Guidance on alternatives to PFOS, PFOA and PFHxS

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Abbreviations and acronyms

AFFF	Aqueous film-forming foams
ALE	Atomic layer etch
APFO	Ammonium perfluorooctanoate
AR-AFFF	Alcohol-resistant aqueous film-forming foams
AR-FFFP	Alcohol-resistant film-forming fluoroprotein foams
BAT	Best available techniques
BEP	Best environmental practices
BOD	Biochemical oxygen demand
BSI	German Sporting Goods Industry
C&L	the ECHA classification & labeling (C&L) inventory
CAS	Chemical Abstracts Service
CEN	European Committee for Standardization
CMP	Composite Mesh Pads
CMR	Carcinogenic, mutagenic or toxic for reproduction
CN4-C1	Methoxycarbonyl-tetracyanocyclopentadienide
CN5	Pentacyanocyclopentiadienide
COD	chemical oxygen demand
Cr	Chromium
D4	Octamethyl cyclotetrasiloxane
D5	Decamethyl cyclopentasiloxane
D6	Dodecamethyl cyclohexasiloxane
ECF	Electrochemical fluorination
ECHA	European Chemicals Agency
EtFOSA	N-Ethyl perfluorooctane sulfonamide
EU	European Union
Eurofeu	European Committee of the Manufacturers of
F3	Fluorine-free foam
F-53	Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate/perfluoro(hexyl ethyl ether sulfonate)
F-53B	Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
FDA	The US Food and Drug Administration
FEP	Fluorinated ethylene propylene polymer
FEVE	Fluoroethylene vinyl ether
FFFC	*Fire* Fighting Foam Coalition
FFFP	Film-forming fluoroprotein foams
FOEN	Federal Office for the Environment (Switzerland)
FTAB	Fluorotelomer sulfonamidealkylbetaine
FTCA	Fluorotelomer carboxylic acid
FTOH	Fluorotelomer alcohol
FTSA	Fluorotelomer sulfonic acid
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GLP	Good Laboratory Practices
HDPE	High-density polyester (HDPE)
HFP	Hexafluoropropylene
ICAO	International Civil Aviation Organization
INCI	International Nomenclature of Cosmetic Ingredients
IPEN	International POPs Elimination Network
ISO	International Organization for Standardization
ABRAISCA	Leaf-Cutting Ant Baits Industries Association
LD_{50}	Lethal dose, 50%

LDPE	Low-density polyester
MSC	Member State Committee
NaPFO	Sodium perfluorooctanoate
NBS	Nitrobenzenesulfonate
NFPA	National Fire Protection Association
NGP	Natural greaseproof paper
NICNAS	National Industrial Chemicals Notification and Assessment
OECD	Organisation for Economic Co-operation and Development
PACF	Perfluoroalkanoyl fluoride
PAN	Pesticide Action Network
PASF	Perfluoroalkanesulfonyl fluoride
PBSF	Perfluorobutanesulfonyl fluoride
PBT	Persistent, bioaccumulative and toxic
PDMS	Polydimethylsiloxanes
PET	Polyethylene terephthalate
PFA	Perfluoroalkoxy polymer
PFAAs	Perfluoroalkyl acids
PFASs	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutane sulfonic acid
PFCs	Per- and polyfluorinated chemicals
PFCA	Perfluoroalkylcarboxylic acid
PFHxA	Perfluorohexanoic acid (or undecafluorohexanoic acid)
PFHxS	Perfluorohexane sulfonic acid
PFHxSF	Perfluorohexane sulfonyl fluoride
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFSA	Perfluoroalkane sulfonic acid
PFPiA	Perfluoroalkyl phosphinic acids
POPs	Persistent organic pollutants
POPRC	Persistent Organic Pollutants Review Committee
ppb	Parts per billion
ppm	Parts per million
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RIE	Reactive-ion etching
RME	Risk management evaluation
SPIN	Substances in Preparations in Nordic Countries
SVHC	Substances of Very High Concern
TBNO	Benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-)
TFE	Tetrafluoroethylene
TN	2-thiophenesulfonic acid, 5-chloro-4- nitro-, ion(1-)
TOP	The total oxidizable precursor assay
TPS	Triphenylsulfonium
UL	Underwriters Laboratories
US EPA	United States Environmental Protection Agency
vPvB	Very persistent and very bioaccumulative
VDF	Vinylidene fluoride
WSC	World Semiconductor Council
ZVO	The German electroplating industry association

1 Introduction

1.1 Objectives

The current document is guidance on alternatives to 1) perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF); 2) perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds; and 3) perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS related compounds. The document was prepared on the basis of the guidance on alternatives to PFOS[1], report on the assessment of alternatives to PFOS[2], and draft guidance on alternatives to PFOA[3].

The ultimate goal is to enhance the capacity of countries, especially developing countries and countries with economies in transition, to phase out the above-mentioned compounds, considering the need for time to phase in alternatives to some of the uses and the fact that alternatives to certain uses may not be currently readily available in all countries.

In this document, the availability, suitability (including technical feasibility, accessibility, health and environmental impact), and implementation of alternatives are described.

1.2 Listing of the chemicals

1.2.1 PFOS, its salts, and PFOSF

PFOS, its salts and PFOSF were listed in Annex B to the Stockholm Convention by decision SC-4/17 in 2009. By decision SC-9/4 in 2019, the Conference of the Parties decided to amend Annex B with regard to specific exemptions and acceptable purposes for PFOS, its salts and PFOSF, as reflected in Table 1 below. The amendment is based on the fact that there is no longer any Party registration for specific exemptions for the production and use of PFOS, its salts and PFOSF for uses in carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, and rubber and plastics. No new registrations may be made with respect to them.

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[1] UNEP/POPS/POPRC.12/INF/15/Rev.1, Consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals (PFOS).

[2] UNEP/POPS/POPRC.14/INF/13, Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride.

[3] UNEP/POPS/COP.10/INF/25, Draft guidance on alternatives to perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds.

Table 1: Listing of PFOS, its salts and PFOSF (SC-9/4) to the Stockholm Convention.

Chemical	Activity	Specific exemption
Perfluorooctane sulfonic acid (CAS No. 1763-23-1), its salts[a] and perfluorooctane sulfonyl fluoride (CAS No. 307-35-7) [a] For example: potassium perfluorooctane sulfonate (CAS No: 2795-39-3); lithium perfluorooctane sulfonate (CAS No: 29457-72-5); ammonium perfluorooctane sulfonate (CAS No: 29081-56-9); diethanolammonium perfluorooctane sulfonate (CAS No: 70225-14-8); tetraethylammonium perfluorooctane sulfonate (CAS No: 56773-42-3); didecyldimethylammonium perfluorooctane sulfonate (CAS No: 251099-16-8)	Production	**Acceptable purpose:** In accordance with Part III of Annex B, production of other chemicals to be used solely for the uses below. Production for uses listed below. **Specific exemption:** None
	Use	**Acceptable purpose:** In accordance with part III of Annex B (UNEP/SC-9/4) for the following acceptable purposes, or as an intermediate in the production of chemicals with the following acceptable purposes: • Insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants *Atta spp.* and *Acromyrmex spp.* for agricultural use only **Specific exemption:** • 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

1.2.2 PFOA, its salts, and PFOA-related compounds

PFOA ($C_7F_{15}COOH$) is a fully fluorinated carboxylic acid (PFCA). PFOA salts include the PFOA anion, and ammonium, sodium or potassium as cations. CAS numbers also exist for the silver and chromium(III) salts (ECHA, 2015a).

PFOA-related compounds, for the purposes of the Stockholm Convention, are any substances that degrade to PFOA. This includes any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C_7F_{15})C as one of the structural elements. It needs to be mentioned that some groups of substances are not included in the Stockholm Convention listing of PFOA, its salts and PFOA-related compounds (see Table 2).

Table 2: Listing of PFOA, its salts and PFOA-related compounds to the Stockholm Convention (SC-9/12).

Chemical	Activity	Specific exemption
PFOA, its salts and PFOA-related compounds mean the following: (i) Perfluorooctanoic acid (PFOA; CAS No. 335-67-1), including any of its branched isomers; (ii) Its salts; (iii) PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety $(C_7F_{15})C$ as one of the structural elements; The following compounds are not included as PFOA-related compounds: (i) C_8F_{17}-X, where X= F, Cl, Br; (ii) Fluoropolymers that are covered by $CF_3[CF_2]_n$-R', where R'=any group, n>16; (iii) Perfluoroalkyl carboxylic and phosphonic acids (including their salts, esters, halides and anhydrides) with ≥8 perfluorinated carbons; (iv) Perfluoroalkane sulfonic acids (including their salts, esters, halides and anhydrides) with ≥9 perfluorinated carbons; (v) Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), as listed in Annex B to the Convention.	Production	• Fire-fighting foam: None • For other production, as allowed for the Parties listed in the Register in accordance with the provisions of part X of Annex A
	Use	In accordance with the provisions of part X of Annex A: • 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 comprise 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 transmission • Manufacture of fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors

1.2.3 PFHxS, its salts and PFHxS-related compounds

In 2022, the Conference of the Parties decided to amend part I of Annex A to the Stockholm Convention on POPs to list therein PFHxS, its salts and PFHxS-related compounds without specific exemptions (see Table 3).

Table 3: Listing of PFHxS, its salts and PFHxS-related compounds to the Stockholm Convention (SC-10/13).

Chemical	Activity	Specific exemption
Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds “Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds” means the following: (i) Perfluorohexane sulfonic acid (CAS No. 355-46-4, PFHxS), including branched isomers; (ii) Its salts; (iii) (iii) Any substance that contains the chemical moiety $C_6F_{13}SO_2^-$ as one of its structural elements and that potentially degrades to PFHxS.	Production	None
	Use	None

1.3 Information source

In preparing the draft report, in addition to the information submitted by Parties and others by 15 May 2023, information in the following documents (and references therein) has been consulted.

General information

- General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals (UNEP/POPS/POPRC.5/10/Add.1) (UNEP, 2009).

For PFOS, its salts and PFOSF

- Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) (UNEP/POPS/POPRC.14/INF/13) (UNEP, 2019c);
- Consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals (UNEP/POPS/POPRC.12/INF/15/Rev.1) (UNEP, 2016b);
- Report on the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride UNEP/POPS/COP.9/INF/12) (UNEP, 2019d);
- Report on the assessment of alternatives to PFOS, its salts and PFOSF (UNEP/POPS/POPRC.10/INF/7/Rev.1) (UNEP, 2014b);
- Fact sheets on alternatives to PFOS, its salts and PFOSF (UNEP/POPS/POPRC.10/INF/8/Rev.1) (UNEP, 2014a);
- Guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals (UNEP/POPS/POPRC.9/INF/11/Rev.1) (UNEP, 2013);
- Technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications (UNEP/POPS/POPRC.8/INF/17/Rev.1) (UNEP, 2012);
- Addendum to the risk management evaluation for perfluorooctane sulfonate (UNEP/POPS/POPRC.4/15/Add.6) (UNEP, 2008);
- Risk management evaluation on perfluorooctane sulfonate (UNEP/POPS/POPRC.3/20/Add.5) (UNEP, 2007);
- Risk Profile of Perfluorooctane sulfonate (UNEP/POPS/POPRC.2/17/Add.5) (UNEP, 2006).

For PFOA, its salts, and PFOA-related compounds

- Consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals (UNEP/POPS/POPRC.12/INF/15/Rev.1) (UNEP, 2016b);

- Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) (UNEP/POPS/POPRC.14/INF/13) (UNEP, 2019c);
- Risk profile on pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds (UNEP/POPS/POPRC.12/11/Add.2) (UNEP 2016c);
- Additional information related to the draft risk profile on pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds (UNEP/POPS/POPRC.12/INF/5) (UNEP 2016a);
- Addendum to the risk management evaluation on pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds (UNEP/POPS/POPRC.13/7/Add.2) (UNEP 2017a);
- Addendum to the risk management evaluation on perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/POPS/POPRC.14/6/Add.2) (UNEP, 2018a).

For PFHxS, its salts, and PFHxS-related compounds

- Risk profile on perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds (UNEP/POPS/POPRC.14/6/Add.1) (UNEP, 2018d);
- Additional information on perfluorohexane sulfonic acid (CAS No: 355-46-4, PFHxS), its salts and PFHxS-related compounds (UNEP/POPS/POPRC.14/INF/4) (UNEP, 2018b);
- Risk management evaluation on perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds (UNEP/POPS/POPRC.15/7/Add.1) (UNEP, 2019a).

1.4 Other available information

The following related information and guidance is available:

- Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and their related compounds listed under the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2021);
- Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/CHW/POP-SIWG.4/4)(UNEP, 2022).

2 Characteristics of the chemicals

2.1 Terminology

In this document, terms such as PFASs, long-chain PFASs, and short-chain PFASs are used. Their definitions will be described here.

In 2011, Buck et al. provided the first clear structural definition of PFASs and recommendations on names and acronyms for over 200 individual PFAS (Buck et al., 2011). As the identified PFASs increase over time, gaps between the structural definition of PFASs from Buck et al. (2011) and the newly identified substances were noticed (OECD, 2021). To have a coherent and consistent logic behind the PFAS definition which adequately reflects all compounds with the same structural traits, i.e. the PFAS universe, OECD provided recommendations in 2021 with regard to the terminology of PFASs (OECD, 2021). The updated PFASs are defined as follows:

> ‘PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS (OECD, 2021).‘

Figure 1 provides an overview of PFAS groups, their structural traits, examples and notes on whether common nomenclatures (including acronyms) exist for them, building on Buck et al. (2011) and the OECD 2018 List (OECD, 2021).

In this case, PFOS and PFHxS belong to the subgroup perfluoroalkane sulfonic acids (PFSAs). PFOA belongs to the subgroup perfluoroalkyl carboxylic acids (PFCAs).

Figure 1: An overview of PFAS groups, their structural traits, examples and notes on whether corresponding common nomenclatures (including acronyms) exist. Source: (OECD, 2021)

Based on the length of the fluorinated carbon chain, many PFASs can be categorized as short- vs. long-chain. Long-chain PFASs refer to (EC & ECHA, 2020):

- PFCAs with carbon chain lengths C8 and higher, including PFOA;
- PFSAs with carbon chain lengths C6 and higher, including PFHxS and PFOS;
- Precursors of these substances.

Accordingly, short-chain PFASs include (EC & ECHA, 2020):

- PFSAs with carbon chain lengths of C5 and lower, including perfluorobutane sulfonic acid (PFBS);
- PFCAs with carbon chain lengths of C7 and lower, including perfluorohexanoic acid (PFHxA);
- Precursors of these substances. Examples are perfluorobutane sulfonyl fluoride-based derivatives (other than PFBS and its salts) and 6:2 fluorotelomer-based compounds.

2.2 Properties of PFOS, its salts, and related compounds

The strong carbon-fluorine bond makes the perfluoroalkyl chain present in PFOS extremely stable and non-reactive. PFOS resists even strong acids and high temperatures and is not degradable in the environment. The basic PFOS structure is persistent, and the more complex PFOS-related chemicals will degrade to the basic PFOS structure during use or in the environment (UNEP, 2016b).

The surfactant properties of PFOS give extremely low surface tension. The perfluorocarbon chain is both oleophobic and hydrophobic. Thus, it repels water, oil and dirt and insulates electricity. Due to the hydrophobic and hydrophilic nature, PFOS and many of its related compounds can be used as surface-active agents in a wide variety of applications. The chemical stability of these substances makes them suitable candidates for applications at high temperatures or environments with strong acids or bases. More information can be found in the PFOS risk profile (UNEP, 2006).

The historical use of PFOS-related compounds in the following applications has been confirmed in the US and the EU: fire-fighting foams, metal plating, surface treatment agents (e.g. for carpets, leather/apparel, textiles, upholstery, paper and packaging, etc.), coatings and coating additives; industrial and household cleaning products, biocides, etc. (UNEP, 2006).

PFOS is persistent and has bioaccumulative and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues; instead, it binds to proteins in blood and the liver. It has the capacity to undergo long-range transport and has demonstrated ecotoxicity and toxicity towards mammals (UNEP, 2006, 2022).

2.3 Properties of PFOA, its salts, and related compounds

PFOA, its salts, and PFOA-related compounds have unique properties such as high friction resistance, dielectrical properties, resistance to heat and chemical agents, low surface energy, and are water, grease, oil and soil repellent. Therefore, they are used in a wide variety of applications and consumer products across many sectors (UNEP, 2016c) (ECHA, 2015a). PFOA and its salts are, or were, most widely used as processing aids in the production of fluoropolymers, e.g. PTFE and specific fluoroelastomers. PFOA-related compounds, including side-chain fluorinated polymers, have been used as surfactants and surface treatment agents (e.g. in textiles, paper and paints, fire-fighting foams, etc.).

PFOA is mobile and persistent in the environment. Studies also indicate the bioaccumulation and biomagnification effect of PFOA (UNEP, 2016c).

Many PFASs, including PFOA, are well absorbed orally and distribute mainly in the serum, the liver and the kidney of human beings (OECD, 2002; UNEP, 2016c, 2018d). There are a number of potential health adverse outcomes associated with PFOA exposure. For example, the International Agency for Research on Cancer (IARC) classified PFOA as possibly carcinogenic to humans (Group 2B), particularly in regard to prostate, testicular, liver and/or kidney cancers (IARC, 2016). The US National Toxicology Program (NTP) concludes that PFOA is presumed to be an immune hazard to humans (NTP, 2016). PFOA alters immune function in humans and may increase hypersensitivity-related outcomes and increased autoimmune disease incidence (NTP, 2016).

2.4 Properties of PFHxS, its salts, and related compounds

PFHxS, its salts, and PFHxS-related compounds have been used in fire-fighting foams, in metal plating, in surface treatment products for cleaning, waxing and polishing as well as in water- and stain-protective coatings for carpets, paper, leather and textiles. PFHxS, its salts, and PFHxS-related compounds have been applied as replacements for PFOS in many cases. In addition, PFHxS is and has been unintentionally produced during the electrochemical fluorination (ECF) processes of some other PFASs.

Environmental monitoring shows that PFHxS is very widely found in the environment (UNEP, 2018d). Similar to its C8 homologue PFOS, PFHxS is extremely persistent and has long-range transport potential (Norwegian Environment Agency, 2018). Numerous studies have reported elevated levels of PFHxS in soil, water and a variety of biota (UNEP, 2019a). Bioaccumulation and biomagnification occur for PFHxS. The estimated serum elimination half-life of PFHxS in humans is higher than other PFASs, with an average of 8.5 years (range 2.2–27 years) (UNEP, 2019a). Animal studies and a study with human mesenchymal stem cells showed an association of PFHxS exposure with reproductive toxicity or developmental toxicity (Gaballah et al., 2018; Shuyu Liu et al., 2020).

3 Alternatives to the use of PFOS, PFOA, and PFHxS

This chapter presents currently known chemical and non-chemical alternatives to the various uses of PFOS, PFOA and PFHxS. The Appendix contains a brief description of the alternatives and their environmental, safety and health properties. For some of these alternatives, a general discussion of properties might be all that is possible owing to a lack of specific information.

3.1 Exempted uses for PFOS, PFOA, and PFHxS

Before the describsion of the alternatives of PFOS, PFOA, and PFHxS, an overview of the current exempted uses for these compounds is listed in Table 4. This information is based on Decision SC-9/4 (for PFOS), SC-9/12 (for PFOA), and SC-10/13 (for PFHxS).

Table 4: An overview of the current exempted uses.

Uses	Detailed information	Compounds	Production or use	Exemption
Insect baits for leaf-cutting ants	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	PFOS[1]	Production & use	Acceptable Purposes
Hard-metal plating	only in closed-loop systems	PFOS	Production	None
			Use	Specific exemption
Fire-fighting foam	Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems	PFOS	Production	None
			Use[2]	Specific exemption
		PFOA[3]	Production	None
			Use	Specific exemption
pharmaceutical products	Use of perfluorooctyl iodide for the production of perfluorooctyl bromide for the purpose of producing pharmaceutical products	PFOA[4]	Production & use	Specific exemption
Semiconductor industry	Photolithography or etch processes in semiconductor manufacturing	PFOA	Production & use	Specific exemption

Uses	Detailed information	Compounds	Production or use	Exemption
Photographic coatings	Photographic coatings applied to films	PFOA	Production & use	Specific exemption
Coating for textile	Textiles for oil and water repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety	PFOA	Production & use	Specific exemption
Medical devices	Invasive and implantable medical devices	PFOA	Production & use	Specific exemption
Manufacture of fluoropolymers [5]	1) Manufacture of PTFE and PVDF, 2) Manufacture of FEP; 3) Manufacture of fluoroelastomers	PFOA	Production & use	Specific exemption

1. in accordance with part III of Annex B, production of other chemicals to be used solely for the use.
2. in accordance with paragraph 10 of part III of Annex B.
3. in accordance with paragraph 2 of part X of Annex A.
4. in accordance with the provisions of paragraph 3 of part X of Annex A.
5. Details see SC-9/12: Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds.

3.2 Insect baits

3.2.1 Introduction and background

Leaf-cutting ants of the genera *Atta* spp. and *Acromyrmex* spp. are native in a large part of Latin America and the southern part of the United States.[4] Leaf-cutting ants are the dominant species in both natural and human-disturbed settings where they occur. Insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B.

Insecticides for control of red imported fire ants and termites were listed as specific exemptions for the production and use of PFOS, its salts and PFOSF in Annex B. According to COP 9 in 2019, SC-9/4, as there were no longer any Parties registered for specific exemptions for the production and use of PFOS, its salts and PFOFS for insecticides for control of red imported fire ants and termites, Parties to the Convention have eliminated the exemptions for PFOS, its salts and related compounds in this use.

