LEARNING COURSE

Alternatives to POPs Annexes A-B

Perfluorooctane sulfonic acid (PFOS)
Perfluorooctanoic acid (PFOA)
Perfluorohexane sulfonic acid (PFHxS)

GGKP, 2024

DISCLAIMER

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POPs listed in Annex A -B

Parties must take measures to eliminate the production and use of the chemicals listed under Annex A.
Specific exemptions for use or production are listed in the Annex and apply only to Parties that register for them.

Parties must take measures to restrict the production and use of chemicals listed under Annex B, in accordance with the provisions of that Annex.

Status of PFOS, PFOA and PFHxS under the Stockholm Convention

- Perfluorooctane sulfonic acid **(PFOS)** is listed in **Annex B (restriction)** since 2009 (decision SC-4/17). Its acceptable uses include as an active ingredient in insect bait to control leaf-cutting ants, in closed-loops systems in metal plating and as fire-fighting foam.
- Perfluorooctanoic acid **(PFOA)**, its salts and PFOA-related compounds are listed in **Annex A (elimination)** since 2019 (decision SC-9/12).
- In 2022, perfluorohexane sulfonic acid **(PFHxS)**, its salts and PFHxS-related compounds were listed in **Annex A (elimination)** (decision SC-10/13).
- Long-chain perfluorocarboxylic acids (LC-PFCAs), their salts and related compounds have been proposed for listing in Annexes A, B and/or C.

REF: https://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/and-polyfluoroalkyl - Stockholm Convention

PFOS, PFOA, PFHxS and related chemicals

PFOS, PFOA and **PFHxS** belong to the family of per- and polyfluoroalkyl substances, which are abbreviated as “PFASs”.

PFOS is a fully fluorinated anion, which is commonly used as a salt or incorporated into larger polymers. PFOS-related chemicals are chemicals that contain the structural element PFOS in their molecular structure and are or were produced with PFOSF as a starting or intermediate material.

Perfluorooctanoic acid (**PFOA**) is part of the per- and polyfluorinated chemicals (PFCs) family. PFOA has been mainly used as polymerization aid in the manufacturing of fluoropolymers and in aqueous fluoropolymer dispersions, which are used for paints, photographic film additives and in the textile finishing industry, and it has also been used in aqueous fire fighting foams.

Perfluorohexane sulfonic acid (**PFHxS**), its salts and PFHxS-related compounds belong to the class of per- and polyfluoroalkyl substances (**PFASs**) and have been widely used in fire-fighting foams, in metal plating, in cleaning, waxing, polish and other surface treatment products, as well as in water- and stain-protective coatings for carpets, paper, leather and textiles. PFHxS, its salts and PFHxS-related compounds are applied as replacements for perfluorooctane sulfonic acid (PFOS) in many cases.

REF: UNEP/POPS/COP.11/INF/22 - UNEP/POPS/POPRC.12/INF/15/Rev.1 - Vierke, L., Staude, C., Biegel-Engler, A. et al. Perfluorooctanoic acid (PFOA) — main concerns and regulatory developments in Europe from an environmental point of view. Environ Sci Eur 24, 16 (2012). https://doi.org/10.1186/2190-4715-24-1 - UNEP/CHW.16/6/Add.2/Rev.1

PFOS, PFOA and PFHxS production

- PFOS, PFOA and PFHxS as other PFASs have been produced for direct use in commercial products and use in industrial product streams.
- PFHxS, its salts and PFHxS-related compounds have been produced from a common parent compound, PFHxSF.
- PFHxSF may be intentionally produced from the electrochemical fluorination (ECF) of hexanesulfonyl chloride.
- PFHxSF may be unintentionally produced as a byproduct from the ECF of octanesulfonyl fluoride or chloride, which is the process to produce perfluorooctane sulfonyl fluoride (PFOSF).
- Global production of PFOSF by 3M (main producer until production ceased in 2003) is estimated at 13.670 metric tonnes.
- The estimated global production of PFOS between 1970-2002 was 96,000 tonnes.
- In 2003, China initiated the production of PFOS and PFOSF. The annual production volumes of PFOS from 2009 to 2011 were 30, 10 and 10 tonnes, respectively, whereas those of PFHxS were 10, 10 and 30 tonnes, respectively.
- The actual production of PFOS, PFOA, and PFHxS and their related substances cannot be quantified and confirmed due to a lack of reporting of production in many countries.

