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Operational issues: intersessional work on substitution and alternatives

Annotated outline for a guidance document on perfluorooctane sulfonate alternatives

Note by the Secretariat

The annex to the present note contains the full annotated outline for a guidance document on alternatives to perfluorooctane sulfonic acid and its derivatives developed by the intersessional working group on substitution and alternatives. A summary of the annotated outline is contained in annex I to document UNEP/POPS/POPRC.5/6. Comments on the outline submitted by Parties and observers are contained in document UNEP/POPS/POPRC.5/INF/14. The annex has been reproduced as received and has not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.5/1.

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Annex

Annotated outline for a study (Guidance document) on alternatives to perfluorooctane sulfonic acid (PFOS) and its derivatives

Purpose of this outline:

It is an appetizer to indicate a proposed content and flow of the **more detailed** Guidance document to be drafted in the autumn of 2009. The information mentioned is mainly from national submissions to POPC and earlier reviews. References are not normally shown here but should appear more in the final text. The tables will be amended.

Acknowledgement:

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Table of Content

Executive summary

This will be the size of about one page containing the most important findings/conclusions.

1. Introduction, background and objectives

This introductory chapter will describe the background of the PFOS issue and objectives of this study of available or potential alternative substances or equipment. It will be based a. o. on the following UNEP POPRC documentation with website links in the reference list:

- Proposal for listing of PFOS in Annex A (letter from Swedish Ministry for the Environment from 14 July 2005).
- Perfluorooctane sulfonate proposal (UNEP/POPs/POPRC.1/9; 24 August 2005)
- Decisions at POPRC-1/7: Perfluorooctane sulfonate
- Conclusions of the Risk Profile of PFOS (21 November 2006)
- Exploration of Management options for PFOS (12 June 2007)
- Conclusions of the Risk Management Evaluation of PFOS (4 December 2007)
- Addendum to the risk management evaluation for PFOS (30 October 2008)

Important to show that yes we need alternatives.

2. Characteristics of PFOS and its derivatives

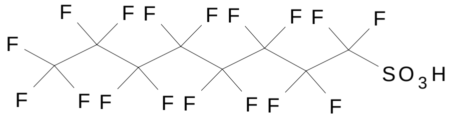
It will be discussed how many PFOS derivatives that is relevant to include in the Guidance document based on previous POPRC papers and other sources. Sweden nominated 96 PFOS related substances. According to the Chinese delegation 66 PFOS related chemicals have been registered in a national inventory in China (Year?). In 2007 in Denmark 92 polyfluorinated substances were registered, among these 13 PFOS derivatives (Jensen et al. 2008).

On 12 April, 2006, OECD made available a "Preliminary List of PFOS, PFAS, PFOA and Related Compounds and Chemicals that May degrade to PFCA [ENV/JM/MONO (2006)15]. OECD, in cooperation with BIAC and other country representatives, has recently drafted the 2009 PFC Survey Questionnaire, "Survey of Product Content and Environmental Release Information on PFOS, PFAS, PFOA, PFCA, their Related Substances and Products/Mixtures Containing these Substances," that will be distributed to participating companies this summer, to report on their 2008 activities.

2.1 PFOS derivatives and precursor mentioned explicit in previous papers

The PFOS derivatives included in the previous POPRC documents will be listed and described shortly:

- Perfluorooctane sulfonic acid (PFOS; CAS no. 1763-23-1):



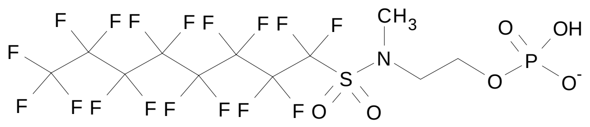
- Potassium perfluorooctane sulfonate (CAS no. 2795-39-3); a perfluoro anionic surfactant; chrome-fume inhibitor and wetting agent in electroplating.

- Lithium perfluorooctane sulfonate (CAS no. 29457-72-5)
- Ammonium perfluorooctane sulfonate (CAS no. 29081-56-9)
- Diethanolammonium perfluorooctane sulfonate (CAS no. 70225-14-8)
- Perfluorooctane sulfonyl fluoride (PFOSF; CAS no. 307-35-7); a major basic chemical for synthesis of PFOS derivatives.

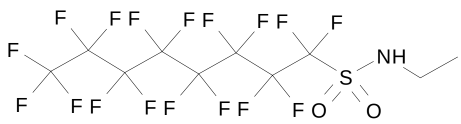
2.2 Additional and often used PFOS derivatives and precursors

From the literature additional relevant PFOS derivatives will be identified and listed e.g.:

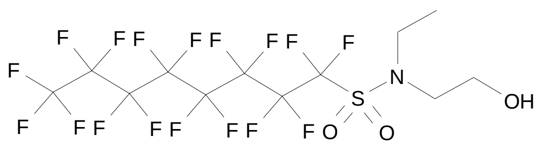
- Tetraethylammonium perfluorooctane sulfonate (CAS no. 56773-42-3); wetting agent for chrome plating (Fluorotensid-248).
- Perfluorooctane sulfonamide (PFOSA, FOSA; CAS no. 754-91-6); basic chemicals for fluorosurfactants (impregnation), electroplating additives and etching agent for metal and plastic.
- *N*-Methyl perfluorooctane sulfonamide (MeFOSA; CAS no. 31506-32-8)
- *N*-Methyl perfluorooctane sulfonamidoethanol (MeFOSE; CAS no. 2448-09-7)
- *N*-Methyl perfluorooctane sulfonamidoethyl acrylate (MeFOSEA; CAS no. 25268-77-3).
- *N*-Methyl perfluorooctane sulfonamidoethyl phosphate; surfactant for packaging:



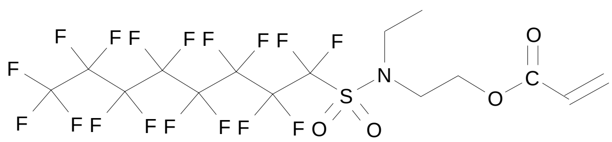
- *N*-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2); surfactant and pesticide for termites, cockroaches and other insects.



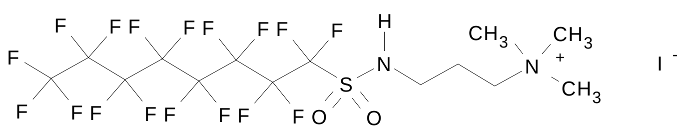
- *N*-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE; CAS no. 1691-99-2); surfactant, intermediate for perfluoroalkyl acrylic ester synthesis:



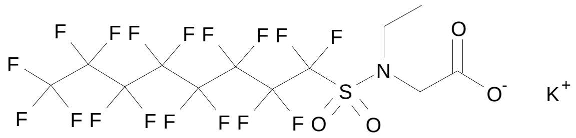
- *N*-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSEA; CAS no. 432-82-5):



- 3-[[(Heptadecafluorooctyl)- sulfonyl]amino]-*N*,*N*,*N*-trimethyl-1-propanaminium iodide/perfluorooctyl sulfonyl quaternary ammonium iodide (CAS no. 1652-63-7); cationic surfactant, wetting agent, fire extinguisher, film coating agent, auxiliary welding agent, anti-scalant for fibre, leather, pesticide etc. (Fluorotenside-134).



- Potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS-no. 2991-51-7); used in cleaning products and pesticides.

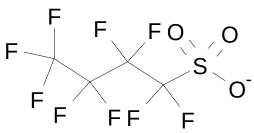


Some more structure formulas are planned.

2.3 Other related polyfluorinated alkyl sulfonates (PFAS)

Other perfluorinated alkyl sulfonates, which have been identified as used for similar or related applications as PFOS and may be used as substitutes, are mentioned briefly. Further discussion in later chapters on substitutes:

- Potassium perfluoroethyl cyclohexyl sulfonate (FC-98; CAS no. 67584-42-3); may be used as an anti-erosion agent <0.1% (mainly 0.0075% to 0.075%) in aviation hydraulic oils, anti-reflective coating and electro-optical liquid crystal displays.
- Perfluorodecane sulfonic acid/sulfonate (PFDS; CAS no. 335-77-3/67906-42-7); precursors used in impregnating agent for tents, sleeping bags, etc.
- Perfluorohexane sulfonic acid (PFHxS; CAS no. 432-50-7); precursors used as PFOS substitutes in impregnation agent for textiles and carpets etc.
- Perfluorobutane sulfonic acid/sulfonate (PFBS; CAS no. 29420-49-3/29420-43-3); precursors used as PFOS substitutes in impregnation agent for textiles and carpets etc



2.4 Chemical, physical, environmental and biological properties of PFOS and its derivatives

This subchapter will contain a brief description of the chemical, physical, environmental and biological properties of PFOS derivatives. More detailed tables will be annexed. These are surfactants with extremely low surface tensions (active at low concentrations), low friction factor, electric insulation, and repellent for water, oil and dirt. These properties have been found to be useful in many applications.

