

# **Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and their related substances listed under the Stockholm Convention on Persistent Organic Pollutants**

March 2021

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## Acknowledgements

The work to review and update the guidelines and guidance on best available techniques and best environmental practices is conducted by the experts on best available techniques and best environmental practices in accordance with the terms of reference set out in annex to decision SC-8/6, thanks to the generous financial support provided by European Union through the European Commission Global Public Goods and Challenges (GPGC) programme and through the in-kind contributions of the nominated experts. The valuable input of the experts nominated by Parties and others to be consulted in the process for review and update of the guidelines and guidance is highly acknowledged. The experts' names are listed in the joint Toolkit and BAT and BEP expert roster, accessible on the Stockholm Convention's website.

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## Preface

This document has been initially developed in 2012 by the United Nations Industrial Development Organization (UNIDO) and the United Nations Institute for Training and Research (UNITAR), working in collaboration with the Secretariat of the Stockholm Convention and with financial support of the Global Environment Facility (GEF). In 2013, further to the request of the Conference of the Parties (COP) to the Stockholm Convention, the document has been revised in the frame of the Stockholm Convention best available techniques (BAT) and best Environmental Practices (BEP) expert process, based on comments received from parties and others, and submitted for consideration by the COP in 2015. The present document supersedes the guidance on BAT/BEP issued in January 2017 (re-issued for technical reasons in March 2017) (<http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-BATBEP-GUID-PFOS-201703.En.pdf>), contains most up-to-date information and knowledge as evaluated and integrated in the guidance by the BAT and BEP experts, and supersedes the previous versions. The initial contribution of contributory organizations and the expert input provided by the BAT and BEP group of experts is highly acknowledged. Before finalization, the draft document was circulated for comments to national stakeholders and others in January 2021.



## Abbreviations and acronyms

6:2 FTS	6:2 fluorotelomer sulfonate
AFFF	aqueous film-forming foam
AR-AFF	alcohol resistant aqueous film-forming foam
AR-FFFP	alcohol-resistant film-forming fluoroprotein
AR-FP	alcohol-resistant fluoroprotein foam
BAT	best available techniques
BEP	best environmental practices
BREF	BAT Reference Document
CCD	charge-coupled device (technology for capturing digital images)
COP	Conference of Parties
Cr(VI)	chromium(VI)
ECF	electrochemical fluorination
EHLA	extreme high speed laser metal deposition
EMS	environmental management system
ETFE	ethylene tetrafluoroethylene, a fluorine-based plastic
EtFOSA	<i>N</i> -ethyl perfluorooctanesulfonamide
EtFOSE	<i>N</i> -ethyl perfluorooctanesulfonamidoethanol
FFFP	film-forming fluoroprotein foam
FOSA	<i>N</i> -alkylperfluorooctanesulfonamide
FOSE	<i>N</i> -alkylperfluorooctanesulfonamidoethanol
FP	fluoroprotein foam
GHS	Global Harmonization System
HVOF	high velocity oxygen fuel process
PBT	persistent, bioaccumulative and toxic
PFAS	per- and polyfluoroalkane substances
PFCA	perfluoroalkane carboxylic acid(s)
PFOS	perfluorooctanesulfonate
PFOSF	perfluorooctanesulfonyl fluoride
PFSA	perfluoroalkane sulfonic acid(s)
POPRC	Persistent Organic Pollutant Review Committee
POPs	persistent organic pollutants

PVD	physical vapour deposition
SDS	safety data sheet
TEA	tetraethylammonium heptadecafluorooctanesulfonate, tetraethylammonium salt of PFOS

## 1 Introduction

This document supersedes the “Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention” as of January 2017 (<http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-BATBEP-GUID-PFOS-201703.En.pdf>), to reflect the provisions of two relevant decisions at Stockholm Convention COP-9 in relation to PFOS, its salts and perfluorooctane sulfonyl fluoride (SC-9/4) and to incorporate perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (SC-9/12).

For the purpose of this document, the term “PFOS, PFOA and their related substances” is used to address the listing of certain persistent organic pollutants as shown in SC-9/4 “perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF)” and SC-9/12 “perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds”.

