



Stockholm Convention on Persistent Organic Pollutants

**Conference of the Parties to the Stockholm
Convention on Persistent Organic Pollutants
Tenth meeting**

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Agenda item 5 (d)

**Matters related to the implementation of the
Convention: implementation plans**

Draft guidance on alternatives to perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds

Note by the Secretariat

As is mentioned in the note by the Secretariat on the implementation plans (UNEP/POPS/COP.10/10), the annex to the present note sets out draft guidance on alternatives to perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. The present note, including its annex, has not been formally edited.

* In accordance with decisions BC-15/1, RC-10/2 and SC-10/2 of the conferences of the Parties to the Basel, Rotterdam and Stockholm conventions, the 2021/2022 meetings of the conferences of the Parties are being held in two segments: an online segment held from 26 to 30 July 2021 and a face-to-face segment to be held from 6 to 17 June 2022 in Geneva.

Annex

**Draft guidance on alternatives to
perfluorooctanoic acid (PFOA), its salts
and PFOA-related compounds**

February 2022

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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
CAS	Chemical Abstracts Service
CMR	Carcinogenic, mutagenic or toxic for reproduction
CEN	European Committee for Standardization
CN4-C1	Methoxycarbonyl-tetracyanocyclopentadienide
CN5	Pentacyanocyclopentadienide
D4	Octamethyl cyclotetrasiloxane
D5	Decamethyl cyclopentasiloxane
D6	Dodecamethyl cyclohexasiloxane
ECHA	European Chemicals Agency
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
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
ISO	International Organization for Standardization
LD ₅₀	Lethal dose, 50%
LDPE	Low density polyester
NaPFO	Sodium perfluorooctanoate
NBS	Nitrobenzenesulfonate
NFPA	National Fire Protection Association
NGP	Natural greaseproof paper
NOAEC	No observable adverse effect concentration
NOAEL	No observable adverse effect level
OECD	Organisation for Economic Co-operation and Development
PACF	Perfluoroalkanoyl fluoride
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)
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
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
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
vPvB	Very persistent and very bioaccumulative
VDF	Vinylidene fluoride
WSC	World Semiconductor Council

1 Introduction

1.1 Objectives

The current document is a consolidated guidance on alternatives to PFOA and its related chemicals. The objective of the current document is to provide a summary of information on currently known alternatives to PFOA, its salts, and PFOA-related compounds. The ultimate goal is to enhance the capacity of developing countries and countries with economies in transition to phase out PFOA, its salts, and PFOA-related compounds, taking into account 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 PFOA, its salts and PFOA-related compounds in Annex A

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty to protect human health and the environment from POPs, i.e., chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment.

Since the Conference of the Parties listed perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds in Annex A to the Convention (decision SC-9/12) in 2019, substantive progress has been made in phasing out of the use of PFOA, its salts and its related chemicals. The use of PFOA, its salts and its related chemicals has been replaced in a number of applications, while some of the use in critical applications, where it is not currently possible without the use of PFOA, may need to continue until safer alternatives are identified.

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 (C₇F₁₅)C as one of the structural elements. However, the following compounds are not included as PFOA-related compounds:

- C₈F₁₇-X, where X= F, Cl, Br;
- Fluoropolymers that are covered by CF₃[CF₂]_n-R', where R'=any group, n>16;
- Perfluoroalkyl carboxylic and phosphonic acids (including their salts, esters, halides and anhydrides) with ≥8 perfluorinated carbons;
- Perfluoroalkane sulfonic acids (including their salts, esters, halides and anhydrides) with ≥9 perfluorinated carbons;
- Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), as listed in Annex B to the Convention.

Specific exemptions

Specific exemptions for the production and use of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds are listed as follows:

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 to the Stockholm Convention.

Use:

In accordance with the provisions of part X of Annex A to the Stockholm Convention:

- 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 to the Stockholm Convention;
- 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 to the Stockholm Convention;
- 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.

1.3 Information source

The information in this document is based on the submissions by Parties and others on alternatives to PFOA, its salts, and PFOA-related compounds received before January 2022.

The current document consolidates the information from the following documents:

- 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);
- SC-9/12: Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP 2019b);
- 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 (PFOF) (UNEP/POPS/POPRC.14/INF/13) (UNEP 2019c).

1.4 Other available information

- General Guidance on POPs Inventory Development (UNEP 2020b);
- 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 2021a);
- Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/CHW/POP-SIWG.4/4) (UNEP 2020c).

2. Characteristics of PFOA, its salts and PFOA-related compounds

2.1 Terminology

In 2011, Buck et al. provided a first clear structural definition of PFASs and recommendations on names and acronyms for over 200 individual PFASs (Buck et al. 2011). As the identified PFASs increases 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 reflect all compounds with the same structural traits, i.e. the PFAS universe, OECD provided in 2021 recommendations 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 a comprehensive 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, PFOA belongs to the subgroup perfluoroalkyl acids (PFAAs) – perfluoroalkyl carboxylic acids (PFCAs).



Figure 1: A comprehensive 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 ones. Long-chains refer to (EC and ECHA 2020):

- Perfluoroalkyl carboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including PFOA;
- Perfluoroalkane sulfonic acids (PFSAs) with carbon chain lengths C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonic acid (PFOS);
- Precursors of these substances.

Accordingly, short-chain PFAS include (EC and 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 PFOA, its salts and PFOA-related compounds

PFOA (C₇F₁₅COOH) is a fully fluorinated carboxylic acid (PFCA, see Figure 1). PFOA salts include the PFOA anion, and cations such as ammonium, sodium or potassium. Chemical Abstracts Service Registry Numbers (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. PFOA-related compounds can be either non-polymers or side-chain fluorinated polymers (Figure 1). This includes any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C₇F₁₅)C as one of the structural elements. It needs to be mentioned that the following groups of substances are not included in the Stockholm Convention listing of PFOA, its salts and PFOA-related compounds:

- C₈F₁₇-X, where X= F, Cl, Br;
- Fluoropolymers that are covered by CF₃[CF₂]_n-R', where R'=any group, n>16;
- Perfluoroalkyl carboxylic and phosphonic acids (including their salts, esters, halides and anhydrides) with ≥8 perfluorinated carbons;
- Perfluoroalkane sulfonic acids (including their salts, esters, halides and anhydrides) with ≥9 perfluorinated carbons;
- Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), as listed in Annex B to the Convention.

Recently, an updated indicative list of substances covered by the listing of PFOA, its salts and PFOA-related compounds was drafted by the Stockholm Convention (UNEP 2021b). The substances which are covered and not covered by the listing of PFOA, its salts and PFOA-related compounds were listed in this document. Moreover, OECD has compiled a Comprehensive Global Database of PFASs.¹ The PFOA-related chemicals are chemicals which have the "Structure Categories" (Table 1) with 7 or more perfluorinated carbons. One will need to check the corresponding "Structure-Category" and "Perfluoroalkyl Chain Length" column in the Comprehensive Global Database of PFASs which was published by OECD in order to filter chemicals that belong to PFOA, its salts and PFOA-related compounds.