Non-polymeric PFASs have been applied in biocides in two ways: (i) as active ingredients: e.g. short-chain PFASs-based sulfonamides in plant growth regulators or herbicides and N-ethyl perfluorooctane sulfonamide (also known as sulfluramid or sulfuramid) in ant baits to control leaf-cutting ants, red imported fire ants, and termites; (ii) as inert ingredients (enhancers) (OECD, 2013).

Information related to PFOS

N-Ethyl perfluorooctane sulfonamide (known as sulfluramid; EtFOSA; CAS No: 4151-50-2) is used as an active ingredient in ant baits to control leaf-cutting ants in many countries in South America as well as for control of red imported fire ants and termites (UNEP, 2011). Sulfluramid was used in insecticides at concentrations of 0.01-0.1% (ABRAISCA, 2016).

Sulfluramid is manufactured by using PFOSF as an intermediate and its structure is related to PFOS. In the environment, it degrades in significant yields to PFOS, although it also has the potential to degrade to PFOA under certain conditions. Since it is produced from PFOSF, it is already covered in the Stockholm Convention, although not mentioned explicitly, under the listing of PFOS, its salts and PFOSF.

Fluorosurfactants may also be used as “inert” surfactants (enhancers used in pesticide formulas as an additive but not constituting active ingredients) in pesticide products (UNEP, 2017a).

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[4] http://www.antweb.org/antblog/2011/03/geographic-range-of-leaf-cutter-ants-don-indianapolis-in-usa.html.

Information related to PFOA

PFOA has also been used in pesticides mainly as inert ingredients. Fiedler et al. (2010) reported that PFOA concentration of one pesticide tested was 14,500 µg/L. Recent study from the United States Environmental Protection Agency (US EPA) found that PFOA has been used in pesticide packaging. Investigations by the US EPA showed that the high-density polyethylene (HDPE) containers of certain pesticides are treated inside and outside through fluorination, which resulted in PFASs, including PFOA, presence in the pesticide[5]. The concentration of PFOA was roughly 250 parts per trillion (ppt) and that of HFPO-DA (hexafluoropropylene oxide dimer acid, a "GenX" replacement for PFOA) ranged from 260 to 500 ppt. The contaminated pesticide has potentially spread over millions of acres. Therefore, in addition to the pesticide MSDSs, samples can be collected and analysed to determine the exact concentrations of the related compounds of the document.

In certain pesticides, PFASs, such as perfluoroalkyl phosphinic acids (PFPiAs), have been used as anti-foaming agents in the solutions (Z. Wang et al., 2016). C_6/C_8 and C_8/C_8 PFPiAs are persistent and may transform into highly persistent PFOA in the environment and are therefore considered PFOA-related compounds (Lee et al., 2012; Z. Wang et al., 2016).

Information related to PFHxS

There is limited information that PFHxS is used in biocides. PFHxS may be present as an impurity of PFOS. PFHxS impurity in PFOS was determined to be 4 – 14.5% (UNEP, 2018d).

3.2.2 Availability of alternatives

Both chemical and non-chemical alternatives have been developed for use in insect baits to control leaf cutting ants. An overview of the available alternatives, both chemical and non-chemical, is presented in Table 5. This compiles information from previously published sources, e.g. UNEP/POPS/POPRC.12/INF/15(UNEP, 2016b); UNEP/POPS/POPRC.14/INF/13 (UNEP, 2019c); and BAT/BEP Experts guidance documents (UNEP, 2017d, 2021).

Non-chemical alternatives/alternative technologies

A wide range of non-chemical methods have also been developed with the aim of controlling leaf-cutting ants. It is noted that Brazil has studied a number of mechanical, cultural, and biological methods since the early 1950s. These are briefly summarised below, and the viability and effectiveness of these approaches are discussed in the following sections:

(a) Biodiversity measures – e.g., through introduction of different and more varied plant species;

(b) Cultural control – conventional soil preparation by ploughing and harrowing leading to the mortality of newly formed Atta nests;

(c) Physical / mechanical controls – i.e., physically excavating the ant nests for queen ant removal;

(d) Barriers – i.e. plastic tape coated with grease, plastic cylinders and strips of aluminium, plastic or metal fastened around the tree trunks;

(e) Natural plant extracts – for example the product Bioisca was registered in Brazil in 2011, based on sapoins and flavones extracted from the plant *Tephrosia candid;*

(f) Biological controls using fungi– e.g., using the pathogenic fungi *Escovopsis sp*, and *Syncephalastrum sp* to control leaf-cutting ants has been suggested, as well as the entomopathogenic *Metarrhizium anisopliae* and the entomopathogenic fungi *Beauveria bassiana* and *Aspergillus ochraceus*; and

(g) Integrated Pest Management – an integrated approach involving improvements in on-farm diversity in conjunction with biological controls such as the pathogenic fungi described above, to minimise damage above economic thresholds.

Developing effective biological and physical controls is challenging because leaf-cutting ants have mechanical and chemical defences that help them to counterbalance the effect of some control measures. For example, exocrine glands and symbiotic bacteria are the main sources of antimicrobials in leaf-cutting ants and are used to counter biological control agents. The combination of multiple methods, such as those that limit the growth of bacteria together with biological control agents could therefore be a promising approach in certain settings.

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[5] US EPA: https://www.epa.gov/pesticides/pfas-packaging.

Chemical alternatives

A number of chemical alternatives have been previously tested as alternatives to sulfluramid, including chlorpyrifos, cypermethrin, a mixture of chlorpyrifos and cypermethrin, fipronil, imidacloprid, abamectin, deltamethrin, fenitrothion, and a mixture of fenitrothion and deltamethrin. It is noted that fipronil and chlorpyrifos are considered more acutely toxic to humans and the environment than sulfluramid, and the effectiveness of these substances has been questioned, thus new alternatives are being studied in Brazil. It is indicated that due to severe toxicological and environmental characteristics, chlorpyrifos use in insect baits is no longer used in insect baits in Brazil to control leaf-cutting ants (Brazil, 2018).

The reported chemical alternatives to sulfluramid currently considered as pesticides for leaf-cutting ants are: fipronil, deltamethrin, fenitrothion and hydramethylnon (see Table 5). In principle these pesticides are available on the world market, but it is noted that they are not all freely available everywhere.[6] It has been indicated that they are all available as commercial products on the Argentinean market. Deltamethrin, fenitrothion and permethrin are registered and used in Brazil in complementary forms, in very specific applications for the control of leaf-cutting ants.

There are two alternative chemical methods that have been developed as a complementary form of insect bait to the control of leaf-cutting ants:[7]

(a) Thermonebulizable solutions (thermal fogging) – generation of ultra-fine droplets in a range of 1µm - 50µm using thermo-pneumatic energy. Via controlled flow through a nozzle, the pesticide solution is injected into the hot exhaust gas stream near the outlet of the resonator causing it to be atomized forming ultra-fine fog droplets. The active ingredient permethrin (CAS No. 52645-53-1) is mixed with diesel or kerosene as a vehicle;

(b) Dried powder formulations **–** deltamethrin is mixed in a talcum powder vehicle and manually applied via hand-held equipment (called “dusters”) into the ant hill holes.

The use of dried powder formulations is limited to a few regions of the country and is far from being used widely. These are recommended only for use as a complementary form in very specific situations, for example, to control some species of *Acromyrmex* colonies and initial colonies of *Atta*.

Table 5: Overview of alternatives to sulfluramid for use in insect baits for the control of leaf-cutting ants from Atta spp. and Acromyrmex spp.

Composition	**CAS No**	**Trade name**	**Manufacturer**	**Class***	**Source(s)**	**Additional details**
Chemical alternatives						
Fipronil	120068-37-3	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC.10/INF/7/Rev.1 (UNEP, 2014b) UNEP BAP/BEP guidance (UNEP, 2017c)	
Fenitrothion (thermal fogging)	122-14-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC.10/INF/7/Rev.1 (UNEP, 2014b) UNEP BAP/BEP guidance (UNEP, 2017c)	

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[6] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[7] See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

Composition	CAS No	Trade name	Manufacturer	Class*	Source(s)	Additional details
Deltamethrin (dried powder)	52918-63-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC.10/INF/7/Rev.1 (UNEP, 2014b) UNEP BAP/BEP guidance (UNEP, 2017c)	
Hydramethylnon	67485-29-4	Amdro® Ant Block	Information gap	4	Brazil (2018) UNEP/POPS/POPRC.10/INF/7/Rev.1 (UNEP, 2014b)	For further information, see for example, http://www.cdpr.ca.gov/docs/risk/rcd/hydrameth.pdf and http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/hydmthn.pdf).
Non-chemical / Alternative Technology						
Biodiversity	N/A	N/A	N/A	N/A	PAN (2018) UNEP/POPS/POPRC.8/INF/17/Rev.1 (UNEP, 2012) UNEP/POPS/POPRC.9/INF/11/Rev.1 (UNEP, 2013)	Can cause the decline and ultimate death of small colonies
Cultural control	N/A	N/A	N/A	N/A	IPEN (2018) ABRAISCA (2018) BAT/BEP Group of Experts, 2017 UNEP/POPS/POPRC.8/INF/17/Rev.1 (UNEP, 2012)	
Physical / mechanical controls	N/A	N/A	N/A	N/A	IPEN (2018) ABRAISCA (2018) BAT/BEP Group of Experts, 2017 UNEP/POPS/POPRC.8/INF/17/Rev.1 (UNEP, 2012)	
Barriers	N/A	N/A	N/A	N/A	IPEN (2018) ABRAISCA (2018) BAT/BEP Group of Experts, 2017	
Natural plant extracts	N/A	Bioisca	Cooperativa De Cafeicultores e Agropecuaristas	N/A	PAN (2018) IPEN (2018) ABRAISCA (2018) BAT/BEP Group of Experts, 2017	

Composition	CAS No	Trade name	Manufacturer	Class*	Source(s)	Additional details
Biological controls using fungi	N/A	N/A	N/A	N/A	PAN (2018) IPEN (2018) ABRAISCA (2018) BAT/BEP Group of Experts, 2017	

* Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: Class 1 (Substances that the committee considered met all Annex D criteria); Class 2 (Substances that the committee considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data); Class 3 (Substances that are difficult for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

3.2.3 Suitability of alternatives

The BAT/BEP Group of Experts guidance (2017) noted that assessment of BAT is difficult because the two species of ants are very different, and more information is available on ways to control the genus *Atta* whereas little information is available on the need of and ways to control the genus *Acromyrmex* (UNEP, 2017c). The guidance states that “alternative technologies are only effective and efficient in specific situations and require specific equipment and different labour skills that those needed to apply toxic bait”. The combination of technologies overall is considered more labour intensive and costly.

Non-chemical alternatives/alternative technologies

A number of biological controls have been investigated and show potential for controlling leaf-cutting ants (UNEP, 2019c). For example, International POPs Elimination Network (IPEN, 2018) cite laboratory studies that suggest the entomopathogenic fungi Metarrhizium *anisopliae* can cause the decline and ultimate death of small colonies and recent research indicates that the entomopathogenic fungi *Beauveria bassiana* and *Aspergillus ochraceus* both show a high degree of control, causing 50% mortality within 4 to 5 days (IPEN, 2018a). However, it should be that while displaying some promising results, these techniques are still at the R&D stage and tests have not resulted in conclusive results on the efficiency or consistency of this approach.

Pesticide Action Network (PAN, 2018) indicated that there was evidence to suggest that biological control agents such as using strains of *Escovopsis* parasitic fungi (Meirelles, Montoya, et al., 2015; Meirelles, Solomon, et al., 2015) or the pathogenic fungus *Syncephalastrum sp.* (Barcoto et al., 2017), could be promising alternatives for the control of leaf-cutting ants (PAN, 2018). At present this is not considered a viable alternative approach as uncertainties over the long-term potential remain. More research is required to establish the potential for this approach in different settings at operational level. The feasibility and potential risks of biological controls, with reference to the use of potentially invasive species and wider ecological impacts need to be carefully considered if proposed approaches involve species that are not already widespread in the local environment.

As noted by PAN (2018) the plant extract product Bioisca, based on an extract of the leguminous plant *Tephrosia candida* (white hoarypea) is currently being used, for instance, in organic farmers in Brazil to control the ant species *Atta sexdens rubropilosa* (*saúva-limão*) and *Atta laevigata* (*saúva cabeçade-vidro*) (PAN, 2018). The product is certified as an organic product by Biodynamic and the efficacy of the product has been validated in various regions of Brazil (PAN, 2018). However, this approach is not currently recommended for large-scale use such as in agriculture, forestry and livestock farming, and the wider operational potential of these products requires further investigation and development.

The potential for baits produced from other natural resources has also been reported (PAN, 2018). Other plant extracts which have shown promise include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata*, neem and sesame oil. Baits prepared with neem oil (azardirachtin) have been reported to reduce ant foraging by 75.5% for *Atta* spp. and 83.5% for *Acromyrmex* spp. in a field trial in Brazil. Baits prepared with sesame oil reduced ant foraging by 55.9% and 67.6% of *Atta* spp. and *Acromyrmex* spp., respectively. Baits prepared with neem and sesame do not kill leaf-cutting ant colonies but reduce forage activity and hence leaf-loss. It is noted that further research is required into the wider technical feasibility and operational consistency of control methods using natural plant extracts before these can be recommended for widespread use and be considered viable alternatives.

For cultural controls, de Britto et al. (2016) indicated that approaches such as crop rotation, ploughing and harrowing, the use of fertilizers and limestone, the digging of nests, and the use of composting have been widely used but are not considered a feasible alternative to controlling leaf-cutting ants in all situations (de Britto et al., 2016). It is also noted that, with the practice of minimum cultivation adopted in several cultivars and reforestation projects, such control has been abandoned. It is also noted that the practice of minimum tillage, which reduces soil preparation throughout the area and is adopted by many forest producers may increase the number of leaf-cutting ant nests (Zanetti et al., 2014).

As noted by PAN (2018), research in Costa Rica has indicated that increasing plant diversity in coffee plantations reduced leaf loss to leaf-cutting ants from 40% in monocultures to <1% in farms with complex plant diversity. De Britto et al. (2016) indicate that the presence of forest understory and native vegetation strips and the consequent bird populations in situ are factors that contribute in reducing the number of ant nests initially, but they need to be thoroughly tested before they can be recommended, and it is noted this is currently in the research phase.

For mechanical controls, the 2017 BAT//BEP guidance states that excavation of the young nests and capturing the ant queens is an effective way to control the leaf-cutting ants in smaller areas. Excavation is recommended only during the third and fourth months after the nuptial flight, when the queens are about 20 cm deep in the soil (UNEP, 2017c; Zanetti et al., 2014). Brazil (2018) indicated that mechanical control by excavating their nests for queen ant removal was no longer recommended for leaf-cutting colonies that are more than 4 months old, this is when the queen will be lodged at depths exceeding 1 meter, thus rendering the technique unviable. It is considered that, in practice, mechanical control will be unviable in areas used for commercial plantations, in reforestation projects and grazing systems (Brazil, 2018).

Barriers are noted as being one of the oldest and most cost-effective control methods used for these ants, but only in small orchards (Zanetti et al., 2014). However, constant inspections and repairs are necessary to protect the trees. This control mechanism is not applicable to agricultural and forest crops because of the high maintenance requirements.[8]

There is uncertainty and contradictory opinion on the potential for integrated pest management to control leaf-cutting ants, and further research and development is clearly required in this area. According to Della Lucia et al. (2013), a lack of economic thresholds and sampling plans focused on the main pest species preclude the management of leaf-cutting ants; such management would facilitate their control and lessen insecticide overuse, particularly the use of insecticidal baits (Della Lucia et al., 2014).

Chemical alternatives

According to de Britto et al. (2016), to be considered an adequate insecticide used to formulate bait for the control of leaf-cutting ants, the substance should fulfil the following criteria: lethal (to ants) at low concentrations or otherwise to prevent the ant from feeding or reproducing; act by ingestion; present a delayed toxic action; be odourless and non-repellent; and paralyze the plant cutting activities, in the first days after application (de Britto et al., 2016).

In Brazil, fipronil is only registered for use in baits to control certain *Atta* species and is suggested this might not be as efficient and seems to display broader toxicity to other animals.[9] There is insufficient available data to determine the overall feasibility of this substance as a replacement for sulfluramid. de Britto et al. (2016) noted that fipronil and other phenylpyrazoles used in the toxic bait formulation, did not show potential for replacing the sulfluramid (de Britto et al., 2016).

A special formulation of hydramethylnon, sold under the trade name Amdro® Ant Block, is currently the only widely available bait product labelled for control of leaf-cutting ants in the USA.[10] de Britto et al. (2016) noted that this product had several drawbacks, including a 30% efficiency, the requirement for multiple applications, and a relatively short useful lifetime. This product has not been registered or used in Brazil for leaf-cutting ants. This product may not be used in agricultural sites (e.g., livestock pastures, gardens, cropland) and may not be suitable for treating large colonies.

It was also suggested that two active ingredients, dechlorane[11] and sulfluramid had displayed full efficiency in the control of leaf-cutting ants, wherein the first is no longer used. Brazil[12] considered therefore sulfluramid to be the

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[8] BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

[9] See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

[10] See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

[11] Dechlorane is a candidate for Annex D evaluation.

[12] UNEP-POPS-POPRC13FU-SUBM-PFOS-Brazil-20180209.En (submitted for UNEP/POPS/POPRC.12/INF/15/Rev.1).

only active ingredient registered for the control of leaf-cutting ants, efficient for all species, that fulfils all of the technical criteria outlined above (Brazil, 2018).

In terms of alternative techniques for leaf cutting ant control, dried-powder dusting with deltamethrin, is noted to have a number of limitations, including:

(a) Cannot be applied to moist/wet soil that will cause clogging and clumping of the powder making it ineffective in reaching far into the nests;

(b) Before application, loose soil needs to be removed from the ant hill;

(c) Not effective in eradicating large nests because the powder will not reach into the depth of all the tunnels.

Dried-powder dusting with deltamethrin is therefore recommended for complementary use to control initial nests of *Atta* species and some *Acromyrmex* species (de Britto et al., 2016).

Thermo-nebulization (thermal fogging) is also noted to display some limitations, including:

(a) Use of specialised equipment and associated high costs;

(b) Greater work force needed (at least three operators per application);

(c) Equipment operational problems and maintenance;

(d) Increased exposure of equipment operators and their colleagues to the insecticides;

(e) Potential contamination of soil and water.

This technique can be applied to control *Atta* spp. in mature nests but cannot be used to control *Acromyrmex* ssp. It is being utilized in specific situations, such as very high infestation rates and initial land preparation for cultivation.[13]

From the discussion above, it can be concluded that there is no single chemical or process alternative approach that will cover all applications. With the variety of different scales of application, differences in the effectiveness against the different ant species, as well as other considerations, a variety of approaches is required. The 2017 BAT/BEP Group of Experts report outlines different best available techniques based on a number of different specific situations (UNEP, 2019c).

Table 6: The UNEP (2017) BAT/BEP Group of Experts recommend the following best practice for control of leaf-cutting ants from Atta spp. and Acromyrmex spp.

Situation	BAT
For initial large area land preparation and high infestation rate on mature *Atta* nests	Thermo-nebulization with permethrin
For small areas, such as small orchards and residential uses	Mechanical Control: Excavation of the young nests and capturing the ant queens
	Barriers" fastened around tree trunks, such as plastic tape coated with grease, plastic cylinders and strips of aluminium
To control nests no larger than 5m^2	Dried-powder dusting with deltamethrin
To control young *Atta* colonies and certain *Acromyrmex* species	Dried-powder dusting with deltamethrin
To control certain *Acromyrmex* species	Dried-powder dusting with deltamethrin
All other	Baits containing sulfluramid

3.2.4 Implementation of alternatives

Observations in 2018 suggested that sulfluramid continued to be used in relatively significant quantities in Brazil or other South or Central American countries (UNEP, 2019c). The alternatives were observed to be not widely implemented yet based on information from 2018 (UNEP, 2019c).

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[13] BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

3.2.5 Conclusion

There is currently difficulty in determining the suitable alternatives for sulfluramid to control leaf-cutting ants (the *Atta* spp. and *Acromyrmex* spp.). The BAT/BEP expert guidance notes that a number of alternative chemicals and approaches are available and are considered best practices for a number of specific applications. Additional research and development of alternatives are encouraged, especially in the field of technical and operational feasibility of the alternatives. In particular, the non-chemical alternatives such as plant extracts and other biological and cultural controls in field studies are needed to be developed and their feasibility as widespread control measures shall be demonstrated.

3.3 Metal plating

3.3.1 Introduction and background

There are two main technologies in metal plating: hard and decorative metal plating. The difference between hard and decorative metal plating is thickness, hardness and deposition of the chrome layer on the plated object. The hard metal plating is addressed as functional against, e.g., corrosion, abrasion etc. The main function of decorative metal plating is primarily a decorative surface finish (UNEP, 2016b).

In hard metal plating, the workpiece is submerged in a chromic acid (hexavalent chromium, Cr(VI)) bath. The electrolytic process causes bubbles and mist to be ejected from the plating bath causing aerosols, consisting of process liquids containing chromic acid, to be dispersed into outdoor ambient air. Cr(VI) is a human carcinogen. In order to reduce the occupational exposure, the risk of respiratory cancers, and the amount of chromium lost, chemical fume suppressants are added to the chromium bath. Fluorosurfactants are used as such suppressants (UNEP, 2019a).

The use of Cr(VI) is not essential for all types of decorative chrome plating because trivalent Cr(III) can be used instead. Trivalent chromium is much less toxic than Cr(VI) and mist-suppressing PFASs are therefore not needed in processes with trivalent chromium (Glüge et al., 2022; US EPA, 2000).

Moreover, fluorosurfactants (including PFOS-related chemicals) were used in other metal-plating applications besides chromium plating.