The basic PFOS structure is extremely persistent and resists strong acids and high temperature. Its precursors degrade to PFOS basic structure.

It is useful to know that PFOS as salt and quaternary ammonium compounds is more hydrophilic, and the acid itself and the substituted sulfonamides are less hydrophilic and more volatile than the salts. Thus, there is a range of properties depending on chemical species.

The cost of some PFOS- substances from various suppliers will be included.

Additional information may be traced in 2002 OECD hazard assessment.[1] and, among others.

2.5 Production and consumption of PFOS and derivatives

The production trend of PFOS will be described based on various sources, including 3M phasing out PFOS production in 2002, and changed to production of shorter chain PFCs. Some sporadic production data exists from national information in POPRC documents.

For example, in 2003 production of PFOSF and PFOS was initiated in China. In 2006 the annual production of PFOSF was more than 200 tons of which about 100 tons was exported to other countries including Brazil and EU. In 2003 Germany and Italy produced <60 and <22 tons PFOS, respectively.

The United States estimates total use to be less than 8 tons/yr (2006), and Ireland reports import and use of 10 kg PFOS during 2006. Switzerland gives several estimates for the current use (March 2007) of PFOS ranging from 230 kg/yr to 5 tons/yr.

Many articles and reports have been published, including the recent publications by AG Paul et. al. (2009) and Bruinen de Bruin et al. (2009).

[1] http://www.regulations.gov/fdmspublic/component/main?main=DocketDetail&d=EPA-HQ-OPPT-2003-0012

3. Legislative initiatives and assessments

Here some information about legislative initiatives on PFOS will be mentioned. Latest overview of country activities is available at UNEP Chemicals website:[2]

3.1 EU

The European Union has by adopting Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006 amended for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates). The restrictions include the following:

- PFOS and related substances (salts, amides, and polymers) are banned from 27 June 2008 as substances or constituents of preparations in concentrations equal to or higher than 0.005%, in semi-finished products and articles at a level of 0.1% except for textiles or coated materials in which the restricted amount of PFOS will be 1 µg/m2.
- Exemptions were provided for the following PFOS uses, as well as for the substances and preparations needed to produce them: photoresist or anti-reflective coatings for photolithography processes, industrial photographic coating, mist suppressants for chromium plating and other electroplating applications, as well as aviation hydraulic fluids;
- Stocks of PFOS-based fire-fighting foams supplied on or before the date 12 months before the legislation comes into force may be used for a period of 54 months until 27 June 2011.

Not later than 27 December 2008 Member States shall establish and communicate to the Commission an inventory.

3.2 Canada

On May 29, 2008, Canada finalized a national regulation to prohibit the manufacture, use, sale, offer for sale and import of PFOS and its salts and substances that contain one of the following groups $C_8F_{17}SO_2$, $C_8F_{17}SO_3$ or $C_8F_{17}SO_2N$ with exemptions provided for certain uses e.g. aqueous fire fighting foam, metal plating, semiconductor and photolithography and use of products containing PFOS produced before the regulation entered into force (Canada Gazette, Part 2, Vol. 142, No. 12, June 11, 2008).[3] Additional information on PFOS can also be found at Environment Canada website.[4]

3.3 USA

In 2000 and 2002 the United States Environmental Protection Agency (US EPA) has issued Significant New Use Rules (SNURs) for 88 PFOS substances which apply to new manufacture and new uses of these substances (40CFR 721.9852). The SNURs allow only three specific, technically essential low volume, low exposure, low release uses to continue: photographic/imaging industry, semiconductor industry, aviation industry; also allowed use as an intermediate to produce other chemical substances to be used solely for the uses listed.

A final SNUR for 183 additional perfluoroalkyl sulfonate substances was published in October 2007. The SNUR continues to apply the 4 excluded uses from the previous SNURs and provides for two new exclusions for ongoing uses: seven chemicals are allowed for use as an etchant, and one chemical is allowed for metal plating and finishing uses. More information is available at the USEPA website.[5] An overview from February 2009 is available.[6]

In August 2008 the California Assembly approved the state Senate bill to ban the use of (grease-proof of fast-food sandwich wrappers, french-fry bags, pizza boxes and other food packaging) food packaging containing perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Senate Bill 1313 would ban persons and companies from manufacturing, selling, or distributing any food contact substance containing PFOS, PFOA, higher homologues, or precursors to these chemicals, in any concentration exceeding 10 parts per billion, however, California's governor Arnold Schwarzenegger vetoed Senate Bill 1313 on 29 September 2008.[7]

3.4 Other countries

In 2007 Norway banned PFOS in fire fighting foams, in textiles and in surface protection agents. But still needs an exemption for hard chrome plating.

Information from other countries will be included if available. However, the focus of this report is on the alternatives to PFOS and the regulation of PFOS has been discussed in previous reports.

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[2] http://www.chem.unep.ch/unepsaicm/cheminprod_dec08/PFCWorkshop/default.htm
[3] http://www.ec.gc.ca/ceparegistry/documents/regs/g2-14212_r1.pdf
[4] http://www.ec.gc.ca/TOXICS/EN/detail.cfm?par_substanceID=230&par_actn=s1"
[5] http://epa.gov/oppt/pfoa/pubs/pfas.html
[6]http://www.chem.unep.ch/unepsaicm/cheminprod_dec08/PFCWorkshop/Presentations/US%20Activities%20on%20PFCs.pdf
[7] http://www.rsc.org/chemistryworld/News/2008/October/01100801.asp

4. Uses of PFOS derivatives where alternatives are available

Historical uses in some countries are ongoing uses in other countries. PFAS in articles/products is still an issue for all countries that import articles/products that contain PFAS, even if PFAS are not manufactured/imported in that country. An estimated timeline of introduction in the various applications will be added. It is not so long ago that we lived in a society without PFOS.

4.1 Textile impregnation and surface protection

Fluorinated chemicals (PFCs) are extensively used by the textile industry and by private consumers for all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, leather, footwear, rugs, mats and carpets etc. to repel water, oil and dirt. Before year 2000 these were the most important application of PFOS derivatives (about 47% of the use in EU) but after the bans in many countries, PFOS has been substituted mainly with shorter-chain analogues and fluorotelomers but also with non-fluoro chemicals (see later). The Chinese delegation reports that 10.000 tons of fluorine-containing textile finishing agents was imported to China in 2006 for treatment of high-quality clothing. It is not clear if it was PFOS or not.

Examples of well-known soil and dirt repellents trade marks for PFCs for carpets are:

- Scotchgard® (3M)
- Zonyl® (DuPont)
- Baygard® (Bayer)
- Foraperle® (Atofina/DuPont)

The PFOS derivatives (normally 2-3% of the fibre weight 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).

Water repellent consumer sprays are available for leather products. A content of PFCs of about 0.025-0.05% of the leather weight is necessary to obtain water repellence.

In the production of textiles, fluorinated chemicals are also used as

- Wetting agents to e.g. enhance dyeing
- A binder in non-woven fabrics
- Anti-foaming agents in textile treatment baths;
- As emulsifying agents for fibre finishes
- Penetration aids for bleaches.

4.2 Impregnation of packaging (paper/cardboard)

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

- 3M (Scotchban®)
- Bayer (Baysize-S/Baysynthol®)
- Ciba (Lodyne®)
- Clariant (Cartafluor®)
- DuPont (Zonyl®)

PFOS derivatives have been used both in food contact applications (plates, food containers, bags (popcorn), and wraps) and in non-food contact applications: folding cartons, containers, carbonless forms, and masking papers.

Paper protection by PFOS derivatives was achieved by using either

- mono-, di- and triphosphate esters of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) or
- *N*-methyl perfluorooctane sulfonamidoethanol acrylate polymers.

Before 2000 about 32% of the total use of PFOS in EU was for paper but now it is not allowed and substituted mainly by other fluorinated chemicals.

4.3 Cleaning agents, waxes and polishes for cars and floors

Fluorinated surfactants are especially used in water-based floor polish products, as these compounds lower the surface tension and contribute to the formation of a hard film with a good adhesion to the floor, mainly on floors of PVC and linoleum.

PFOS derivatives have historical been used as surfactants to 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 carwashes. PFOS derivatives have also been used in carpet spot cleaners.

A PFOS derivative often used in cleaning agents, floor polish and auto polish products has been the potassium salt of *N*-ethyl-*N*-[(heptadecafluorooctyl)sulfonyl] glycine (CAS-no. 2991-51-7). The concentration of that substance in the final product was in general between 0.005% and 0.01% but might have been 10 times higher.

4.4 Surface coating, paint and varnish

PFOS derivatives have had several historical uses (before 2000 about 18% of the PFOS use in EU) in coating, paint and varnishes at reduction of surface tension, for example for substrate wetting, levelling, as dispersing agents, and for improving gloss and antistatic properties. They can be used as additive in dyestuff and ink, e.g. as foam generators. Furthermore, they can be used as pigment grinding aids or as agents to combat pigment flotation problems. Fluorosurfactants are much more expensive (to be elaborated on in the text) than other surfactants available for paint, and were only used for special purposes, where an extremely smooth surface was necessary e.g. in coating of electronics. The concentrations used were below 0.01% (w/w).