### 1.1 Purpose

This guidance builds on decisions SC-7/8 and SC-8/6 by the Conference of the Parties “for the review and update of guidelines and guidance to address releases from unintentional production and best available techniques and best environmental practices for the chemicals listed in Annexes A, B and/or C to the Stockholm Convention” and BAT/BEP requirement for PFOS, its salts and PFOSF as laid down in annex B, part III (2) referring to Annex C with the following definitions:

- i. “Best available techniques” means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole. In this regard:
- ii. “Techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;
- iii. “Available” techniques means those techniques that are accessible to the operator and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and
- iv. “Best” means most effective in achieving a high general level of protection of the environment as a whole;
- v. “Best environmental practices” means the application of the most appropriate combination of environmental control measures and strategies.

Article 3, paragraph 6 of the Stockholm Convention, requests Parties that have a specific exemption and/or acceptable purpose in accordance with Annexes A or B to the Convention to take measures to ensure that any production or use under such exemption or purpose is carried out in a manner that prevents or minimizes human exposure and releases to the environment (e.g., applying BAT and BEP).

This guidance document has been developed and is updated to guide Parties in their actions to prevent or reduce releases of perfluorooctane sulfonic acid (PFOS), its salts, PFOSF and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds from production and use under the specific exemptions and acceptable purposes listed in the Convention at its ninth meeting in 2019 (COP-9, SC-9/4 for PFOS and SC-9/12 for PFOA). These provisions entered into force on 3 December 2020.

This document includes most up-to-date information and knowledge with status at COP-9. Please consult previous versions of the guidance document for information on expired exemptions (<http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceonBATBEPfortheuseofPFOS/tabid/3170/Default.aspx>).

Because information by Parties and observers on the specific exemptions referred to in paragraph 1 of the decision SC-9/13 for PFOA, PFOA salts and PFOA-related compounds will be available in 2026 the current version focuses on uses similar to PFOS as a pragmatic approach for inclusion of new information as available, noting that there will most likely be information gaps for this chemical group.

**Chapter 1** outlines the purpose and structure of this document.

**Chapter 2** is a brief overview of identity, production, and uses of PFOS, PFOA and their related substances, the relevant provisions under the Stockholm Convention and a summary of required measures under these provisions. Furthermore, Table 3 and

Table 4 summarize whether or not alternatives are available and in use for each acceptable purpose and specific exemption. Table 5 and Table 6 provide a comprehensive summary of BAT and BEP for each acceptable purpose and specific exemption.

**Chapter 3** includes high level BAT and BEP principles for general chemical management, general pesticide management and guidance for the management of PFOS and PFOA and related substances in particular.

**Chapters 4** provides guidance for the acceptable purpose for PFOS-related substances (Note: there are none for PFOS and none for PFOA and PFOA-related compounds).

**Chapter 5** provides guidance for BAT and BEP measures for specific exemptions applicable to both, PFOS, PFOA and their related substances. Subsequent subchapters provide details for specific exemptions applicable to PFOS, its salts and PFOA and then to PFOA, its salts and PFOA-related compounds.

Each section within these chapters provides a general description (Background) of the process/application in which PFOS or PFOA and their related substances are used, including information on available alternatives for that use, and specific BAT and BEP guidance for management of PFOS or PFOA and their related substances and their alternatives in the respective process/application.

## 2 Substances covered under this document

PFOS and PFOA are referred to as per- or polyfluoroalkyl substances (PFAS) and belong to the group of non-polymers in the subgroup of perfluoroalkyl acids (PFAA). PFOS belongs to the subgroup of perfluoroalkane sulfonic acids (PFSA) and PFOA belongs to the subgroup of perfluoroalkane carboxylic acids (PFCA) (Buck *et al.* 2011). Both groups contain only C and F atoms in the PFAA moiety.

In this document, the following definitions/classifications are used:

- PFOS, its salts and PFOSF are characterized by the  $C_8F_{17}$ -moiety directly attached to the sulfonic acid group or that can degrade to PFOS or are or were produced with PFOSF as an intermediate chemical;  
 For molecular structures, see Table 1: Examples of PFOS and PFOS-related substances. Please note, these substances are a mix of linear and branched isomers. The structural formula in the table is shown for the linear compounds only..
- PFOA, or its salts are substances having a linear or branched perfluoroheptyl group ( $C_7F_{15}$ )C moiety and PFOA-related compounds which are substances having a linear or branched perfluorooctyl group with the moiety ( $C_8F_{17}$ )C as one of the structural elements and that can degrade to PFOA.  
 Note: According to decision SC-9/12, the characteristic moiety for PFOA-related compounds is ( $C_7F_{15}$ )C; however, it shall be noted that ( $C_7F_{15}$ )C as a degradation product (after defluorination and oxidation to carboxylic acid) can only be generated from compounds with the moiety ( $C_8F_{17}$ ).  
 For chemical identity and molecular structures, see Error! **Not a valid bookmark self-reference.** includes 8:2 fluorotelomer alcohol (8:2 FTOH) and 8:2 fluorotelomer (meth)acrylate (8:2 FTMAC) which are polyfluorinated substances containing an ethyl alcohol group, with the general structure  $F(CF_2)_nCH_2CH_2OR$ , where  $n = 8$  (note: not conform with the listing in (iii) above). These substances can degrade to form PFOA (Buck *et al.* 2011].
- Table 2: Examples of PFOA and PFOA-related compounds and chapter 2.1.2.

### 2.1 List of specific substances and relation to Stockholm Convention

#### 2.1.1 Perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctanesulfonyl fluoride (PFOSF)

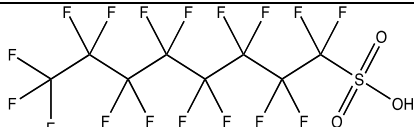
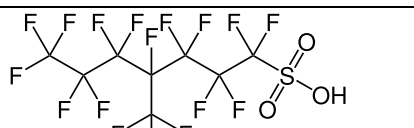
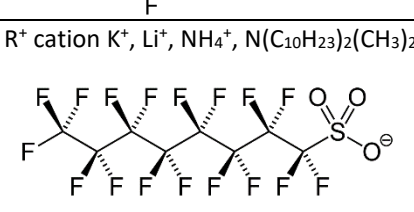
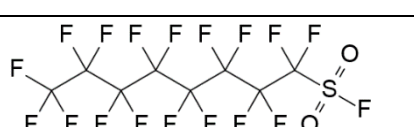
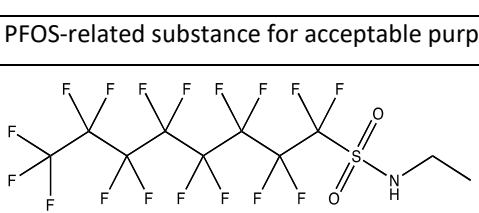
PFOS, its salts and PFOSF is listed in Part III of Annex B of the Convention. The chemical has been listed at COP-4 in 2009 and the listing was amended by COP-9 in 2019. The last listing entered into force on 3 December 2020.

Perfluorooctyl sulfonate ( $F-(CF_2)_8-SO_3^-$ ) is a fully fluorinated (perfluorinated) anionic substance, which is commonly used as a salt or in the acid form (perfluorooctane sulfonic acid, PFOS). PFOS is not known to occur naturally and is synthesized from perfluorooctanesulfonyl fluoride (PFOSF,  $F-(CF_2)_8-SO_2F$ ). PFOSF (in the scientific literature often referred to as POSF) is a key intermediate to produce “PFOS-related substances”, i.e. all substances that contain one or more  $C_8F_{17}SO_2$ -groups and that can, or is assumed, to degrade to PFOS in the environment (UNEP/POPS/COP.7/INF/26). For example, PFOSF is the key intermediate to produce PFOS and PFOS-related substances, such as N-alkyl perfluorooctanesulfonamides (FOSAs,  $F-(CF_2)_8-SO_2-NH(alkyl)$ ) or N-alkyl perfluorooctanesulfon-amidoethanols (FOSEs,  $F-(CF_2)_8-SO_2-$

N(alkyl)(CH<sub>2</sub>CH<sub>2</sub>OH)) in the electrofluorination process (ECF). FOSA derivatives are typically non-polymeric substances, such as EtFOSA which is used as a pesticide. FOSEs are key intermediates to produce other PFOS-related substances, for example, EtFOSE (N-ethyl perfluorooctanesulfonamidoethanol; F-(CF<sub>2</sub>)<sub>8</sub>-SO<sub>2</sub>-N(C<sub>2</sub>H<sub>5</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH)) is the key intermediate to produce PFOS-related fluorinated polymers such as poly(meth)acrylates and polyurethanes. See Figure 1 for an overview of the process scheme and how it relates to the major product categories. The structural formulae are shown in **Error! Reference source not found.** below.