Information related to PFOS

PFOS salts are or have been commonly used as surfactants, wetting agents and mist-suppressing agents in chrome metal plating processes (UNEP, 2019a). The harsh environment of the metal plating processes requires the surfactant to be stable in the presence of hot chromic acid and resist decomposition during the electrolysis. Perfluorinated surfactants, such as PFOS, demonstrate a good resistance, remain stable and maintain their activity over a long period (Posner, 2013).

The PFOS-related compounds most commonly used in chromium plating were tetraethylammonium perfluorooctane sulfonate (CAS No. 56773-42-3, with trade names such as Fluorotenside-248, SurTec 960, FC-248 and FT-248m) and potassium perfluorooctane sulfonate (CAS No. 2795-39-3, with the trade name FC-80). Lithium, diethanolamine, and ammonium salts of PFOS may also be used for chromium plating (Cheremisinoff, 2016). New plating chemistry using chromium-III instead of chromium-VI is available for decorative chromium plating applications. Although chromium-III technology is available for decorative plating, it has not been widely adopted by industry due to cost/performance. PFOS typically remains in the chromium-plating solution after the metal-plating process.

Information related to PFOA

Not relevant.

Information related to PFHxS

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 (UNEP, 2018c). It is not clear from the publicly available information, how extensively the substance is used in metal plating. However, some patents (3M (Minnesota Mining and Manufacturing Co. USA), 1981; Dainippon (Dainippon Ink and Chemicals, Inc., 1979, 1988; Hengxin (Hubei Hengxin Chemical Co., 2015) were identified for the use of PFHxS, its salts and various PFHxS-related compounds in metal plating as mist suppressants, suggesting that such use may have occurred.

Furthermore, due to the unintentional production of PFHxS during the ECF process (Z. Wang et al., 2017), 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.

3.3.2 Availability of alternatives

In UNEP (2019b), the alternatives to PFOS and related chemicals for metal plating have been assessed and presented.

Non-chemical alternative technologies

A number of non-chemical (alternative approaches) have been outlined, with the intention of either replacing the use of Cr(VI) in the plating process completely, altering the technique used in the plating/coating process, or providing alternative approaches of preventing the release of Cr(VI) during the process.

These include the use of PTFE-coated balls on top of the bath, and the use of mesh or blanket covers for plating baths. The composite mesh pads (CMP) system collects and transports chromium emissions through a mesh blanket-type pad where the chromium particles are condensed and collected, primarily through physical means. A CMP system typically consists of several mesh-pad stages. Early stages remove large particles, intermediate stages remove smaller particles and final stages remove microscopic particles. The CMP system is effective at removing droplets and eliminating the discharge of chromic acid mist. Control devices such as packed bed scrubbers, or chromic acid fume scrubbers[14] could also be used to catch aerosols from chromium plating.

Cr(VI) emissions could be reduced substantially by avoiding air convection (Glüge et al., 2022; P.B. Poulsen et al., 2011). Some companies used closed systems with underpressure and found almost no chromic-acid aerosols. No PFASs are therefore necessary as mist suppressants (Blepp et al., 2016; Glüge et al., 2022).

An example of an alternative plating/coating process is the High Velocity Oxygen Fuel (HVOF) process, which is a thermal spray coating technique for hard chrome plating (Mehta et al., 2017). It is known to be globally available and is considered effective and with low costs.

Research shows the possibility of metal chrome coating by dipping instead of electroplating. It uses a version of the Reduction Expansion Synthesis (RES) process, Cr-RES, which can create a micron-scale Cr coating on an iron wire (Pelar et al., 2018).

Additional alternative technologies available include:

- Chrome plating based on nanotechnologies (http://www.greencoat.it/);
- A 2-layer system developed by Hauzer Techno Coating (https://www.hauzertechnocoating.com/en/). Hauzer deposits chromium layers on plastics with Cromatipic technology as an alternative to electroplating.
- Topocrom® coating process. The coating process takes place in a closed reactor. The workpiece is rotated constantly. The process fluids are pumped continuously through the reactor to achieve important quality advantages.
- Hexigone system. It is a chrome-free way of tackling corrosion. The protection response is smart, fast and highly effective - pigments lay dormant in the micro-reservoir system until they can sense corrosion activity and subsequently release the inhibitor ‘on demand.’ (https://www.hexigone.com/).

However, it is unclear whether these techniques can be used for hard metal plating as well as decorative metal plating.

The use of Cr(III) instead of Cr(VI) for certain decorative chrome plating processes has made PFAS use in decorative chrome plating obsolete. Attempts to use Cr(III) also for hard chromium plating are ongoing for the development of

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[14] https://www.monroeenvironmental.com/air-pollution-control/packed-bed-wet-scrubbers/.

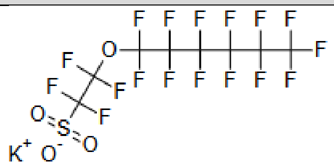
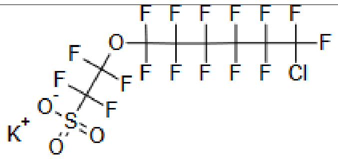
an environmentally friendly alternative to hexavalent chromium in chrome plating.[15] Atotech and Faraday Technology are working on a trivalent chromium plating process for functional applications (Glüge et al., 2022).

Chemical alternatives

Poulsen et al. (2011) have demonstrated that the fluorinated alternative Fumetrol® 21 from Atotech, which is based on 1H,1H,2H,2H-perfluorooctane sulfonic acid (6:2 fluorotelomer sulfonic acid (6:2 FTSA); CAS No. 27619-97-2) reduces the Cr(VI) emission. This alternative PFASs will ultimately degrade to a mixture of perfluorocarboxylic acids that have alkyl chains with no more than six perfluorinated carbon atoms.

In China, other alternatives to PFOS exist, namely F53 and F53-B (Table 7). Scientific studies have been performed on their environmental impact and ecotoxicity (Shuai Liu et al., 2021; Shi et al., 2017; UNEP, 2016b; S. Wang et al., 2013; Z. Wang et al., 2015; Yu et al., 2021). One study shows that F53-B induces embryotoxicity and disrupts cardiac development in zebrafish embryos (Shi et al., 2017). Moreover, Yu et al. (2021) suggest the associations of Cl-PFESAs (such as F53-B) concentrations with metabolic syndrome, including hyperglycemia, raised blood pressure, elevated triglycerides, elevated waist circumference and reduced high-density lipid cholesterol.

Table 7: Identities of F53 and F53-B.

Name	Acronym	Structure	CAS
Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) ethane sulfonate	F53		754925-54-7
Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	F53-B		73606-19-6

Fluorine-free alternatives such as alkylsulfonate and olea amine ethoxylates (CAS 26635-93-8) are also available (ECHA, 2019a). The German electroplating industry association (ZVO, 2018) indicated the availability of PFOS-free alternative products from 10 German suppliers. It is noted that information is lacking regarding the exact identity and composition of these chemical compounds; however, it is indicated that three are fluorinated and seven are non-fluorinated alternatives (UNEP, 2019c).

An overview of the chemical and non-chemical alternatives is summarised in Table 8.

Table 8: Overview of alternatives to PFOS and PFHxS for use in the metal plating sector.

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
Non-chemical alternative processes							
Physical covers (netting, balls) for metal plating baths (chromium (VI))	N/A	Yes	Yes	Information gap	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1 BAT/BEP Expert Guidance	N/A	E.g., Mesh or blankets (Composite Mesh Pads) placed on top of the bath Not recommended or considered BEP

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[15] https://www.pfonline.com/blog/post/nucor-invests-in-environmentally-friendly-chrome-plating.

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
Add-on air pollution control devices	N/A	Yes	Yes	https://www.monroeenvironmental.com/air-pollution-control/packed-bed-wet-scrubbers/	BAT/BEP Expert Guidance	N/A	E.g., Composite Mesh Pads (CMP), Chromic Acid Fume Scrubber, or Packed Bed Scrubbers
Novel plating processes	N/A	Yes	Yes	www.topocrom.com www.greencoat.it https://www.hauzertechnocoating.com/en/ www.hexigone.com/ High Velocity Oxygen Fuel) Process	BAT/BEP Expert Guidance	N/A	
Trivalent chromium or Cr(III) plating.	N/A	Yes	Yes	Atotech, Faraday Technology	BAT/BEP Expert Guidance	N/A	
Chemical alternatives							
-Fluorinated alternatives							
6:2 fluorotelomer sulfonic acid (6:2 FTSA) (Hard metal)	27619-97-2	Yes	No	• 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)	UNEP/POPS/POPRC.10/INF/7/Rev.1; BAT/BEP Guidance; Poland (2018); Germany (2018).	3	It is not resistant to chrome sulfuric acid pickling and hard chrome baths.

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
6:2 fluorotelomer sulfonate (6:2 FTSA) (Decorative)	27619-97-2	No	Yes	• 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)	UNEP/POPS/POPRC.10/INF/7/Rev.1; BAT/BEP Guidance	3	
F53 (Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) ethane sulfonate)	754925-54-7	Yes	Yes		C. Huang et al. (2010); Z. Wang et al., (2013)		Available in China
F53-B (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo) ethane sulfonate)	73606-19-6	Yes	Yes		C. Huang et al. (2010); Shi et al. (2017); Z. Wang et al., (2013)		Available in China
-Fluorine-free alternatives							
Alkane sulfonates	N/A	Yes	Yes	• TIB Suract CR-H (TIB Chemicals AG))	BAT/BEP Expert Guidance		Not resistant to hard chromium plating, less effective in decorative chromium plating
Oleo amine ethoxylates	26635-93-8	No	Yes	• ANKOR® Wetting Agent FF (Enthone)) • Antispray S (Coventya)	BAT/BEP Expert Guidance	N/A	(Z)-Octadec-9-enylamine,ethoxylated (Oleylaminethoxylat)

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
Other non-fluorinated alternatives	N/A	Yes	Yes	• CL-Chromeprotector BA (CL Technology GmbH) • Antifog V4 (Chemisol GmbH & Co. KG) • Non Mist-L (Uyemura)	BAT/BEP Expert Guidance	N/A	No information on chemical identity

*Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: Class 1 (Substances that the committee considered met all Annex D criteria); Class 2 (Substances that the committee considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data); Class 3 (Substances that are difficult for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

3.3.3 Suitability 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.

Non-chemical alternatives

It is indicated by information provided by Germany (2018) that regarding PTFE-coated balls on top of the bath, the state of knowledge is that this alternative will 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. Information provided by Germany (2018) also indicates that the use of mesh or blanket covers requires further research before this can be considered an effective control measure.

It has been estimated by a company that in ~20% of applications, the High Velocity Oxygen Fuel (HVOF) methods of spraying chromium layers can replace hard chromium layers deposited by electroplating (German Environment Agency (UBA), 2017). HVOF is known to be globally available and is considered effective and with low costs. Mehta et al. (2017) noted that the HVOF method displays high deposition efficiency and good quality finish (high density, low porosity), but has the disadvantage of requiring high-temperature application. German Environment Agency (UBA) (2017) mentioned that layers deposited using this method may be more porous and less resistant to corrosion.

Chemical alternatives

It was reported that alternatives to the PFOS derivatives are considered to be less stable and durable in the chrome bath than PFOS. Thus, they may not reach the necessary surface tension, and additionally, they degrade further through oxidation, which is not the case for PFOS due to its extremely persistent properties (UNEP, 2016b).

The use of closed systems with underpressure reduces the reproductive hazard of Cr(VI) from the level of "Repr. 1B/H360D" (may damage the unborn child) to "Repr. 2/H361f" (suspected of damaging fertility) (Glüge et al., 2022). It also reduces the environmental hazard as no PFAS or other hazardous substances are needed in this process (Glüge et al., 2022).

The use of Cr(III) instead of Cr(VI) in electroplating constitutes a shift to a less hazardous substance without the carcinogenic, mutagenic and reproductive toxicity properties of Cr(VI) (ECHA, 2016; Glüge et al., 2022). Atotech launched a hard-chrome plating process with trivalent chromium and stated that the process exhibits the same benefits as hexavalent-chromium processes[16]. Besides Atotech, Faraday stated that the trivalent chromium plating process has already passed the tests specified for aerospace applications. They are currently further optimising the process such that the coating microstructure and appearance is equivalent to that of hexavalent-chromium coatings (Glüge et al., 2022).

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[16] https://www.atotech.com/atotech-launches-the-first- trivalent-chromium-hard-chrome-general-metal-finishing/ (accessed

ZVO (2018) considered there are no other reliable alternatives on the market at the moment. Non-fluorinated alternatives are not economically viable because their use causes additional risks with respect to safety, process stability and device preservation. ZVO (2018) noted that fluorine-free alternatives tested were not stable enough in the hard chrome plating bath, but could be used for decorative chrome plating, for which alternative processes based on chromium (III) exist already.

It is noted that numerous products, for example, based on short-chain PFASs, have been tried for the application in hard metal plating, but all alternatives have proven to be less effective and less stable than PFOS under the harsh conditions of this process.[17] For example, Capstone® FS10 (6:2 FTSA) from DuPont, could only partly be applied in decorative metal plating due to its slightly higher surface tension when compared to PFOS (UNEP, 2016b).

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). 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. The final EU-wide restriction of PFHxA and PFHxA-related compounds is being formulated. Acute and repeated-dose mammalian and aquatic toxicity has been reported for 6:2 FTSA.

FluoroCouncil (2018) considered that the technical feasibility of the alternatives is specific to the industrial metal plating process in practice. Users have adopted alternatives that meet their industrial use requirements. According to the current state of knowledge noted in the BAT/BEP guidance, the use of fluorine-free alternative substances should be considered on a case-by-case basis.

As outlined in a report by Amec Foster Wheeler and Bipro (2017), a number of limitations have been noted for the use of PFOS-free alternatives in metal plating (UNEP, 2016b):

- The performance is not equal to PFOS-based suppressants, particularly for fluorine-free alternatives; [18]
- Plating baths may need to be dosed at higher concentrations than the PFOS salts to meet specific surface tension requirements and might be less stable and therefore may have to be replenished more frequently.[19] This may have significant cost implications;
- Use of alternatives may cause corrosion of lead anodes that will then need to be replaced more frequently. This may have significant cost implications;
- Products can reduce Cr(VI) to Cr(III) in the chromium electrolyte, which can lead to serious faults in the chromium coating;
- Short-chain PFASs could pose similar risks to the environment and human health as PFOS, and that use of short-chain PFASs leads to the occurrence of very persistent degradation products in the environment (e.g., PFHxA in water bodies; see Germany submission 2018; POPRC 13 follow-up). PFOS can be retained more easily than alternatives by activated carbon techniques or the use of ion exchangers, so there is a danger of higher levels of environmental release;
- Fluorinated alternatives to PFOS could potentially have similar properties to PFOS and could therefore lead to regrettable substitutions.

Oosterhuis et al. (2017) provided cost estimate data for the substitution of persistent organic pollutants, including PFOS, for safer alternatives. It was indicated that for metal plating, alternatives appeared to be available at limited additional cost, in some cases close to zero or even negative but always less than $1000 per kilogram.

3.3.4 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 industry association (FluoroCouncil, 2018) indicated that short-chain PFASs such as 6:2 FTSA and potassium perfluorobutane

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[17] See UNEP/POPS/POPRC.12/INF/15/Rev.1.

[18] BAT/BEP Group of Experts 2017; (UNEP/POPS/POPRC.12/INF/15/Rev.1).

[19] BAT/BEP Group of Experts 2017; (UNEP/POPS/POPRC.12/INF/15/Rev.1).

sulfonate have been reviewed globally and approved by regulators and have been commercially available from numerous suppliers worldwide for over a decade. Poland (2018) and Germany (2018) indicated 6:2 FTSA being commercially available in those countries.

The use of Cr(III) instead of Cr(VI) for certain decorative chrome plating processes is available. For example, Norway has reported the industry phase-out of the use of PFOS-containing wetting/anti-mist agents by using the Cr(III) process instead of the Cr(VI) process where possible.

3.3.5 Conclusion

The short-chain PFASs such as 6:2 FTSA show environmental concern. The fluorine-free alternatives are partially not economically viable because their use could cause additional risks with respect to safety, process stability and device preservation. The non-chemical alternatives might have the potential for wide application in metal plating.

Based on the publicly available information, time is needed to fully evaluate the performance, cost-efficiency, health and environmental impacts of the alternative in metal plating, especially hard plating.

3.4 Fire-fighting foams

3.4.1 Introduction and background

There are generally two types of fire-fighting foams, Class A and Class B fire-fighting foams.

Class A fire-fighting foams are used to extinguish fires caused by wood, paper, wooden structures and wildland. Class A foams generally do not contain PFASs, and are composed of hydrocarbon surfactants which are designed to spread, penetrate and cling to the carbonaceous fuels more easily than plain water (Magrabi et al., 2002).

Class B firefighting foams, on the other hand, are formulated to be most efficient at extinguishing liquid hydrocarbon fuel fires, such as oil and diesel. Class B foams are designed to progressively spread on flammable liquids to cool the burning fuel and starve the flame zone of fuel and oxygen vapours (Magrabi et al., 2002).

Class B fluorinated foams

Typical Class B fluorinated foams are aqueous film-forming foams (AFFF), fluoroprotein foams (FP) and alcohol-resistant aqueous film-forming foams (AR-AFFF):

- AFFF suppress and secure fires involving petroleum-based products such as liquid natural gas and rubber; and flammable and combustible liquids such as diesel fuel, crude oil, and gasoline. 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 (Johnson Controls, 2020);
- FP are oleophobic (oil shedding), which makes them particularly well-suited for sub-surface injection near the base of a Class-B flammable liquid storage tank (Johnson Controls, 2020);
- AR-AFFF suppress and secure fires on hydrocarbon fuels as well as polar solvent fuels such as methanol, ethanol and acetone (Johnson Controls, 2020).

PFASs were the key components in the formulation of AFFF because they lower the surface tension at the air-foam interface and form a film over the hydrocarbon fuel to prevent reignition (UNEP, 2016a). The formation of the water film was exclusively provided by PFASs (UNEP, 2019c).

Information related to PFOS and PFOA

In the past, the industry favoured the use of C8-based PFASs, including PFOA and PFOS (UNEP, 2017a, 2018a). Fluorotelomer-based derivatives such as 8:2 fluorotelomer alcohol (8:2 FTOH), carboxylic acid (8:2 FTCA) and sulfonic acid (8:2 FTSA) are also found in the C8-based fire-fighting foams (EC & ECHA, 2020).

Use of fire-fighting foams to fight large fires and accidental spills may cause considerable local persistent contamination of ground- and surface waters. Fire-fighting foams represent the area with high risks of huge (accidental) releases directly to the environment.

Due to the high risks of fire-fighting foams containing long-chain PFASs, regulations have been developed in many parts of the world to avoid or minimize the production, use, discharge and disposal of such foams. The production of new fire-fighting foams that contain or may contain PFOS, PFOA, their salts and their-related compounds is not exempted under the Stockholm Convention (SC-9/4 and SC-9/12). However, the use of fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, is exempted in certain conditions (details see SC-9/4 and SC-9/12).

According to the European Committee of the Manufacturers of Fire Protection Equipment and Fire Fighting Vehicles (Eurofeu), the European and North American fire-fighting foam industry has fully implemented the US EPA 2010/2015 Stewardship Program with a total phaseout of production of C8-based AFFF although stockpiles still exist. This indicates that fluorinated foams manufactured up to 2015 may contain C8 perfluorinated substances; after that, 'C6 Pure' policies have been implemented (Eurofeu, 2018).

The European Commission allows PFOA, its salts and PFOA-related compounds to be used in Class B fire-fighting foams for already installed in systems until 4 July 2025, subjecting to certain conditions (European Commission, 2020a). After this date, maximum concentrations of 25 parts per billion (ppb) for PFOA and its salts, or 1000 ppb for a combination of PFOA-related compounds, are imposed for fire-fighting foams placed to market in the EU (European Commission, 2020a). The Swedish Chemicals Agency (2015) commented that residual concentrations of C8 substances (substances with 8-carbon chain (C8) structure), including PFOA and related substances, can be 0.01% wt/wt in the final commercial product (KEMI, 2015). Canada also provides exemptions for trace quantities of PFOA within fluorotelomer-based AFFF (UNEP, 2018a).

Information related to PFHxS

AFFF with PFHxS as the active perfluorinated compound has also been on the market in the past (Table 8 in (ECHA, 2019a)). Historically, 3M produced PFHxS for compounds incorporated in fire-fighting foams (Olsen et al., 2005; UNEP, 2017e). According to (Olsen et al., 2005), 3M produced PFHxS (or PFHS) as a building block for compounds incorporated in fire-fighting foams, and this information is in accordance with patents from 3M (3M (Minnesota Mining and Manufacturing Co. USA), 1992) and from another potential historical producer which were reviewed in Norwegian Environment Agency M-961/2018 (Norwegian Environment Agency, 2018). In particular, (3M (Minnesota Mining and Manufacturing Co. USA), 1992) indicates that PFHxS-related compounds and PFOS were likely used in the same AFFF formulations, i.e., previously known as “PFOS-based AFFFs” (e.g., FC-600) (UNEP, 2018d). It is also well supported by measurements of environmental media at AFFF-impact sites (Backe et al., 2013; Baduel et al., 2017; Barzen-Hanson et al., 2017; Bräunig et al., 2017; Houtz et al., 2013; Lanza et al., 2017), where similar or higher levels of PFHxS than that of PFOS were detected, and in some cases, elevated levels of PFHxS-related compounds were identified. It is possible that such “PFOS-based AFFFs” containing PFHxS-related compounds have been discontinued after 3M ceased its global production in 2000–2002 (3M, 2000a); however, production by companies other than 3M cannot be excluded (UNEP, 2018d). There may still be substantial stockpiles of such legacy AFFF formulations around the world (UNEP, 2011; Zushi et al., 2017). Furthermore, Shanghai Vatten has recently developed and commercialised at least one new PFHxS-related amphoteric surfactant for foam fire-extinguishers (UNEP, 2018d; Vatten, 2018). Some AFFF produced in 2015 in China contain PFHxS as a substitute for PFOS (UNEP, 2019a).