4.5 Oil production and mining

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, jet fuel and hydrocarbon solvents, and to enhance the amount of recovery in copper and gold mines. According to information from the Chinese Delegation to the Stockholm Convention PFOS is still used as surfactant in old oil fields in China to recover trapped oil in small pores between rock particles. No information about essentiality.

5. Commercial uses where alternatives need to be developed

In this chapter the data will be checked for consistency with COP4. If available the volume of these uses will be mentioned and country compared.

5.1 Photo industry

In the photographic industry PFOS-related compounds are used in the manufacturing process of film, photo paper and -plates. The PFOS-related compounds function as dirt rejecters and friction control agents. Furthermore, they reduce surface tension and static electricity. Imaging materials that are more sensitive to light (i.e. high speed films) are more in need of the properties provided by 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 $\mu g/cm^2$.

Due to a reduction of the use of films caused by use of digital cameras, the use of PFOS within this area is not expected to grow. World consumption of PFOS used in colour film production process is down from 23 tons in 2000 to 8 tons in 2004. Present annual consumption in EU photographic industry is 1 ton PFOS. This reduction by 83% in the EU since 2000 has had according to industry an estimated cost of 20-40 mio. €/year.

PFOS is still used probably in minor quantities in X-ray film for photo imaging for medical use and industrial use (NDT). It is also used in films for professional purposes such as the movie industries. Alternatives to PFOS are claimed not to achieve the same high quality. Use of PFOS in industrial photographic coating is exempted from the PFOS ban in EU.

In addition, PFOS-related compounds have previously been used in developers for photographical film. According to the EU Directive this application is banned now. Japanese photo industries also informed that PFOS is not used for photo processing anymore in Europe, Japan, North America and other areas. Since photo processing solutions using PFOS were highly technical products, they were produced and supplied by a limited number of manufacturers terminating PFOS for their photo processing products. The replacement may be new digital technology.

5.2 Electric and electronic parts

Electric and electronic equipment requires hundreds of parts and thousands of processes. PFOS based chemicals are used in the fabrication of digital cameras, cell phones, printers, scanners, satellite communications, and radar systems etc. The PFOS-related compounds are process chemicals and the final products are mostly PFOS-free.

5.3 Semiconductor industry

PFOS reduces the surface tension and reflection of etching solutions, important for precise photolithography in the semiconductor industry (photoresist and photomask) for ultra-fine patterning and antireflective coatings. The PFOS-related compounds in such uses are a part of the process chemicals and are not a part of the final products.

The World Semiconductor Council (industry) is committed to end non-critical uses in the UNECE region by May 2007 and everywhere in May 2009. The annual use of PFOS in EU semiconductor industry before 2000 was 470 kg with emissions of 54 kg.

PFOS (<5 kg PFOS/yr) is used in the Japanese semiconductor industry for etching of high-frequency compound semiconductors and piezoelectric ceramic filters. Alternative method in the same level of quality is not currently available and more research and development is needed to achieve quality requirement. According to a submission from Japan alternative methods are expected to be available in 2014 (UNEP/POPS/POPRC.4/INF/17).

According to information from the Chinese delegation the semiconductor industry in China uses 30-40 kg PFOS/yr for photoresist, anti-reflective coating, de-glueing agent and developing agent, and in 2007 the industry sales were 100 billion Yuan.

5.4 Aviation hydraulic fluids

Hydraulic oils with content (about 0.1%) of potassium perfluorooctane sulfonate has been used in both civil and military airplanes since the 1970s (a published patent was from 1972) in order 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 EU for this use was about 730 kg.

5.5 Pesticides

N-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2) is surfactant and pesticide for termites, cockroaches and other reptile insects. Sulfluamid may be used in wood and cellulose products such as paper and cardboard?

Fluorosurfactants may also be used as “inert” surfactant (enhancer) in pesticide products, e.g. 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) has been approved in the US.[8] Both chemicals have more uses as seen on page 2. Because PDOS derivatives previously were considered rather inert and non toxic, they were used. The present extent of that use is not known.

The use to manufacture of baits for ants and in insecticides against beetles and ants is obsolete in EU and the US EPA did cancel the registration of sulfluramid in May 2008.[9] However, according to information submitted to the Stockholm Convention 3 tons sulfluramid is used for pest control (cockroaches, white ants and fire ants) in China, and sulfluramid is also used in Brazil in 95% of all baits; amount not reported.

5.6 Medical devices

Video endoscopes are used to examine and treat patients in hospitals. Around 70% of the video endoscopes used worldwide or about 200 000 endoscopes contain a CCD[10] colour filter that contains a small amount of (150 ng) PFOS. Repairing such video endoscopes requires a CCD colour filter containing PFOS, according to submission from the Japanese delegation.

PFOS is also used as an effective dispersant when contrast agents are incorporated into an ethylene tetrafluoroethylene copolymer (ETFE) 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 indwelling needle catheters).

5.7 Metal plating

The discussion will separated in decorative chrome plating vs. hard metal plating. Previously, PFOS was used for both processes but new technology applying Cr-III instead of Cr-VI have made PFOS use in decorative chromium plating obsolete.

PFOS is used as wetting/anti-mist agent for chromium plating. PFOS works by lowering the surface tension and form a single foam film barrier of a thickness of about 6 nm on the surface of the chromic acid bath, which retains aerosol (fog) formation, and thus reduces airborne loss of hexavalent chromium from the bath and decreases exposure of workers to this carcinogenic agent. The use of PFOS as wetting agent for hard chromium plating has been considered essential, and this use is exempted from the PFOS bans already enforced in some countries.

The PFOS derivative mostly used in hard chrome plating is the quaternary ammonium salts tetraethylammonium perfluorooctane sulfonate (e.g. Fluorotenside-248), typically in a 10% solution but also the potassium, lithium, diethanolamine, and ammonium salts of perfluorooctane sulfonic acid may be used. During the process the tenside is broken down and after about 7 months only about 1% of the original content is left. Thus the bath has occasionally to

[8] http://www.fluoridealert.org/pesticides/pfos.pfoas-page.htm
[9] http://www.epa.gov/fedrgstr/EPA-PEST/2008/May/Day-16/p10919.htm
[10] Charge-coupled-device = technology for capturing digital images

be refilled with fluorotensides, when the operator finds the foam layer insufficient to withhold the Cr-VI aerosols. Alternatives to the PFOS derivative will be less stable in the bath.

In the industry the PFOS tensides seem to be marketed as safe products without information about the hazards or the content of PFOS.[11] Thus the incentive to find alternative substances and processes is low. Because the fluorotensides are not classified dangerous, this use in Denmark is not reported to the Product Registry, and the full extent is not known to the authorities.[12]

When the bath is "burnt out", it is e.g. in DK sent to a chemical waste plant, where the chromium is precipitated and disposed at a landfill. The PFC residues currently probably still escape to the waste water and end up in sewage sludge, which sometimes is used as fertilizer of agricultural soil. A great part of PFC used in this industry will probably end up in the nature. High levels of PFOS recently were found in agricultural soils in the US[13] and in Germany. On the other hand the German national metal plating organisation ZVO states that in Germany only 20% is lost.[14]

- In EU the annual use for this purpose is 10 tons PFOS.
- Information from the Chinese delegation show that 25 tons PFOS/yr is used in the Chinese chrome plating industry. The industry turnover is 30 billion Yuan. A phase-out could worsen the health of 100.000 Chinese workers, according to Chinese authorities.
- Canada reports an estimated 3 metric tons imported from USA and used for metal plating in 2004.
- France reports 200 kg used for metal plating during 2006.

Besides the use for chromium plating fluorinated surfactants (including PFOS?) are also used as

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

5.8 Fire-fighting foam

When it comes to extinguish a liquid fuel fire at airports, and oil refineries/storage, fire-fighting foams with fluorosurfactants, are very effective. These are:

- Fluoro-protein foams used for hydrocarbon storage tank protection and marine applications,
- Aqueous film forming foams (AFFF) used for aviation, marine and shallow spill fires; developed in the 1960s
- Film forming fluoro-protein 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 fluoro-protein foams (AR-FFFP), which also are multi-purpose foams. Developed in the 1970s

Normally, a mixture of fluorinated surfactant and a hydrocarbon-based surfactant are 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 0.5-1.5% but can be higher.

The fluorinated surfactant used in aqueous fire-fighting foams (AFFF) forms an aqueous film covering the oil surface for stopping oil-fires at chemical plants, fuel storage, airports, underground parking and tunnels. A PFOS compound used: 3-[[(Heptadecafluorooctyl)- sulfonyl]amino]-*N*,*N*,*N*-trimethyl-1-propanaminium iodide (DuPont).