Table 1: Structure categories which belong to PFOA-related compounds in the OECD Comprehensive Global Database of PFASs.

Structure Category	Name
101	perfluoroalkyl carbonyl halides
103	other perfluoroalkyl carbonyl-based nonpolymers
103.01	perfluoroalkyl carbonyl amides/amido ethanols and other alcohols
103.02	perfluoroalkyl carbonyl silanes
103.03	perfluoroalkyl carbonyl (meth)acrylate
104	other perfluoroalkyl carbonyl-based side-chain fluorinated polymers
104.01	perfluoroalkyl carbonyl (meth)acrylate polymers
303	perfluoroalkyl phosphinic acids (PFPIAs), their salts and esters
304	bis(perfluoroalkyl) phosphinyl-based nonpolymers
304.01	bis(perfluoroalkyl) phosphinyl amids (PFPIAMs)
401	perfluoroalkyl iodides (PFAIs)
402	n:2 fluorotelomer-based non-polymers
402.01	n:2 fluorotelomer iodides (n:2 FTIs)
402.02	n:2 fluorotelomer olefins (n:2 FTOs)

¹ Comprehensive Global Database of PFASs: <http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/>.

Structure Category	Name
402.03	n:2 fluorotelomer alcohols (n:2 FTOHs)/thiols
402.04	n:2 fluorotelomer alcohol, phosphate esters (PAPs)
402.05	n:2 fluorotelomer-based silanes
402.06	n:2 fluorotelomer-based (meth)acrylate
402.07	n:2 fluorotelomer sulfonic acids (n:2 FTSAAs)
402.08	n:2 fluorotelomer sulfonyl-based compounds
402.09	n:2 fluorotelomer phosphonic/phosphinic acids
402.1	n:2 FTOH ethoxylates
402.11	n:2 FT amine, amino and derivatives
402.12	n:2 FT-thiol derivatives
402.5	n:2 fluorotelomer carboxylic acids (FTCAs)
402.51	n:3 acids
402.52	FTAL
403	n:2 fluorotelomer-based side-chain fluorinated polymers
403.01	n:2 fluorotelomer-based (meth)acrylate polymers
403.02	n:2 fluorotelomer-based urethane polymers
403.03	n:2 fluorotelomer-based siloxanes/silicon polymers
403.04	n:2 fluorotelomer-based sulfonyl (meth)acrylate polymers
405	n:1 fluorotelomer-based side-chain fluorinated polymers
405.01	n:1 fluorotelomer-based (meth)acrylic polymers
406	fluorotelomer epoxides and derivatives
406.01	fluorotelomer epoxides
406.02	fluorotelomer epoxides derivatives
601	perfluoroalkyl silanes
602	perfluoroalkyl alcohols
603	perfluoroalkyl alcohol-based side-chain fluorinated polymers
701	hydrofluorocarbons (HFCs), semifluorinated alkanes (SFAs) and their derivatives
701.1	HFCs and derivatives
701.2	SFAs and derivatives
702	hydrofluoroethers (HFEs) and derivatives
702.1	HFEs
702.2	HFE-based silanes
702.3	other HFE-based derivatives
703	hydrofluoroolefins (HFOs)
704	semi-fluorinated ketons
705	side-chain fluorinated aromatics

2.3 Properties of PFOA, its salts and PFOA-related compounds

Properties of PFOA are summarized in Table 2 (UNEP 2017a) and Table 3 (UNEP 2016a).

Table 2: Identity of PFOA.

CAS number:	335-67-1
CAS name:	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-
IUPAC name:	Pentadecafluorooctanoic acid
EC number:	206-397-9
EC name:	Pentadecafluorooctanoic acid
Molecular formula:	C ₈ HF ₁₅ O ₂
Molecular weight:	414.07 g/mol
Synonyms:	Perfluorooctanoic acid; PFOA; Pentadecafluoro-1-octanoic acid; Perfluorocaprylic acid; Perfluoro-n-octanoic acid; Pentadecafluoro-n-octanoic acid; Pentadecafluorooctanoic acid; n-Perfluorooctanoic acid; 1-Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro

Table 3: Overview of relevant physicochemical properties of PFOA.

Property	Value	Reference/Remark
Physical state at 20°C and 101.3 kPa	Solid	Kirk (1995)
Melting/freezing point	54.3 °C 44–56.5 °C	Lide (2003) Beilstein (2005) cited in ECHA (2013)
Boiling point	188 °C (1013.25 hPa) 189 °C (981 hPa)	Lide (2003) Kauck and Diesslin, (1951)
Vapour pressure	128 – 96,500 Pa (59.25 - 190.80 °C) for PFO (liquid phase); 5.2 - 40.7 Pa (25 - 45° C) for PFO (Solid phase)	Kaiser et al. (2005) Barton et al. (2009)
Water solubility	9.5 g/L (25° C) 4.14 g/L (22°C)	Kauck and Diesslin (1951) Prokop et al. (1989)
Dissociation constant	<1.6, e.g., 0.5	Vierke et al. (2013)
pH-value	2.6 (1 g/L at 20 °C)	ECHA (2015a) (reliability not assignable)

2.4 Environmental fate and health effects of PFOA

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; UNEP 2018b). 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 regard to prostate, testicular, liver and/or kidney cancers (IARC 2016). The US National Toxicology Program (NTP) concludes that PFOA is presumed to be immune hazards to

humans (NTP 2016). PFOA alters immune function in humans and may increase hypersensitivity-related outcomes and increased autoimmune disease incidence (NTP 2016).

2.5 Production, trade, and use of PFOA, its salts and PFOA-related compounds

2.5.1 Production and trade

PFOA, its salts and PFOA-related compounds have been produced since the 1950s. The production took place first in the U.S. and then expanded to Italy in 1968 and Belgium (starting earliest in 1971) (Wang et al. 2014a). After 1975, production expanded further and took place in countries such as Germany, Japan, Russia and China (Wang et al. 2014a).

The ammonium salt (Ammonium perfluorooctanoate, APFO) and the sodium salt (Sodium perfluorooctanoate, NaPFO) have been largely used as processing aids in the polymerization of certain fluoropolymers (e.g., PTFE, FEP) (3M Company 2000; Prevedouros et al. 2006; Wang et al. 2014a). Wang et al. (2014a) estimated that the sum historical global consumption of APFO/NaPFO for the production of fluoropolymers was approximately 600–4,000 metric tons from 1951 to 2015.