3.4.2 Availability of alternatives

There are generally two categories of alternatives: a) fluorine-free alternatives and b) short-chain fluorinated alternatives.

Fluorine-free alternatives

Since 2000, significant developments have been made to produce new generations of fire-fighting foams, consisting of water-soluble non-fluorinated polymer additives and increased levels of hydrocarbon detergents, i.e., formulations that do not use any fluorine-based chemistry, including usages as surfactants or other components.

The Best Available Techniques (BAT) and Best Environmental Practices (BEP) Guidance for use of PFOS and related chemicals under the Stockholm Convention on Persistent Organic Pollutants (POPs) confirms that non-fluorinated foams exist and are in use (UNEP, 2017c). This technology is not new but has advanced considerably over the last 5-10 years since the realisation of problems associated with PFASs (UNEP, 2017c).

Most of the fluorine-free foams (F3) are intended for use on class B fires as well as class A fires (EC & ECHA, 2020). Only very general hints on replacement substances or substance groups have been identified for F3 foams, which can be grouped into four classes: hydrocarbons, detergents, siloxanes and proteins (EC & ECHA, 2020).

The substances that are being used to produce these alternative foams show similarities across different companies/products. A list of F3 foams that are available and are used in the EU market is given in Table 9 based on a study published by the European Commission and European Chemicals Agency (EC & ECHA, 2020).

Table 9: List of alternative F3 foam products available on the EU market.

Manufacturer/supplier	Product
Bio-EX	ECOPOL(Class A & B), BIO FOR (Class A), BIO FOAM (Class B), BIO T (training foam)
Solberg	RE-HEALING™ 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)
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)

There is relatively little publicly available information on the chemical structure or properties of the fluorine-free alternatives. A number of manufacturers and commercial products of safety-certified F3 foams have been identified, where the details of the precise formulations are not divulged due to confidential business information (see Table 6 in UNEP/POPS/POPRC.14/INF/8). However, patents for F3 foams provide more insights. For example, in the Solberg patent the following ingredients are listed: Diethylene glycol butyl ether, xanthan gum, starch, carbonised sugar, diethanolamine lauryl sulfate, sodium decyl ethoxy sulfate, cocamidopropyl betaine, cocamidopropyl hydroxysultaine, sodium octyl sulfate, sodium decyl sulfate, alkyl polyglucoside (Patent US20080196908) (SOLBERG SCANDINAVIA AS, 2008). To be simplified, it contains carbonised saccharide composition, a cross-linking agent or inorganic salt, a surfactant, and water (SOLBERG SCANDINAVIA AS, 2008).

The benefits of using F3 foams are related to the reduction of long-term impact on the environment, while short-term impact related to acute toxicity due to biochemical oxygen demand (BOD) and chemical oxygen demand (COD) is not significantly different from the fluorine-containing foams (IPEN, 2018c). F3 foams are biodegradable while AFFFs contain persistent fluorinated substances.[20]

Short-chain fluorinated alternatives

C6-based compounds including 6:2 fluorotelomers such as perfluorohexane ethyl sulfonyl betaine (UNEP, 2019c), and C4-based fluorinated compounds (Place & Field, 2012) have also been used in fire-fighting foams. Studies indicate that fluorotelomers eventually degrade to perfluorinated acids in nature, e.g., 6:2 fluorotelomer sulfonate (6:2 FTS) is known to degrade to PFHpA and PFHxA but not PFHxS (N. Wang et al., 2011).

3.4.3 Suitability of alternatives

Fluorine-free alternatives

Performance

The operational capabilities of fluorine-free Class B firefighting foams (F3s) which are suitable for liquid hydrocarbon and polar-solvent fuel fires, have continued to advance and expand in use dramatically since their initial development in the early 2000s (IPEN, 2018c).

Castro (2017) reported the results of testing data on F3 foams. It indicated there were significant differences in the performance between PFAS-containing AFFFs and F3 foams depending on the types of fire. For heptane and diesel fires, the time required for F3 foams to control the fires relative to AFFF was 5–6% slower, but for Jet A1 fuel and gasoline, it was 50–60% slower.

However, recent tests confirm that F3 foams are as effective, or better, and meet industry-established fire-fighting performance certifications. Information provided by the Solberg Company confirms that PFAS-free fire-fighting foams that are being used to effectively extinguish fuels and with no environmental concerns of persistence, bioaccumulation or toxic breakdown products have shown to perform the same ability to extinguish Class B fires as traditional AFFFs (UNEP, 2018a). Independent fire tests conducted by the Southwest Research Institute found that Solberg's Re-Healing RF3 foam was effective in extinguishing Jet A fuel, meeting the Performance Level B testing requirements of the ICAO Fire Test Standard (Huczek, 2017).

In 2012, a testing program led by the UK Civil Aviation Authority noted that F3 foams are ICAO Level B approved and indicated that a new generation of fluorine-free firefighting foams using compressed air foam systems CAFS[21] proved to be as effective and efficient as the currently used PFAS-containing AFFFs.[22]

Civilian airports and offshore companies around the world have introduced F3 foams and are satisfied with the performance (UNEP, 2018a).

According to a review undertaken by the Queensland Government in Australia, many F3 foams are acknowledged as meeting the toughest among the fire-fighting standards and exceeding film-forming fluorinated foam performance in various circumstances (State of Queensland, 2016b). It is indicated that modern development in F3 foams has substantially decreased any difference in performance levels (IPEN, 2018c).

Hazards

Based on the assessed substances, non-fluorinated alternatives are likely to be of lower environmental concern, primarily due to biodegradation (EC & ECHA, 2020). However, the Member State Committee (MSC) of the ECHA has approved the classification of siloxanes (cyclic D4, D5, D6) as substances of very high concern (SVHC). Other (linear) siloxanes are currently undergoing PBT assessment. The experts in the MSC rated D4 as persistent, bioaccumulative (it accumulates in the food chain), and toxic (PBT), but they assigned only persistent and bioaccumulative (Very persistent and very bioaccumulative, vPvB) properties to D5 and D6.

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[20] https://echa.europa.eu/fluorine-free-foams.

[21] Simple systems in which high pressure air is injected into the water/foam solution before leaving the piping leading to the turret or hose line.

[22] https://www.internationalairportreview.com/article/11655/ensuring-a-safer-future-for-the-aviation-industry/.

Cost

Based on current data, prices of fluorine-free and fluorine-containing AFFFs are comparable (information provided by Dr. Roger Klein at POPRC-14)(UNEP, 2018a).

The FFFC (2018b) commented that short-chain fluorotelomer-based AFFFs have a shelf-life of 10–25 years, while a manufacturer of fluorine-free alternatives (SOLBERG, 2014) quotes a shelf-life of 20 years (UNEP, 2018a). Comments from the Netherlands note that, based on discussions with a fire brigade in the Netherlands, fires at private facilities are rare, and AFFF should not be used for training; it can mean that stockpiles reach full life expectancy without use, meaning shelf-life is an important consideration (UNEP, 2018a).

Castro (2017) comments that for the application of foams, particularly on petrol and jet A1 fuels that significantly more fluorine-free foam (from $2.31/min/m^2$ to $3.75/min/m^2$) foam is needed to bring fires under control at an equivalent speed to PFAS-containing AFFFs. IPEN commented in the RME that the wider environmental remediation costs of AFFFs should also be taken into account (UNEP, 2018a). This would include the externalised costs of continued reliance on PFAS-containing foams, including the costs of groundwater remediation, as well as the societal costs of subsistence and commercial fisheries, and environmental and public health associated with contamination of aquatic environments (IPEN Comments on 2nd draft RME, (UNEP, 2018a)). 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 (see State of Queensland (2016b, 2016a)), as indicated above, which include infringement of operating license conditions, reputational and brand image damage (Klein, 2013; UNEP, 2018a).

Socioeconomic effects were the drivers for developing the Queensland's foam policy to phase out PFAS-containing fire-fighting foams by 2019. These effects include: contaminated sites are numerous and increasing; water and soil clean-up costs are very high (e.g., single airport spill 2017, €47M); waste treatment, disposal and destruction are very expensive; drinking water supplies are at risk; seafood/fisheries can become restricted; livestock and horticultural products can become unsaleable; an increasing number of legal actions and claims (against manufacturers and end users) (UNEP, 2018a).

Short-chain fluorinated alternatives

Performance

Shorter-chain PFAS-based firefighting foam provides fast control of all flammable liquid fires under different situations (Peshoria et al., 2020). 6:2 fluorotelomer-based firefighting foams are shown by recent extensive and rigorous NFPA Research Foundation and US Naval Research Laboratory testing to be the most effective foams currently available to fight flammable liquid fires occurring in many military, industrial, and aviation situations (American Chemistry Council, 2018).

Hazards

There is an increasing concern among authorities in Europe regarding risks for health and the environment exhibited by short-chain PFASs. These concerns are due to persistence, high mobility in water and soil and potential toxic properties of these substances. Already now short-chain PFASs are ubiquitously present in the environment, even in remote areas (UNEP, 2017b). 6:2 fluorotelomers have been used in firefighting foams. They can transform to PFHxA and thus are PFHxA-related compounds. 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. The final EU-wide restriction of PFHxA and PFHxA-related compounds is being formulated.

3.4.4 Implementation of alternatives

Foam users currently have two types of alternatives: modern fluorinated foams that contain only short-chain PFASs and fluorine-free foams (F3).

Based on the study from the European Commission (EC) and ECHA, most F3 foams use either hydrocarbons or detergents in the foams (EC & ECHA, 2020).

Siloxane- and protein-based fire-fighting foams maybe still in the phase of development. No commercial F3 foams containing these substances were identified in the task of a study carried out by the European Commission and ECHA (EC & ECHA, 2020).

F3 foams certified to different ICAO levels (required for use at civilian airports) are available on the market (FFFC, 2017) and are already introduced at airports in practice (UNEP, 2017a). For example, the UK Civil Aviation Authority notes that F3foams are ICAO Level B approved and found that F3 foams were just as efficient as AFFF in large-scale fire tests; while the Copenhagen Airport replaced AFFF with Solberg RF Re-Healing foam for environmental reasons (UNEP, 2018a).

F3 foam has been in use in fire trucks at London Heathrow Airport without any operational deficiencies. The following advantages of using F3 foam were described: The airport returned to full operations very quickly following two incidents, with no clean-up costs; operational and environmental responsibilities were met; regular training built confidence in the new product (UNEP, 2018a).

Commercial airports in Sweden and Norway have replaced PFAS-based fire-fighting foams with F3 foams because of environmental safety concerns. Since 2008, AFFF has no longer been used at fire drills at the Swedavia airports in Sweden, and in 2011 Swedavia started to use fluorine-free alcohol-resistant foam (Moussol FF 3/6) (Norström et al., 2015). Moussoll-FF 3/6 is degraded to carbon dioxide and water in the environment. It is considered effective in fire suppression required at airports where high safety standards have to be fulfilled. Norwegian airports and military properties have also introduced F3 foams (Norway Comments on 3rd draft RME, (UNEP, 2018a)).

The major international hubs such as Dubai, Dortmund, Stuttgart, London Heathrow, Manchester, Copenhagen, and Auckland have transitioned to F3 foams. All of the 27 major airports in Australia have transitioned to F3 foams, while airports in Europe, such as Billund, Guernsey, Bristol, Blackpool, Köln, and Bonn are also using F3 foams (IPEN, 2018c).

In October 2018, the U.S. Senate approved a five-year reauthorisation for the Federal Aviation Administration which changed the performance standards for fire-fighting foams to allow the use of F3 foams at civilian airports (US Congress, 2018).

Private sector companies using F3 foams include BP, ExxonMobil, Total, Gazprom, Statoil, BHP Billiton, Bayern Oil, 3M, BASF, Chemours, AkzoNobel, Stena Line, Pfizer, Lilly, Weifa, JO Tankers, and ODFJEL (IPEN, 2018c).

In the oil and gas sector, F3 foams are being extensively used. For instance, Statoil in Norway has transitioned to F3 foams throughout all of its operations. Some military users including the Danish and Norwegian Armed forces, have moved to F3 foams. For example, the Royal Danish Airforce has transitioned to F3 foams several years ago (IPEN, 2018c).

3.4.5 Conclusion

The size of in-use stockpiles for fire-fighting foams containing PFHxS and PFHxS-related compounds may be significant, and it is highly recommended not to use up stockpiles or installed fire-fighting foams containing PFHxS and PFHxS-related compounds before the entry into force with the aim of avoiding disposal and decontamination costs.

Both short-chain fluorinated foams, as well as fluorine-free alternatives, are available on the market.

Foam manufacturers support the use of both fluorinated and fluorine-free products in appropriate applications and feel strongly that both products are necessary for the fire protection needs of society. No single type of foam meets all the needs encountered by end users. It is incumbent upon foam users to choose the type of foam product that best meets their needs based on fuel type, size and geometry of the fire, environmental concerns and legislative requirements (FFFC, 2019).

Concerns have been highlighted about the mobility and potential environmental impacts of short-chain fluorinated compounds in fire-fighting foams. Concerns have also been raised on the significant socioeconomic costs related to site decontamination.

Lifetime costs for using AFFFs, fluoroproteins (FPs), or film-forming fluoroproteins (FFFPs) outweigh those of fluorine-free foams (F3) because of potential site remediation cost, treatment of contaminated drinking water, an increasing number of legal actions and claims (against manufacturers and end users), etc.

Some concerns were expressed about the importance of effective fire-fighting foam for liquid fuel fires, the potential unavailability of suitable alternatives and the cost of their use and implementation, considering that some time to move to alternatives without fluorinated compounds may be needed.

3.5 Use of perfluorooctyl iodide (PFOI) for the production of perfluorooctyl bromide (PFOB) for the purpose of producing pharmaceutical products

3.5.1 Introduction and background

Information related to PFOS and PFHxS

Not relevant.

Information related to PFOA

PFOB is used as a processing aid (solvent) to produce "micro-porous" pharmaceutical products. This allows to obtain a drug which is very small and contains low-density phospholipid porous particles as a functional component, indispensable for the efficient delivery of the active substance/medicine in a smaller amount of dry powder to the lesion (lung) in a short time via inhalation, also known as pressurized metered-dose inhaler (pMDI) medicines.

PFOB is not restricted under the Stockholm Convention. However, PFOI, which is used to produce PFOB, is a substance that can degrade into PFOA, i.e., a PFOA-related compound.[23] PFOI may be present in the final drug as residue at around 200 parts per million (ppm) which exceeds the threshold of 1 ppm set in the REACH Restriction (ECHA, 2018).

PFOB is produced from PFOI which results from the production of 6:2 fluorotelomer-based substances. The production of PFOI takes place at one single site in Japan and is then transported to another site in Japan for use as an intermediate in the production of PFOB.[24]

Since PFOB-based technology may allow pharmaceutical companies to develop more effective treatments via inhalation for a wider scope of clinical applications, use of PFOI for the production of PFOB is exempted for the purpose of producing pharmaceutical products, in accordance with the provisions of paragraph 3 of part X of Annex A[25] to the Stockholm Convention.

3.5.2 Availability of alternatives

Recently, there is a patent application in the US to produce PFOB with PFOA residue less than 25 ppb or less. The method is to produce PFOB by PFOI with bromination to produce PFOB. The reaction product is PFOB with PFOA impurities. Then this product goes to alkali-washing to reduce PFOA impurities to below 25 ppb.[26] There is, however, no information on PFOI impurities content in the final PFOB product.

3.5.3 Suitability of alternatives

Four scenarios to reduce or eliminate PFOI impurities in PFOB were assessed by AstraZeneca, the major user of PFOB (ECHA, 2018).

- PFOB which is further purified to reduce residual levels of PFOI;
- PFOB that is manufactured via alternative synthetic routes;

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[23] ECHA Report on the request to review a derogation request for the restriction of PFOA, its salts and PFOA-related substances (entry 68 of Annex XVII to REACH), Annex 1 Chemical Safety Report for the Use of PFOB Containing up to 200 ppm PFOI.

[24] UNEP/POPS/POPRC.13/7/Add.2.

[25] Decision SC-9/12.

[26] US 2020/0157028 A1 Composition containing $C8F17Br$ and method for producing $C8F17Br$.

- Use of similar molecules to PFOB;
- Use of structurally different alternatives to PFOB.

Scenario a: further PFOB purification. The chemical conversion is already 99.9% efficient, which is exceptional and there is little scope to improve this conversion rate. Efforts will continue to reduce the levels of PFOI, but it should be recognized that the process is already well-optimized (ECHA, 2018). This option will be pursued in any case, but is very unlikely to provide PFOB that meets the impurity thresholds in the EU regulation (ECHA, 2018).

Scenario b: PFOB that is manufactured via alternative synthetic routes. PFOB could be manufactured via analogous molecules such as sulfonic equivalents, but this could be considered even less desirable than the current intermediate, PFOI. It is also highlighted that the current route for PFOB uses a by-product that would otherwise need to be incinerated. There is a risk that alternative chemical routes will force the synthesis of undesired chemicals for use as intermediates, whereas the existing process consumes an inevitable by-product that is otherwise incinerated. From a technical perspective, alternative synthetic routes to make PFOB are possible, but these are less desirable than the current synthetic route. From economic feasibility, use of alternative synthetic routes will mean identifying a supplier who is able to supply alternative intermediates that can be converted to PFOB. This will infer uncertain costs which may result in a less desirable situation than now (ECHA, 2018).

Scenario c: perfluorooctyl ethane (PFOE) is considered as suitable for PFOB replacement. However, PFOE can bioaccumulate and is metabolized in the human body, PFOE is less stable than PFOB, and PFOE is made from PFOI, so the switch makes little sense (ECHA, 2018). This option is not viable.

Scenario d: the use of structurally different alternatives to PFOB. There are no suitable substances have been identified to date with similar physical properties as PFOB.

According to information provided, the current production process starting from PFOI is considered the only reasonable way to produce PFOB. If an alternative to PFOB was to be found, the development process to incorporate it into the pharmaceutical products typically would require ten years to complete the three phases of human trials and the regulatory review process.

3.5.4 Implementation of alternatives

Alternatives to the production process using PFOI for the production of PFOB for the purpose of producing pharmaceutical products are currently not available.

3.5.5 Conclusion

No alternative to PFOB as a processing aid has been found for pharmaceutical product manufacturing. Use of PFOI for the production of PFOB for the purpose of producing pharmaceutical products, is exempted in accordance with the provisions of paragraph 3 of part X of Annex A to the Stockholm Convention.

3.6 Semiconductor industry

3.6.1 Introduction and background

PFASs have been used in the semiconductor industry for applications such as photoresists, anti-reflective coatings, immersion topcoats, and overcoats used in the photolithographic process. Other uses of PFASs in the semiconductor industry include, e.g., developer and rinse solutions (Glüge et al., 2022). PFASs are used in these solutions to lower the contact angle of the solutions and, thus, reduce watermark defects after dry spinning (Glüge et al., 2022).

Information related to PFOS

PFOS has been used in the semiconductor industry for applications including photo-resists, and anti-reflective coatings (ARCs) for semiconductors and etching agents for compound semi-conductors and ceramic filters, which were listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B (SC-4/17). During the ninth Meeting of the Conference of the Parties to the Stockholm Convention in 2019, the exemption for use in the semiconductor industry has been eliminated. The Semiconductor Industry Association (SIA, 2018) reported that the semiconductor industry globally has successfully completed the phase-out of PFOS, and therefore the industry no longer has a need for use exemptions for this set of applications (UNEP, 2019c).

Information related to PFOA

Like PFOS, PFOA and related compounds can be found in the semiconductor industry. They are contained in equipment used to manufacture semiconductors and are used in the photolithography and etching processes during the semiconductor production (UNEP, 2017a).

Considering the complexity of supply chains for the equipment, the low PFOA content (around 10 kg for the whole industry sector according to the industry), and high potential costs for early equipment adaptation or replacement, exemptions of PFOA, its salts and related compounds in photolithography or etch processes in semiconductor manufacturing are granted to the Parties to the Stockholm Convention (UNEP, 2019b). In the EU, according to Regulation (EU) 2020/784 of April 8 (2020), an exemption of PFOA, its salts and related compounds was granted to the substances, mixtures and articles in photolithography or etch processes in semiconductor manufacturing until 4 July 2025.

PFOA emission control measures are documented in the OECD Emissions Scenario Document No. 9, Photoresist Uses in Semiconductor Manufacturing (OECD, 2010; SIA, 2016).

Under the auspices of the World Semiconductor Council (WSC), companies in the global semiconductor industry announced a commitment to phase out the use of PFOA in their manufacturing processes by 2025. As a follow-up to the successful efforts on phasing-out PFOS, the WSC is committing to transitioning away from the use of PFOA and PFOA-related compounds in chemical formulations in semiconductor manufacturing. The process of identifying and qualifying replacement chemicals can be extremely complex, and it is essential that companies be given sufficient time to work through this process.[27] The WSC intends to complete this work by a target date of 2025. However, additional time may be needed to complete the final replacement process for PFOA-related compounds due the complexity of replacing these substances in all applications.

Information related to PFHxS

There is limited information on the specific processes in the manufacture of electronics and semiconductors that PFHxS is used. However, PFHxS was detected in the wastewater of a semiconductor industry park (PFHxS: 133330 μg/m³ (Lin et al., 2010) and in a receiving river of a semiconductor industry park at a concentration of 2100 ng/L (Lin et al., 2009).

3.6.2 Availability of alternatives

PFOS, PFOA, PFHxS, their salts and related compounds have been mostly used in the photolithographic process and in the developer and rinse solutions.