Today, most fire-fighting foams are manufactured without use of PFOS but with fluorochemicals/telomers based on a C_4 or a C_6 alkyl chain, however, according to information from the Chinese Delegation more than 50 enterprises in China which produce Aqueous Film Forming Foam (AFFF) consume more than 100 tons of PFOS per year. AFFF was phased-in in China in the 1990s as alternative technology for halons, which are ozone depleting substances, and with support from the international community.

As fire-fighting foams have long shelf life (10-20 years or longer) PFOS-containing fire-fighting foams may still be used everywhere at actual accidental oil fires. In 2004 the EU stocks of fire-fighting foams with PFOS was 122 tons. Canada reports an estimated 3 tons of PFOS in stockpiles of fire fighting foams, of which 10% (300 kg in 2004) is

[11] Personal information from Prof. Per Møller, Technical University of Denmark, March 16, 2009.
[12] Personal information from Frank Jensen DEPA, March 17, 2009.
[13] Renner R. EPA finds record PFOS, PFOA levels in Alabama grazing fields. EST 2009; 43: 1246-1247.
[14] Personal information from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), D-40724 Hilden; March 6, 2009.

estimated to be expended each year. In Japan, the stocks of AFFF are 19 000 tons (80% are stored in 40 000 underground parking areas), and the maximum production capacity is 2100 t/y.

Cheaper but apparently less effective fire-fighting foams without fluorosurfactants have been developed with the main purpose of using them during training exercises.

6. Alternative substances and processes; technology and costs

This chapter will include identification and description of possible/potential alternative chemicals, processes or products for various uses. If an alternative chemical is not available, may be the process or product could be changed? Or may be the product is not essential? The task is to examine which alternatives are available, feasible, used, and with experiences.

Further, to evaluate technical properties/fitness for use/durability of the alternatives for each separate application. Also socio-economic assessment of the alternatives; differences between branches, size of enterprise, countries, and regions; product essentiality; economic constrains, societal costs. Finally, environmental, health and safety aspects/risk will be mentioned in that extend information is available. There is often lack of public data for the environmental properties of the alternatives compared to PFOS itself. That is also a reason, why rigid selection criteria are not useful. We should not expect that possible alternatives are without hazards, but at least not as hazardous as PFOS. Especially in the start alternatives could also be more expensive – that should also be accepted to get rid of a very hazardous chemical. Trustful economically data will probable also be scarce.

A list of the sources researched to determine whether or not an alternative is available.

- Information from international organizations such as UNEP and OECD
- Information from industries and industry associations
- Information from authorities
- Information from NGO's
- Internet search
- Literature search
- Contacts to identified producers of alternatives.

The scope of the search will provide a useful parameter to consider when concluding "there are no alternatives".

If possible, it might be interesting to include information on the research pipeline and when alternatives for certain uses might appear in time.

6.1 Textile impregnation and surface protection

The alternatives to PFOS for impregnation of textile fabrics, leather, carpets, rugs and upholstery are mainly:

- Other polyfluorinated compounds such as perfluorobutane sulfonate (PFBS) based substances, fluortelomer-based polymers, or polytetrafluoroethylene (PTFE).
- Silicone-based products.
- A mixture of silicones and stearamidomethyl pyridine chloride, eventually together with carbamide (urea) and melamine resin.

3M Company markets a Scotchgard™ Protector for fabric (Universal Spray) without perfluorooctanoyl chemistry but containing 1-5% of a trade secret fluorinated urethane.

Analyses on 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 PFOS at all. The analyses indicate that perfluorinated acids and telomere alcohols are now used as alternatives to PFOS in impregnating agents (Information from SFT 2009).

6.2 Impregnation of packaging (paper/cardboard)

The possible alternatives identified for impregnation of paper and cardboard for use in packaging are telomer-based substances and polyfluoroalkyl phosphate or phosphonate type compounds but grease-proof paper did also exist before PFOS was introduced.

In a survey conducted by the Norwegian Food Safety Authority in 2006, it was concluded that no fluorinated substances are used in fast food packaging in Norway. The Norwegian paper producer Nordic Paper is using mechanical processes to produce extra dense paper which inhibit leakage of fat through the paper (Information from SFT 2009).

6.3 Cleaning agents and waxes and polishes for cars and floors

As the fluorinated compounds have the same function in waxes as in paint, to lower the surface tension and contribute to the formation of a hard film with a good adhesion, it may be possible to use the same substitutes as within the paint and varnish industry.

The possible alternatives identified for cleaning agents, waxes and floor polishes are:

- Different C4-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)
- Telomer-based surfactants and polymers
- Fluorinated polyether's: PolyFox™ (OMNOVA Solutions Inc); a line of fluorosurfactants which are polymers with a molecular weight greater than 1,000 based on ether links and with C2F5 or CF3 as the starting material.
- A shift to softer waxes may eliminate the use of PFOS-compounds entirely. In these products, the fluorinated surfactants are substituted with non-ionic or anionic surfactants, which have good wetting properties.

6.4 Paint and varnish

The possible alternatives identified for paints and varnishes are surfactants based on:

- C4 compounds based on perfluorobutane sulfonate (PFBS) especially within the area of electronic coating,
- Polyether-modified polydimethyl siloxane,
- Fluorinated polyether's (PolyFox™) as in cleaning agents above,
- Propylated aromatics (naphthalenes and biphenyls) can be used as water repelling agents for different applications such as rust protection systems, marine paints, resins, printing inks, and coatings of electrical applications,
- Aliphatic alcohols (e.g. fatty alcohol polyglycol ether sulfate, eventually together with a sulfosuccinate),
- Silicone polymers, such as non-ionic modified silicone polyether mixed with di-2-ethylhexyl (dioctyl) sulfosuccinate in ethanol and water,
- Sulfosuccinates, e.g. the sodium salt of di-2-ethylhexyl sulfosuccinate dissolved in ethanol and water is an alternative in wood primers and printing inks.
- Telomer-based surfactants.

The information received from different suppliers specifically within the paint and varnish industry suggests that fluorinated surfactants in general are much more expensive alternatives compared to other surfactants. Therefore, fluorosurfactants are only used for special purposes in paint and varnishes, where it is necessary to gain such a low surface tension, which no other (non-fluorinated) alternatives can achieve, e.g. in product where an extremely smooth surface is necessary.

6.5 Pesticides

In Brazil, according to the Brazilian Delegation, damages corresponding to losses of up to 14.5% of trees per hectare have been estimated without the use of ant pesticide (sulfluamid). The cost of an attack of leaf-cutting ants is estimated to US$ 6.7 billion in wood. Considering that the sugar cane planted area in Brazil is of approximately 6 millions of hectares, the cost in this sector is estimated to US$ 1,82 billion/year. Other affected agricultural products likely to be affected at high costs are soybean and maize. Also the capacity of supporting livestock heads/hectare is likely to be reduced, if forage for grazing is reduced by ants.

There are three alternatives registered in Brazil for the control of leaf cutting ants: fipronil, endosulfan and chlorpyrifos. However, endosulfan is a candidate for addition to the Stockholm Convention, and the others are considered more acutely toxic for human health and the environment. The effectiveness of some of these products has been questioned. Therefore, new alternatives are being studied in Brazil.

It is not clear, what is used as alternatives today, in countries where banned. Ant baits with S-methoprene and pyriproxyfen are registered in New Zealand to control exotic ants for air and ground applications. These pesticides are not killing adult ants but inhibit growth and make them unable to reproduce. Exotic and leaf-cutting ants are different, thus it is not clear, if these or other insect growth regulators are effective against both pests.[15] Synthetic piperonyl compounds seem to kill most of the exposed leaf-cutting ants and may be an alternative.[16] A combination of these two agents could be even more efficient. It is very unlikely that efficient and safe alternatives don't exist.

[15] Information from the Brazilian Delegation.
[16] Victor et al. Pest Manag Sci 2001; 57:603-608.

6.6 Oil production and mining

Currently no information about alternatives in the oil and mining industry but the amount presently used is probably small and represent dispersive uses and should be prioritized for phase-out.. At COP4, several government delegates questioned this use of PFOS saying that oil production and mining occurred in their countries without the use of PFOS. This indicates that there are alternative processes that do not require PFOS.

6.7 Photo industry and imaging

The possible alternatives identified for the photographic industry are:

- Digital techniques
- Telomer-based products
- C3 and C4 perfluorinated compounds
- Hydrocarbon surfactants
- Silicone products.

For some still allowed uses of the PFOS-related compounds within the photographic industry no sufficient alternatives have been identified so far. These uses are as surfactants, electrostatic charge control agents, friction control agents, dirt repellent agents and adhesion control agents for mixtures used in coatings applied to films, papers, and printing plates.

Required properties to alternatives for keeping the same quality as PFOS compounds includes: dynamic surface tension capability, antistatic property, solubility, photo-inactivity and stability against heat and chemicals.

The cost of replacement of PFOS has been estimated by industry to 20-40 mio. €.

