes will decrease in the long run with a growing market and increasing competition.

222. The necessity or “public good” of a use could also be a factor in determining whether it should continue or be phased out even in the absence of apparently good alternatives. Of course PFOS has useful applications, but none for which feasible alternatives appear to be lacking.

## VI. Conclusions, recommendations and future developments

### Low surface tension is the key

223. In addition to stability, a key factor in the performance of fluorosurfactants is their extremely low surface tension, which currently cannot be matched with other surfactants. PFOS is the optimal substance with regard to that property. Owing to environmental and health concerns, however, surfactants without fluorine content could be used as alternatives if such low surface tension levels are not needed. Given the relatively high prices of fluorosurfactants, switching can in some cases also have economic benefits.

### Substitutes for PFOS are available

224. Fluorinated or non-fluorinated alternatives exist for nearly all current uses of PFOS. While the alternatives may be slightly more expensive and less effective, they will normally be less hazardous. In Japan only three essential applications are left for PFOS: 1) etching agent for semiconductors, 2) semiconductor resists and 3) photo films for industrial purposes.<sup>86</sup>

225. The most common PFOS alternatives in use are fluorotelomers, which are precursors for PFCA. Formerly, C<sub>8</sub>-fluorotelomers were a frequent choice; they have been shown, however, to degrade into PFOA, which also has hazardous properties. For that reason the major global producers of fluorochemicals have agreed with the United States Environmental Protection Agency to phase out C<sub>8</sub>-fluorotelomers before 2015. As a result, there has been a shift to the less hazardous C<sub>6</sub>-, C<sub>4</sub>- and C<sub>3</sub>-perfluoroalkylated chemicals.

### Need for better alternatives

226. For some uses non-fluorinated chemicals have been introduced as alternatives; examples include silicones, aliphatic alcohols and sulfosuccinates. It might also be that a particular use or product is no longer essential, or that a process could be changed to eliminate the need for PFOS, as has happened in the photographic industry and in chrome plating.

### Need for incentives

227. There is a need for incentives to develop safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for their development. The international requirements applying to all parties to the Stockholm Convention, which must be implemented in national law, constitute one such incentive. The development of national law is an important tool for promoting incentives to identify and use alternative substances and processes. Postponing the development of national law until perfect alternatives are available is not wise because manufacturers may not develop alternatives if they are not forced to do so.

### Complex assessment

228. A comparative assessment of PFOS and its possible alternatives with regard to technical, socio-economic, environmental, health and safety considerations is a very complex process requiring a large amount of data and other information, and more than is normally available. Often the information available about PFOS is much more extensive than information about the possible alternatives, which may be newly developed substances or formulations covered by trade secrets. Furthermore, information on the alternatives will also often be non-peer-reviewed and of lower scientific quality. There may be a need for a mechanism for continuously updating information regarding the alternatives' substitution properties and hazards. Such a mechanism should be consistent with Article 9, subparagraph 1 (b), of the Convention regarding the exchange of information on alternatives to persistent organic pollutants.

<sup>86</sup> Presentation by Takashi Fukushima, Japanese Ministry of Economy, Trade and Industry, at the national workshop on nine new persistent organic pollutants subject to the Stockholm Convention and the implementation of the Convention in China, Beijing, 1–2 July 2010.

229. Available useful economic data may also be scarce and biased. The sparse information received to date, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. Specifically in the coatings and paints area, the non-fluorinated alternatives are cheaper. Higher costs of alternatives are not always a problem; in fact, sometimes the high cost of not continuing the use of small amounts of PFOS can be a problem for the industry.

### **Need for more public data and information on alternatives**

230. Much fewer data are currently available publicly on the alternatives than on PFOS. Much of the information is from patent literature, and the identities of actual chemicals used are often not disclosed. This reinforces the need for implementation of paragraph 1 of Article 9 on the information exchange regarding alternatives to persistent organic pollutants.

231. Chemicals with structures similar to those of the listed PFOS substances could cause concerns similar to those related to the latter substances. This should be considered in evaluating alternatives.

232. Increasing effort will be needed to study the toxicological and environmental properties of alternatives and to make the resulting information public and trustworthy by publishing it in peer-reviewed scientific journals.

233. A strategic integrated approach to testing is needed to speed development of the data required to understand the issues and concerns relating to the various types of alternatives. According to the United States Environmental Protection Agency, testing can be done scientifically without necessarily testing every alternative chemical for every endpoint.

### **Need for better communication in the value chain**

234. It is important that the issues associated with PFOS as a globally recognized persistent organic pollutant, including the health and environmental risks, be made fully known to suppliers and industries. Producers need to have better knowledge about the use of PFOS in processes, products and articles. It is also important to provide information to customers and consumers so that they can develop informed opinions about the possible need to change products or processes. Industries that are proactive in phasing out the use of a very hazardous chemical such as PFOS are likely to reap future market advantages.

### **Need for more international cooperation**

235. PFOS and its substitutes are being studied and evaluated in parallel by authorities in many countries. More international cooperation can save resources and speed up processes. The OECD Parallel Process for the Notification of New Chemicals is one useful approach (for new chemicals) to consider in developing international collaboration on assessing potential alternatives to PFOS and other polyfluorinated chemicals of concern.

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