Photolithographic process

Short-chain (four carbon atoms or less) PFASs are considered as available. PFBS or functionalized fluoroethanesulfonates have been used as photoacid generators (PAGs) in the photolithographic process. IPEN (2018a) noted that patent literature also indicated active work in this area. Substitutes do exist for non-critical uses, and the semiconductor industry has phased out of PFOS/PFASs in these uses.

Regarding non-fluorinated alternatives, Glüge et al. (2021) summarized the current available non-fluorinated alternatives in the photolithographic process. Possible alternatives include 1) nitrobenzenesulfonate (NBS); 2) acceptor-substituted thiosulfonate anions such as benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-) (TBNO) or 2-thiophenesulfonic acid, 5-chloro-4- nitro-, ion(1-) (TN); 3) aromatic anions, such as pentacyanocyclopentiadienide (CN5) or methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1); and 4) triphenylsulfo nium (TPS). Other related patents include US20090181319 (Li et al., 2009) and US8034533 (Sen Liu & Varanasi, 2011), which describe fluorine-free photo-resist compositions as alternatives to PFOS/PFASs for such uses. Moreover, Fuji markets photo-resists that are “PFOS- and PFAS-free”.[28]

In addition, non-chemical alternatives for photolithography process in the form of other manufacturing processes are being discussed in research. A new dry etch technology being commercially introduced is atomic layer etch (ALE),

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[27] Joint statement of 23rd meeting of the World Semiconductor Council.

[28] http://www.fujifilmusa.com/products/semiconductor_materials/photo-resists/krf/index.html.

which selectively removes materials at the atomic scale. These can be plasma or thermal-based systems, or a hybrid of both (UNEP, 2019c). Suppliers of these technologies include Applied Materials, Hitachi High-Technologies, Lam Research, and TEL.

Developer and rinse solutions

A patent from BASF (Klipp et al., 2012) refers to the aforementioned patent US20080299487 (Chang, 2008) and discloses that a new liquid (and a method of using it) for immersion photolithography of photoresist layers has been developed that allows for a high aspect ratio for line-space dimensions of 20 nm and below without causing pattern collapse, line edge roughness, and watermark defects, without the use of fluorinated surfactants (Glüge et al., 2022).

3.6.3 Suitability of alternatives

Photolithographic process

Short-chain PFASs: significant evidence has shown potential health and environmental problems of short-chain PFASs, including enhanced mobility, uptake in crops, binding to proteins, increasing levels of exposure, difficulty to capture and to clean up once released into the environment (Brendel et al., 2018; Ritscher et al., 2018; UNEP, 2018a). Among the short-chain PFASs, PFBS is persistent (ECHA, 2019c). ECHA committee agrees PFBS is substance of very high concern. Animal studies support identification of thyroid, developmental, and kidney endpoints as potential health effects following repeated exposures of PFBS salt in utero and/or during adulthood (US EPA, 2021).

Fluorine-free alternatives have some technical limitations which are currently prohibitive to high-volume manufacturing (Glüge et al., 2022). The potential health and environmental concern of fluorine-free photoresist is not clear for all alternatives. Data from the ECHA Classification & Labeling (C&L) Inventory indicated that NBS has no carcinogenic, mutagenic or toxic for reproduction (CMR) properties (Glüge et al., 2022). Environmental hazard data were estimated for NBS, TBNO, TN, and CN5, all of which indicate lower environmental hazard than for PFASs (Glüge et al., 2022).

Non-chemical alternatives: ALE, a next-generation etch technology that removes materials at the atomic scale, is one of the several tools used to process advanced devices in a fab. ALE moved into production for select applications around 2016. The technology is still not widely deployed because it’s a slow process. Now the industry is looking at new applications for ALE in memory and logic, as well for III-V materials and exotic metals (UNEP, 2019c).

Developer and rinse solutions

The alternative described by Klipp et al. (2012) seems to fulfil the technical functions needed and has potential also for future developments in the semiconductor industry (Glüge et al., 2022). No information is available on the hazards of the alternatives proposed.

3.6.4 Implementation of alternatives

IBM began its PFOS/PFOA phase-out in 2003, eliminated PFOS and PFOA in its wet etch processes in 2008, and went on and eliminated PFOS/PFOA in all its photolithography processes in 2010 (UNEP, 2019c). Information on the relative performance has not been made available. Taiwan Semiconductor Manufacturing Company (TSMC) is the world's largest dedicated independent (pure-play) semiconductor foundry. According to the TSMC 2020 Corporate Social Responsibility Report, TSMC succeeded substituting all PFOA-related substances and added PFASs with one to four carbons were substances that required disclosure in 2020.[29]

3.6.5 Conclusion

The semiconductor industry is working on phasing out PFOA, its salts and PFOA-related compounds. Success has been achieved by some companies such as TSMC.

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[29] https://esg.tsmc.com/download/file/2020-csr-report/english/pdf/e-all.pdf.

There is a lack of publicly available information on the properties of many of the possible alternatives, including whether they have POP characteristics. Information on the chemical profiles and other properties of the alternatives needs to be made available, so that the health and environmental impacts of the alternatives can be assessed.

Emissions of PFOA, its salts and related compounds in the semiconductor industry needs to be managed according to the Emissions Scenario Document No. 9, Photoresist Uses in Semiconductor Manufacturing (OECD, 2010; SIA, 2016).

3.7 Photo-imaging

3.7.1 Introduction and background

Information related to PFOS

Photo-imaging was listed as an acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B (4/17). During the ninth Meeting of the Conference of the Parties to the Stockholm Convention in 2019, the exemption for use in the semiconductor industry has been removed. In the photographic industry, PFOS, its salts and PFOSF have been used in themanufacturing of film, photographic paper and photographic plates (UNEP, 2019c).

The PFOS-related compounds that have been reported to have been used for this purpose, are tetraethylammonium perfluorooctanesulfonate (CAS No. 56773-42-3), used in the manufacture of photographic film, and FOSA quaternary ammonium iodide (CAS No. 1652-63-7), used in the manufacture of photographic film, paper and plates (UNEP, 2019c).

PFOS, its salts and PFOSF are favoured in these photo imaging applications due to their lack of photo-activity and ability to provide critical functionality (such as controlling surface tension, electrostatic charge, friction, and adhesion, and repelling dirt). Imaging materials that are very sensitive to light (e.g., high-speed films) benefit particularly from these properties (UNEP, 2019c).

Information related to PFOA

Similar to PFOS, PFOA salts and related compounds play an essential role in manufacturing and performance of certain imaging products because these chemicals provide critical antistatic, surfactant, friction control, and dirt-repellent qualities. It is important to note that these substances also provide important safety features by controlling the build-up and discharge of static electricity. Therefore, they prevent employees from injury, prevent damage of equipment and products, and remove fire and explosion hazards (I&P Europe, 2016b; van der Putte et al., 2010).

According to the Imaging and Printing Association Europe (I&P Europe), control measures have been adopted voluntarily to pursue the development of alternatives (UNEP, 2017a). Since 2000, the industry has reformulated/discontinued a large number of products, resulting in a world-wide reduction in the use of PFOA-related compounds of more than 95% (I&P Europe, 2016a).

At the POPRC-13 meeting in 2017, representatives of the European photographic imaging industry suggested that exemptions for photographic coatings applied to paper and for use in printing plates were no longer needed (UNEP, 2018a). However, it was also noted that for developing countries, such information was lacking.

Moreover, PFOA-related compounds are considered necessary for the application of coating layers during the manufacture of some remaining conventional photographic film products (i.e., products in which the image formation is based on silver halide technology) (UNEP, 2017a).

Although replacements do not currently exist for the remaining few applications, further reduction in the use of these substances is anticipated as the transition continues towards digital imaging (I&P Europe, 2016a).

According to I&P Europe, the non-availability of PFOA-related compounds for the manufacture of the remaining relevant imaging products will adversely affect involved customer groups such as healthcare and military. In view of the healthcare sector for example, it could be financially challenging for hospitals and doctor's offices with tight budget restraints to invest in new technologies necessitated by discontinuation of current conventional photographic products. It can be expected that such an impact is larger in developing countries(I&P Europe, 2016a).

Based on the information, the exemption of PFOA, its salts and related compounds in photographic coatings applied to films is agreed upon by the Conference of the Parties to the Stockholm Convention (UNEP, 2019b). Within the EU risk management approach, an exemption is granted for photographic coatings applied to films until 4 July 2025 (European Commission, 2020b).

Information related to PFHxS

There is limited information on the specific processes in the photo-imaging that PFHxS is used.

3.7.2 Availability of alternatives

Non-chemical/technological alternatives

PFOA use in photo-imaging has been reduced by more than 95% worldwide since 2000 (I&P Europe, 2016a). Further reduction in use of these substances is anticipated as the transition continues towards digital imaging. Digital techniques have substantively reduced the use of photographic and X-ray films (UNEP, 2016b).

IAEA and WHO[30] note that the rapid adoption of digital technology in healthcare results from “efficiencies inherent in digital capture, storage and display and the competitive cost structures of such systems when compared to alternatives involving film” and “digital image management is currently the preferred method for medical imaging.” (IPEN, 2018b).

Chemical alternatives

The possible alternatives identified for the photographic industry are: shorter-chain fluorotelomer-based products; C3 and C4 perfluorinated compounds; hydrocarbon surfactants; and silicone products (Pia Brunn Poulsen et al., 2005).

I&P Europe (2018) indicated that the search towards alternatives for C8 PFASs typically involved a “preferred replacement hierarchy”, favouring non-fluorinated hydrocarbon alternatives, followed by non-perfluorinated substances, further followed by perfluorinated substances with shorter chain lengths (C3 or C4) (UNEP, 2019c).

3.7.3 Suitability of alternatives

I&P Europe (2018) considered that some known possible alternatives that have been identified in other areas, e.g., silicone products and siloxane compounds, are in practice not usable as alternatives in the manufacture of conventional photographic products (UNEP, 2019c). However, the presence of chemical alternatives on the market suggests that commercial products are readily available for photo-imaging applications. However, the lack of available information on specific products and formulation means that the level of availability and accessibility of alternatives, the health and environmental impacts of alternatives, remains unclear.

An estimation of costs with regard to the replacement of the remaining relevant uses of PFOA-related compounds in the photo and printing industry cannot be estimated. The formulas of imaging coatings are proprietary and differ from company to company and from product to product. Thus, each company will identify different costs when changing formulation compositions, which may take several years of effort with respect to research and development (not only the performance of substances is evaluated when developing alternatives, but also environmental, health and safety issues). Economic costs associated with substitution of PFOA-related compounds concerning few remaining critical relevant uses in the imaging and photographic sector are considered prohibitive by the industry. The remaining critical uses are described as niche products in markets that I&P Europe members plan to diminish (I&P Europe, 2016a).

3.7.4 Implementation of alternatives

According to I&P Europe Imaging and Printing Association, since 2000, the corresponding European industry has reformulated/discontinued a large number of products. As a result of which PFOA or PFOA-related compounds are

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[30] IAEA, WHO (2015) Worldwide implementation of digital imaging in radiology, IAEA Human health series No. 28, http://www-pub.iaea.org/MTCD/Publications/PDF/Pub1647web.pdf.

no longer used in photographic coatings applied to paper and in printing plates manufactured by their members. Information from other geographies has not been made available.

IPEN (2018a) further noted that the switch to digital technologies also includes developing countries, who report a rapid implementation of digital imaging technology for healthcare, citing examples of this use in Gabon, South Africa, Kenya and Kazakhstan.

3.7.5 Conclusion

Since 2000, the industry has reformulated/discontinued a large number of products, resulting in a world-wide reduction in the use of PFOA and its-related compounds of more than 95% (I&P Europe, 2016a).

The chemical compositions and trade names of the chemical alternatives are not available. Further assessment of the technical and economic feasibility, environmental and health effects, availability, accessibility, etc. are not possible.

The PFOA RME suggested that developing chemical alternatives of photographic coatings applied to films that are viable replacements is very challenging and requires significant research and development investment (UNEP, 2017a). In practice, the most effective alternative approach to using PFOS/PFOA/PFASs in photo imaging is the technological shift to digital photography.

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

3.8.1 Introduction and background

PFASs have been used in formulas/mixtures for the oil- and water-repellent finishing of textiles, leather, apparel, carpet and upholstery.

Robel et al. (2017) found that PFAS-treated textiles contained 0.1–2.5% unbound residues including volatile and ionic PFASs. It is also found that 8:2 FTOH, which is a precursor of PFOA, has been the dominant residue in the studied textiles (Robel et al., 2017). These unbound residues or impurities can be released to the environment via air and water during the use and waste phase of the treated textile.

It was noted in UNEP/POPS/POPRC.12/INF/15/Rev.1 that major manufacturers in conjunction with global regulators have agreed to discontinue the use of long-chain PFASs and move to short-chain PFASs in these applications (UNEP, 2019c). As such, fluorinated alternatives to PFOS, PFOA and PFHxS in these uses are readily available, technically and economically feasible, and have been widely implemented already.

Information related to PFOS

The main PFOS-related compounds used for the surface treatment of textiles and carpets were the acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) (UNEP, 2011). A restriction of use of PFOS and its related compounds in textiles was introduced after PFOS, its salts were listed in the Annex B of the Stockholm Convention. As in other areas, PFOS and its related compounds are replaced by short-chain fluorinated compounds and other fluorine-free alternatives.

Information related to PFOA

Industry associations noted that especially in the field of professional, technical and protective textiles and other advanced textiles, alternatives which meet the high performance demand by legal requirements and by customers are currently not available (UNEP, 2019c). Some examples are shown as follows.

The textile industry reported that the C8 PFASs chemistry is able to fulfill the high requirements related to repellency of dangerous liquids and dusts while having a minor detrimental effect on flame retardations. This preferable combination of the two effects cannot be obtained by C6 PFAS-based products (TM, 2016; VTB-SWT, 2016). Moreover, it was stated that technical protective textiles protect workers from being contaminated by liquids or dangerous substances (e.g., infectious liquids). Moreover, serious health issues might occur in case of neglected re-impregnation, which is required due to a decrease in protection performance over time (TM, 2016; VTB-SWT, 2016).

The personal protective equipment used by firefighters, also called “turnout gear”, is manufactured from textiles that are made from fluoropolymers (one group of PFASs) or extensively treated by PFASs in the form of side-chain fluorinated polymers (Henry et al., 2018). These chemicals are used in firefighter textiles primarily to impart durable water- and oil- resistance (Holmquist et al., 2016). This resistance prevents the turnout gear from becoming water soaked and adding significant weight to the turnout gear each firefighter must carry during a fire event. These PFASs include fluoropolymer materials such as PTFE used as a moisture barrier in the inner layers of turnout gear. Typically, a cloth thermal liner surrounds the PTFE layer, and it is not usually PFAS-treated. There is always an outer shell (on both jacket and pants) that contains additional PFASs in the form of side-chain fluorinated polymers built into the fabric or additional PFAS treatments applied after the fabric is woven.

Based on the above-mentioned information, PFOA, its salts and related compounds are allowed in textiles for oil-and water-repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety in Annex A to the Stockholm Convention (UNEP, 2019b). In the EU, PFOA, its salts and PFOA-related compounds are allowed in textiles for worker protection from dangerous liquids until 4 July 2023 (European Commission, 2018).

For carpets, leather, apparel, upholstery, and non-technical textiles used in outdoor applications (e.g., awnings and outdoor furnishing, camping gear), alternatives are available and an exemption is not justified.

Information related to PFHxS

Historically, 3M used PFHxS-related compounds in some of its aftermarket (post-production) carpet protection products (Olsen et al., 2005). In a formulation of ScotchGard™ Carpet Protector, produced by 3M (US), but discontinued in 1999, PFHxS-related compounds were major constituents that were intentionally added to the carpet protector (Beesoon et al., 2012).

It was reported that water-proof textile finishes based on PFHxS-related compounds such as CAS No: 68259-15-4 (tridecafluoro-N-methylhexanesulfonamide), CAS No: 68555-75-9 (tridecafluoro-N-(2-hydroxyethyl)-N-methylhexanesulfonamide), and CAS No: 67584-57-0, (2-[methyl[(tridecafluorohexyl) sulfonyl]amino]ethyl acrylate)) have been developed (Hengxin, 2018; J. Huang et al., 2013), as alternatives to PFOS-based compounds (J. Huang et al., 2013).

3.8.2 Availability of alternatives

Alternatives for use in carpets, leather, apparel, upholstery, and non-technical textiles include fluorinated and fluorine-free chemical alternatives, as well as non-chemical alternatives.

Non-chemical alternatives

Considering the information provided by IPEN and ACAT (2018), bioinspired 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 (Wong et al., 2011).

Moreover, carpets using stain-free fibers are stain-resistant without coating (Glüge et al., 2022). For example, the yarn producer, Aquafil, offers stain-free fibers based on the nylon-6 fiber “Econyl StayClean”.[31] This fiber is made from nylon waste that was depolymerised and recycled (Glüge et al., 2022; Nordic Council of Ministers, 2017). No PFASs are added to the recycled fiber. Another yarn manufacturer, Universal Fibers, describes the use of a “sulfonated nylon copolymer” for PFAS-free stain protection (Glüge et al., 2022; Vallette et al., 2017).

Fluorine-free chemical alternatives

Most prominent fluorine-free alternatives are reported to be high molecular weight polydimethylsiloxanes (PDMS), mixtures of silicones and stearamide methyl pryriden chloride (sometimes in combination with carbamide (urea) and melamine resins), waxes and paraffin (usually consisting of modified melamine-based resins), and dendrimers that are being developed to imitate the ability of the lotus blossom to repel water. Other alternatives to provide similar

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[31] Econyl. Econyl Stay Clean http://www.econyl.com/stay-clean/.

water-repellency are available and include textile surface treatment applications based on acrylate, methacrylate adipate and urethane polymers (UNEP, 2019c; VTB-SWT, 2016).

There is a range of fluorocarbon-free, water-repellent commercial finishing agents for textiles on the market, such as BIONIC-FINISH®ECO and RUCO-DRY® ECO marketed by Rudolf Chemie Ltd., Geretsried/ Germany; and ecorepel® marketed by SchoellerTechologies AG, Sevelen/Switzerland (UNEP, 2019c). More examples are listed below.

- Rudolf Chemie, BIONIC-FINISH®ECO and RUCO®-DRY ECO: https://www.rudolf.de/en/technology/bionic-finish-eco/bionic-finishr-eco-product-selection/
- Schoeller, ecorepel®: https://www.schoeller-textiles.com/en/technologies/ecorepel
- Daikin, PFC-free water repellent: https://www.daikinchem.de/products-and-performance/unidyne-xf-pfc-free-water-repellencyNicca: https://www.niccausa.com/fluorine-free-water-repellent/
- Chemours : https://www.teflon.com/en/products/repellents?_ga=2.203631952.1143916487.1595398495-1030182489.1585293077
- Archroma: https://www.archroma.com/solutions/protection-workwear
- Maflon: https://www.maflon.com/
- OrganoTex from OrganoClick: https://organotex.com/
- AquaSil™ Tex from OrganoClick : https://organoclick.com/eng-oc-aquasil-tex-hydrofoberingsmedel-for-nonwoven-och-teknisk-textil/

The BIONIC-FINISH®ECO introduced by Rudolph Group is a fluorocarbon-free, water-repellent treatment for textiles.[32] BIONIC-FINISH®ECO is composed of a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers (UNEP, 2016b).[33] The exact identity of the chemical has not been provided by the company.

There is a lack of information on the hazards associated with durable water-repellent hyper-branched polymers, or dendrimers.

Furthermore, 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 (Shabanian et al., 2020).

Short-chain fluorinated alternatives

Short-chain ("C6") fluorotelomer-based side-chain fluorinated polymers, such as high molecular-weight acrylic polymers, which contain 6:2 fluorotelomer functional groups on the side chain to provide repellent performance(UNEP, 2019c). Examples of the suppliers who offer these products commercially are:

- Daikin: https://www.daikinchem.de/products-and-performance/water-oil-repellency;
- Asahi: https://www.agc-chemicals.com/jp/en/fluorine/products/detail/use/index.html?pCode=JP-EN-F001;
- Chemours: https://www.teflon.com/en/products/repellents?_ga=2.203631952.1143916487.1595398495-1030182489.1585293077;
- Archroma: https://www.archroma.com/solutions/protection-workwear;
- Nicca: http://www.niccausa.com/product_data_sheet/ni-805/;
- Rudolf Chemie: http://www.rudolf.de/en/products/textile-auxiliaries/finishing/;
- Maflon: Hexafor from Maflon: https://www.maflon.com/;
- Thetaguard and Thetapel from ICT: http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/;
- OrganoTex: http://organoclick.com/products/performance-textiles-nonwoven.

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[32] https://www.rudolf.de/en/technology/bionic-finish-eco/.

[33] There are still data gaps but some data are available in UNEP/POPS/POPRC.8/INF/17/Rev.1.

Short-chain ("C4") perfluoroalkane sulfonyl fluoride-based side-chain fluorinated polymers, such as high molecular-weight acrylic polymers containing perfluorobutane sulfonyl functional groups on the side chains to provide repellent performance (UNEP, 2019c). An example of suppliers who offer these products commercially is 3M (Scotchgard™ with C4 technology): https://www.scotchgard.com/3M/en_US/scotchgard/built-in-protection/.

Perfluoropolyether based polymer

Solvay has developed a product named Fluorolink® P56[34], 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.

3.8.3 Suitability of alternatives

Fluorine-free alternatives

Fluorine-free alternatives were reported to be unable to repel oil, which might limit their potential for substitution in textile applications that require repellence towards non-polar liquids, such as medical textiles in surgical gowns and drapes, in operating rooms, doctor and nurse apparel and for laboratory personnel that are required to be protected from blood and body fluids as carriers for infections and viruses (Schellenberger et al., 2018). This is in line with information provided in the assessment of alternatives to PFOS that was updated in 2018 (UNEP/POPS/POPRC.14/INF/8). However, in the same study, it was shown experimentally that some fluorine-free and even biodegradable durable water repellents could provide some degree of stain repellence (Schellenberger et al., 2018).