6.8 Electric and electronic parts

Historical uses of PFOS in electric and electronic parts include belts and rollers in printers and copying machines. For most of these not well-known uses, alternatives are available or are under development. However, several uses have been identified by industry for which alternatives will not soon be available. One such use is in the intermediate transfer belt and PFA rollers of colour copiers and printers. Intermediate transfer belts contain up to 100 ppm of PFOS, while PFOS in the amount of 8×10^{-4} ppm is contained in an additive used in producing PFA rollers.

6.9 Semiconductor industry

Small amounts of PFOS-based compounds are required during the following critical photolithography applications in manufacturing semiconductor chips:[17]

- photoresists as photo-acid generators (PAGs) and/or surfactants; and
- anti-reflective coatings (ARCs) as uniquely performing surfactants.

These applications are crucial to achieving the accuracy and precision required to manufacture miniaturized, high performance semiconductor chips. According to the industry there are presently no alternatives available that would allow for the comprehensive substitution of PFOS in these critical applications, which have been exempted from PFOS bans until now.

The new photolithography technologies use less photoresist per wafer, and PFOS concentrations in the photoresist have dramatically decreased in the new formulations. Thus the total use of PFOS is decreasing, lowering the total amount of releases. In 2002 for the whole of Europe, only an estimated 43 kg of PFOS were released in the effluent from these critical uses.

Development cost of a new photoresist system is estimated to 700 million $ for an industry which had a global sale of 248 billion $ in 2006.

Additional PFOS applications include developers and edge bead removers. Substitutes do exist for these non-critical uses, and the semiconductor industry is committed to phase them out. Substitution requires varying lengths of time. According to the industry smooth substitution requires often more than 10 years, and substitution without approval from customer's tending to stop customers production lines. Customers expect that alternatives will perform the same function as the PFOS-containing items.

There may be one additional specialized application, for which PFOS use according to industry has no current substitute. It is use in liquid etchant in the photomask rendering process.[18] For photomask etching with strong acids non-fluorosurfactants are not stable enough, and shorter chain fluorosurfactants have not sufficient low surface

[17] Information from the European Semiconductor Industry Association.
[18] Photomasks are optically transparent fused quartz blanks imprinted with a pattern defined with chrome metal and are the templates used to scribe the circuit pattern into the photoresist.

tensions. In some instances a dry etching process without surfactants may be used. However, such process is not useable for LCD panels in large size (more than 1m by 1m).

6.10 Aviation hydraulic fluids

At present there is uncertainty about alternative substances within this area. Aviation hydraulic fluids without fluorinated chemicals exist, and other fluorinated chemicals than PFOS can be used. A search for alternatives has been said to be going on for 30 years (before PFOS was considered a problematic substances), and about 2500 different compounds should have been tested but unfortunately, neither fluorotelomers nor non-fluorinated chemicals tested have met the required demands, and the high safety standards within this industry.[19]

This is unlikely to be true now. The potassium salt of perfluoroethyl cyclohexyl sulfonate (CAS-no. 67584-42-3) is a not PFOS-related perfluorinated compound, which has been used in the hydraulic oils instead of PFOS. However, the former producer of this chemical (the 3M Company) has ceased the production of that substance. Further, there are plenty of available aviation hydraulic fluids without fluorinated additives based on e.g. phosphate esters.[20]

6.11 Medical devices

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

Since about 2000, when the effects of PFOS on the environment were identified as a problem, radio-opaque ETFE manufacturers have been working with chemical material suppliers to find alternatives. The 2006 OECD survey identified use of perfluorobutane sulfonate (PFBS) as 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.

6.12 Metal plating

The industry association ZVO in Germany describes the availability of PFOS-free alternative products from 10 German supplier companies.[21] Three products are fluorinated chemicals and seven are fluorine-free chemicals. Information is lacking about the exact chemicals. All 10 products can be used for decorative chromium plating, for which alternative chromium-(III) processes already exist.

For hard plating the process with chromium-(III) process does not function. Neither do the seven fluorine-free chemical alternatives; they are not persistent enough in the extreme environment in the chromic acid bath. The fluorine-containing alternatives, which can be used, will also be persistent but still less hazardous than PFOS, especially with a shorter CF_2-chain. In Denmark the company ATOTECH market Fumetrol® 140 with PFOS and Fumetrol® 21 without PFOS but with another, not disclosed, fluorinated chemical.

The Norwegian Galvano Industry Organisation (NGLF) has reported that their suppliers no longer provide wetting/anti-mist agent for chromium plating. They provide PFOS-free tensides instead. NGLF consider the performance of those alternatives to be insufficient and is currently developing better alternatives to PFOS and alternative technology to solve the problem with airborne loss of hexavalent chromium from the baths. The metal plating industry association in Norway estimated the cost of substituting Cr^{6+} with Cr^{3+} in the plating baths to be approximately 100 000 NOK (~15-16000 USD) per bath. But NGLF reports that the industry have started to phase out the use of PFOS containing wetting/mist agent, by using the chromium (III)-process instead of the chromium (VI)-process, where possible (Information from SFT, 2009).

Larger closed tanks, or increased ventilation combined with extraction of chromium-(VI) from filters have been suggested as alternative solutions for the applications, where a use of chromium-(III) is not yet possible. Increased ventilation has been suggested as a solution but that will result in increased energy consumption and CO_2-emission and loss of chromium from the bath. It is not considered to work in practice. Other solutions should be investigated e.g. physical covers (net, balls) over the bath to diminish the hydrogen burst and catch the aerosols.

6.13 Fire-fighting foam

Manufacturers, distributors and users of aqueous film-forming foam (AFFF) fire fighting agents and their chemical components have formed a not-for-profit trade association: The Fire Fighting Foam Coalition (FFFC).[22] FFFC helps to ensure that accurate industry information about PFOS alternatives, including telomer-based products, is disseminated to appropriate audiences. The industry position is published in the journal: Asia PACIFIC FIRE, Issue 26, from June 2008.

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

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[19] UK RFA 2004.
[20] http://www.freepatentsonline.com/6319423.html and www.freepatentsonline.com/WO2006138081.html
[21] Personal information from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), D-40724 Hilden; March 6, 2009.
[22] http://www.fffc.org/

- Non-PFOS based fluorosurfactants with shorter chain length such as
  - C6-fluorotelomers e.g. polyfluoroalkyl sulfonyl betaine. See also Chapter 7.2.
  - Dodecafluoro-2-methylpentan-3-one (CF3-CF2-C(=O)-CF(CF3)2) (3M).
- A return to the previous technology with fluorine-free fire-fighting foams, which are e.g.
  - 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 training (Trainol); new products with glycols (Hi Combat ATM from AngusFire).[23]
  - Protein-based foams (e.g. Sthamex F-15) which will not be as effective for flammable liquid fuel fires. Mainly used for training, but also some marine actual uses.

It has been claimed that fire-fighting foams made from fluorinated surfactants have technically shown to be the only technology, which can quickly and effectively extinguish fires from highly combustible and flammable materials. However, a European foam producer indicates that it produces fluorine-free foams that perform as well during testing as PFOS based foams.

In Norway, the offshore industry has voluntarily and systematic phased out the use of PFOS before the ban in 2007. PFOS containing fire fighting foam is also phased out by other users. The now most used alternatives in Norway are PFOS-free telomer-based fluorosurfactants. But there are also commercial available fluoro-free alternatives on the market in Norway. They are called Arctic Re-healing Foam RF and developed by 3M Australia. The Norwegian producer, Solberg Scandinavian AS, states that it is not as good as AFFF, and will not be an alternative at offshore installations or for the petroleum industry, but that the fire fighting performance is close to AFFF and is a good alternative for other uses. It is approved to the control and extinguishment of Class B flammable liquid hydrocarbon and polar fuel fires. Arctic Re-healing Foam RF meets the requirements of CEN/EN-1568 specifications, part 3 and 4 (Information from SFT 2009).

A British survey (RFA 2004) states that for fire-fighting foams the fluorine-free alternatives are approximately 5-10% more expensive than the fluorosurfactant based foams. According to a manufacturer of the fluorine-free alternatives the price would fall, if the market size increased. A more deliberately shift towards fluorine-free fire-fighting foam alternatives will probably eliminate the difference in cost.

The cost of replacement and destruction of PFOS in fire-fighting foam storages in the EU has been estimated to 6000 € per tons or about 700 000 € in total. In Japan's case, PFOS replacement with alternatives in an environmentally appropriate way (including collection, refilling, transportation, storage and incineration) costs 1.7 million JPN (13 000 Euros) per tonnes or 22 billion JPN (170 million Euros) in total Japan.

7. Description of environmental safety and health properties of alternative substances

The key to the performance of the fluorosurfactants is the extremely low surface tension, which currently cannot be matched with other surfactants. However, due to high prices of the fluorosurfactants and due to environmental reasons, other surfactants can be used as alternatives, if it is not a technical must to achieve such low surface tension levels.

After the phase-out of PFOS, many of PFOS-based products were converted to C8-based telomers. Since 2006, the major manufacturers of C8-based telomers are working toward elimination of C8-based and longer-chain-based PFCs by 2015. It would be helpful to separate C8-based fluorotelomers from other alternatives.