Moreover, the total historical production of PFAI, which is a PFOA-related compound, was estimated to be as high as 171,000 metric tons from 1961 and 2015 (Wang et al. 2014a). Perfluorooctyl iodide (PFOI) has been used since 1961 to produce fluorotelomer-based substances, such as polyfluoroalkyl phosphate diesters (diPAPs), FTSA and FTOHs. These fluorotelomer-based substances have been widely used as surface treatment agents and fluorinated surfactants. Many fluorotelomer-based compounds (e.g. 8:2 and longer-chain homologues) can break down to PFOA and thus are PFOA-related compounds.

Due to concerns about the adverse impact of PFOA on humans and the environment, PFOA, its salts, and PFOA-related compounds were listed on the Stockholm Convention in 2019. They have been and are being substituted in many applications by alternatives (UNEP 2017a).

All production of PFOA and its salts in the European Union (EU) has now ceased, and manufacturing in Japan and the U.S. should have also stopped by the end of 2015 (ECHA 2015a). Meanwhile, there has been a geographical shift of industrial sources of PFOA from primarily North America, Europe, and Japan to emerging economies, and China has become the largest emitter of PFOA/APFO (Meng et al. 2017).

The following table (Table 4) summarizes information related to the production of PFOA, its salts (such as APFO) and FTOHs according to several literature sources (UNEP 2016c).

Table 4: Production of PFOA, its salts, APFO and PFOA-related compounds

Year/Period	Production	Volume [in metric ton/year]	Reference
1992–2002	PFOA production 3M [in US]	113	UNEP (2016c)
2009	Estimated worldwide production of FTOH	11,000–14,000	German Environment Agency (UBA) (2009)
2014	Production of PFOA-related compounds in the EU (actual volume is likely to be greater)	100–1,000	ECHA, (2015a)
2003	Production of PFOA and its salts in China	30	Li et al. (2015)
2012	Production of PFOA and its salts in China	90	Li et al. (2015)

Data concerning imports and exports of PFOA are limited, and no information concerning the global trade flows has been identified owing to industry confidentiality claims (ECHA 2015a).

2.5.2 Uses

PFOA, its salts and related compounds have been used in a wide variety of commercial applications and consumer products across many sectors (ECHA 2015a; OECD 2013).

PFOA has been predominantly used in the form of APFO in aqueous solution as an emulsifier and processing aid in the manufacture of many fluoropolymers. It is therefore a contaminant in many PFAS products (Emmett et al. 2006).

PFOA-related compounds can be either:

- Non-polymeric substances for use in firefighting foams, paints, and photographic films, etc. (OECD 2013; van der Putte et al. 2010). PFOA-related compounds has also been used, as a surfactant and processing aid, in the manufacture of semiconductors used in the photolithographic process (ECHA 2015a; van der Putte et al. 2010) and as a replacement to perfluorooctane sulfonic acid (PFOS) (ECHA 2015a);
- Side-chain fluorinated polymers, which have been used to as water- and oil-proof surface protector for textiles, leather, food contact paper and paperboard, and so on. They are also used in paints (e.g., exterior and interior architectural paints), non-woven medical garments, ski waxes, floor waxes, stone/wood sealants, adhesives, thread sealant tapes, etc. (Glüge et al. 2020; Liu et al. 2014; Posner 2012).

Among PFOA-related compounds, "Fluorotelomers" is a term often used in the literature, referring to substances produced with the telomerization process and are widely used as surface treatment agents and fluorinated surfactants. Fluorotelomers can be PFOA-related compounds if they contain the respective perfluorocarbon chain length longer than 7. It was reported that historically, 80% were used in polymeric forms and 20% in non-polymeric forms (Wang et al. 2014a).

ECHA (2015a) provides estimation on the amounts of PFOA and its salts as well as on PFOA-related compounds used in the EU in different sectors/industries (Table 5).

Table 5: Usage of PFOA, its salts and PFOA-related compounds in different sectors in the EU

	Sector/Industry	Usage in the EU [in metric tons]
PFOA-related compounds	Textile and leather treatment	~1,000
	Paper treatment	>150–200
	Fire-fighting agents	>50–100
	Paints and inks	>50–100
	Others uses	>0.1–0.5
PFOA and its salts	Manufacture of fluoropolymers	<20
	Photo industry	1.0
	Semiconductor industry	<0.05
	Other uses 0.5-1.5 t	0.5-1.5

Reference: (ECHA 2015a)

2.6 Waste streams likely to contain PFOA, its salts and PFOA-related compounds and recommended management/destruction options

Wastes consisting of, containing or contaminated with PFOA, its salts or PFOA-related compounds may be found in a number of physical forms, including (UNEP 2020a):

- Solid obsolete stockpiles of PFOA, its salts and PFOA-related compounds in original packages which are no longer usable because their shelf life has been exceeded or the packaging has deteriorated;
- Soil and sediments;
- Solid waste (food contact materials, paper, textiles, leather, rubber and carpets);
- Production wastes from PFASs;
- Fire suppression equipment;
- Wastewater from industrial and municipal processes;
- Solid residues from wastewater cleaningsuch as activated carbon treatment;
- Sludge, including sewage sludge;
- Landfill leachate;
- Liquid industrial and household cleaning products;
- Liquid fluids (aviation hydraulic fluids).

Waste streams of importance in terms of potential volume or concentration are as follows (UNEP 2020a):

- Sludge and wastewater from fluoropolymer production and processing activities;
- Sludge and wastewater from metal plating and photographic industrial activities;
- Sludge and wastewater from municipal treatment plants;
- Landfill leachate;
- Leather and upholstery;
- Carpets;
- Fire-fighting foams equipment;
- Textiles;
- Obsolete stockpile.

For the environmental sound management of wastes, the following documents can be consulted:

- General technical guidelines on the environmentally sound management of consisting of, containing or contaminated with persistent organic pollutants (UNEP/CHW.14/7/Add.1/Rev.1.) (UNEP 2019a);
- Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/CHW/OEWG.12/INF/8) (UNEP 2020a).

A number of fluoropolymer and fluoroelastomer producers in many parts of the world have developed and implemented various technologies to recover PFOA and other PFAS emulsifiers from their production process, including treatment of off-gases, wastewater streams and fluoropolymer dispersions, so as to reduce emissions and exposure to them (Smith et al. 2014).

Moreover, the Best Available Techniques (BAT) and Best Environmental Practices Technologies (BEP) in terms of emission control measures are summarized in section IV of (FOEN 2017). Some of these technologies may also be used to treat waste streams and products of other relevant industries to reduce emissions and exposure of PFOA and related compounds (FOEN 2017).

3. Alternatives to the use of PFOA, its salts and PFOA-related compounds

As discussed in subsequent sections, the risk management evaluation (RME) of PFOA, its salts and PFOA-related compounds under the Stockholm Convention highlighted that many chemical alternatives are available to replace these substances and commercially in use globally (UNEP 2017a; UNEP 2018a).