PFOS is persistent and has substantial bioaccumulation and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues; instead, it binds to proteins in blood and liver. It has the capacity to undergo long-range transport and has demonstrated ecotoxicity and toxicity towards mammals (UNEP/POPS/POPRC.2/17/Add.5).

Table 1: Examples of PFOS and PFOS-related substances. Please note, these substances are a mix of linear and branched isomers. The structural formula in the table is shown for the linear compounds only.

Structural formula	Substance name and abbreviation	Formula
PFOS chemicals as listed in the Stockholm Convention		
	Perfluorooctane sulfonic acid (linear) PFOS	F-(CF <sub>2</sub> ) <sub>8</sub> -SO <sub>3</sub> <sup>-</sup>  C <sub>8</sub> F <sub>17</sub> -SO <sub>3</sub> <sup>-</sup>
	4-Perfluorooctane sulfonic acid (branched) PFOS	F-(CF <sub>2</sub> ) <sub>8</sub> -SO <sub>3</sub> <sup>-</sup>  C <sub>8</sub> F <sub>17</sub> -SO <sub>3</sub> <sup>-</sup>
	potassium perfluorooctane sulfonate; lithium perfluorooctane sulfonate; ammonium perfluorooctane sulfonate; didecyldimethylammonium perfluorooctane sulfonate	F-(CF <sub>2</sub> ) <sub>8</sub> -SO <sub>3</sub> <sup>-</sup> C <sub>8</sub> F <sub>17</sub> -SO <sub>3</sub> <sup>-</sup>
	Perfluorooctanesulfonyl fluoride PFOSF	F-(CF <sub>2</sub> ) <sub>8</sub> -SO <sub>2</sub> FS  C <sub>8</sub> F <sub>17</sub> -SO <sub>2</sub> F
PFOS-related substance for acceptable purpose		
	N-ethylperfluorooctanesulfonamide EtFOSA Also: sulfluramid	F-(CF <sub>2</sub> ) <sub>8</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> CH <sub>3</sub>  C <sub>8</sub> F <sub>17</sub> -SO <sub>2</sub> -N(H)C <sub>2</sub> H <sub>5</sub>

## 2.1.2 PFOA, its salts and PFOA-related compounds

PFOA, its salts and PFOA-related compounds were listed into Annex A of the Convention by COP-9 in 2019 (SC-9/12).

The listing includes perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds with the following meaning (see **Error! Not a valid bookmark self-reference.** includes 8:2 fluorotelomer alcohol (8:2 FTOH) and 8:2 fluorotelomer (meth)acrylate (8:2 FTMAC) which are polyfluorinated substances containing an ethyl alcohol group, with the general structure  $F(CF_2)_nCH_2CH_2OR$ , where  $n = 8$  (note: not conform with the listing in (iii) above). These substances can degrade to form PFOA (Buck et al. 2011].

Table 2: Examples of PFOA and PFOA-related compounds for examples):

- i. Perfluorooctanoic acid (PFOA; CAS No: 335-67-1), including any of its branched isomers;
- ii. Its salts;
- iii. PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety  $(C_7F_{15})C$  as one of the structural elements (SC-9/12);

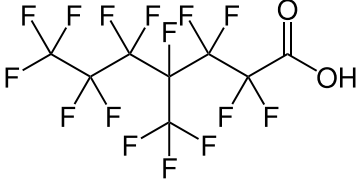
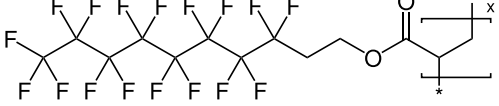
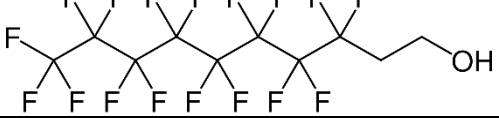
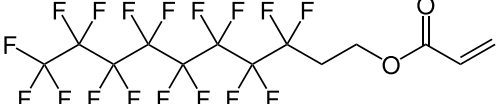
Explicitly excluded are the following compounds with:

- i.  $C_8F_{17}-X$ , where  $X = F, Cl, Br$ ;
- ii. Fluoropolymers that are covered by  $CF_3[CF_2]_n-R'$ , where  $R' = \text{any group}$ ,  $n > 16$ ;
- iii. Perfluoroalkyl carboxylic and phosphonic acids (including their salts, esters, halides and anhydrides) with  $\geq 8$  perfluorinated carbons;
- iv. Perfluoroalkane sulfonic acids (including their salts, esters, halides and anhydrides) with  $\geq 9$  perfluorinated carbons;
- v. Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), as listed in Annex B to the Convention.