In evaluation of listed alternatives, intermediates, precursors, and end products should also be evaluated.

A strategic integrated approach to testing is needed to speed development of the data needed to understand the issues/concerns with the various types of alternatives. EPA believes this can be done scientifically without necessarily testing every alternative chemical for every endpoint. More information on this approach that US EPA is taking is available at http://epa.gov/oppt/pfoa/pubs/altnewchems.html.

OECD Parallel Process is one useful approach to consider in developing international collaboration on assessing potential alternatives to PFCs of concern.

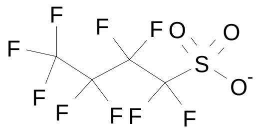
Some of these alternatives are new chemicals and some are existing chemicals in US.

For some of these, a general discussion of properties as group might not be sufficient; i.e., specific chemicals within the same group might have different health and environmental effects from others in the group.

[23] http://www.kiddecanada.com/utcfs/Templates/Pages/Template-50/0,8061,pageId%3D2587&siteId%3D463,00.html

7.1 Shorter chain perfluoroalkyl sulfonates

The Novec™ products are polymeric anionic fluorinated surfactants, which are based on perfluorobutane sulfonates (PFBS; C_4-chemistry):



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 or in low viscosity systems. Generally, this surfactant has a lower surface tension than hydrocarbon silicone surfactants. It can also be used in a less amount than the hydrocarbon surfactants. The compounds are said to influence the second layer coating adhesion less than silicon or conventional fluorinated surfactants.

Besides the paint and coatings industry the Novec products should be useful as surfactants in electronic coating, in industrial commercial cleaning, and cleaners for solder flux residue. They have also been identified as alternatives in connection with impregnation of textiles, leather and carpets.

Health effects

It is claimed that PFBS does not have the serious toxic effects associated with PFOS and other long-chain analogues, but data published in peer reviewed literature is scarce.

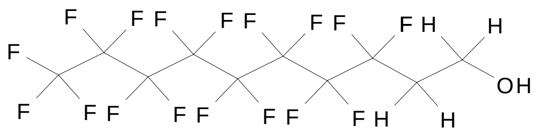
Environmental effects

PFBS is as persistent as other perfluorinated compounds, and it is detected in increasing concentrations in some water bodies, including the North Sea, however, bioaccumulation in wildlife and humans seems to be much less than for PFOS.

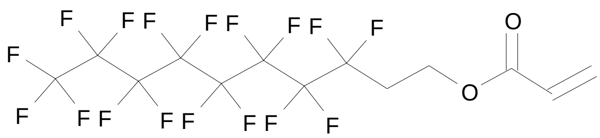
7.2 Fluorotelomers and perfluorophosphates

In general, fluorotelomers are the most common alternatives to PFOS-compounds. They are not fully fluorinated but contain also more reactive hydrocarbon parts.

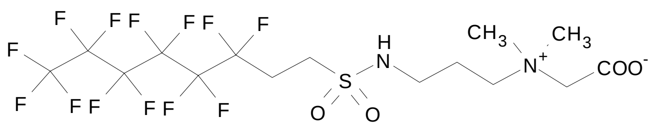
- One of the basic structures is 8:2 fluorotelomer alcohol (8:2 FTOH) also named 1*H*,1*H*,2*H*,2*H*-perfluorodecanol:



- An acrylate of that telomer 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) is marketed by DuPont as an telomer intermediate under the trade name of Zonyl® TA-N:



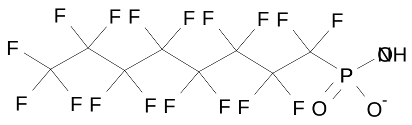
- DuPont manufactures a range of fluorotelomers designed for fire-fighting foam formulations called DuPont™ Forafac® products with 65-95% C_6-fluorinated amphoteric telomers based on perfluorohexyl ethyl sulfonamide are used for fire extinguishing formulations:[24] A possible formula for an amphoteric compound:



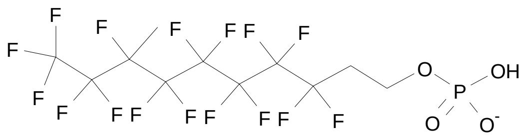
- The polyfluoroalkyl phosphonic acids and phosphoric acids and their diesters (PAPs and diPAPs) used mainly in packaging have recently been discovered in the environment and in people.[25] Some formula:

[24] http://www2.dupont.com/Forafac/en_US/index.html

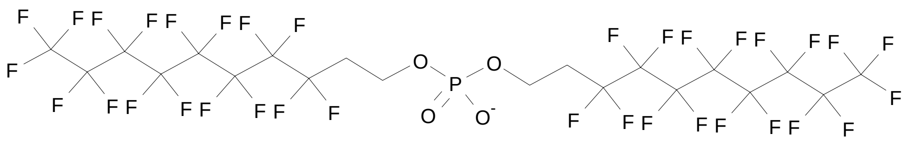
- Perfluorooctyl phosphonate



- 8:2 PAP



- 8:2 Di-PAPs



DuPont market more Zonyl products in this group e.g. Zonyl® 9027 a spot and dirt repellent, which is a telomer B phosphate diethanolamine (CAS no. 65530-63-4).

Health effects

Some data exists on adverse effects seen in experimental animals and laboratory tests of precursors and final degradation products: perfluorocarboxylic acids/salts such as PFOA. For some PFCAs, there are known adverse health impacts. For example, perfluorooctanoate (PFOA) has been shown to be tumorigenic and immunotoxic in laboratory animals. However, for other PFCAs, there is no toxicological or ecotoxicological data available though they have been regularly detected in human blood, umbilical cord blood, and breast milk.

Environmental effects

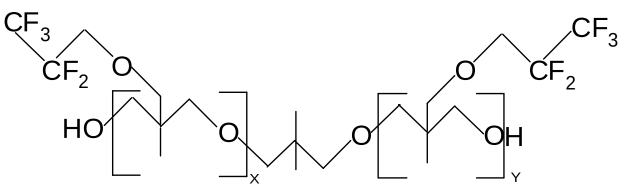
Precursors degrade to perfluorinated carboxylic acids such as PFHpA, PFOA and PFNA in organisms and nature. These have been widely detected in the environment and wildlife.

7.3 Fluorinated polyethers

OMNOVA Solutions Inc. produces under the trade name PolyFox™ a family of short-chain fluorosurfactants based on fluorinated polyethers.

The PolyFox fluorosurfactants are polyethers with a molecular weight greater than 1,000 and with C_2F_5 or CF_3 perfluoroalkyl side chain structures.

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



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

[25] D'eon JC, Crozier PW, Furdui VI, Reiner EJ, Libelo EL, and Mabury SA. Observation of a Commercial Fluorinated Material, the Polyfluoroalkyl Phosphoric Acid Diesters, in Human Sera, Wastewater Treatment Plant Sludge, and Paper Fibers. Environ Sci Technol online April 29, 2009.

PolyFox fluorosurfactants have found use in aqueous and solvent-borne semiconductor coating formulations. In a number of examples, excellent wetting, flow and leveling properties have been afforded to semiconductor coatings.

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_3, -C_2F_5) side chains reduces refractive index additionally, and PolyFox materials have found use as antireflection layers in photoresist and LCD screen applications.

The PolyFox formulation is currently being used as a surfactant in floor polish products in the USA, Europe and Asia.

Health effects

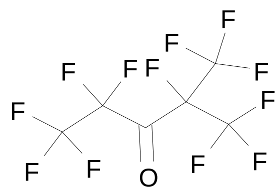
The acute toxicity is low but the fluorinated polyethers may irritate skin and the respiratory system. Generally, there is a lack of data.

Environmental effects

Fluorinated polyethers have a high molecular weight that makes them less available for transport across bio-membranes and therefore less biologically available. Furthermore, the polymer backbone linkage of the PolyFox molecules is an ether link, which is more environmentally stable than e.g. the ester linkages of PFOS and telomer-based fluorosurfactants. This makes the PolyFox molecule more resistant to degradation to lower molecular carboxylic acids. Since PolyFox products are made with shorter fluorinated alkyl chain lengths (C_2F_5 or CF_3 structures), which means they cannot produce the longer perfluorinated acids such as PFOA. PolyFox has low acute toxicity to aquatic organisms.

7.4 Shorter chain perfluoroalkyl ketones

According to 3M's website, a C_6-fluorinated compound Novec™ 1230 is used in their Fire Protection Fluid. The compound is dodecafluoro-2-methylpentan-3-one:



Health effects

There is a lack of data.

Environmental effects

There is a lack of data.

7.5 Fluorinated co-polymers

Fluorinated chemical for impregnation of indoor car upholstery: Foraperle® 225 (DuPont): CAS no. 203743-03-7 which contains the compound 2-Propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate, γ-ω-perfluoro-C_{10}-C_{16}-alkyl acrylate and stearyl methacrylate.