REF: UNEP/POPS/COP.11/INF/22 - UNEP/POPS/POPRC.12/INF/15/Rev.1 - UNEP/CHW.16/6/Add.2/Rev.1

PFOS uses (as per Annex B)

Acceptable purposes

- In accordance with Part III of this Annex for the following acceptable purpose, or as an intermediate in the production of chemicals with the following acceptable purpose:
  - Insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants from Atta spp. and Acromyrmex spp. for agricultural use only.

Specific exemptions

- Metal plating (hard-metal plating) only in closed-loop systems
- Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 10 of part III of Annex B.

REF: Stockholm Convention - UNEP/CHW.16/6/Add.2/Rev.1

PFOA, its salts and PFOA-related compounds uses (as per Annex A)

Specific exemptions

- Photolithography or etch processes in semiconductor manufacturing.
- Photographic coatings applied to films.
- Textiles for oil- and water-repellency for the protection of workers from dangerous liquids that pose risks to their health and safety.
- Invasive and implantable medical devices.
- Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 2 of part X of Annex A.
- Use of perfluorooctyl iodide for the production of perfluorooctyl bromide for the purpose of producing pharmaceutical products, in accordance with the provisions of paragraph 3 of part X of Annex A.
- Manufacture of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) for the production of:
  - High-performance, corrosion-resistant gas filter membranes, water filter membranes and membranes for medical textiles
  - Industrial waste heat exchanger equipment
  - Industrial sealants capable of preventing leakage of volatile organic compounds and PM2.5 particulates
- Manufacture of polyfluoroethylene propylene (FEP) for the production of high-voltage electrical wire and cables for power transmisión.
- Manufacture of fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors.

REF: Stockholm Convention - UNEP/CHW.16/6/Add.2/Rev.1

PFHxS uses

- PFHxS, its salts and PFHxS-related compounds can be used as effective surfactants and/or surface protectors.
- PFHxS, its salts and PFHxS-related compounds have been intentionally used at least in the following applications:
  - Aqueous film-forming foams (AFFF) for firefighting
  - Metal plating
  - Finishes for textiles, leather and upholstery
  - Polishing agents and cleaning/washing agents
  - Coatings, impregnation, or proofing (for protection from dampness, fungus, etc.)
  - Within the manufacturing of electronics and semiconductors
- Other potential uses may include pesticides and flame retardants, application in the oil industry, and in hydraulic fluids.

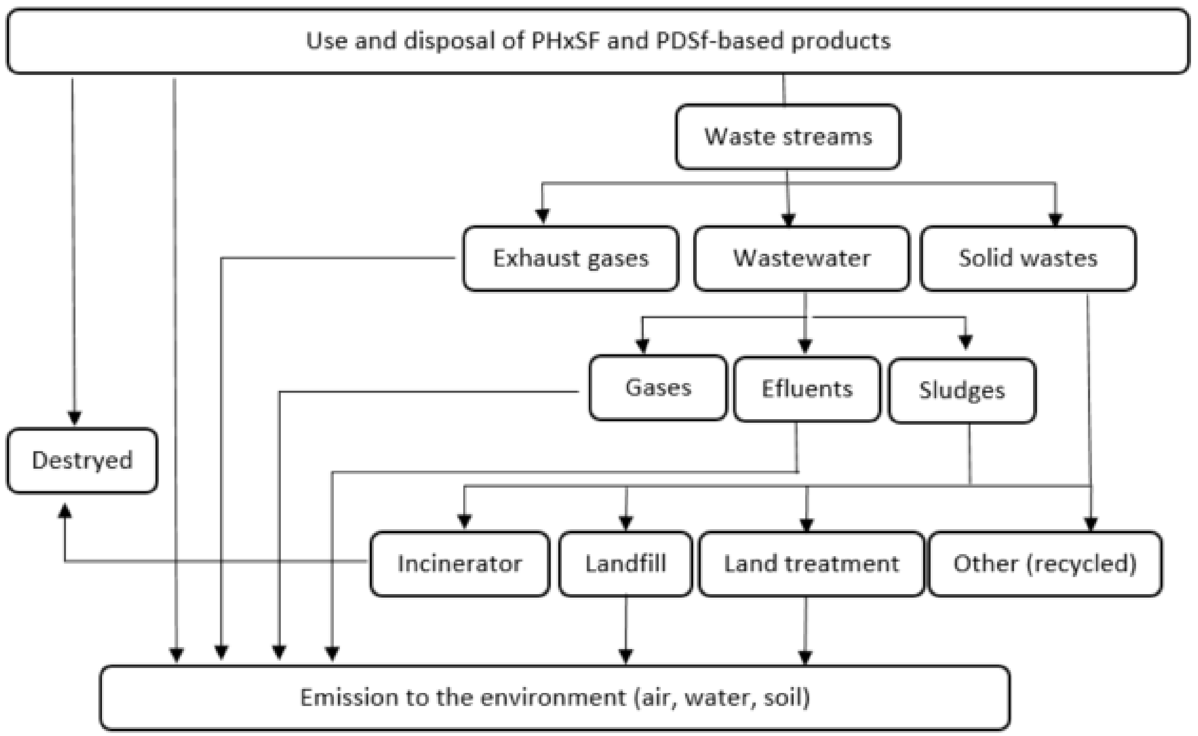
REF: UNEP/POPS/COP.11/INF/22 - UNEP/CHW.16/6/Add.2/Rev.1