**Error! Not a valid bookmark self-reference.** includes 8:2 fluorotelomer alcohol (8:2 FTOH) and 8:2 fluorotelomer (meth)acrylate (8:2 FTMAC) which are polyfluorinated substances containing an ethyl alcohol group, with the general structure  $F(CF_2)_nCH_2CH_2OR$ , where  $n = 8$  (note: not conform with the listing in (iii) above). These substances can degrade to form PFOA (Buck et al. 2011].

Table 2: Examples of PFOA and PFOA-related compounds. Please note that the PFOA-related substances do not have the moiety as specified in SC-9/12.

Structural formula	Substance name and abbreviation	Formula
PFOA		
	Perfluorooctanoic acid (linear) L-PFOA	$F-(CF_2)_7-COOH$ $C_7F_{15}-COOH$

	Perfluorooctanoic acid (branched) example br-PFOA	$F-(CF_2)_7-COOH$ $C_7F_{15}-COOH$
	Fluorinated polymer with C <sub>8</sub> based perfluoroalkyl side chains <sup>1</sup>	
	8:2 fluorotelomer alcohol 8:2 FTOH	$C_8F_{17}-CH_2-CH_2OH$
	8:2 fluorotelomer (meth)acrylate 8:2 FTMAC	$C_8F_{17}-CH_2-CH_2-O-C(O)C(CH_3)=CH_2$

## 2.2 Production and use of PFOS, its salts and PFOSF

In 2009, PFOS, its salts and PFOSF were listed in Annex B to the Convention with specific exemptions and acceptable purposes for production and use in accordance with Part III of Annex B. Production and use shall be eliminated by all Parties except those that have registered for the specific exemptions or acceptable purposes listed in Part I of Annex B. The amended list from 2019 (SC-9/4) of uses for acceptable purposes or specific exemptions pursuant to Part I of Annex B is given in Table 3 below. The register of specific exemptions and the register of acceptable purposes for PFOS and PFOS-related substances have been established and are maintained on the Convention's website: <http://chm.pops.int/Implementation/Exemptions/AcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx> (for acceptable purposes) and <http://chm.pops.int/Implementation/Exemptions/SpecificExemptions/ChemicalslistedinAnnexBRoSE/PFOSRoSE/tabid/4644/Default.aspx> (for specific exemptions)

Table 3: Acceptable purposes and specific exemptions for production and use of PFOS and PFOS-related substances according to Part I of Annex B to the Stockholm Convention (SC-9/4); entry into force on 3 December 2020.

Acceptable purposes	Specific exemptions
1. Insect baits with sulfluramid (CAS No: 4151-50-2) as an active ingredient for control of leaf-cutting ants from <i>Atta spp.</i> and <i>Acromyrmex spp.</i> for agricultural use only	1. Metal plating (hard metal plating) only in closed-loop systems 2. Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems

<sup>1</sup> section III of decision SC-9/12 and in UNEP/POPS/POPRC.13/INF/6/Add.1



Acceptable purposes have no limited time frame, unless specified otherwise by the Conference of the Parties. Specific exemptions expire five (5) years after the date of entry into force of the chemical under the Convention unless the Party indicates an earlier date when registering for an exemption.

Paragraph 10 of Part III of Annex B sets further provisions as “each Party that has registered for an exemption pursuant to Article 4 for the use of PFOS, its salts and PFOSF for fire-fighting foam shall:

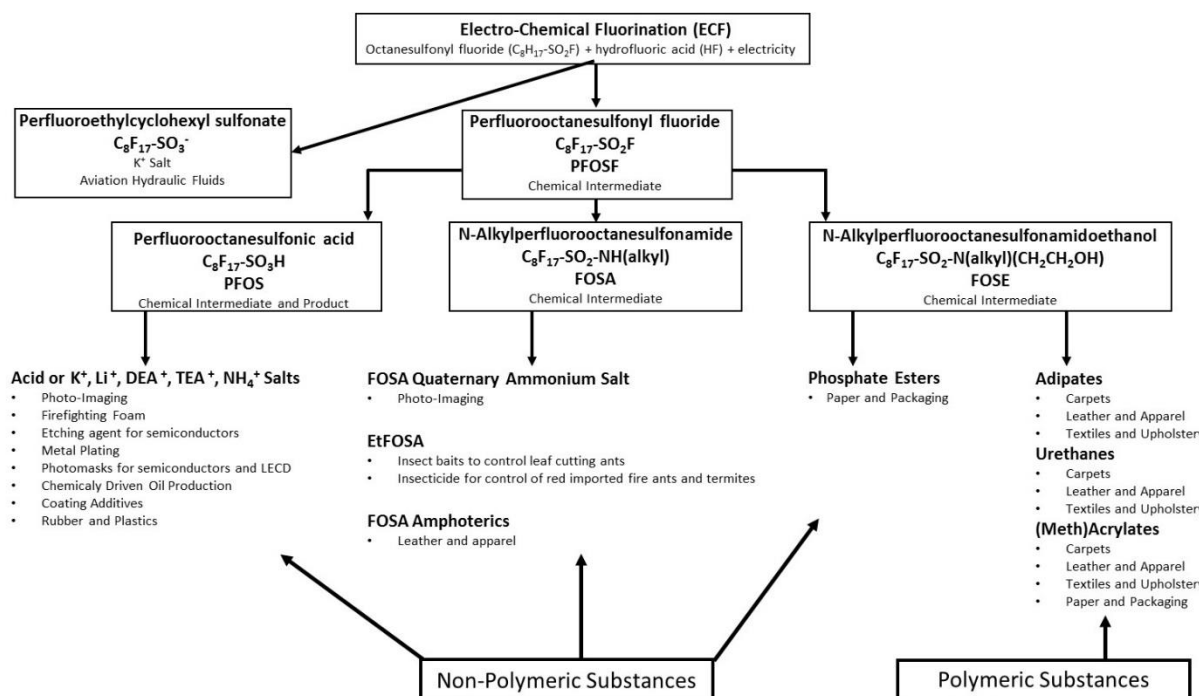
- (a) Notwithstanding paragraph 2 of Article 3, ensure that fire-fighting foam that contains or may contain PFOS, its salts and PFOSF shall not be exported or imported except for the purpose of environmentally sound disposal as set forth in paragraph 1 (d) of Article 6;
- (b) Not use fire-fighting foam that contains or may contain PFOS, its salts and PFOSF for training;
- (c) Not use fire-fighting foam that contains or may contain PFOS, its salts and PFOSF for testing unless all releases are contained;
- (d) By the end of 2022, if it has the capacity to do so, restrict uses of fire-fighting foam that contains or may contain PFOS, its salts and PFOSF to sites where all releases can be contained;
- (e) Make determined efforts designed to lead to the environmentally sound management of fire-fighting foam stockpiles and wastes that contain or may contain PFOS, its salts and PFOSF, in accordance with paragraph 1 of Article 6, as soon as possible.”

Figure 1 shows the process scheme to produce PFOSF and the major product categories and applications of PFOS and PFOS-related substances (with modifications from OECD 2002). Electro-chemical fluorination (ECF) was licensed by 3M in the 1940s (Banks et al. 1994). ECF produces a mixture of even- and odd-numbered carbon chain lengths of approximately 70% linear and 30% branched substances (Concawe 2016, Buck et al., 2011).

Since most FOSE is incorporated into higher molecular weight polymers, it comprises only a portion of the mole fraction of the entire polymer in the final product. However, it should be noted that the secondary reactions used to produce non-polymeric or polymeric FOSE derivatives do not necessarily produce pure products. Typically, 1%-2% of the final product is comprised of unreacted or partially reacted fluorinated starting materials or intermediates that are carried forward into the final product as impurities (3M 2000). Furthermore, these products may also contain PFOA as an impurity (Jiang *et al.* 2015).

Figure 1: Process scheme and major product categories and applications of PFOSF, PFOS and PFOS-related substances, such as FOSA and FOSE and the non-polymeric and polymeric

derivatives (OECD 2002, UNEP 2017). See also Figure 2 (left) for further details on the electro-chemical fluorination step.