Available alternatives for grease- and dirt-repellent agents are limited (UNEP, 2018a). However, a new study reported that fabricating oil-repellent textile finishes using PDMS finish 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 (Shabanian et al., 2020).

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. The main ingredient in most products is paraffin oil/wax (mixtures of long-chain alkanes), which is considered harmless in pure form. Some products also contain isocyanates, dipropylene glycol, and metal salts, which may be harmful (UNEP, 2017a).

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. However, certain siloxanes, D4, D5 and D6, are persistent and widespread in the environment. Mostly, they are detected in urban areas and in the aquatic environment. High levels have been found in the livers of fish, which were caught close to outlets of sewage treatment plants. 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. In Canada, it is concluded that D4 is entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity (see the PFOA RME). In the EU, D4, D5 and D6 are identified as Substances of Very High Concern (SVHCs) under the REACH regulation based on their PBT and/or vPvB properties. Moreover, the experts in the MSC rated D4 as persistent, bioaccumulative (it accumulates in the food chain), and toxic (PBT), but they assigned only persistent and bioaccumulative (vPvB) properties to D5 and D6. The ecological risks arising from industrial uses of cyclic siloxanes in Australia have recently been assessed by National Industrial Chemicals Notification and Assessment in Australia (NICNAS, 2018); this assessment concluded that D4, D5 and D6 are persistent in the air and sediment compartments, and that D4 and D5 can bioconcentrate in fish. Although a small fraction of cyclic siloxanes in use is emitted to the aquatic environment, these emissions are not currently considered to pose a direct risk to aquatic life in Australia (NICNAS, 2018).

There are no data on the health properties of the active substances and other components of dendrimer-based repellents, but producers of commercial products have provided health data in the material safety data sheets and made some proposals for classification of the product. According to information from producers, these products

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[34] https://www.solvay.com/en/product/fluorolink-p-56.

should not be classified as harmful to the environment, but it is not possible to evaluate these statements on the basis of available information. The compositions of the products were not specified sufficiently for an assessment. Some of the products include unknown siloxanes, cationic polymers, isocyanates, or irritating organic acids. In summary, the available information for this group of chemicals is insufficient for an assessment of the possible health effects of the impregnation agents.

Short-chain fluorinated alternatives

Shor-chain side-chain fluorinated polymers showed excellent water repellence and durability (Schellenberger et al., 2018; UNEP, 2019c). A strong decline in oil repellence and durability with perfluoroalkyl chain length was shown for short-chain side-chain fluorinated polymers (Schellenberger et al., 2018).

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 (Brendel et al., 2018; Ritscher et al., 2018; UNEP, 2018a).

6:2 FT-based side-chain fluorinated polymers can transform to PFHxA and thus are PFHxA-related compounds. 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. The final EU-wide restriction of PFHxA and PFHxA-related compounds is being formulated.

PFBS is persistent (ECHA, 2019c). ECHA committee agrees PFBS is a substance of very high concern. Animal studies support the identification of thyroid, developmental, and kidney endpoints as potential health effects following repeated exposures to PFBS salt in utero and/or during adulthood (US EPA, 2021).

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 in order to meet high safety standards; this will result in additional emissions of PFASs due to the larger amounts of used chemicals compared to the C8-chemistry (VTB-SWT, 2016). In this context, it was mentioned that 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 (Euratex, 2016; UNEP, 2018a).

3.8.4 Implementation of alternatives

Generally speaking, the alternatives are available in the market for casual, outdoor and sports activities. Textile producers also become aware of the importance of fluorine-free alternatives. According to a survey carried out by the Association of the German Sporting Goods Industry (BSI) representing the interests of German sport article manufacturers, one of the most important performance characteristics needed for fibers in the coming 5-10 years is PFC-free, together with other characteristics such as biodegradability and ability to measure the materials footprint (BSI, 2021).

3.8.5 Conclusion

Short-chain fluorinated alternatives, fluorine-free alternatives and non-chemical alternatives are available on the market and have been widely used. It is noted that in many cases, the specific identities of some of the developed alternatives have not been disclosed due to trade secrets.

Short-chain fluorinated alternatives show increasing concerns due to their potential toxicity, persistence, mobility and difficulty to be treated. The health and ecological risks of some fluorine-free alternatives also remain unclear.

3.9 Invasive and implantable medical device

3.9.1 Introduction and background

Information related to PFOS

Not relevant

Information related to PFOA

PTFE is a fluoropolymer and, over the years, has proven itself a useful coating used in almost all industries. In the medical field, PTFE is commonly used to coat surgical instruments as well as medical components such as catheters, guidewires, and implantable medical devices. As stated above, ammonium or sodium perfluorooctanoate (APFO and NaPFO) has been used as processing aids in the production of PTFE.

Certain PTFE-containing medical devices, including invasive and implantable devices, might contain PFOA residual/impurity from the manufacturing process of PTFE. Information submitted to ECHA (2015a) indicates that amounts of PFOA and PFOA-related compounds in the final products are estimated to be extremely low. In implantable devices, one manufacturer previously estimated that the total amount of PFOA present in all devices put on the market in the EU during the period 2018–2025 without the restriction would amount to 20 g (it is however unclear if this amount includes only PFOA or also PFOA-related compounds) (UNEP, 2018a). This was extrapolated to 100g total worldwide by the industry assuming that the EU occupies 20% of the market assuming similar usage in other non-EU geographies (MedTech Europe, 2018).

Use of PFOA, its salts and/or PFOA-related compounds for invasive and implantable medical devices is exempted in Annex A of the Stockholm Convention.[35] In EU, the same is exempted until 4 July 2025 (European Commission, 2020a).

Information related to PFHxS

Not relevant

3.9.2 Availability of alternatives

A number of PFOA-free PTFE medical devices are now available in the market, including invasive and implantable devices.

- Boyd Coatings: https://www.hydromer.com/medical-healthcare/;
- Surface Solution: http://www.surfacesolutionsgroup.com/coatings/;
- Merit Medical: https://meritoem.com/documents/#product-brochures;
- Tegra Medical: https://www.tegramedical.com/product-category/coated-wire/zero-pfoa-green-ptfe-wire/;
- Wytech: https://wytech.com/wire-components/;
- Precision Coating: https://www.precisioncoating.com/medical-coating-services/ptfe-medical-device-coated-applications.

PTFE-free coatings for invasive and implantable medical devices are also available:

- Rho-coat⍰⍰: https://www.cambusmedical.com/rho-coat/.

More information can be found in section 3.10 Manufacture of fluoropolymers.

3.9.3 Suitability of alternatives

The main issue for alternatives was the resistance to saline solutions, but also some low-friction technical issues may still exist (Nesbitt, 2017). The second generation of PFOA-free PTFE products have resolved the bonding issue by changing manufacturing processes related to surface preparation, coating viscosity and solids content, humidity, airborne particulates, spray pressure, temperature, electrostatic voltage, spray pattern, coating line humidity and line speed, among others (Nesbitt, 2017; UNEP, 2018a). Nesbitt (2017) also noted that processes following these altered practices had resulted in zero Class 1 FDA recalls (UNEP, 2018a).

The main societal effects related to the continued use of PFOA-based PTFE or a restriction on PFOA-based PTFE for medical devices relates to the availability of devices for use in the healthcare sector (MedTech Europe, 2018). MedTech Europe (2018) and Euromed (2015), both highlighted that regulations within the healthcare sector were stringent, and alteration of substances within devices might lead to retesting, including potential clinical trials. This

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[35] Decision SC-9/12.

delays the transition process to alternative products. However, alternatives that do not use or contain PFOA have already passed medical regulations in at least some geographies and are commercially available.

Following the recall of two OEM's guidewire products, some in the medical device industry expressed concern and cast aspersions indiscriminately towards PFOA-free PTFE. The medical PTFE coating industry suffered a loss of confidence. In fact, some manufacturers of medical guidewires considered coating their products with something other than PTFE.

More information can be found in section 3.10 Manufacture of fluoropolymers.

3.9.4 Implementation of alternatives

Limited information is available on the implementation of alternatives.

Canada (2018) stated that the main use of PFOA within medical devices is as a process aid in the emulsion polymerization of PTFE; however, Canada states that PFOA-free PTFE products are now available on the market. IPEN and ACAT (2018) also commented that PFOA-free PTFE products had been commercialized and are available on the market within the USA.

In the EU public consultation, industry stakeholders indicated that substitution is ongoing but was a lengthy process given the complexity of the supply chains and the certification processes (ECHA, 2015b). In the specific case of implantable medical devices, one manufacturer requested a transition period of 15 years (ECHA, 2015b). This request was supported by a socio-economic analysis comparing the costs of not using the devices with the avoided emissions. ECHA found that, even if all costs were not clearly justified and might include some overestimation, this socio-economic analysis demonstrated that a shorter transition period than requested would not be cost-effective (ECHA, 2015b).

3.9.5 Conclusion

PFOA-free medical devices are available in the market, maybe not for all products. Due to the complexity of the supply chains and the certification processes, a long period is needed to ensure a cost-effective transition to alternatives.

3.10 Manufacture of fluoropolymers

3.10.1 Introduction and background

Information related to PFOS

Not relevant.

Information related to PFOA

Fluoropolymer producers have used APFO and NaPFO as processing aids in the (emulsion) polymerization processes of PTFE, FEP, PFA and certain fluoroelastomers. In addition, ammonium perfluorononanoate (APFN) was applied in the emulsion polymerization of PVDF (Prevedouros et al., 2006; UNEP, 2017a).

PFOA, its salts and related substances are exempted in Annex A (UNEP, 2019b)to the Stockholm Convention for the manufacturing of fluoropolymers in the following application:

- PTFE and 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 $PM_{2.5}$ particulates;
- FEP for the production of high-voltage electrical wire and cables for power transmission;
- Fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors.

On 15 June 2020, the EU published Regulation (EU) 2020/784 that amends current EU legislation restricting the use of POPs. The regulation sets a maximum concentration of 25 ppb for PFOA and any of its salts, and a maximum concentration of 1000 ppb for a combination of PFOA-related compounds. Time-limited exemptions exist until 4 July

2023 for the manufacture of PTFE and PVDF for specific applications which are accordingly exempted in Annex A[36] to the Stockholm Convention (European Commission, 2020a).

PTFE has excellent dielectric properties, specifically low group velocity dispersion (Mishra & Yagc, 2008) which makes it widely used as an insulator in connector assemblies and cables, and in printed circuit boards used at microwave frequencies. Because of its extreme non-reactivity and high temperature rating, it is used as chemically-inert liners. The surface of PTFE material is smooth and slippery which allow improved flow of highly viscous liquids. PTFE is also used in non-stick cooking ware, surfactant, oil and water repellent in textile, carpet and upholstery, bearings, gears, slide plates, seals, gaskets, bushings due to its low friction, in medical applications such as for cardiovascular grafts, heart patches, ligaments for knees due to highly inert and nontoxic properties and as membrane for special filters, analytical instruments, and in fuel cells (Drobny, 2008).

PVDF exhibits excellent mechanical properties, and when compared with perfluorinated polymers, it has much higher resistance to elastic deformation under load (creep), much longer life in repeated flexing, and improved fatigue resistance. PVDF exhibits excellent resistance to most inorganic acids, weak bases, and halogens, oxidizing agents even at elevated temperatures, and to aliphatic, aromatic, and chlorinated solvents. Strong bases, amines, esters, and ketones cause its swelling, softening, and dissolution, depending on conditions (Drobny, 2008).

FEP has outstanding electrical properties, practically identical to those of PTFE within its recommended service temperature. Its volume resistivity remains unchanged even after prolonged soaking in water. FEP resists most chemicals and solvents, even at elevated temperatures and pressures. Acid and bases are not absorbed at 200°C (392°F) and exposures of 1 year.[37] Organic solvents are absorbed only a little, typically 1% or less, even at elevated temperatures and long exposure times. The absorption does not affect the resin and its properties and is completely reversible. The only chemicals reacting with FEP resins are fluorine, molten alkali metal, and molten sodium hydroxide.

Information related to PFHxS

Not relevant.

3.10.2 Availability of alternatives

Process/technology alternatives

Various fluoropolymer manufacturers are exploring and have patented a number of PFAS-free aqueous emulsion polymerization processes (Hintzer & Schwertfeger, 2014; UNEP, 2017a). These include: (1) emulsifier-free polymerization of amorphous standard co/terpolymers comprising tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and vinylidene fluoride (VDF); and (2) development of so-called “surfmers” (which are surfactants that can also act as monomers in the polymerization action) for specific classes of fluoropolymers.

Asahi Glass developed aqueous fluoropolymer dispersions for producing an aqueous dispersion (latex) of fluorinated polymer from a monomer to emulsion polymerization in the presence of hydrocarbon anionic emulsifier having a critical micelle concentration of at most 0.09 mass % in an aqueous medium (UNEP, 2017a). As the monomer, a fluorinated monomer and as the case requires, another monomer (copolymer) is used. The composition of the monomer is determined depending upon the type of fluorinated polymer to be produced.[38]

3M developed aqueous fluoropolymer dispersions whereby the dispersion was free of fluorinated surfactant having a molecular weight of less than 1000 g/mol or contains the fluorinated surfactant having a molecular weight of less than 1000 g/mol in an amount of not more than 0.025% by weight based on the total weight of solids in the dispersion.[39] In this method, high molecule weight fluorinated surfactant (equal or more than 1000 g/mol) is used instead of PFOA and its salts. Examples of high molecular weight anionic and fluorinated surfactants comprise

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[36] Decision SC-9/12.

[37] Teflon™ FEP information bulletin, https://www.teflon.com/en/-/media/files/teflon/teflon-fep-film-tech-bulletin.pdf.

[38] US patent application Pub. No.: US 2016/0108225 A1 for assignee of Asahi Glass Company Limited.

[39] United States patent application Pub. No.: US 20040186219A1.

polymeric surfactants and include perfluoropolyether having one or more anionic groups, such as carboxylic acid groups or salts thereof examples of perfluoropolyether surfactants.[40]

Non-fluorinated emulsifiers/surfactants as alternatives

Non-fluorinated emulsifiers for VDF-containing polymers such as polyvinyl/acrylic acids, derivatives of polyethylene/propylene glycols, alkylphosphate esters, vinyl acids, siloxanes, silanes, long-chain hydrocarbon acids, and derivatives of sugars are developed (Hintzer & Schwertfeger, 2014; UNEP, 2017a).

Companies have developed fluoro-polymerization processes which do not use fluorinated surfactants. DuPont developed an aqueous polymerization of perfluoromonomer using hydrocarbon surfactants. This process does not use PFASs as processing aids. This method can be used to produce PTFE and PVDF.[41]

Arkema developed production process of aqueous fluoropolymer dispersions using non-ionic nonfluorinated emulsifier (UNEP, 2017a). The emulsifiers used in the invention are those that contain segments of polyethylene glycol, polypropylene glycol, and/or polytetamethylene glycol. The process can produce a wide range of fluoropolymer: the fluoropolymer may be a homo- or copolymer and the dispersion may contain a mixture of different fluoropolymers.[42]

Moreover, method of polymerization uses one or more alkyl sulfate surfactants was developed in aqueous fluoropolymer dispersions in particular to emulsion polymerization method for producing fluoropolymer latex.[43]

Fluorinated alternatives

The companies Arkema, Asahi, BASF Corporation, Clariant, Daikin, 3M/Dyneon, DuPont and Solvay Solexis agreed under the US EPA 2010/15 Stewardship program to manufacture fluoropolymers without using PFOA (CAS No. 335-67-1) as a processing aid by the end of 2015 (UNEP, 2018a). Therefore, there has been a shift to other PFASs (Glüge et al., 2020).

Most producers have developed their own alternatives. Commercialized fluorinated alternatives are functionalized PFPEs including amongst others, (I)ADONA from 3M/Dyneon ($CF_3OCF_2CF_2CF_2OCHFCF_2COO^-NH_4^+$; CAS No: 958445-44-8; (Gordon, 2011)); (II) GenX or C3 Dimer salt[44] from DuPont ($CF_3CF_2CF_2OCF(CF_3)COO^-NH_4^+$; CAS No: 62037-80-3; (UNEP, 2017a)); (III) cyclic or polymeric functionalized PFPEs from Solvay (Marchionni et al., 2010; Pieri et al., 2011; Spada & Kent, 2011); (IV) EEA-NH_4 from Asahi ($C_2F_5OC_2F_4OCF_2COO^-NH_4^+$; CAS No: 908020-52-0; (EFSA, 2011b); and (V) $CF_3OCF(CF_3)CF_2OCF(CF_3)COO^-NH_4^+$ from Daikin (Hintzer & Schwertfeger, 2014).

C3 Dimer salt (GenX), ADONA and EEA-NH_4 are applied as alternatives for the use of PFOA as polymerization processing agent where it is applied as emulsifying agent enabling reactants from the aqueous phase and reactants from the hydrophobic phase to get into contact in an emulsion and react with each other (ECHA, 2015a).

Several major Chinese fluoropolymer producers have also developed alternative substances to replace PFOA in their fluoropolymer (or fluoroelastomer) production processes. These possible alternative substances remain to be PFASs and can be divided into two sub-groups(UNEP, 2017a): (1) shorter-chain homologues of PFOA-related compounds (e.g., 6:2 fluorotelomer carboxylic acid (FTCA) (Xu et al., 2011) and perfluorobutanesulfonyl fluoride (PBSF)-based substances (Lu et al., 2011), and (2) perfluoroalkylether acids (Lu et al., 2011; H. Wang et al., 2015; Xie et al., 2010; J. Zhang et al., 2012)). Examples of such perfluoroalkylether acids include $CF_3O(CF_2CF(CF_3)O)(CF_2OO)(C(CF_3)FO)COO^-$ (Xie et al., 2010; J. Zhang et al., 2012).

3.10.3 Suitability of alternatives

Three PFOA-alternatives with ether moieties (GenX, ADONA and EEA-NH_4) were assessed in the EU restriction process (ECHA, 2015a).

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[40] United States patent application Pub. No.: US 20040186219A1.

[41] US patent application Pub. No.: US 2012/0116003 A1 for assignee of E.I. Du Pont Nemours and Company.

[42] United States Patent No. US 9,068,071 B2 for assignee of Arkema Inc.

[43] US Patent application Pub. No.: US 2014/0179868 A1.

[44] IUPAC name: Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate; CAS No: 62037-80-3.

GenX is listed as a Substances of Very High Concern (SVHC) under ECHA. US EPA published in 2021 an updated Human Health Toxicity Assessments for GenX Chemicals which confirmed health effects including on the liver, kidneys, the immune system, development of offspring, and an association with cancer based on animal studies following oral exposure. [45]The assessment resulted in the final chronic oral reference dose for GenX chemicals of 0.000003 mg/kg-day which is lower than that in the 2018 draft (0.00008 mg/kg-day) based on new studies. To be mentioned that the chronic oral reference dose for GenX is even lower than that of PFOA and PFOS (0.000003 mg/kg-day for GenX versus 0.00002 mg/kg-day for PFOA and PFOS) although EPA is currently re-evaluating toxicity information for PFOA and PFOS and the oral reference doses of PFOA and PFOS are subject to change.

Toxicokinetic data of C3 Dimer salt GenX indicate little or no metabolism, but rapid excretion in some species. It is presumably cleared non-metabolized within 2–7 days (mouse), 10–11 h (monkey) and 4–48 h (rat). C3 Dimer salt is classified as skin irritating and eye damaging. Moreover, repeated administration resulted in liver enlargement and hepatocyte hypertrophy as well as liver cell necrosis at 0.5 mg/kg/day in male mice. With respect to carcinogenicity, a two-year rat study gave tumors at higher doses (≥50 mg/kg/day). With regards to environmental risks (data were taken from the registration dossier) related to C3 Dimer salt, it was concluded that the substance is probably not acutely toxic (LC/EC50>100 mg/L) or chronically toxic (NOEC>1 mg/L) to aquatic organisms. Regarding all available information, a full PBT assessment including assessment of the criteria persistence, bioaccumulation and toxicity according to the EU chemicals legislation (for guidance see (ECHA, 2017)) cannot be performed. However, the registrant acknowledges in the chemical safety report (CSR) that the C3 Dimer salt fulfils the persistence (P) and the toxicity (T) criteria based on specific target organ toxicity after repeated exposure (STOT RE 2) (UNEP, 2017a).

With respect to ADONA, it turned out that the substance is persistent (UNEP, 2017a). No data related to carcinogenicity were available. Concerning environmental risks related to ADONA using data from the REACH registration dossier, it was concluded that the substance is probably not acutely toxic (LC/EC50>100 mg/L) or chronically toxic (NOEC>1 mg/L) to aquatic organisms. Regarding all available information, a full PBT assessment cannot be performed. Based on the data for environmental toxicity, the substance does not fulfil the T criterion. The registration dossier lacks toxicological information relevant to humans. Based on a document from the European Food Safety Authority from 2011, 3M reported that the elimination half-life of ADONA was between 12 and 34 days from the bodies of three workers, while it takes about four years in humans to clear half of the PFOA (EFSA, 2011a; The Intercept, 2016; Z. Wang et al., 2015).

EEA-NH_4 is considered persistent (UNEP, 2017a; Z. Wang et al., 2015). Provided data is not sufficient to conclude on bioaccumulation (B). Regarding environmental risks (data were taken from the registration dossier) related to EEA-NH_4 no acute toxicity (LC/EC50>100 mg/L) to aquatic organisms was determined. On the basis of all available information, a full PBT assessment cannot be performed. Based on the data for environmental toxicity, the substance does not fulfil the T criterion. Toxicity data on human health were provided in the registration. The registrant points out that the substance is classified as toxic for reproduction category 2. Thus, the substance fulfils the T-criterion of Annex XIII and it remains a PBT suspect (ECHA, 2015a).