Waste streams likely to contain POP-PFASs and recommended management/destruction options

- It is likely that POP-PFASs are released into the environment throughout their life cycles.
- Air emissions from production of POP-PFASs can be an important source of pollution.
- Waste management activities have been identified as one route through which POP-PFASs can enter the environment, mainly through industrial and municipal wastewater discharges to surface waters and through leachate from landfills.
- The primary media for the release of POP-PFASs from waste management activities are likely to be water, sediments and soils.

Waste streams likely to contain PFHxS and recommended management/destruction options

- Emissions of PFHxS to the environment occur at all its life-cycle stages, but are assumed to be highest during service life and in the waste phase.
- Historically, major emissions of PFHxS and PFHxS-related compounds were most likely due to its unintentional presence in PFOS manufactured by ECF. PFHxS might also be present in stockpiles of PFOS or products/chemical mixtures containing PFOS, that are still not disposed of.



Waste streams likely to contain PFHxS and recommended management/destruction options

- The absorption of PFHxS by granular activated carbon (GAC) is much less effective at small concentrations of GAC than it is for PFOS.

- To have economical destructive treatment, PFHxS must first be concentrated from the high-volume/low-concentration wastes as usually encountered in contaminated firefighting water and groundwater.

Alternatives to PFOS, its salts and PFOSF; PFOA, its salts and PFOA-related compounds; and PFHxS, its salts and PFHxS-related compounds

- Assessment of alternatives to PFOS and PFOA indicates that many uses are expected to be similar to those for PFOS and PFOA.
- Alternatives to PFHxS, its salts and PFHxS-related compounds include:
  - Short-chain and other PFASs
  - Fluorine-free chemicals
  - Non-chemical (physical) alternatives such as new processes, new technologies and new product design

REF: UNEP/POPS/COP.11/INF/22

Fire-fighting foams

- Two types of fire-fighting foams:
  - **Class A**: Used to extinguish fires caused by wood, paper, wooden structures and wildlands. Generally do not contain PFASs. They are composed of hydrocarbon surfactants which are designed to spread, penetrate and cling to carbonaceous fuels more easily than plain water.
  - **Class B**: Formulated to be most efficient at extinguishing liquid hydrocarbon fuel fires, such as oil and diesel. Are designed to progressively spread on flammable liquids to cool the burning fuel and starve the flame zone of fuel and oxygen vapours. In the past, these foams contained PFASs, including PFOA, its salts and related compounds. Fluorine-free foams (F3) are currently available on the market.