The use of PFOS or its salts is no longer allowed, according to decision SC-9/4. For country-specific information and additional uses not covered by the listing in Annex B, the report to Stockholm Convention COP-9 should be consulted (UNEP/POPS/COP.9/INF/12, Table 5 and Table 6. Further, reference is made to the national reports under Article 15 of the Stockholm Convention.

### 2.3 Production and use of PFOA, its salts and PFOA-related compounds

In 2019, PFOA, its salts and PFOA-related compounds were listed in Annex A to the Convention with specific exemptions for production and use in accordance with the provisions of Part X of Annex A. Production and use shall be eliminated by all Parties except those that have notified the Secretariat of the intention to produce and/or use them for the specific exemptions (except fire-fighting foam in accordance with Article 4.). The list of uses for specific exemptions pursuant to Part X of Annex A is given in Table 5:

Availability of alternatives to PFOS for acceptable purpose and specific exemption applications (based on UNEP/POPS/COP.7/INF/26, DEFRA 2004, Willand 2020). below (UNEP 2019a). According to decision SC-9/13, information on the specific exemptions concerning use, production, efficacy and efficiency of possible control measures, alternatives and status of control and monitoring capacity will be submitted by Parties and observers to the Secretariat in 2025.

Table 4: Specific exemptions for production and use of PFOA and PFOA-related substances according to the Stockholm Convention (SC-9/12) (UNEP 2019a).

Activity	Specific exemption
Production	<ul style="list-style-type: none"> <li>• Fire-fighting foam: None</li> <li>• For other production, as allowed for the Parties listed in the Register in accordance with the provisions of part X of this Annex</li> </ul>
Use	<p>In accordance with the provisions of part X of this Annex:</p> <ul style="list-style-type: none"> <li>• Photolithography or etch processes in semiconductor manufacturing</li> <li>• Photographic coatings applied to films</li> <li>• Textiles for oil and water repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety</li> <li>• Invasive and implantable medical devices</li> <li>• 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 this Annex</li> <li>• 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 this Annex</li> <li>• Manufacture of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) for the production of:             <ul style="list-style-type: none"> <li>○ High-performance, corrosion-resistant gas filter membranes, water filter membranes and membranes for medical textiles</li> <li>○ Industrial waste heat exchanger equipment</li> <li>○ Industrial sealants capable of preventing leakage of volatile organic compounds and PM2.5 particulates</li> </ul> </li> <li>• Manufacture of polyfluoroethylene propylene (FEP) for the production of high-voltage electrical wire and cables for power transmission</li> <li>• Manufacture of fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors</li> </ul>

Part X of Annex A sets further provisions for a Party for the use of PFOA, its salts and PFOA-related compounds for fire-fighting foam:

- (a) Notwithstanding paragraph 2 of Article 3, ensure that fire-fighting foam that contains or may contain PFOA, its salts and PFOA-related compounds shall not be exported or imported except for the purpose of environmentally sound disposal as set forth in paragraph 1 (d) of Article 6;
- (b) Not use fire-fighting foam that contains or may contain PFOA, its salts and PFOA-related compounds for training;
- (c) Not use fire-fighting foam that contains or may contain PFOA, its salts and PFOA-related compounds for testing unless all releases are contained;

- (d) By the end of 2022, if it has the capacity to do so, but no later than 2025, restrict uses of fire-fighting foam that contains or may contain PFOA, its salts and PFOA-related compounds to sites where all releases can be contained;
- (e) Make determined efforts designed to lead to the environmentally sound management of fire-fighting foam stockpiles and wastes that contain or may contain PFOA, its salts and PFOA-related compounds, in accordance with paragraph 1 of Article 6, as soon as possible.

The register of specific exemptions for PFOA, its salts and PFOA-related compounds is maintained at <http://chm.pops.int/Implementation/Exemptions/SpecificExemptions/PFOARoSE/tabid/8363/Default.aspx> (open since 3 December 2020)

With regard to the specific exemption for the use of perfluorooctyl iodide for the production of perfluorooctyl bromide for the purpose of producing pharmaceutical products, at its thirteenth ordinary meeting and at every second ordinary meeting thereafter, the Conference of the Parties shall review the continued need for this specific exemption. This specific exemption shall in any case expire at the latest in 2036 according to Part X, paragraph 3 of decision SC/9-12 (UNEP 2019b).