3.1 Fire-fighting foams

3.1.1 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 fire-fighting 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). In the past, Class B foams contained fluorinated surfactants or fluoropolymers, including PFOA, its salts and PFOA-related compounds (Cousins et al. 2016). Nowadays, fluorine-free foams (F3) are available in the market. Hereafter, only Class B fire-fighting foams are discussed.

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).

In the past, various perfluoroalkanoyle fluoride (PACF)-, perfluoroalkanesulfonyl fluoride (PASF)-, and fluorotelomer-based derivatives were added (i) as film formers in AFFF and film-forming fluoroprotein foams (FFFP) (German Environment Agency (UBA) 2013), (ii) as fuel repellents in FP, and (iii) as foam stabilizers in FFP and AR-AFFF (Cousins et al. 2016).

PFASs are 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).

In the past, the industry favored the use of C8-based PFASs, including PFOA and PFOS (UNEP 2017a; UNEP 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 and 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 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 PFOA, its salts and PFOA-related compounds is not exempted under the Stockholm Convention (UNEP 2019b). 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 accordance with paragraph 2 of part X of Annex A to the Stockholm Convention on POPs (UNEP 2019b).

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).

3.1.2 Availability of alternatives

Shorter-chain fluorinated alternatives

Most foam manufacturers have reformulated their foam products to contain only shorter-chain (C6 or below) PFASs (FFFC 2018a; Klein 2012; Kleiner and Jho 2009). DuPont, for example, commercialized two AFFFs based on 6:2 fluorotelomer sulfonamidealkylbetaine (6:2 FTAB) or 6:2 fluorotelomer sulfonamideaminoxide (Wang et al. 2013). Suppliers offering a portfolio of shorter-chain fluorotelomer-based surfactants include Chemguard, Chemours and Dynax (UNEP 2017c 2017a). In addition, C6-based compounds includes PFHxS, Dodecafluoro-2-methylpentan-3-one, and 6:2 fluorotelomers such as perfluorohexane ethyl sulfonyl betaine (UNEP 2019c), C4-based fluorinated compounds (Place and Field 2012) have also been used in fire-fighting foams.

Fluorine-free alternatives

The BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on 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 realization 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 and ECHA 2020). Only very general hints on replacement substances or substance groups have been identified for F3 foams, which can be grouped into four substance classes: hydrocarbons, detergents, siloxanes and proteins (EC and ECHA 2020).

The substances that are being used to produce these alternative foams show similarities across different companies/products. A list of fluorine-free foams that are available and used in the EU market is given in Table 6 based on a study published by the European Commission and European Chemicals Agency (EC and ECHA 2020).

Table 6: List of alternative fluorine-free foam products available on the EU market

Manufacturer/supplier	Product
Bio-EX	ECOPOL (Class A and 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 and B), Sthamex® (Class A and B), UltraWet® (Class A), Training foam, Test foam.
3F	Smart Foam® including: FREEDOL SF, FREEFOR SF (Class A), HYFEX SF, FREDEX SF (Class A and B), FREEGEN SF, T-FOAM SF (training foam)
Angus fire	Respondol ATF (Class A and Class B), Jetfoam (Class B), Syndura (Class B), Trainol (traing foam), TF (training foam)
Auxquimia	UNIPOL-FF™ (Class A and B), SF-60 L (Class A and B), H-930 (Class A and B), RFC-105 (Class A and 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

Manufacturer/supplier	Product
Fomtec	P 3% AR (Class A and B), Enviro Plus (Class B), Enviro ultra (Class B), Enviro 3% ICAO (Class B), Enviro eMax (Class A and B), Enviro USP (Class A and B)
National Foam	Muni ^{®F3} Green (Class A and B), Universal ^{®F3} Green (Class A and 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 and B), BoldFoam A+ (Class A), BoldFoam AM (Class A), B-Water (Class A)

3.1.3 Suitability of alternatives

Shorter-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:

The belief that the short-chain C6 and lower PFASs are harmless if released is untrue (Holmes 2017; UNEP 2018a). 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). C6 compounds are detected in the environment including the Arctic, human and wildlife, which makes its use in fire-fighting foams undesirable (UNEP 2017d).

Short-chain anionic and zwitterionic PFASs are expected to migrate downstream of source areas faster than their longer-chain counterparts and will likely break through granulated active-carbon system (Barzen-Hanson et al. 2017). Barzen-Hanson et al. (2017) stated that it may pose challenges for using *ex-situ* remediation techniques because systems designed to capture PFOS and PFOA (such as granulated active-carbon) will not be effective for short-chain PFASs.

Fluorine-free alternatives

Performance:

The operational capabilities of fluorine-free Class B firefighting foams 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 2018b).

Castro (2017) reported the results of testing data on fluorine-free foams. It indicated there were significant differences in the performance between PFAS-containing AFFFs and non-fluorinated foams depending on the types of fire. For heptane and diesel fires, the time required for fluorine-free foams to control the fires relative to AFFF was 5–6% slower, but for Jet A1 fuel and gasoline it was 50–60% slower. For fluorine-free fire-fighting foams, the application rate to control a fire is higher than for PFAS-containing AFFFs, but the application rate had no impact on the extinguishing rate. The authors attributed these observations to the PFAS-containing AFFFs having good foam repellence against hydrocarbons when applied in forceful application. It was suggested that the lack of good oil-repellence properties for fluorine-free foams could mean, even if the fuel is covered with the foam blanket, some fuel may still be picked up and become contaminated, impeding full rapid extinguishment and potentially increasing

the risk of re-ignition. It was concluded that fires on fuels with lower flash points are more difficult to control with fluorine-free foams.

However, recent tests confirm that fluorine-free 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 ICAO Fire Test Standard (Huczek 2017).

In 2012, a testing program led by the UK Civil Aviation Authority noted that fluorine-free foams are ICAO Level B approved and indicated that a new generation of fluorine-free firefighting foams using compressed air foam systems CAFS² proved to be as effective and efficient as the currently used PFAS-containing AFFFs.³

Civilian airports and offshore companies around the world have introduced fluorine-free foams and are satisfied by the performance (UNEP 2018a).

According to a review undertaken by the Queensland Government in Australia, many fluorine-free foams are acknowledged as meeting the toughest amongst 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 fluorine-free foams has substantially decreased any difference in performance levels (IPEN 2018b).

Hazards:

Based on the assessed substances, non-fluorinated alternatives are likely to be of lower environmental concern, primarily due to biodegradation (EC and ECHA 2020).

Some siloxanes were identified by ECHA's Member State Committee as Substances of Very High Concern (SVHC) with persistent, bioaccumulative and toxic (PBT) and/or very persistent and very bioaccumulative (vPvB) properties (such as octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6)). Other (linear) siloxanes such as octamethyltrisiloxane are currently undergoing PBT-assessment by ECHA.