Fire-fighting foams – Class B fluorinated foams

- Typical fluorinated foams are:
  - Aqueous film-forming foams (**AFFFs**). Applications include military and civilian ships, military bases and airfields, airport crash-fire-rescue, refineries, tank farms and other operations involving the transport, processing, or handling of flammable liquids
  - Fluoroprotein foams (**FPs**). Well suited for sub-surface injection near the base of a Class-B flammable liquid storage tank.
  - Alcohol-resistant aqueous film-forming foams (**AR-AFFFs**). Suppress and secure fires on hydrocarbon fuels as well as polar solvent fuels such as methanol, ethanol and acetone.

Alternatives to PFOS, its salts and PFOSF; PFOA, its salts and PFOA-related compounds; and PFHxS, its salts and PFHxS-related compounds

Fire-fighting foams – Class B fluorinated foams

Alternatives

Fluorine-free foams (F3)

- Intended for use on class B fires as well as class A fires
- Very general hints on replacement substances or substance groups have been identified for F3 foams
- Main benefit is related to the reduction of long-term impact on the environment, while short-term impact related to acute toxicity
- F3 foams are biodegradable while AFFFs contain persistent fluorinated substances

Short-chain fluorinated foams

- C6-based compounds and C4-based fluorinated compounds

REF: UNEP/POPS/COP.11/INF/22

Fire-fighting foams – Class B fluorinated foams

Fluorine-free foams (F3)

Manufacturer/supplier	Product
Bio-EX	ECOPOL(Class A & B), BIO FOR (Class A), BIO FOAM (Class B), BIO T (training foam)
Solberg	RE-HEALINGTM FOAM (Class B)
Dr. Sthamer	vaPUREx® (Class B), MOUSSOL®FF (Class A & B), Sthamex® (Class A & B), UltraWet® (Class A), Training foam, and Test foam.
3F	Smart Foam® including FREEDOL SF, FREEFOR SF (Class A), HYFEX SF, FREEDEX SF (Class A & B), FREEGEN SF, T-FOAM SF (training foam)
Angus fire	Respondol ATF (Class A & Class B), Jetfoam (Class B), Syndura (Class B), Trainol (training foam), TF (training foam)
Auxquimia	UNIPOL-FF™ (Class A & B), SF-60 L (Class A & B), H-930 (Class A & B), RFC-105 (Class A & B), CAFOAM (Class A), TF-136 (training foam)

REF: UNEP/POPS/COP.11/INF/22

Fire-fighting foams – Class B fluorinated foams

Fluorine-free foams (F3)

Manufacturer/supplier	Product
Chemguard	CHEMGUARD® NFF (Class B), Class A plus, Extreme (for Class A fires)
Fireade	FireAde®, FireAde® Class A Foam, FireAde® Training
Firechem	FIRECHEM Fluorine Free Foam
Fomtec	P 3% AR (Class A & B), Enviro Plus (Class B), Enviro ultra (Class B), Enviro 3% ICAO (Class B), Enviro eMax (Class A & B), Enviro USP (Class A & B)
National Foam	Muni®F3 Green (Class A & B), Universal®F3 Green (Class A & B), Avio®F3 Green KHC (Class B)
Orchidee	Bluefoam
Aberdeen Fire Fighting Foam	Aberdeen Foam F3 (Class B), Aberdeen AR-F3 (Class B), Aberdeen Foam 1% Class A, Aberdeen Foam Training Foam (Synthetic)
VS FOCUM	Silvara(Class A & B), BoldFoam A+ (Class A), BoldFoam AM (Class A), B-Water (Class A)

REF: UNEP/POPS/COP.11/INF/22

Fire-fighting foams – Class B fluorinated foams

Suitability of alternatives – fluorine-free alternatives

Performance

- For fluorine-free fire-fighting foams, the application rate to control fire is higher than for PFAS-containing AFFFs, but the application rate had no impact on the extinguishing rate.
- PFAS-free fire-fighting foams that are being used to effectively extinguish fuels have shown to perform the same ability to extinguish Class B fires as traditional AFFFs.
- New generation of fluorine-free firefighting foams using compressed air foam systems CAFS proved to be as effective and efficient as the currently used PFAS-containing AFFFs.
- Modern development in F3 foams has substantially decreased any difference in performance levels.

Hazards

- Non-fluorinated alternatives are likely to be of lower environmental concern, primarily due to biodegradation.