Serum elimination half-lives of GenX (in rats and mice) and ADONA (in rats and humans), were reported (ECHA, 2014; EFSA, 2011a). Provided elimination half-lives were shorter compared to the one for PFOA, but it was considered impossible to draw a conclusion on the bioaccumulation potential of these two compounds due to the fact that no quantitative serum elimination half-life threshold is defined in regulations as a criterion for bioaccumulation, the interspecies variation has not been elucidated and the studies were often conducted with different dosing methods (e.g., oral vs. intravenous, single vs. repeated dose). As a consequence, it is reported that serum elimination half-lives between substances cannot be directly compared (Z. Wang et al., 2015).

Moreover, some short-chain PFASs alternatives, such as ADONA and F-53B, are stable in the total oxidizable precursor (TOP) assay and represent terminal products that are likely as persistent as historically used PFASs (C. Zhang et al., 2019). In other words, ADONA and F-53B transferred to stable terminal products after being treated with a strong oxidizer (persulfate) and were not disintegrated. This again indicates the persistence of ADONA and F-53B in the environment. Sun et al. (2016) also found that removal of GenX contained in raw drinking water was negligible in a drinking water treatment plant after coagulation, ozonation, biofiltration, and disinfection.

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[45] https://www.epa.gov/chemical-research/human-health-toxicity-assessments-genx-chemicals.

According to ECHA, most of the stakeholders stated that there are no technical differences between fluoropolymers produced with PFASs alternatives and fluoropolymers produced with PFOA (or stakeholders do not know whether there are any differences) (ECHA, 2015a). Fluoropolymer manufacturers stated during the EU public consultation that the production costs varied from none to 20% increase when applying the alternatives (ECHA, 2015a). The increase is a result of higher costs of the alternatives as well as higher amounts of the alternatives needed to manufacture one unit of fluoropolymer. Some downstream users mentioned that no cost effects occurred after the substitution from PFOA to alternatives.

3.10.4 Implementation of alternatives

Fluoropolymer manufacturers are exploring novel processes to eliminate the use of PFASs in aqueous emulsion polymerization. For the production of PVDF, processes with fluorine-free emulsifiers have been implemented by multiple manufacturers (Glüge et al., 2022).[46] [47] Fluorine-free emulsifier-based processes for manufacturing other fluoropolymers, including fine-powder and dispersion PTFE, have been patented, but are not yet implemented (Glüge et al., 2022).

PFOA-free PTFE is available in the market.[48] Zero-PFOA FEP is also available in the market.[49] However, no information is available on the exact implementation of individual alternatives, apart from the general information available above.

The current progress of replacing PFOA by Chinese fluoropolymer and fluoroelastomer producers remains unclear, except that Zhonghao Chenguang reported having selected and industrialized a perfluoroalkylether acid-based alternative to PFOA for its production processes of PTFE and fluoroelastomers since 2007 (Xie et al., 2009).

3.10.5 Conclusion

PFAS alternatives, such as GenX, ADONA and EEA-NH_4 are still persistent. Provided data was not sufficient to conclude on their bioaccumulation (B). Some PFASs alternatives such as GenX have been recognized as being similarly problematic as PFOA. Assessment and regulations are necessary to evaluate and regulate the life-cycles of these alternatives. Information related to the composition and implementation of other alternatives in the fluoropolymer production needs to be made available.

3.11 Other applications: Paper and packaging

3.11.1 Introduction and background

PFASs have been applied to paper since the early 1960s (Posner, 2013). These chemicals were used in the paper, food packaging and commercial packaging where these PFASs confer mainly fat, but also stain and water repellence properties (OECD, 2020).

In food packaging industry, the applications particularly target fatty foods, especially those intended to be heated in packaging or stored for an extended period. Examples include fast food-contact paper such as for French fries and hamburgers, microwave popcorn bags, baking paper, baking cups and moulds, sandwich and butter paper, chocolate paper, and paper for dry foods and pet foods.

A chemical barrier for food contact materials against grease and water is achieved either by the addition of chemicals to the pulp during paper production (internal sizing) or as a surface treatment to the paper (external sizing) (OECD, 2020).

Several companies indicated that they proactively took the decision to avoid the use of PFASs entirely for paper and board food contact materials and to look for alternatives to PFASs (OECD, 2020). US FDA currently does not allow

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[46] Kynar500FSF. Fluorosurfactant Free Kynar® PVDF Resin https://www.kynar500.com/en/product-information/fluorosurfactant-free/.

[47] Solvay. Solvay Launches Non-Fluorosurfactant Technologies in the U.S. https://www.solvay.com/en/press-release/solvay-launches-non-fluorosurfactant-technologies-in-us.

[48] https://www.greblon.com/en/technology/ptfe-ceramics.

[49] https://www.precisioncoating.com/medical-coating-services/medical-fep/.

long-chain PFASs in food contact materials applications; they removed the last legacy PFOA-related substances from “21 CFR 176.170-Components of paper and paperboard in contact with aqueous and fatty foods” in 2016 (see 81 Fed. Reg. 5–8).

Information related to PFOS

Paper protection by PFOS-related compounds has been achieved by using one of the following (UNEP, 2011):

(a) Mono-, di- or triphosphate esters of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE);
(b) N-Methyl perfluorooctane sulfonamidoethanol acrylate polymers.

Before 2000, about 32% of the total use of PFOS in the EU was for paper coating; the use of PFOS for this purpose was prohibited in 2006 (UNEP, 2011).

According to COP 9, SC-9/4, as there were no longer any Parties registered for specific exemptions for the production and use of PFOS, its salts and PFOFS for paper and packaging, no new registrations may be made with respect to them. Parties to the Convention have eliminated the exemptions for PFOS, its salts and related compounds in paper and packaging.

Information related to PFOA

Uses of non-polymeric PFOA-related compounds are known to provide a water, grease and soil protection as surfactants (wetting agents) in the paper and packaging industry. Parties to the Stockholm Convention do not exempt the use of PFOA, its salts and PFOA-related compounds in food contact materials.

Information related to PFHxS

According to the Norwegian Environment Agency (Norwegian Environment Agency, 2018), PHxSF may be present in packaging. There is data indicating that food packaging materials constitute a source of human PFHxS exposure(ECHA, 2020). However, there is only limited information regarding measured PFHxS concentration in food packages.

3.11.2 Availability of alternatives

Alternatives in paper and board can be divided into short-chain fluorinated alternatives, fluorine-free chemical alternatives, and fluorine-free physical alternatives.

Fluorine-free chemical alternatives

Biopolymers or vegetable-oil based bio-waxes

Solenis produces a number of barrier formulations which are marketed under the trade name TopScreen™. TopScreen™ formulations are used in food contact materials and are either water-based synthetic biopolymers or vegetable-oil based biowaxes (OECD, 2020). Both the biowax and synthetic polymer products confer grease- and water-repellence properties, although the synthetic formulation can give better water resistance for the same application volumes. In addition, TopScreen™ formulations confer water vapour moisture (WVM) resistance. This is particularly important for fast food packaging such as hamburgers to prevent water vapour from escaping from the hamburger bun, which would result in a dry bun (OECD, 2020).

Internal sizing agents such as alkyl ketene dimer and styrene acrylic emulsion can be used in conjunction with TopScreen™ products acting as a first water resistant barrier, onto which formulations such as TopScreen™ can be applied (OECD, 2020). The biowax formulations can be used for candy twists, fast food wrapping, bread bags, meat and cheese wraps, and corrugated board for fruit, vegetables and frozen fish (OECD, 2020). TopScreen™ grease-proof barriers and TopScreen™ water barriers are suitable for packaging applications that require specific water/moisture barrier properties or grease resistance for polyethylene-free cups, paper and linerboard used for fresh and refrigerated/frozen foods, animal feed/pet food and greasy/oily foods (OECD, 2020).

Silicone

Silicone is used to an increasing extent in food contact materials (OECD, 2020). Examples are baking moulds, kitchen utensils, teats and surface coating on baking and food paper. In bakeware silicone products can be made flexible and yet still able to retain their shape (OECD, 2020). Silicone is thermostable and chemically resistant. Paper for food contact can be coated with silicone in order to ensure the paper can be released from the food, for example muffin cases for home baking (NFI, 2017).

Other fluorine-free chemicals

Other fluorine-free coatings that are used to improve the grease resistance of paper and board include aqueous dispersions of copolymers (styrene and butadiene), aqueous dispersions of waxes (other than that of TopScreen^{TM}), starch, clay, stone (calcium carbonate mixed with a resin), chitosan or water soluble hydroxyethylcellulose (OECD, 2020).

Additional sizing agents include talc-filled water-based polyacrylate, pigment-filled hydrophobic monomer dispersions, polyvinyl alcohols and montmorillonite/polyethylene-coatings and modified wheat protein (OECD, 2020).

Fluorine-free physical alternatives

There are three groups for physical barrier of non-fluorine alternatives: cellulose based paper, paper with plastic or aluminium layer and others.

Cellulose-based paper

Common types of cellulose-based paper with an intrinsic mechanical barrier against grease are:

- **Natural greaseproof paper (NGP),** which is made by intensively refining wood pulp. NGP is mainly used as grease and water-resistant paper in food processing and packaging that is intended for contact with fatty foodstuffs such as baking paper, food trays and containers such as muffin cups (OECD, 2020);
- **Microfibrillar cellulose, cellulose nanofibrils and cellulose nanocrystals,** which are produced by refining cellulose using mechanical processes such as high pressure homogenization, grinding, and refining (OECD, 2020). This is then used as a coating on paper or plastic;
- **Vegetable parchment.** Vegetable parchment initially has a fairly open structure, but when the paper is passed through a bath of concentrated sulfuric acid, the cellulose fibres react with the acid and almost melt together (OECD, 2020; Twede & Selke, 2005). The sheet structure is dense with a small number of pores (Giatti, 1996; OECD, 2020). Vegetable parchment offers a very high barrier to water and fat (Pudumjee, 2020) and is suitable for use as food wrappers and liners (OECD, 2020).

Plastic, aluminium and polylactic acid

Another method to make a physical barrier is achieved by laminating an extra layer of plastic or aluminium onto the material that will be used in food contact materials. The disadvantage of lamination, however, is that the paper-making plants must have laminating machines adding extra costs. The resulting food contact material is also difficult to recycle, although one company is known to be recovering plastic from laminated paper (OECD, 2020).

Other physical alternatives

Other physical alternatives to food packaging paper and food paper consumption include a material used in conjunction with cellulose-based paper or instead of cellulose-based paper such as elephant grass, palm leaves, bamboo, clay and wheat straw (OECD, 2020).

Short-chain fluorinated alternatives

The long-chain PFASs previously used in food contact materials were generally a mixture of C8, C10 and C12 chain-length PFASs. These have been progressively replaced by short-chain PFASs, which are mainly based upon C6 technology as regulatory pressure has grown since 2000 (OECD, 2020). The FluoroCouncil (2018) indicated there were two principal alternatives for impregnation of paper and cardboard for that were in global use to provide oil- and grease-repellent properties to paper and paper packaging. These include: (a) Short-chain (“C6”) fluorotelomer-based side-chain fluorinated polymers, with high molecular-weight acrylic polymers that contain 6:2 fluorotelomer functionality to provide repellent performance and (b) perfluoropolyether-based oil- and grease repellent products (UNEP, 2019c).

OECD (2020) provides a list of PFAS chemical alternatives which are allowed to be used in food-contact paper in Switzerland (included on the list of Federal Department of Home Affairs FDHA), Germany (included on the list of Bundes Insitut fur Riskiobewertung, BfR) and the US (included on the list of the US Food and Drug Administration, FDA).

3.11.3 Suitability of alternatives

Given the technical suitability of some of the alternatives highlighted by the OECD (2020) report, it is important to understand their hazard profiles. Therefore OECD published in 2022 a report concerning the hazard profiles of PFASs and Alternatives in Food Packaging (OECD, 2022b). Across the range of alternatives, both short-chain PFASs and some fluorine-free alternatives can meet the grease barrier performance that is required across the range of food contact applications (OECD, 2020).

Fluorine-free alternatives

Fluorine-free alternatives that met the grease/water-repellence performance requirements for the applications considered in this study included physical alternatives such as NGP and chemical alternatives such as TopScreen^{TM} products (OECD, 2020).

Silicone-based alternatives are known to be water-repellent but generally reported not to meet the required grease-repellent performance properties for use in a wide range of food contact materials (Dixit et al., 2006; Nordic Council of Ministers, 2018; OECD, 2020; Wacker Chemical Corp., 2017). Also, whilst silicone alternatives have good release properties, they are often not suitable for industrial-scale baking because they require extensive cleaning to avoid them sticking to the finished food articles(OECD, 2020). Parchment paper and wax paper have similar disadvantages (OECD, 2020).

For silicone-based alternatives, there may be a quantity of siloxanes as residual content after polymerisation or chemical reaction compounds formed during the process. There is also the possibility that siloxanes are formed during the use of silicone products e.g., by repeated used of baking mould at high temperatures. Certain siloxanes such as D4, D5 and D6 are identified as Substances of Very High Concern in the EU under the REACH regulation based on their PBT and/or vPvB properties (ECHA, 2019b).

For paper laminated with extra layer of plastic, and other fluorine-free alternatives which may contain plastic (e.g., styrene-acrylic copolymers, hydrophobic monomer dispersions, polyvinyl alcohols and polyethylene coatings), there is the disadvantage of plastic usage. There has been a trend in OECD countries to seek to reduce or eliminate the use of these materials for food-on-the-go for reasons of non-sustainability (OECD, 2020).

The challenge of using alternatives is exclusively based upon cost. The production cost increased by 12% when short-chain fluorinated alternatives are used compared to long-chain PFASs. Compared to long-chain PFASs, the production cost increased by 24% and 48% when fluorine-free chemical alternatives and physical alternatives are used, respectively (OECD, 2020).

Short-chain fluorinated alternatives

There is a rising concern about the adverse health and environmental effect of short-chain PFASs. The US Food and Drug Administration (FDA) is aware of the potential human health risks from dietary exposure resulting from authorized fluorinated food contact substances that contain 6:2 FTOH. In December 2020 a voluntary phase-out of 6:2 FTOH in food contact materials was announced by FDA.[50]

3.11.4 Implementation of alternatives

The shift to short-chain PFASs has progressively taken place since 2000. In Europe, it may be assumed that the large majority of food paper and board is treated with short-chain PFASs to confer grease and water resistance (OECD, 2020). The remaining market share uses fluorine-free chemical alternatives and physical alternatives. In the US, there is growing pressure to phase out the use of PFASs from food contact materials. Despite this pressure, it would

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[50] https://www.fda.gov/food/cfsan-constituent-updates/fda-announces-voluntary-phase-out-industry-certain-pfas-used-food-packaging.

be a reasonable assumption that fluorine-free chemical alternatives occupy a similarly low market share in the US as in Europe (OECD, 2020).

It took a number of years for PFASs manufacturers to develop short-chain PFASs technology that meets the required specification for use in food contact materials. Discussions with PFASs manufacturers have indicated that the replacement of long-chain to short-chain PFASs and possibly in the future to fluorine-free technology is not a linear process (OECD, 2020). Instead, it would require a stepwise approach to develop the new technology, scale this up to production levels and verify that the technology can be used optimally and cost-effectively by paper and board manufacturers (OECD, 2020).

3.11.5 Conclusion

The alternatives of PFOA, its salts and PFOA-related compounds are available in the market of food contact materials. The challenge of using alternatives is exclusively based upon cost. In the US, there is growing pressure to phase out the use of PFASs from food contact materials. Replacement of long-chain to short-chain PFASs and possibly in the future to fluorine-free technology is not a linear process and will require a stepwise approach (OECD, 2020).

3.12 Other applications: Coatings, paints, inks and varnishes

3.12.1 Introduction and background

Historically, PFAS-related chemicals had several uses in coatings, paints and varnishes to reduce surface tension, for example, for substrate wetting, for levelling, as dispersing agents and for improving gloss and antistatic properties or to impart water- and oil repellency, as well as additives in dyes and ink, as pigment grinding aids and as agents to combat pigment flotation problems (UNEP, 2019c). For example, these are mainly water-based paints where a reduction of the surface tension of the paint is needed to achieve wetting of the surface where the paint is applied to.

However, since 2002 there has been a trend amongst global manufacturers to replace long-chain PFASs, such as PFOA, its salts and the potential precursors with chemicals containing shorter perfluoroalkyl chains or with non-perfluoroalkyl products. Both fluoropolymers and short-chain PFASs are used in coatings, paints and varnishes but they carry out different functions. Typically, fluoropolymers are added to coatings, paints and varnishes to provide resistance to corrosion, weathering, abrasion and scratching, UV and overall provide durability. Fluoropolymers used include PTFE, PVDF and, to a lesser degree, fluoroethylene vinyl ether (FEVE). Short-chain PFASs that are used generally act as levelling and wetting agents, have anti-blocking properties or confer oil and water repellence. Table 10 summarizes the uses of PFASs in coatings, paints and varnishes (OECD, 2022a).

Since fluorosurfactants are much more expensive than other surfactants, they are only used for special purposes where low surface tension is necessary and when other (fluorine-free) alternatives fail, e.g., in applications where an extremely smooth surface is necessary. Moreover, it has been reported that PFOA-alternatives are not yet available in anti-reflective coatings used in the semiconductor industry.

The concentration of the fluorinated substances in the paint/ink can be up to 1 %, depending on the specific application. However, in most cases it is considered to be much lower, e.g., within the range of 0.05 % (ECHA, 2015a).

Table 10: Uses of PFASs in coatings, paints and varnishes. Source: OECD (2022).

OECD Product Categories		**Applications**	**Use examples**	**Fluoropolymers**	**Other PFASs** (Non-polymeric PFASs)
Coatings	Powder coatings	Architectural	Exterior surfaces of bridges, buildings	PTFE, PVDF, ethylene chlorotrifluoroethylene (ECTFE), FEVE, FEP	None identified
		Chemical industry	Lining of reaction vessels, metal surface coating		None identified
	Radiation curable coatings	Electronics	Phone and tablet screens,	PTFE, PVDF	Perfluoropolyether and polyurethane (PU) blend
	Other coatings	Cable and wiring	Commercial indoor local area network (LAN) cables, cables in aircraft	PTFE, FEP, perfluoroalkoxy (PFA), ECTFE and ETFE	None identified
		Anti-reflective coatings	Coating for semi-conductors	FP with a short fluoroalkyl side chain which is less than C4	PFOA, PFOS*
		Ant-graffiti coatings	Walls, public transport, bridges	PTFE has been used	None identified
		Renewable Energy	Solar panels, wind turbine blades	FEP, ETFE, FEVE, ECTFE	Formulations of fluorosulphonamides
Paints	Aerosol spray paints	Automotive paints	Car coatings	PTFE	None identified
		Architectural, Chemical industry	Architecture: bridges, construction Chemical: metal surface protection	PVDF, PTFE, FEVE	None identified
	Water-based paints	Architectural, Chemical industry, Domestic	Architecture: bridges, construction Chemical: lining of vessels, metal surface protection Domestic: doors, walls	PVDF, FEVE, ECTFE, PTFE, FEP	C4-PFBS and C4-fluorinated ethers**, C6-based PFASs
	Solvent-based paints				

OECD Product Categories		**Applications**	**Use examples**	**Fluoropolymers**	**Other PFASs** (Non-polymeric PFASs)
Varnishes	Floor and surface finishes/ lacquers and stains	Domestic, Construction Printing	Protection for stone and tiles, work surfaces, floor polishes, table-top waxes, night-reflective road, pavement and traffic signs and reflective sheeting, printing inks, wood and cellulose shrinkage/swelling protectors	None identified	C4-based PFASs e.g. perfluoro-1-butanesulfonyl fluoride (PBSF), fluorinated polyethers**, short-chain PFASs mixtures with silicone†. None identified for printing inks. Wood protectors: fluorinated hydrocarbons, fluorinated acrylic or methacrylic acid esters, fluoroalkane sulfonic acids and salts of fluorinated carboxylic acids

Key to table: *Still used in in semiconductor manufacturing and very limited derogations exist for PFOA in the Stockholm Convention(UNEP, 2017c). PFOS is no longer used in semiconductor manufacturing. ** For example, methyl nonafluorobutyl ether and methyl nonafluoroisobutyl ether and Polyfox. † For example, Silres 38. C4 and C6 refer to the number of carbon atoms in the molecule (OECD, 2022a).

Information related to PFOS

PFOS-related compounds were used in coatings, paint and varnishes to reduce surface tension in building materials, on metal surfaces, etc. Uses were, but not limited to, substrate wetting, for levelling, as dispersing agents, improving gloss and antistatic properties. PFOS-related compounds could be used as additives in dyes and ink, as pigment grinding aids, and as agents to counteract pigment flotation problems.

The concentrations used were below 0.01 wt %. Information from suppliers in the paint and varnish industries suggested that fluorosurfactants were in general much more expensive than other alternative surfactants (Cheremisinoff, 2016).

Information related to PFOA

PFOA, its salts and related compounds have been used in coatings by smartphone manufacturers requested for pulsed plasma nano-coating (ECHA, 2015b).

Comments from the industry submitted during the EU public consultation indicated that PFOA and related compounds are present in latex inks used in professional printers. This use only continues in printers that are no longer manufactured, and therefore a phase-out is already underway (UNEP, 2017a).

Information related to PFHxS

One PFHxS-related compound (CAS No: 67584-61-6, 2-[methyl[(tridecafluorohexyl)sulfonyl]amino]ethyl methacrylate) was reportedly used in impregnation/coating for protection from dampness, fungus, etc. at least in four products between 2003 and 2009 in Denmark (SPIN (Substances in Preparations in Nordic Countries), 2018).