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 has 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 application of foams, particularly on petrol and jet A1 fuels that significantly more fluorine free foam (from 2.31/min/m² to 3.75/min/m²) 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 externalized 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 fluorine-free 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

² 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.

³ <https://www.internationalairportreview.com/article/11655/ensuring-a-safer-future-for-the-aviation-industry/>.

horticultural products can become unsaleable; increasing number of legal actions and claims (against manufacturers and end users) (UNEP 2018a).

3.1.4 Implementation of alternatives

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

Based on the study from the European Commission and ECHA, most fluorine-free foams use either hydrocarbons or detergents in the foams (EC and ECHA 2020). Siloxane- and protein-based fire-fighting foams maybe still in the phase of development. No commercial fluorine-free foams containing these substances was identified in the task of a study carried out by European Commission and ECHA (EC and ECHA 2020).

Fluorine-free 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 fluorine-free foams are ICAO Level B approved and found that fluorine-free 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).

Fluorine-free foam has been in use in fire trucks at London Heathrow Airport without any operational deficiencies. The following advantages of using fluorine-free foam were described: The airport returned to full operations very quickly following two incidents, with no clean-up costs; Operational and environmental responsibilities 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 fluorine-free 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). Moussol-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 fluorine-free 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 fluorine-free foams. All of the 27 major airports in Australia have transitioned to fluorine-free foams, while airports in Europe such as Billund, Guernsey, Bristol, Blackpool, Köln Bonn are also using fluorine-free foams (IPEN 2018b).

Private sector companies using fluorine-free 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 2018b).

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

3.1.5 Conclusion

Foam manufacturers support the use of both fluorinated and fluorine-free products in appropriate applications and feel strongly that both types of products are necessary for the fire protection needs of society. No single type of foam meets all 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).

The evidence presented within the RME suggests that chemical alternatives to PFOA-containing AFFF exist and are actively in use globally. These include short-chain PFAS-based foams and fluorine free alternatives. From the point of view of environmentally sound management, fluorine-free products with proven efficacy should be the preferred option.

Based on the information compiled and reviewed within the RME, the size of in-use stockpiles for fire-fighting foams containing PFOA and PFOA-related compounds may be significant, considering that such compounds can also be present as impurities in shorter-chain 6:2 fluorotelomer technologies.

Concerns have been highlighted about the mobility and potential environmental impacts of shorter-chain PFASs in fire-fighting foams. Concerns have also been raised on the significant socioeconomic costs related to site decontamination and it is highly recommended not to use up stockpiles or installed fire-fighting foams containing

PFOA and PFOA-related compounds for training purposes before the entry into force with the aim of avoiding disposal and decontamination costs.

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 may be needed to move to alternatives without PFASs.

3.2 Semiconductor industry

3.2.1 Introduction and background

PFOA has 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 PFAS in the semiconductor industry include, e.g., developer and rinse solutions (Glüge et al. 2021). 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. 2021).

Industry stakeholders have identified the use in semiconductor industry as potentially critical. The Semiconductor Industry Association (SIA) surveyed its member companies and found that several companies continue to use PFOA and related chemicals in the photolithography process, a key step in the manufacturing process to produce advanced semiconductors (SIA Comments on 1st draft RME, (UNEP 2017a)). This sector is responsible for a very low share of total emissions of PFOA and PFOA-related compounds. The volume used in the sector is a minor part of the total volumes used in the EU and the substances are reported to be used under strictly controlled conditions.

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.

Photolithography is the critical process in defining the level of sophistication and performance of semiconductor devices. PFOA is stringently managed in the photolithography process. There is no release to the workplace due to the use of closed systems processes. Solvent waste is collected at the factories and sent for incineration. Further exhaust systems with abatement equipment (scrubber) are used. There is very minimal release to the environment via wastewater. Based on an industry figure of usage per annum of <50kg, overall emissions through wastewater based on expert engineer knowledge of the process technology and waste stream would give rise to estimated 4kg per annum. This is a conservative estimation – a worst case scenario (van der Putte et al. 2010).

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.⁴ 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 to the complexity of replacing these substances in all applications.

3.2.2 Availability of alternatives

PFOA, its salts and PFOA-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

⁴ Joint statement of 23rd meeting of the World Semiconductor Council.

(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 pentacyanocyclopentadienide (CN5) or methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1); and 4) triphenylsulfonium (TPS). Other related patents include US20090181319 (W. Li et al. 2009) and US8034533 (S. Liu and 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”.⁵

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), 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. 2021).

3.2.3 Suitability of alternatives

Photolithographic process

Short-chain PFASs: As discussed in section 3.1.3, 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 2019b). 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. 2021). The potential health and environmental concern of fluorine-free photoresist is not clear for all alternatives. CandL data for NBS indicated that this substance has no carcinogenic, mutagenic or toxic for reproduction (CMR) properties (Glüge et al. 2021). Environmental hazard data were estimated for NBS, TBNO, TN, and CN5, all of which indicate lower environmental hazard than for PFAS (Glüge et al. 2021).

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 fulfill the technical functions needed and has potential also for future developments in the semiconductor industry (Glüge et al. 2021). No information is available on the hazards of the alternatives proposed.

3.2.4 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 world's largest dedicated independent (pure-play) semiconductor foundry. According to the TSMC 2020 Corporate

⁵ http://www.fujifilmusa.com/products/semiconductor_materials/photo-resists/krf/index.html.

Social Responsibility Report, TSMC succeeded substituting all PFOA-related substances and added PFASs with one to four carbons were substances that required disclosure in 2020.⁶

3.2.5 Conclusion

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

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).

3.3 Photographic coatings applied to films

3.3.1 Introduction and background

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 employee 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 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 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 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).

3.3.2 Availability of alternatives

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 (Poulsen et al. 2005).

⁶ <https://esg.tsmc.com/download/file/2020-csr-report/english/pdf/e-all.pdf>.

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

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 use of photographic and X-ray films (UNEP 2016b).

IAEA and WHO⁷ 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 2018a).

3.3.3 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 suggest that commercial products are readily available for photoimaging applications. However, the lack of available information of 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 regards 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).

3.3.4 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 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.

3.3.5 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 effecting alternative approach to using PFOS/PFOA/PFASs in photo imaging is the technological shift to digital photography.

⁷ 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>.

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

3.4.1 Introduction and background

PFOS- and PFOA-related compounds 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 textile 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 residues in the studied textiles (Robel et al. 2017). These unbound residues or impurity 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 PFOA and its related compounds in these uses are readily available, technically and economically feasible, and have been widely implemented already.

However, 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 PFAS 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 for 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.

3.4.2 Availability of alternatives

Alternatives for use in carpets, leather, apparel, upholstery, and non-technical textiles include short-chain or other fluorinated alternatives, fluorine-free alternatives and non-chemical alternatives. In the following paragraphs, relevant alternatives are briefly summarized.