Cost

- Prices of fluorine-free and fluorine containing AFFFs are comparable.
- Short-chain fluorotelomer-based AFFFs have a shelf-life of 10–25 years, while a manufacturer of fluorine-free alternatives quotes a shelf-life of 20 years.
- Lifetime costs for using AFFFs, FPs, or FFFPs far outweigh those of F3 foams because of legal and financial liabilities of using a PFAS-based foam.

Fire-fighting foams – Class B fluorinated foams

Suitability of alternatives – short-chain fluorinated alternatives

Performance	Hazards
• Shorter-chain PFAS-based firefighting foam provides fast control of all flammable liquid fires under different situations.	• Concerns are due to persistence, high mobility in water and soil and potential toxic properties of short-chain PFASs. • The Committees for Risk Assessment and Socio-Economic Analysis under the EU REACH support Germany’s proposal to restrict the use of PFHxA and related substances that are very persistent and mobile in the environment and can damage the human reproductive system.

REF: UNEP/POPS/COP.11/INF/22

Fire-fighting foams – Class B fluorinated foams

Implementation of alternatives

- F3 foams certified to different ICAO levels (required for use at civilian airports) are available on the market.
- Major international hubs such as Dubai, Dortmund, Stuttgart, London Heathrow, Manchester, Copenhagen and Auckland have transitioned to F3 foams.
- In 2018, the US Senate approved a five-year reauthorization for the Federal Aviation Administration (FAA), which changed the performance standards for fire-fighting foams to allow the use of F3 foams at civilian airports.
- In the oil and gas sector, F3 foams are being extensively used.

Metal plating

- Two main technologies in metal plating
  - **Hard metal plating**
  - **Decorative metal plating**
- The difference between hard and decorative metal plating is thickness, hardness and deposition of the chrome layer on the plated object.
- In chrome metal plating, the workpiece is submerged in a chromic acid (hexavalent chromium, Cr(VI), a human carcinogen) bath. PFOS salts are or have been commonly used as surfactants, wetting agents and mist-suppressing agents in chrome metal plating processes, as a measure to improve safety working conditions.
- After the production and use of PFOS are severely restricted due to industrial phase-out and its listing in Annex B to the Stockholm Convention, PFHxS salt has been used as an alternative to PFOS for metal plating.
- Due to the unintentional production of PFHxS during the ECF process, it is likely that the PFOS-containing mist/fume suppressants used for metal plating contain amounts of unintended PFHxS, its salts and/or PFHxS-related compounds.
- PFHxS and PFOS belong to the same group (PFSA) but have different chain lengths; it is likely that the alternatives to PFOS also can be applied to PFHxS.

Metal plating

Non-chemical alternative technologies

- Use of PTFE-coated balls on top of the bath, and the use of mesh or blanket covers for plating baths are effective at removing droplets and eliminating the discharge of chromic acid mist.
- Cr(VI) emissions could be reduced substantially by avoiding air convection.
- High Velocity Oxygen Fuel (HVOF) process, which is a thermal spray coating technique for hard chrome plating. Globally available, effective and low costs.
- Metal chrome coating by dipping instead of electroplating.
- Attempts to use Cr(III) also for hard chromium plating are ongoing for the development of an environmentally friendly alternative to hexavalent chromium in chrome plating.

REF: UNEP/POPS/COP.11/INF/22

Metal plating

Chemical alternative technologies

- There is little information related to the chemical alternatives to PFHxS in metal plating, so chemical alternatives of PFOS are considered.
- Two types
  - Fluorinated
  - Non-fluorinates

Alternatives to PFOS, its salts and PFOSF; PFOA, its salts and PFOA-related compounds; and PFHxS, its salts and PFHxS-related compounds