CAS no. 65530-65-6: Dodecyl methacrylate polymer with α-fluoro-ω-[2-[(1-oxooctadecyl)oxy]ethyl]-poly(difluoromethylene) used in a concentration of 0.085 to 0.45%.

DuPont market a lot Zonyl® products for various purposes. Some are co-polymers e.g. Zonyl® G Fabric Protector for textiles consisting of 2-methyl-2-propenoic acid dodecyl ester, polymer with α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl poly(difluoromethylene) (CAS no. 65605-58-5).

Health effects

There is a lack of data. Polymers are generally of low availability/uptake and have low toxicity. The ultimate degradation products may be perfluoroalkanoic acids (PFAAs).

Environmental effects

There is a lack of data. Probably only the degradation products are hazardous.

7.6 Silicone polymers

Worlée-Chemie produces silicone polymers, which in the paint and ink industry in several cases can be used as alternative wetting agents to fluorosurfactants. WorléeAdd 340 is a low viscous non-ionic special modified silicone polyether can improve for 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 efficient improving wetting, spreading and levelling of water-borne coatings and eliminating surface defects without foam stabilising. It is further claimed that the compound normally has no negative effect on recoating.

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 the penetration into absorbing surfaces also is improved.

Health effects

Harmful by inhalation and exposure may induce serious damage to eyes. Lack of data.

Environmental effects

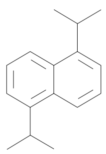
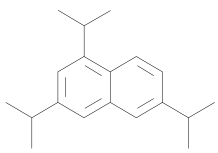
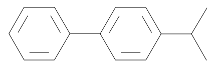
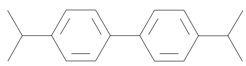
The silicone polymers are toxic to aquatic organisms and are bioaccumulative. Lack of data.

7.7 Propylated aromatics

The company “Rütgers Kureha Solvents” produces different aromatic surfactants with the trade name Ruetasolv®, based on propylated naphthalenes and biphenyls, which can be used as water repelling agents for different applications, such as corrosion protection systems, marine paints, resins, printing inks, coatings, electrical, electronically and mechanical applications.

They may also act 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 as follows: Epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate polymers, mineral oils, bitumen, etc.

The propylated aromatic products are all colourless liquids with a boiling point at about 300 °C and a very low solubility in water.

Ruetasolv DI   Ruetasolv TTPN   Ruetasolv BP 4201   Ruetasolv BP 4103

Health effects

The isopropylated naphthalene- and biphenyl compounds are irritating substances, and the biphenyl compounds may produce skin sensitisation or dermatitis. Furthermore, one of the biphenyl compounds is known to cause CNS damage as well as liver and kidney damage.

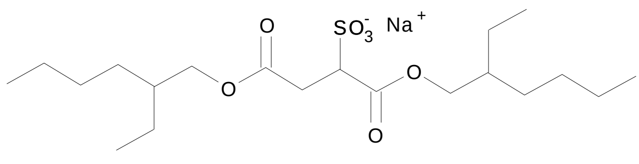
Environmental effects

The biphenyls and the naphthalenes are potentially bioaccumulative. The biphenyl moiety seems to be easily biodegradable, whereas the naphthalene moiety only slowly biodegrades. The sparse information suggests that the biphenyls are acutely toxic to aquatic organisms, whereas the naphthalene has no acute toxic effects in the investigated fish species.

7.8 Sulfosuccinates

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.

The chemical structure of the sodium salt of di(2-ethylhexyl) sulfosuccinate:



In the product from BASF the sulfosuccinate is mixed with water and ethanol (Lutensit® A-BO), and in the product Hydropalat® 875 from Cognis the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol. 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 paints and coatings. The identity of the sulfosuccinate is not disclosed.

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 optimising the colour acceptance of aqueous pigment concentrates in different coatings. The product has a medium foam formation.

The product from Münzing Chemie can be used as wetting agent for aqueous systems is claimed to have good wetting properties, no increase in foam and good re-coatability. The surface tension is claimed to be moderate. Application areas are decorative paint, wood and furniture coatings, automotive and repair coating, industrial coatings, printing inks and overprint varnishes.

Health effects

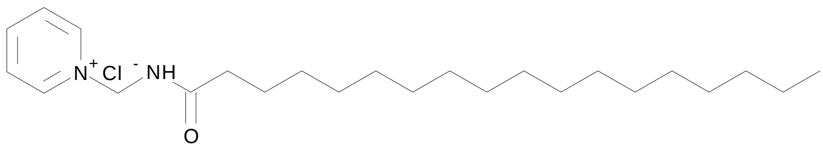
Sulfosuccinates are irritants to eyes, skin and the respiratory system. Dermatitis has been observed as a long-term effect as well as CNS depression. The substance is mildly harmful to toxic, if swallowed.

Environmental effects

Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate but is harmful to aquatic organisms.

7.9 Stearamidomethyl pyridine chloride

A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, earlier marketed by ICI as Velan PF:



The substance is 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 fibers and 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 has an unpleasant odor and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970 s when government regulations on such substances increased. Further information about properties is lacking.

Health effects

There is a lack of data.

Environmental effects

There is a lack of data.

7.10 Fatty alcohol polyglycol ether sulfate

Possible replacements to fluorosurfactants to some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor® FAS 30 is sodium salt of fatty alcohol polyglycol ether sulfate.

Health effects

The fatty alcohol polyglycol ether sulfate is acutely toxic by ingestion but is not considered to be irritating.

Environmental effects

The fatty alcohol polyglycol ether sulfate is readily biodegradable and does not seem to be toxic to aquatic organisms.

8. Comparative (technical, socioeconomic, environmental, health and safety) assessment of the PFOS and its possible alternatives

This chapter will include selection/demonstration of best alternatives and prioritization to be written based on previous text. A principle could be substitution of PFOS in lower quality consumer products before professional uses. Cost indication may be biased by coming mainly from industry.

In general, very little information about the price of the alternatives was found in the Danish survey (Poulsen et al. 2005), even though the producers of alternative products were asked specifically about this information. However, the sparse information received suggests that the alternatives in general are about the same price as the PFOS-related compounds or even cheaper. One company mentioned in particular that the price of the alternatives intentionally is kept at the same level as the PFOS-related compounds.

According to an article on perfluorinated surfactants,[26] the cost of fluorinated surfactants is higher than that of hydrocarbon surfactants. Within a specific application, fluorinated surfactants are typically cost effective, as their relatively high price is offset by the low concentrations needed to achieve the desired effect. Nevertheless, the authors of the article assess, that due to the high prices of fluorinated surfactants, fluorosurfactant applications are limited to problems that the conventional, lower-priced surfactants cannot address. Other sources confirms that fluorinated compounds are only used, if no other alternatives are found fit for use.

If this study finds that there are no feasible alternatives for a particular use, then the original use should also be examined. The necessity or 'public good' of a use should be a factor in determining whether it should continue, even in the absence of apparent alternatives. It would be helpful if the study could consider the necessity or 'public good' of PFOS uses for which feasible alternatives appear to be lacking.

If possible, it would be interesting to engage end users of the function provided by PFOS. For example, some hospitals may already use an alternative catheter than the one that requires PFOS for manufacture. This may also be mentioned in the document as a strategy to search for alternatives.

If the study concludes that an alternative is not appropriate, it would be useful to explain why it may not be technically or scientifically viable. This should also include how the proposed use is distinct from other examples of alternatives for similar uses. If known, an assessment of what is in the research pipeline for alternatives should be provided.

9. Conclusions, recommendations and future developments

Will contain the final wrap-up of conclusions and recommendations, regards what to do further, including opportunities for international cooperation.

There is a need for incentives to develop alternative substances and processes and to identify the driving forces for developing alternatives. Some increasing effort will be needed to study the toxicological and environmental properties of alternatives. Presently, the amount of data on the alternatives is much less that for PFOS.

Legislation and classification is an important tool to promote incentives to find alternative substances and processes, but as the development of legislation is time consuming and could impact industries in many ways, it is important that the issue of PFOS as a globally recognized POP substance is made fully known to suppliers and industries.

It is crucial with better knowledge among producers about PFOS in processes, products and articles. Information to customers, consumers can also be important in order to create a opinion about the need to change a product or process. Industries that are proactive and phase-out a very hazardous chemical such as PFOS are likely to get future market advantages.

10. Reference list (to be amended)

To be decided, if specific references should be footnotes or end notes.