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/>.

In certain medical applications, IPEN and ACAT submitted information in 2018 that technically feasible alternatives that meet regulatory requirements and do not contain PFOA are available for some products such as surgical gowns and drapes (IPEN and ACAT 2018). These products are usually based on C6 fluorinated polymers.

- 3M™ Steri-Drape:
http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSu9n_zu8l00xm8mBl8t94v70k17zHvu9lxtD7xt1evSSSSSS-
- Daikin: <https://www.daikinchem.de/products-and-performance/water-oil-repellency>.
- Halyardhealth: <https://products.halyardhealth.com/surgical-solutions/surgical-gowns/breathable-high-performance-gowns/halyard-microcool-breathable-high-performance-surgical-gown-with-secure-fit-technology.html>.
- Asahi: <https://www.agcchem.com/news/2016/june-1-2016-asahiguard-ag-e600-repellent-provides-sustainable-solution-for-nonwoven-medical-textiles>.

Short-chain (“C4”) PASF-based side-chain fluorinated polymers, such as high molecular-weight acrylic polymers, contain 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™): https://www.scotchgard.com/3M/en_US/scotchgard/built-in-protection/.

Other fluorinated alternatives

Solvay has developed a product named Fluorolink® P56⁸ 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.

Fluorine-free 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 paraffins (usually consisting of modified melamine-based resins), and dendrimers that are being developed to imitate the ability of the lotus blossom to repel water. Alternatives to provide similar water-repellency are available and include textile surface treatment applications based on acrylate, methacrylate adipate and urethane polymers (UNEP 2019c; VTB-SWT 2016).

According to the RME, there is a range of fluorocarbon-free, water-repellent commercial finishing agents for textiles such as BIONIC-FINISH® ECO and RUCO-DRY® ECO marketed by Rudolf Chemie Ltd., Geretsried/Germany; and ecorepel® marketed by Schoeller Technologies 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-repellency>;
Nicca: <https://www.niccausa.com/fluorine-free-water-repellent/>;

⁸ <https://www.solvay.com/en/product/fluorolink-p-56>.

- 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://www.organoclick.com/site/assets/files/1594/tds_oc-aquasil_tex_30x_eng.pdf.

The BIONIC-FINISH®ECO introduced by Rudolph Group is a fluorocarbon-free, water-repellent treatment for textiles.⁹ BIONIC-FINISH®ECO is composed of a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers (UNEP 2016b).¹⁰ 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).

Non-chemical alternatives

Considering 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. 2021). For example, the yarn producer, Aquafil, offers stain-free fibers based on the nylon-6 fiber “Econyl StayClean”.¹¹ This fiber is made from nylon waste that was depolymerized and recycled (Glüge et al. 2021; 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 a PFAS-free stain protection (Glüge et al. 2021; Vallette et al. 2017).

3.4.3 Suitability of alternatives

Short-chain fluorinated alternatives

Short-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 2019b). 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).

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

⁹ <https://www.rudolf.de/en/technology/bionic-finish-eco/>.

¹⁰ There are still data gaps but some data are available in UNEP/POPS/POPRC.8/INF/17/Rev.1.

¹¹ Econyl. Econyl Stay Clean <http://www.econyl.com/stay-clean/>.

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 emits 4–8 times more PFASs compared to using the C8-chemistry (Euratex 2016; UNEP 2018a).

Fluorine-free alternatives

In some cases, when applying fluorine-free alternatives, quality requirements of technical textiles cannot be fulfilled due to, for example, decreased water-, oil- and/or dirt-repellent properties, inadequate abrasion and/or inadequate wash resistance. Schellenberger et al. (2018) reported that non-fluorinated alternatives such as silicone, silicon functionalized polyurethane, paraffin wax and hyper-branched polymer with hydrocarbon-modification were unable to repel oil.

However, water-repellency ratings were similar across the range of all finished fabrics tested. They all demonstrated a high level of resistance to wetting, and several nonfluorinated repellent fabrics provided similar water repellency as long-chain (C8) PFAS or short-chain (C6) PFAS finished fabrics (Hill et al. 2017).

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 (Polydimethylsiloxanes) are used as water repellent agent 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. Certain siloxanes 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 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. The ecological risks arising from industrial uses of cyclic siloxanes in Australia have recently been assessed (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 are 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 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 should not be classified as harmful for 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.

3.4.4 Implementation of alternatives

Generally speaking, the alternatives are available in the market for casual, outdoor and sport activities and PFOA, its salts and PFOA-related compounds have been increasingly replaced by short-chain fluorinated compounds and fluorine-free compounds. The 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 the 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).

3.4.5 Conclusion

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). Exemption is thus granted to PFOA, its salts and related compounds in textiles for oil and water repellency for the protection of workers from dangerous liquids by the Parties to the Stockholm Convention. However, PFOA, its salts and PFOA-related compounds are not allowed to be used for carpets, leather, apparel, upholstery, and non-technical textiles (e.g., outdoor applications) under the Stockholm Convention.

PFOA, its salts and PFOA-related compounds have been increasingly replaced by short-chain fluorinated compounds and fluorine-free compounds in the field of casual, outdoor and sport activities. However, short-chain fluorinated alternatives (C6 and C4) show increasing concerns due to their toxicity, persistence, mobility and difficulty to be treated. The health and ecological risks of some fluorine-free alternatives remain unclear.

3.5 Manufacture of fluoropolymers

3.5.1 Introduction and background

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 A¹² to the Stockholm Convention (European Commission 2020a).

PTFE has excellent dielectric properties, specifically low group velocity dispersion (Mishra and Yagc 2008) which makes it widely used as 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 an 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.¹³ 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

¹² Decision SC-9/12.

¹³ Teflon™ FEP information bulletin, <https://www.teflon.com/en/-/media/files/teflon/teflon-fep-film-tech-bulletin.pdf>.

reversible. The only chemicals reacting with FEP resins are fluorine, molten alkali metal, and molten sodium hydroxide.

3.5.2 Availability of alternatives

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 ($\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCHF}_2\text{COO}^-\text{NH}_4^+$; CAS No: 958445-44-8; (Gordon 2011)); (II) GenX or C3 Dimer salt¹⁴ from DuPont ($\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^-\text{NH}_4^+$; CAS No: 62037-80-3; (UNEP 2017a)); (III) cyclic or polymeric functionalized PFPEs from Solvay (Marchionni et al. 2010; Pieri et al. 2011; Spada and Kent 2011); (IV) EEA-NH₄ from Asahi ($\text{C}_2\text{F}_5\text{OC}_2\text{F}_4\text{OCF}_2\text{COO}^-\text{NH}_4^+$; CAS No: 908020-52-0; (EFSA 2011b)); and (V) $\text{CF}_3\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^-\text{NH}_4^+$ from Daikin (Hintzer and Schwertfeger 2014).