Metal plating

Chemical alternative technologies

Fluorinated alternatives		
Composition	**Hard plating. Trade names (manufacturer)**	**Decorative plating. Trade names (manufacturer)**
6:2 fluorotelomer sulfonic acid (6:2 FTSA)	Capstone (Chemours) FS10 Proquel OF (Kiesow) ANKOR® Dyne 30 MS (Enthone) ANKOR® Hydraulics (Enthone) ANKOR® PF1 (Enthone) Fumetrol® 21 (Atotech) Fumetrol® 21 LF 2 (Atotech) HelioChrome® Wetting Agent FF (Kaspar Walter) Maschinenfabrik GmbH & Co. KG) PROQUEL OF (Kiesow Dr. Brinkmann) Wetting Agent CR (Atotech)	ANKOR® Dyne 30 MS (Enthone) Cancel ST-45 (Plating Resources, Inc.) FS-600 High Foam (Plating Resources, Inc.) FS-750 Low Foam (Plating Resources, Inc.) Fumetrol 21 (Atotech) SLOTOCHROM CR 1271 (SchlötterGalvanotechnik) UDIQUE® Wetting Agent PF2 (Enthone) Wetting Agent CR (Atotech)
F53 (Potassium 1,1,2,2- tetrafluoro-2- (perfluorohexyloxy) ethane sulfonate)		
F53-B (potassium 1,1,2,2-tetrafluoro-2- (perfluorohexyloxo) ethane sulfonate)		

REF: UNEP/POPS/COP.11/INF/22

Metal plating

Chemical alternative technologies

Fluorine-free alternatives		
Composition	**Hard plating. Trade names (manufacturer)**	**Decorative plating. Trade names (manufacturer)**
Alkane sulfonates	TIB Suract CR-H (TIB Chemicals AG))	
Oleo amine ethoxylates		ANKOR® Wetting Agent FF (Enthone)) Antispray S (Coventya)
Other non-fluorinated alternatives	CL-Chromeprotector BA (CL Technology GmbH) Antifog V4 (Chemisol GmbH & Co. KG) Non Mist-L (Uyemura)	

Metal plating

Suitability of alternatives – non-chemical alternatives

Performance

- In ~20% of applications, the High Velocity Oxygen Fuel (HVOF) methods of spraying chromium layers can replace hard chromium layers deposited by electroplating. HVOF is known to be globally available and is considered effective and with low costs.

Hazards

- PTFE-coated balls on top of the bath are likely to not reduce chromium emission from the chroming bath but, in contrast, chromium emissions appear to increase, as compared to emissions released in cases where no mist suppression is applied at all.

Cost

- HVOF requires high-temperature application. German Environment Agency (UBA) (2017) mentioned that layers deposited using this method may be more porous and less resistant to corrosion.

REF: UNEP/POPS/COP.11/INF/22

Metal plating

Suitability of alternatives – chemical alternatives

Performance

- Alternatives to the PFOS derivatives are considered to be less stable and durable in the chrome bath than PFOS.
- Additionally, they degrade further through oxidation, which is not the case for PFOS due to its extremely persistent properties.
- The use of closed systems with underpressure reduces the reproductive hazard of Cr(VI). It also reduces the environmental hazard as no PFAS or other hazardous substances are needed in this process.

Hazards

- Germany (2018) indicated that 6:2 FTSA is not considered a viable alternative due to environmental concerns relating to degradation to become the stable perfluorohexanoic acid (PFHxA).

Cost

- Non-fluorinated alternatives are not economically viable because their use causes additional risks with respect to safety, process stability and device preservation.
- Use of alternatives may cause corrosion of lead anodes that will then need to be replaced more frequently.
- Alternatives appeared to be available at limited additional cost.

REF: UNEP/POPS/COP.11/INF/22

Metal plating

Implementation of alternatives

- There is only limited information regarding the implementation of alternatives of PFHxS in metal plating.
- Most information is related to the alternatives of PFOS.
- Chemical alternatives of PFOS are currently available for hard metal plating and decorative plating.
- The use of Cr(III) instead of Cr(VI) for certain decorative chrome plating processes is available.

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

- Finishing agents based on PFASs are widely used in textiles to achieve water, oil and dirt repellency of the material, while at the same time maintaining breathability.
- Water-proof textile finishes based on PFHxS-related compounds have recently been developed.

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Non-chemical alternatives

- Bio-inspired slippery liquid-infused porous surfaces, based on substances found in the Nepenthes plant, although still in the development phase, have a broad application that includes biomedical devices, optical sensing, fluid/fuel handling, and anti-fouling; and can be developed into viable alternatives for surface treatments.
- Carpets using stain-free fibers are stain-resistant without coating.