Recent information from the Republic of Korea and further investigations have revealed the use of a polymer containing PFHxS (most likely unintentional as a constituent in a PFOS-polymer, CAS No.127133-66-8) in a car coating spray product produced in the EU and imported to the Republic of Korea (RPA, 2019). It was reported in 2016 that 20 tonnes of the polymer in the product were imported into the country from 2013 to 2015.

3.12.2 Availability of alternatives

Non-fluorinated alternatives

Coatings

A number of non-fluorinated alternatives to powder coatings are commercially available and some of these are marketed as PTFE-free (Micro Powders, 2021; OECD, 2022a). These include high density polyester (HDPE)-based products that contain nano ceramic and nano aluminium oxide, polyurethane (PU), polyvinyl chloride (PVC), polyolefin[51] and epoxy powders(OECD, 2022a).
Silica-based coatings such as silicone polymers can be used as alternatives to radiation curable coatings in electronics as they have similar properties and therefore can carry out the same function as PFASs used in this application (OECD, 2022a).
In solar panel frontsheet and backsheet coatings, alternatives such as polyester, polyamides and polyethylene terephthalate (PET) have been identified. However, it has been suggested that fluoropolymer coatings in this application are more durable due to being less susceptible to degradation from UV and moisture, and therefore most cost-efficient in the long term (OECD, 2022a).

Paints

Non-PFASs alternatives exist for fluorosurfactants such as silicone-based coatings (OECD, 2022a) without the use of fluoropolymers and hydrocarbons (3M, 2016). Alternatives for binders in paints to confer the durability and other required performance characteristics include acrylic, a popular choice which is a water-based latex paint, polyester-based formulations such as tetrashield PC-4000, PU, alkyds, phenolic or silicone alkyds, phenolic, vinyl and epoxy coatings (OECD, 2022a). Another alternative is a low density polyester (LDPE)-based formulation that contains nano aluminium oxide (OECD, 2022a). This is claimed to confer unsurpassed scratch and scuff resistance (OECD, 2022a)

Varnishes

Silica-based coatings such as silicone polymers made of silanes and siloxanes have been used in varnishes for their low surface tension as surfactants, without the use of fluoropolymers (OECD, 2022a). Additionally, sulfosuccinates have been used in varnishes, specifically as wood primers, in water-based applications for their low surface tension. Both are used to confer wetting and levelling properties (OECD, 2022a).

Other non-fluorinated alternatives

- Propylated naphthalenes and propylated biphenyls, which can be used as water-repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications;
- Fatty alcohol polyglycol ether sulphate, sometimes together with a sulfosuccinate.

Fluorinated alternatives:

As shown in Table 10, fluoropolymers and non-polymeric PFASs are used in coatings, paints and varnishes. The available PFOA alternatives in this field thus refer to PFOA-free fluoropolymers and short-chain PFASs. More information related to PFOA-free fluoropolymers can be found in section 3.10. Some examples of the alternatives are listed here.

- 6:2 fluorotelomer-based side-chain fluorinated polymers. Examples of suppliers who offer these products commercially are:

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[51] A polyolefin is a type of polymer produced from a simple olefin (also called an alkene with the general formula CnH2n) as a monomer. For example, polyethylene is the polyolefin produced by polymerizing the olefin ethylene. Polypropylene is another common polyolefin which is made from the olefin propylene.

    - Chemgard: http://www.chemguard.com/specialty-chemicals/product-applications/wetting-leveling.htm;
    - Chemours: https://www.chemours.com/en/brands-and-products/capstone/products/fluorosurfactants;
    - Dynax: https://dynaxcorp.com/products/coatings-and-ink-applications/.
- Short-chain PBSF-based side-chain fluorinated polymers. Examples of suppliers who offer these products commercially is 3M. https://www.3m.com/3M/en_US/company-us/all-3m-products/?N=5002385+8745513+8711017+8721867+3294857497andrt=r3;
- Fluorinated polyethers;
- Oxetane Fluorosurfactants, an oligomeric poly(oxetane) backbone with short (≤ C_4F_9) perfluoroalkyl groups;

3.12.3 Suitability of alternatives

Chemical alternatives for this use have been developed and are indicated to be available, technically and economically feasible and widely implemented already (UNEP, 2019c).

There is an increasing concern among authorities in Europe regarding risks for health and the environment exhibited by short-chain PFASs. These concerns are due to persistence, high mobility in water and soil and potential toxic properties of these substances. Already now short-chain PFASs are ubiquitously present in the environment, even in the remote areas (UNEP, 2017b).

3.12.4 Implementation of alternatives

Results from consultation with industry indicate that short-chain PFASs are already commonly used in paint applications. Information from suppliers in the paint and varnish industries suggested that fluorosurfactants were in general much more expensive than other alternative surfactants (Cheremisinoff, 2016). A market overview that comprehensively shows the relative market penetration of non-fluorinated alternative substances compared to fluoro-based substances in each of the coating, paint and varnish segments has not been possible to construct from publicly available information (OECD, 2022a). To be mentioned, there is no longer exemption of PFOA, its salts and related compounds in paints and inks in EU and no exemption exists under the Stockholm Convention.

3.12.5 Conclusion

Chemical alternatives, especially short-chain fluorinated alternatives for this use have been developed and widely implemented already. However, there is an increasing concern regarding risks to health and the environment exhibited by short-chain PFASs. Some non-fluorinated alternatives are already commercially available.

4. Summary

This guidance describes the issues relating to the alternatives to 1) PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF); 2) PFOA, its salts and PFOA-related compounds; and 3) PFHxS, its salts and PFHxS related compounds. It summarizes the availability, suitability and implementation of the alternatives. Considerations related to persistence, bioaccumulation, potential for long-range environmental transport and adverse effects have been considered when dealing with possible alternatives.

Generally speaking, there are three types of alternatives to PFOS, PFOA, PFHxS and their related compounds: short-chain fluorinated compounds, fluorine-free compounds and non-chemical alternatives (including physical, mechanical and biological approaches). Alternatives are technically and economically available in many industries or applications, including fire-fighting foam, photolithography and developer solution in the semiconductor industry, the manufacture of fluoropolymers such as PTFE and FEP, and implantable and invasive medical devices. In some fields, however, there are either no technically available alternatives or the cost-effectiveness is too low. This includes insect baits, textile finishing for the protection of workers, photographic coatings applied to films, and the use of PFOI for the production of PFOB. In some applications, although chemical alternatives are available, the toxicity and environmental concerns of the alternatives shall be further studied. The detailed descriptions of alternatives are summarized in the Appendix.

Many chemical alternatives are short-chain fluorinated compounds. C6 and C4 chemistries adequately meet the criteria for replacement of most C8 and higher homologue uses. These short-chain fluorinated compounds include (Schubert, 2013):

- 6:2 fluorotelomer-based chemicals;
- Perfluorobutanesulfonyl fluoride (PBSF)-based derivatives;
- Mono- and polyfluorinated-ether-functionality compounds;
- Fluorinated oxetanes;
- Other fluorinated polymers.

However, significant evidence has shown the potential health and environmental effects of short-chain PFASs including enhanced mobility, uptake in crops, binding to proteins, increasing levels of exposure, difficulty in capturing and cleaning up once released into the environment (Brendel et al., 2018; Ritscher et al., 2018; UNEP, 2018a). One of the short-chain alternatives, PFHxA, has been identified to have PBT/vPvB properties or properties of an equivalent level of concern in Germany (German Federal Institute for Occupational Safety and Health, 2019). 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. The final EU-wide restriction of PFHxA is being formulated.

Fluorine-free alternatives are also available in many industries. They have a very broad scope, including hydrocarbon surfactants, detergents (fire-fighting foam), siloxanes (fire-fighting foam, water-proof finishing), high molecular weight polydimethylsiloxanes (PDMS) (water-proof finishing), waxes (water-proof finishing, food contact material), paraffins (water-proof finishing), sulfosuccinates (paint and ink), propylated naphthalenes or biphenyls (paint and ink), fatty alcohol polyglycol ether sulphates (paint and ink), etc. A large body of peer-reviewed, Good Laboratory Practices (GLP) study data for the alternatives exist. One can consult the OECD/UNEP Global PFC Group for the information related to specific alternatives (https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/).

Moreover, information is lacking in some applications. For instance, a lack of specific information provided for chemical alternatives in terms of their trade names, chemical composition, availability, accessibility, technical and economic feasibility, environmental and health effects. There was also a lack of willingness from stakeholders to release such information. In order to evaluate the chemical alternatives in terms of their availability, accessibility, technical and economic feasibility, and environmental and health effects, the trade names and chemical composition of alternatives and their implementation status are essential information. A lot can still be done to narrow or close the data gaps, for instance, by improved communication with industries on the alternatives, better labelling of the product content, and more intensive assessment of the compounds, including products containing alternatives, when information is lacking, not shared, or proprietary, by e.g. non-targeted analysis.

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Appendix Overview of the alternatives to PFOA, its salts, and PFOA-related compounds.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
Insect baits	Non-chemical alternative technology such as mechanical, cultural, and biological control methods	These control methods have been developed but are not fully commercialised or available in all locations.	Low
Insect baits	Chemical alternatives such as thermo-nebulization with permethrin and dried-powder dusting with deltamethrin	Wide range of commercially available alternatives on the market; techniques for application (e.g. dry powder formulation) have been developed. These alternatives are noted to have a number of limitations, but are recommended to be used for small areas, to control young *Atta* colonies, etc.	
Metal plating	A number of process-based approaches to replace PFOS are also identified and are commercially available e.g. High Velocity Oxygen Fuel (HVOF) process. Cr(III) plating is available as an alternative to Cr(VI) plating for some decorative plating applications.		
Metal plating	fluorine-free alternatives are commercially available	Fluorine-free are still the subject of R&D activity and are less readily available.	H412 - Harmful to aquatic life with long lasting effects[52].
Metal plating	Wide range of short-chain fluorinated chemicals (e.g. 6:2 FTSA)	Technical and economical available	6:2 FTSA is not considered a viable alternative due to environmental concerns relating to degradation to become the stable PFHxA. The final EU-wide restriction of PFHxA and PFHxA-related compounds is being formulated. Acute and repeated-dose mammalian and aquatic toxicity has been reported for 6:2 FTSA.

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[52] "COMPOUND SUMMARY 3-Pentanone, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-". PubChem. Retrieved April 8, 2021 https://pubchem.ncbi.nlm.nih.gov/compound/Perfluoro_2-methyl-3-pentanone#section=Hazards-Identification.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
Fire-fighting foam	Hydrocarbons and detergents (fluorine-free)	Technical and economical available No remediation cost after application	Low concern
Fire-fighting foam	Siloxanes (fluorine-free)	Not available in the market (EC & ECHA, 2020)	Some siloxanes (cyclic D4, D5, D6) are persistent, bioaccumulative and toxic.
Fire-fighting foam	Protein (fluorine-free)	Not available in the market (EC & ECHA, 2020)	Low concern
Semiconductor industry	Short-chain fluorinated alternatives. No specific details of the composition	Information not available.	Many short-chain PFAS are persistent and toxic; they have high mobility, but assumed to be less bioaccumulative than long-chain PFAS.
Photographic coating in paper and for use in printing plates	Short-chain fluorinated alternatives, such as C3 and C4 perfluorinated compounds. No specific details of the composition	Technical and economical available	Many short-chain PFAS are persistent and toxic; they have high mobility, but assumed to be less bioaccumulative than long-chain PFAS.
Photographic coating in paper and for use in printing plates	Hydrocarbon surfactants (fluorine-free), No specific details of the composition	Technical and economical available	No information available
Photographic coating in film	No technically available chemical alternatives.	N/A	N/A
Photographic coating in film	Digitalization may reduce and eliminated this use category (physical alternative)	Switch to digital technologies also includes developing countries, who report a rapid implementation of digital imaging technology for healthcare (IPEN, 2018b)	N/A
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	Short-chain fluorotelomer based substances	Technical and economical available	They can degrade to fluorinated substances which are persistent. 6:2 FT-based side-chain fluorinated polymers can transform to PFHxA and thus are PFHxA-related compounds. PFHxA and related substances are persistent and mobile in the environment and can damage the human reproductive system according to Germany's proposal to restrict the use of these substances.
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	Substances contain perfluorobutane sulfonyl functional groups on the side chains to provide repellent performance	Technical and economical available	PFBS is persistent and bioaccumulative (but less bioaccumulative than PFOA and PFHxS) (ECHA, 2019c). ECHA committee agrees PFBS is substance of

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
	detailed composition unknown		very high concern. Animal studies support identification of thyroid, developmental, and kidney endpoints as potential health effects following repeated exposures of PFBS salt in utero and/or during adulthood (US EPA, 2021).
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	High molecular weight polydimethylsiloxanes (PDMS, fluorine-free)	Technical and economical available	Such polymers could contain residual amounts of monomeric cyclic siloxanes such as D4, D5 or D6 and oligomeric siloxanes which are persistent, bioaccumulative and toxic.
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	Urethane polymers (fluorine-free)	Technical and economical available	Low concern
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	BIONIC-FINISH®ECO introduced by Rudolph Group is a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers (fluorine-free). The exact identity of the chemical is not available	Superhydrophobic surfaces, but do not provide oil-, dirt-, or soil repellence	Lack of information on the hazards
Water- and oil-proof finishing for carpets, leather and apparel, non-technical textiles and upholstery	Waxes and paraffins (fluorine-free)	Durable water repellence but do not provide oil-, dirt-, or soil repellence	Low concern
Water- and oil-proof finishing for the protection of workers	No technically available alternatives	N/A	N/A
Manufacture of fluoropolymer	GenX/HFPO-DA (short-chain fluorinated alternative)	Technical and economical available	GenX is listed as a Substances of Very High Concern (SVHC) under ECHA. US EPA published in 2021 an updated Human Health Toxicity Assessments for GenX Chemicals which confirmed health effects including on the liver, kidneys, the immune system, development of offspring, and an association with cancer

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
			based on animal studies following oral exposure. [53]
Manufacture of fluoropolymer	ADONA (short-chain fluorinated alternative)	Technical and economical available	Persistent. Concerning environmental risks related to ADONA using data from the REACH registration dossier, it was concluded that the substance is probably not acutely toxic (LC/EC50>100 mg/L) or chronically toxic (NOEC>1 mg/L) to aquatic organisms. Regarding all available information, a full PBT assessment cannot be performed.
Manufacture of fluoropolymer	EEA-NH_4 (short-chain fluorinated alternative)	Technical and economical available	Persistent, do not fulfill the toxic (T) criterion under the REACH regulation Provided data was not sufficient to conclude on not bioaccumulating (B).
Manufacture of fluoropolymer	Non-fluorinated emulsifiers for VDF-containing polymers such as polyvinyl/acrylic acids, derivatives of polyethylene/propylene glycols, alkylphosphate esters, vinyl acids, siloxanes, silanes, long-chain hydrocarbon acids, and derivatives of sugars are developed (Hintzer & Schwertfeger, 2014; UNEP, 2017a)	Lack of information	Lack of information
Manufacture of fluoropolymer	Du Pont developed an aqueous polymerization of perfluoromonomer using hydrocarbon surfactant (fluorine-free). This process does not use fluorosurfactant as processing aid. This method can be used to produce PTFE and PVDF.[54]	Lack of information	Lack of information
Manufacture of fluoropolymer	Arkema developed aqueous fluoropolymer dispersions which non-ionic non fluorinated emulsifier is used to	Lack of information	Lack of information

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[53] https://www.epa.gov/chemical-research/human-health-toxicity-assessments-genx-chemicals.

[54] US patent application Pub. No.: US 2012/0116003 A1 for assignee of E.I. Du Pont Nemours and Company.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
	produce fluoropolymer emulsions (UNEP, 2017a). The emulsifiers used in the invention are those that contain segments of polyethylene glycol, polypropylene glycol, and/or polytetamethylene glycol (fluorine-free).		
Manufacture of fluoropolymer	Sanayei (2014) developed aqueous fluoropolymer dispersions using one or more alkyl sulfate surfactant (fluorine-free) in particular to emulsion polymerization method for producing fluoropolymer latex[55].	Lack of information	Lack of information
Manufacture of fluoropolymer	Various fluoropolymer manufacturers are exploring and have patented a number of fluorinated emulsifier-free aqueous emulsion polymerization processes (Hintzer & Schwertfeger, 2014; UNEP, 2017a). These include: (1) emulsifier-free polymerization of amorphous standard co/terpolymers comprising TFE, HFP and VDF; and (2) development of so-called “surfmers” (which are surfactants that can also act as monomers in the polymerization action) for specific classes of fluoropolymers.	Lack of information	Lack of information
Invasive and implantable medical device	See the part of “Manufacture of fluoropolymer”	See the part of “Manufacture of fluoropolymer”	See the part of “Manufacture of fluoropolymer”
Use of PFOI for the production of PFOB	No technically available alternatives	N/A	N/A
Paper and board food contact materials	Short-chain fluorotelomer-based	Technical and economical available	They can degrade to fluorinated substances

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[55] US Patent application Pub. No.: US 2014/0179868 A1.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
	side chain (“C6”) fluorinated polymers		which are persistent and toxic.
Paper and board food contact materials	Perfluoropolyether-based oil- and grease repellent products	Technical and economical available	Lack of information
Paper and board food contact materials	Water-based synthetic barrier coatings for cupstockor and vegetable-oil based biowaxes under the trade name TopScreen™ (fluorine-free)	Technical and economical available,	Low concern. They are compostable, with EN 13432 certification for most packaging applications.
Paper and board food contact materials	Silicone (fluorine-free)	Technical available	There may be siloxanes residual in the product. Certain siloxanes are under regulatory scrutiny in the EU as substances of very high concern (ECHA, 2019b).
Paper and board food contact materials	Aqueous dispersions of copolymers (styrene and butadiene), aqueous dispersions of waxes (other than that of TopScreen™), starch, clay, stone (calcium carbonate mixed with a resin), chitosan or water soluble hydroxyethylcellulose (HEC) (fluorine-free) (OECD, 2020)	Lack of information	Lack of information
Paper and board food contact materials	Cellulose-based paper such as natural greaseproof paper and vegetable parchment (physical alternative)	Technical available, elevated production cost	Low concern
Paper and board food contact materials	Material with an extra layer of plastic or aluminum laminate (physical alternative)	Technical available, elevated production cost	For plastic lamination, there is the disadvantage of plastic usage.
Coatings, paints and varnishes	6:2 fluorotelomer-based side-chain fluorinated polymers	Technical and economical available	They can degrade to fluorinated substances which are persistent and toxic.
Coatings, paints and varnishes	Short-chain (“C4”) side-chain fluorinated polymers, e.g., based on PBSF functional group on the side chains	Technical and economical available	Perfluorobutane sulfonate (*PFBS*) can be a final degradation product of perfluorobutane sulfonyl fluoride (*PBSF*)-based chemicals. PFBS is persistent and bioaccumulative (but less bioaccumulative than PFOA and PFHxS) (ECHA, 2019c). ECHA committee

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
			agrees PFBS is substance of very high concern. Animal studies support identification of thyroid, developmental, and kidney endpoints as potential health effects following repeated exposures of PFBS salt in utero and/or during adulthood (US EPA, 2021).
Coatings, paints and varnishes	Fluorinated polyethers	Technical and economical available	Lack of information
Coatings, paints and varnishes	Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate (fluorine-free)	Technical and economical available	Sodium salt of di-(2-ethylhexyl) sulfosuccinate is not considered persistent, bioaccumulative and toxic (PBT)/very persistent and very bioaccumulative (vPvB)Toxic to terrestrial vertebrates [56]
Coatings, paints and varnishes	Silicone polymers, such as polyether-modified polydimethyl siloxane (PDMS), mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (fluorine-free)	Technical and economical available	PDMS is persistent, but not toxic. Some intermediates for the synthesis of silicone polymers (such as D4, D5 and D6 and specific linear siloxanes) are identified as Substances of Very High Concern (SVHCs) under the REACH regulation based on their PBT and/or vPvB properties.
Coatings, paints and varnishes	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 (fluorine-free)	Lack of information	Lack of information. Diisopropylnaphthalene (DIPN), 1- Isopropyl-2-phenyl-benzene and Triisopropylnaphthalene (TIPN) are likely to fulfil the bioaccumulation criteria according to Annex D in the Stockholm Convention. Diisopropylnaphthalene (DIPN) and 1-Isopropyl-2-phenyl-benzene are likely to fulfil the Annex D for ecotoxicity according to the Stockholm Convention. However it was concluded that these substances are not likely to meet all the annex D criteria and are most likely not POPs. Diisoproplynaftalene

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[56] https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-bis_2-ethylhexyl_sulfosuccinate.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
			(DIPN) is undergoing Substance Evaluation (SE) due to PBT/vPvB concerns.
Coatings, paints and varnishes	Fatty alcohol polyglycol ether sulphate (fluorine-free)	Lack of information	Low concern
Coatings, paints and varnishes	PTFE-free powder coatings: HDPE-based products that contain nano ceramic and nano aluminum oxide, polyurethane (PU), polyvinyl chloride (PVC), polyolefin and epoxy powders (fluorine-free)	Technical available	Low concern
Coatings, paints and varnishes	Solar panel frontsheet and backsheet coatings: polyester, polyamides and polyethylene terephthalate (PET) have been identified (fluorine-free).	These alternatives might be not as durable and cost-efficient as fluoropolymer coatings	Low concern
Coatings, paints and varnishes	Binders in paints: acrylic, water-based latex paint, polyester-based formulations such as tetrashield PC-4000, PU, alkyds, phenolic or silicone alkyds, phenolic, vinyl and epoxy coatings. Another alternative is a low-density polyester (LDPE)-based formulation that contains nano aluminum oxide (fluorine-free).	Technical available	Low concern