C3 Dimer salt (GenX), ADONA and EEA-NH₄ 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 $\text{CF}_3\text{O}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})(\text{CF}_2\text{OO})(\text{C}(\text{CF}_3)\text{FO})\text{COO}^-$ (Xie et al. 2010; J. Zhang et al. 2012).

Non-fluorinated emulsifiers/surfactants as alternatives

Non-fluorinated emulsifiers for vinylidene fluoride (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 and 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.¹⁵

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 polytetramethylene 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.¹⁶

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.¹⁷

Process/technology alternatives

Various fluoropolymer manufacturers are exploring and have patented a number of PFAS-free aqueous emulsion polymerization processes (Hintzer and Schwertfeger 2014; UNEP 2017a). These include: (1) emulsifier-free polymerization of amorphous standard co/terpolymers comprising tetrafluoroethylene (TFE), hexafluoropropylene (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.

¹⁴ IUPAC name: Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate; CAS No: 62037-80-3.

¹⁵ US patent application Pub. No.: US 2012/0116003 A1 for assignee of E.I. Du Pont Nemours and Company.

¹⁶ United States Patent No. US 9,068,071 B2 for assignee of Arkema Inc.

¹⁷ US Patent application Pub. No.: US 2014/0179868 A1.

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 the fluorinated polymer to be produced.¹⁸

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.¹⁹ 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 polymeric surfactants and include perfluoropolyether having one or more anionic groups, such as carboxylic acid groups or salts thereof examples of perfluoropolyether surfactants.²⁰

3.5.3 Suitability of alternatives

Three PFOA-alternatives with ether moieties (GenX, ADONA and EEA-NH₄) were assessed in the EU restriction process (ECHA 2015a).

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.²¹ 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 reevaluating 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 P and the T criterion 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; Wang et al. 2015).

EEA-NH₄ is considered persistent (UNEP 2017a; Wang et al. 2015). Provided data is not sufficient to conclude on not bioaccumulating (B). Regarding environmental risks (data were taken from the registration dossier) related to EEA-NH₄ 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

¹⁸ US patent application Pub. No.: US 2016/0108225 A1 for assignee of Asahi Glass Company Limited.

¹⁹ United States patent application Pub. No.: US 20040186219A1.

²⁰ United States patent application Pub. No.: US 20040186219A1.

²¹ <https://www.epa.gov/chemical-research/human-health-toxicity-assessments-genx-chemicals>.

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 (Wang et al. 2015).

Moreover, some short-chain PFAS 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 another word, ADONA and F-53B transferred to stable terminal products after 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 neglectable in a drinking water treatment plant after coagulation, ozonation, biofiltration, and disinfection.

According to ECHA, most of the stakeholders stated that there are no technical differences between fluoropolymers produced with PFAS 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 substitution from PFOA to alternatives.

3.5.4 Implementation of alternatives

Fluoropolymer manufacturers are exploring novel processes to eliminate the use of PFAS in aqueous emulsion polymerization. For the production of PVDF, processes with fluorine-free emulsifiers have been implemented by multiple manufacturers (Glüge et al. 2021).^{22,23} 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. 2021).

PFOA-free PTFE are available in the market.²⁴ Zero-PFOA FEP is also available in the market.²⁵ 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 to have selected and industrialized a perfluoroalkylether acid-based alternative to PFOA for its production processes of PTFE and fluoroelastomers since 2007 (Xie et al. 2009).

3.5.5 Conclusion

PFAS alternatives, such as GenX, ADONA and EEA-NH₄ are still persistent. Provided data was not sufficient to conclude on their bioaccumulation (B). Some PFAS alternatives such as GenX have been recognized being similarly problematic as PFOA. Assessment and regulations are necessary to evaluate and regulate the life-cycles of these alternatives. Information related to composition and implementation of other alternatives in the fluoropolymer production needs to be made available.

²² Kynar500FSF. Fluorosurfactant Free Kynar® PVDF Resin <https://www.kynar500.com/en/product-information/fluorosurfactant-free/>.

²³ Solvay. Solvay Launches Non-Fluorosurfactant Technologies in the U.S. <https://www.solvay.com/en/press-release/solvay-launches-non-fluorosurfactant-technologies-in-us>.

²⁴ <https://www.greblon.com/en/technology/ptfe-ceramics>.

²⁵ <https://www.precisioncoating.com/medical-coating-services/medical-fep/>.

3.6 Invasive and implantable medical device

3.6.1 Introduction and background

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.²⁶ In EU, the same is exempted until 4 July 2025 (European Commission 2020a).

3.6.2 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.hydrumer.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 3.5 Manufacture of fluoropolymers.

3.6.3 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 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.

²⁶ Decision SC-9/12.

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 3.5 Manufacture of fluoropolymers.

3.6.4 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 have 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).

3.6.5 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, long period is needed to ensure a cost-effective transition to alternatives.

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

3.7.1 Introduction and background

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.²⁷ PFOI may be present in 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 intermediate in the production of PFOB.²⁸

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 A²⁹ to the Stockholm Convention.

²⁷ 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.

²⁸ UNEP/POPS/POPRC.13/7/Add.2.

²⁹ Decision SC-9/12.

3.7.2 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.³⁰ There is, however, no information on PFOI impurities content in the final PFOB product.

3.7.3 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;
- 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 European Union 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 incur 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. This option is not viable.

Scenario d: the use of structurally different alternatives to PFOB. There are no suitable substances that 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.

3.7.4 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.

3.7.5 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.

³⁰ US 2020/0157028 A1 Composition containing C8F17Br and method for producing C8F17Br.

3.8 Other applications: Food contact materials

3.8.1 Introduction and background

PFASs, including PFOA have been used in paper and board food packaging since the 1950s. Certain PFASs are intentionally applied to paper and board packaging where these PFASs confer mainly fat, but also stain and water repellence properties (OECD 2020). 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 PFAS (OECD 2020). US FDA currently does not allow long-chain PFASs in food contact materials applications; they removed the last legacy PFOA-related substances from 21 CFR 176.170 in 2016 (see 81 Fed. Reg. 5–8).

Parties to the Stockholm Convention do not exempt the use of PFOA, its salts and PFOA-related compounds in food contact materials.

3.8.2 Availability of alternatives

Alternatives to PFOA, its salts and PFOA-related compounds in paper and board can be divided into short-chain fluorinated alternatives, fluorine-free chemical alternatives, and fluorine-free physical alternatives.

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. 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 Institut für Risikobewertung, BfR) and the US (included on the list of the US Food and Drug Administration, FDA).

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 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 the most stable 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™), 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 aluminum 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 fibers react with the acid and almost melt together (OECD 2020; Twede and 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, aluminum and polylactic acid

Another method to make a physical barrier is achieved by laminating an extra layer of plastic or aluminum 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).