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Chemical alternatives - Fluorine-free

- There is a range of fluorocarbon-free, water-repellent commercial finishing agents for textiles on the market.
- There is a lack of information on the hazards associated with durable water-repellent hyper-branched polymers, or dendrimers.
- A new study reported that fabricating oil-repellent textile finishes using perfluorocarbon-free surface chemistries is possible by adding a secondary, smaller length-scale texture to each fibre of a given weave, when the texture size, spacing and surface chemistry are properly controlled.

REF: UNEP/POPS/COP.11/INF/22

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Chemical alternatives – short-chain fluorinated

- Short-chain (“C6”) fluorotelomer-based side-chain fluorinated polymers and Short-chain (“C4”) perfluoroalkane sulfonyl fluoride-based side-chain fluorinated polymers provide repellent performances.

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Chemical alternatives – perfluoropolyether-based polymer

- Solvay has developed a product named Fluorolink® P5617, which imparts water and oil repellency and stain release properties to the treated surfaces. Fluorolink® P56 is a waterborne dispersion of an anionic polyurethane based on a perfluoropolyether backbone.

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Suitability of alternatives – fluorine-free alternatives

Performance

- Unable to repel oil. However, it was shown experimentally that some fluorine-free and even biodegradable durable water repellents could provide some degree of stain repellence.
- Available alternatives for grease- and dirt-repellent agents are limited.

Hazards

- Paraffin repellents are liquid emulsions that should not be classified as hazardous to health according to the producers. However, some of the identified ingredients seem to be harmful.
- PDMS are used as water-repellent agents which are inert and have in general no adverse effects. Various siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and specific linear siloxanes, are intermediates for the synthesis of silicone polymers used for textile impregnation. Siloxanes are generally removed from the aqueous phase by sedimentation and exhibit a long half-life in sediments. In soils, siloxanes are transformed depending on the conditions into hydroxylated forms, which still may be persistent.
- Available information for this group of chemicals is insufficient for an assessment of the possible health effects of the impregnation agents.

REF: UNEP/POPS/COP.11/INF/22

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Suitability of alternatives – short-chain fluorinated alternatives

Performance

- Excellent water repellence and durability.

Hazards

- Several scientific literature sources conclude that short-chain fluorinated alternatives (C6 and C4) raise various concerns including persistence, long-range / high mobility in water and soil, potential toxic properties, difficult to capture and to clean up once released into the environment.
- PFBS is persistent.
- Throughout the entire life cycle, technical textiles treated with 6:2 fluorotelomer-based finishes often emit 4–8 times more PFASs compared to using the C8-chemistry.

Cost

- Stakeholders state that protective textiles finished with the C6-chemistry need large amounts of C6-products for the initial finishing and repeated professional re-impregnation with further C6-products after each washing step to meet high safety standards.

REF: UNEP/POPS/COP.11/INF/22

Water- and oil-proof finishes for carpets, leather and apparel, textiles and upholstery

Implementation of alternatives

- Alternatives are available in the market for casual, outdoor and sport activities.
- Textile producers also become aware of the importance of fluorine-free alternatives.

Polishing agents, cleaning/washing agents, and coatings for protection from dampness, fungus, etc.

- For the uses of PFHxS, its salts and PFHxS-related compounds in this category, there is a lack of information, but there are indications that these uses could be related to cleaning, polishing, sealers, coatings, etc., both in the building and car maintenance sectors.
- Historically, PFOS-related chemicals had several uses in coating, paint and varnishes to reduce surface tension, as dispersing agents and for improving gloss and antistatic properties. PFHxS has been used as an alternative to PFOS after PFOS was listed in Annex B of the Stockholm Convention.

Polishing agents, cleaning/washing agents, and coatings for protection from dampness, fungus, etc.

Chemical alternatives – fluorine-free

Many global suppliers are offering fluorine-free alternatives, including:

- Hydrocarbon wax-based repellents consisting of paraffin-metal salt formulations;
- Hydrophobic modified hyper-branched polyurethanes which are also called dendrimers;
- Polysiloxane-based products;
- Resin-based repellents consisting of fatty acid-modified melamine resins;
- Fatty alcohol polyglycol ether sulphate, sometimes together with a sulfosuccinate;
- 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;
- Patent regarding a fluorine-free polishing agent was granted in 2016 (Asahi Glass Co., 2016). The polishing agent includes a particle of a metal oxide, a water-soluble polyamide, an organic acid and water.