- Stockholm Convention. Risk management evaluation on perfluorooctane sulfonate, 4. December 2007. UNEP/POPS/POPRC.3/20/Add.5.
- Stockholm Convention. Risk profile on perfluorooctane sulfonate, 21 November 2006. UNEP/POPS/POPRC.2/17/Add.5.
- UK 2004 Risk Reduction Strategy for PFOS. Risk & Policy Analysts Limited (RPA) in association with BRE Environment. Perfluorooctane Sulphonate – Risk reduction strategy and analysis of advantages and drawbacks. Final Report prepared for Department for Environment, Food and Rural Affairs and the Environment Agency for England and Wales, August 2004. http://www.defra.gov.uk/environment/chemicals/pdf/pfos-riskstrategy.pdf
- Poulsen PB, Jensen AA, Wallström E. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project no. 1013. DEPA, 2005. http://www.mst.dk/Udgivelser/Publications/2005/06/87-7614-668-5.htm
- Perfluorinated substances and their uses in Sweden, 2006. http://www.kemi.se/upload/Trycksaker/Pdf/Rapporter/Report7_06.pdf

[26] Moody CA, Field JA. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. Environ Sci Technol 2000; 34: 3864-3870.

- PFOA in Norway, 2007. Survey of national sources, 2354, SFT 2007. http://www.sft.no/publikasjoner/2354/ta2354.pdf
- Jensen AA, Poulsen PB, Bossi R. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, 99. DEPA, 2008. http://www.mst.dk/Udgivelser/Publications/2008/10/978-87-7052-845-0.htm
- Results of the 2006 OECD Survey on Production and Use Of PFOS, PFAS, PFOA, PFCA, Their Related Substances and Products/Mixtures Containing These Substances. http://appli1.oecd.org/olis/2006doc.nsf/linkto/env-jm-mono(2006)36
- PFOS Regulatory Impact Analysis Statement. Canada Gazette Part II (Vol. 142, No. 12) on June 11, 2008. http://www.ec.gc.ca/ceparegistry/documents/regs/g2-14212_rias1.pdf
- 2007 OECD workshop on Perfluorocarboxylic Acids (PFCAs) and Precursors report http://www.olis.oecd.org/olis/2007doc.nsf/LinkTo/NT00002AB6/$FILE/JT03229256.PDF
- June 2008 Fluorosurfactants Conference: http://pft.fh-fresenius.de/
- OECD. Perfluorooctane Sulfonate (PFOS) and related chemical products. http://www.oecd.org/document/58/0,,en_2649_34375_2384378_1_1_1_1,00
- Shuji Tamura presentation. “Substitution and alternatives”, October 2008.
- Ryo Usami presentation: “Case study on PFOS”, October 2008.
- Presentations at the International workshop on managing perfluorinated chemicals and transition to safer alternatives. 12-13 February 2009, Geneva, Switzerland.
- Overview of Existing Information on PFOS Production, Use, Emissions and Pathways to the Environment and Cost/Benefits with alternatives/substitutes. 2006-01-25.[27]
- Paul AG, Jones KC, Sweetman AJ. A First Global Production, Emission, and Environmental Inventory For Perfluorooctane Sulfonate. Environ Sci Technol 2009; 43(2):386–392.
- Bruinen de Bruin Y, Zweers P, Bakker J, Beekman M. Estimation of emissions and exposures to PFOS used in industry. A PFOS use inventory in metal plating and fire fighting. Bilthoven: RIVM Report 601780002/2009.

[27] http://www.unece.org/env/lrtap/TaskForce/popsxg/2006/Overview%20of%20existing%20information%20on%20PFOS%20emissions%20and%20pat..pdf

Overview of possible tables (to be filled out and elaborated on further in the final report)

Applications	**PFOS derivatives used**	**Alternative chemicals, processes or products; Which alternatives are used, experiences**	**Fitness for use Evaluation of technical properties/fitness for use/availability/durability of the alternatives for each separate application**	**EH&S**	**Socio-economic assessment of the alternatives; differences between branches, size of enterprise, countries, and regions; product essentiality; economic constrains, societal costs**
Impregnation of clothing, footwear, carpets, and furniture based on leather or textiles,					
Impregnation of packaging (paper/cardboard)					
Cleaning agents Waxes and polishes for cars and floors (skies?)					
Paint and varnish					
Hydraulic oils					
Fluxing agent					
Oil industry					
Photo industry		Digital pictures			A reduction by 83% in the EU since 2000 has had an estimated cost of 20-40 mio. €/yr.
Electric and electronic parts - belts and rollers for printers and copying machines - piezoelectric ceramic filters					
Semiconductor industry - Photomask and photoresist - high-frequency compound semiconductors					
Medical devices - CCD colour filters for use and repair of video endoscopes - catheters for angiography and indwelling needle catheters					
Pesticides - production of ant baits					
Decorative metal plating		Cr(III) plating			
Hard metal plating		Permanganic acid etching and Cr(III) plating			In China the industry turnover is 30 billion Yuan.
Fire-fighting foam					

Alternatives to PFOS-compounds

Alternative compound	Product trade name	Company	Used in / used for
Perfluorobutane sulfonate (PFBS) or based on different C_4-perfluorocompounds	Novec ™ Scotchgard™	3M	Paint and coatings industry. As electronic coating. Industrial and commercial cleaning. Cleaner for solder flux residue. Degreasing applications. Cleaners and stain protectors for carpets, leather, furniture, automotives, hard surfaces and other apparels
Dodecafluoro-2-methylpentane-3-one	Novec™ 1230	3M	Fire-fighting foam
Fluorotelomer alcohols and esters	Zonyl®	DuPont™	Coating, printing, textile and chemical industries
C_6 fluorotelomer sulfonamide compounds (80%)	FORAFAC™ 1157; 1183	DuPont	Fire-fighting foam
Hexadecyl methacrylate polymers with 2-hydroxyethyl methacrylate, γ-ω-perfluoro-C_{10}-C_{16}-alkyl acrylate and stearyl methacrylate	Foraperle 225	DuPont	impregnation of indoor car upholstery
CF_3 or C_2F_5 fluoroalkyl polyethers	PolyFox™	OMNOVA Solutions Inc.	Surfactant and flow-, level-, and wetting additive for coating formulations. Also used in floor polish.
Propylated aromatics (naphthalenes or biphenyls)	Ruetasolv™	Rütgers Kureha Solvents Gmbh	Water repelling agents for rust protection systems, marine paints, coatings, etc.
Fatty alcohol polyglycol ether sulfate	Emulphor™	BASF	Levelling and wetting agents
Sulfosuccinate	Lutensit™	BASF	Levelling and wetting agents
Sulfosuccinate	EDAPLAN™ LA 451	Münzing Chemie	Paint and coating industry: Wetting agents for water based applications – e.g. wood primers
Sulfosuccinate	HYDROPALAT™ 875	Cognis	Paint and coating industry: Wetting and dispersing agents
Silicone polymers	WorléeAdd™	Worlée-Chemie	Wetting agents in the paint and ink industry

Properties of chemical alternatives

Substance name(s)	CAS no.	EINECS no.	Formula	M.W.	M.P. (°C)	B.P.	Water solubility	LD_{50} mg/kg (o, r)	Hazard symbol	Risk phrase	Safety phrase	$ Price /kg
Sodium di(2-ethylhexyl) sulfosuccinate; sodium dioctyl sulfosuccinate; Docusate sodium	577-11-7 1639-66-3	209-406-4	$C_{20}H_{37}NaO_7S$	444.6	153-157	Wax like	15 g/L (25 °C)	1900	Xn	22; 36/37/38	26; 37/39	500
Fatty alcohol polyglycol ether sulfate; Emulphor® FAS 30					Yellowish liquid	>100 °C	50 g/L (23°C)	>2000				
1-(Stearamidomethyl) pyridinium chloride; Velan PF	4261-72-7	224-240-2	$C_{24}H_{43}N_2OCl$	411.06								
Bis(1-methylethyl) naphthalene; Ruetasolv DI	38640-62-9		C16H20		Colourless liquid	290-300 °C	Not miscible	> 3900				
Diisopropyl-1,1'-biphenyl; Ruetasolv	69009-90-1		C18H22		Colourless liquid	300-335 °C	Not miscible					

BP 4201												
(1-Methylethyl)-1,1'-biphenyl; Ruetasolv BF 4103	25640-78-2		C15H16		Colourless liquid	293-315 °C	Not miscible					
Ruetasolv TPPN	35860-37-8		C13H14		Colourless liquid	255-265 °C	Not miscible					
Mix. 1-/2-Isopropyl naphthalene	38640-62-9		C19H26		Colourless liquid	325-350 °C	Not miscible					
Perfluorobutane sulfonate (PFBS) or based on different C_4-perfluorocompounds Novec™ (3M)								> 2000				
Dodecafluoro-2-methylpentan-3-one Novec™ (3M)	756-13-8		CF_3-CF_2-C(O)-$CF(CF_3)_2$; $C_6F_{12}O$		Clear colourless liquid	49 °C						
Hexadecyl methacrylate polymers with 2-hydroxyethyl methacrylate, γ-ω-perfluoro-C_{10}-C_{16}-alkyl acrylate and stearyl methacrylate Foraperle 225 (DuPont)	203743-03-7											
DuPont FORAFAC 1203	161278-39-3				Brown liquid	95 °C		>5000		R52/53		
silicone polyether	67674-67-3								Xn Xi N	R20 R51/53 R41		
PolyFox												