3.8.3 Suitability of alternatives

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). 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 PFAS and Alternatives in Food Packaging (OECD 2022b).

Short-chain fluorinated alternatives

There is a rising concern about the adverse health and environmental effect of short-chain PFASs. 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.³¹

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™ 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 use 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 2019a).

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).

3.8.4 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 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 PFAS manufacturers to develop short-chain PFAS technology that meets the required specification for use in food contact materials. Discussions with PFAS 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).

3.8.5 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).

³¹ <https://www.fda.gov/food/cfsan-constituent-updates/fda-announces-voluntary-phase-out-industry-certain-pfas-used-food-packaging>.

3.9 Other applications: Coatings, paints and varnishes

3.9.1 Introduction and background

Historically, PFAS-related chemicals including PFOA had several uses in coating, paint and varnishes to reduce surface tension, for example, for substrate wetting, for levelling, as dispersing agents and for improving gloss and antistatic properties 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 7 summarizes the uses of PFAS 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 semi-conductor 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 7: Uses of PFAS in coatings, paints and varnishes. Source: OECD (2022)

	OECD Product Categories	Applications	Use examples	Fluoropolymers	Other PFASs (Non-polymeric PFAS)
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 fluoro-sulphonamides
	Paints	Aerosol spray paints	Automotive paints	Car coatings	PTFE
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	PVDF, FEVE, ECTFE, PTFE, FEP	C4-PFBS and C4-fluorinated ethers**, C6-based PFAS
Solvent-based paints			Chemical: lining of vessels, metal surface protection Domestic: doors, walls		

	OECD Product Categories	Applications	Use examples	Fluoropolymers	Other PFASs (Non-polymeric PFAS)
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 PFAS e.g. perfluoro-1-butanefluoride (PBSF), fluorinated polyethers**, short-chain PFAS 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 semiconductor manufacturing and very limited derogations exist for PFOA in the Stockholm Convention (UNEP 2017c). PFOS is mainly 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).

3.9.2 Availability of alternatives

Fluorinated alternatives:

As shown in Table 7, fluoropolymers and non-polymeric PFASs are used in coatings, paints and varnishes. The available PFOA alternatives in this field thus refers to PFOA-free fluoropolymers and short-chain PFASs. More information related to PFOA-free fluoropolymers can be found in section 3.5. 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:
 - 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+3294857497 andrt=r3;
- Fluorinated polyethers;
- Oxetane Fluorosurfactants, an oligomeric poly(oxetane) backbone with short ($\leq C_4F_9$) perfluoroalkyl groups;

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 nanoceramic and nano aluminium oxide, polyurethane (PU), polyvinyl chloride (PVC), polyolefin³² 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-PFAS 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.

3.9.3 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).

3.9.4 Implementation of alternatives

Results from consultation with industry indicate that short-chain PFASs are already commonly used in paint applications. 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).

³² A polyolefin is a type of polymer produced from a simple olefin (also called an alkene with the general formula C_nH_{2n}) 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.

There is no longer exemption of PFOA, its salts and related compounds in paints and inks in EU and the Stockholm Convention.

3.9.5 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 for 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 of PFOA, its salts and PFOA-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 taken into account when dealing with possible alternatives.

Generally speaking, there are three types of alternatives to PFOA, its salts and PFOA-related compounds: short-chain fluorinated compounds, fluorine-free compounds and physical (non-chemical) alternatives. Alternatives are technically and economically available in many industries or applications including fire-fighting foam, photolithography and developer solution in semiconduction industry, manufacture of fluoropolymer such as PTFE and FEP, and implantable and invasive medical devices. In some fields, however, there is either no technically available alternatives or the cost-effectiveness is too low. This includes textile finishing for the protection of workers, photographic coatings applied to films, and use of PFOI for the production of PFOB. 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 potential health and environmental effects 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). One of the short-chain alternatives, PFHxA, has been identified to have PBT/vPvB properties or properties of 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, detergent (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, environmental and health effects; the trade names and chemical composition of alternatives, the implementation status of the alternatives 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, more intensive assessment of the compounds, and more international cooperation.

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

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
Fire-fighting foam	Dodecafluoro-2-methylpentan-3-one	Technical and economical available Remediation cost may occur after uncontrolled application	H412 - Harmful to aquatic life with long lasting effects ³³ .
Fire-fighting foam	6:2 fluorotelomers such as perfluorohexane ethyl sulfonyl betaine	Technical and economical available Remediation cost may occur after uncontrolled application	High mobility. Can degrade to fluorinated substances which are persistent (Shaw et al. 2019). Not enough information referring to the toxicity and bioaccumulation.
Fire-fighting foam	PFHxS,	Technical and economical available Remediation cost may occur after uncontrolled application	PFHxS is persistent, bioaccumulative, toxic to animals including humans and transported to locations far from its production and use (UNEP 2018b).
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 and 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 and ECHA 2020)	Low concern
Semiconductor industry	Short-chain fluorinated alternatives. No specific details of the composition	Information not available.	Many short-chain PFASs are persistent and toxic; they have high mobility, but assumed to be less bioaccumulative than long-chain PFASs.
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 PFASs are persistent and toxic; they have high mobility, but assumed to be less bioaccumulative than long-chain PFASs.

³³ "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
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 2018a)	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 detailed composition unknown	Technical and economical available	PFBS is persistent and bioaccumulative (but less bioaccumulative than PFOA and PFHxS) (ECHA 2019b). 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).
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

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
			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 based on animal studies following oral exposure. ³⁴
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

³⁴ <https://www.epa.gov/chemical-research/human-health-toxicity-assessments-genx-chemicals>.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
			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 and 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. ³⁵	Lack of information	Lack of information
Manufacture of fluoropolymer	Arkema developed aqueous fluoropolymer dispersions which non-ionic non fluorinated emulsifier is used to produce fluoropolymer	Lack of information	Lack of information

³⁵ 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
	emulsions (UNEP 2017a). The emulsifiers used in the invention are those that contain segments of polyethylene glycol, polypropylene glycol, and/or polytetramethylene 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 ³⁶ .	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 and 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”

³⁶ US Patent application Pub. No.: US 2014/0179868 A1.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
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 side chain ("C6") fluorinated polymers	Technical and economical available	They can degrade to fluorinated substances 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 cupstock or 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 2019a).
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.

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
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	<p>Perfluorobutane sulfonate (PFBS) can be a final degradation product of perfluorobutane sulfonyl fluoride (PBSF)-based chemicals.</p> <p>PFBS is persistent and bioaccumulative (but less bioaccumulative than PFOA and PFHxS) (ECHA 2019b). 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).</p>
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 ³⁷
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

³⁷ 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
			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. Diisopropylnaphthalene (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	Technical available	Low concern

Industry or application	Alternatives	Availability and social-economic efficiency	Health and environmental concern
	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).		