Polishing agents, cleaning/washing agents, and coatings for protection from dampness, fungus, etc.

Chemical alternatives – short-chain fluorinated alternatives

There are also short-chain fluorinated chemicals on the market, such as:

- (“C4”) Side-chain fluorinated polymers in coating and coating additives. For example, C4- compounds derived from perfluorobutane sulfonyl fluoride;
- Short-chain fluorotelomer-based side-chain fluorinated polymers (UNEP, 2019c);
- Side-chain fluorinated oxetane polymers.

Polishing agents, cleaning/washing agents, and coatings for protection from dampness, fungus, etc.

Suitability of alternatives

Performance

- Excellent water repellence and durability.

Hazards

- Certain siloxanes are persistent and widespread in the environment.
- The biphenyls and the naphthalenes have high octanol/water partition coefficients (log KOW), and the bioconcentration factor for the substances is greater than 100 (potentially bioaccumulative).
- The sparsely 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.

Cost

- No additional cost occurred for using non-fluorinated alternatives.

REF: UNEP/POPS/COP.11/INF/22

Polishing agents, cleaning/washing agents, and coatings for protection from dampness, fungus, etc.

Implementation of alternatives

Chemical alternatives for this use have been developed and are available, technically and economically feasible, and widely implemented already.

Manufacturing of electronics and semiconductors

- There is no available information on the specific processes in the manufacture of electronics and semiconductors that PFHxS is used, and it is therefore necessary to review all the information available on PFOS within the manufacture of electronics and semiconductors.
- Small amounts of PFOS-based compounds are required during the following critical photolithography applications in manufacturing semiconductor chips:
  - Ultra-fine patterning/photo resists as photo-acid generators and surfactants
  - Anti-reflective coatings as uniquely performing surfactants

Manufacturing of electronics and semiconductors

Availability of alternatives

- Short-chain (four carbon atoms or less) PFASs are considered as available alternatives.
- Regarding non-fluorinated alternatives, current available non-fluorinated alternatives in the photolithographic process include:
  - nitrobenzenesulfonate (NBS)
  - acceptor-substituted thiosulfonate anions (benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-) (TBNO) or 2-thiophenesulfonic acid, 5-chloro-4- nitro-, ion(1-) (TN))
  - aromatic anions (pentacyanocyclopentiadienide (CN5) or methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1));
  - triphenylsulfo nium (TPS)
- Non-chemical alternatives for the photolithography process in the form of other manufacturing processes are being discussed in the research.

Alternatives to PFOS, its salts and PFOSF; PFOA, its salts and PFOA-related compounds; and PFHxS, its salts and PFHxS-related compounds

Manufacturing of electronics and semiconductors

Suitability of alternatives

Performance	Hazards	Cost
• Fluorine-free alternatives have some technical limitations, which are currently prohibitive to high-volume manufacturing. • ALE, a next-generation etch technology that removes materials at the atomic scale, is one of several tools used to process advanced devices in a fab. Is still not widely deployed because it's a slow process. ALE is not used for every device in the fab.	• Significant evidence has shown potential health and environmental problems of short-chain PFASs.	• No additional cost occurred for using non-fluorinated alternatives.

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Manufacturing of electronics and semiconductors

Implementation of alternatives

- There is no publicly available information regarding the implementation of alternatives of PFHxS, its salts and PFHxS-related compounds.

Final remarks

- Compared to PFOS and PFOA, there is much less information related to the production, use and alternatives of PFHxS, its salts and PFHxS-related compounds.
- As PFHxS and PFOS belong to the same group of PFSAs, and PFHxS has been used as an alternative to PFOS, alternatives to PFOS are additionally considered as (potential) alternatives to PFHxS.
- A large body of peer-reviewed scientific data for the alternatives exists.
- A lot can still be done to narrow or close the data gap on the trade names and chemical composition, availability, accessibility, technical and economic feasibility, and environmental and health effects of alternatives, for instance, by improved communication with industries on the alternatives, better labelling of the compounds, more thorough and detailed assessment of the compounds, and more international cooperation.