Information on PFASs reduction and elimination by the eight major leading companies under the US EPA's PFOA Stewardship Programme can be accessed at <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas>.

There are two production processes for PFOA (i) electrochemical fluorination and (ii) telomerization. PFOA and related compounds can be produced by ECF from heptylacid chloride ( $C_7H_{15}COCl$ ) to yield perfluorooctanoyl fluoride ( $C_7F_{15}COF$ ), which is further reacted to make PFOA and its salts (see Figure 2 below from Buck et al., 2011).

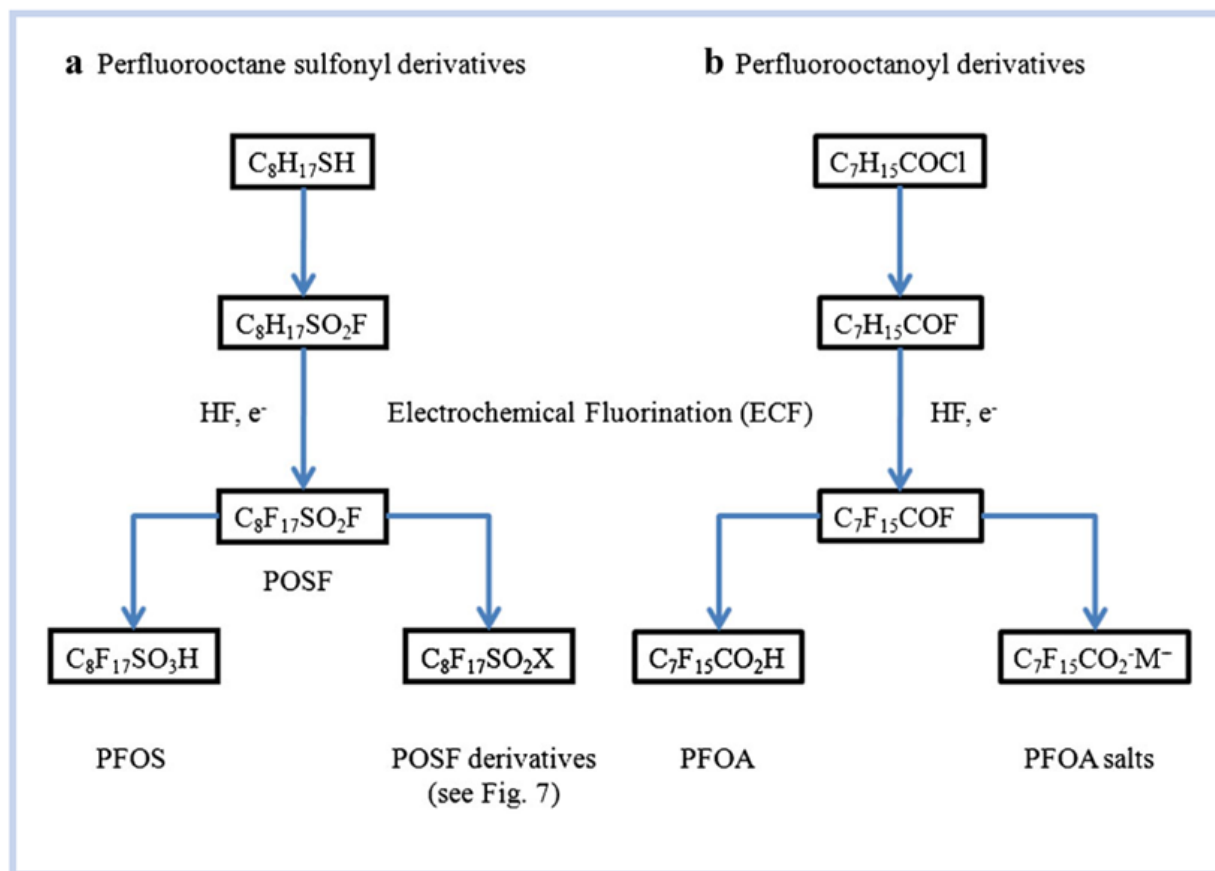


Figure 2: Synthesis, by electrochemical fluorination, of building blocks leading to PFOS, PFOA and derivatives (Buck et al. 2011)

Telomerization was developed in the 1970s (Benskin et al. 2012) and yields mainly even numbered, straight carbon chain isomers (Kissa 2001; Parsons et al. 2008).

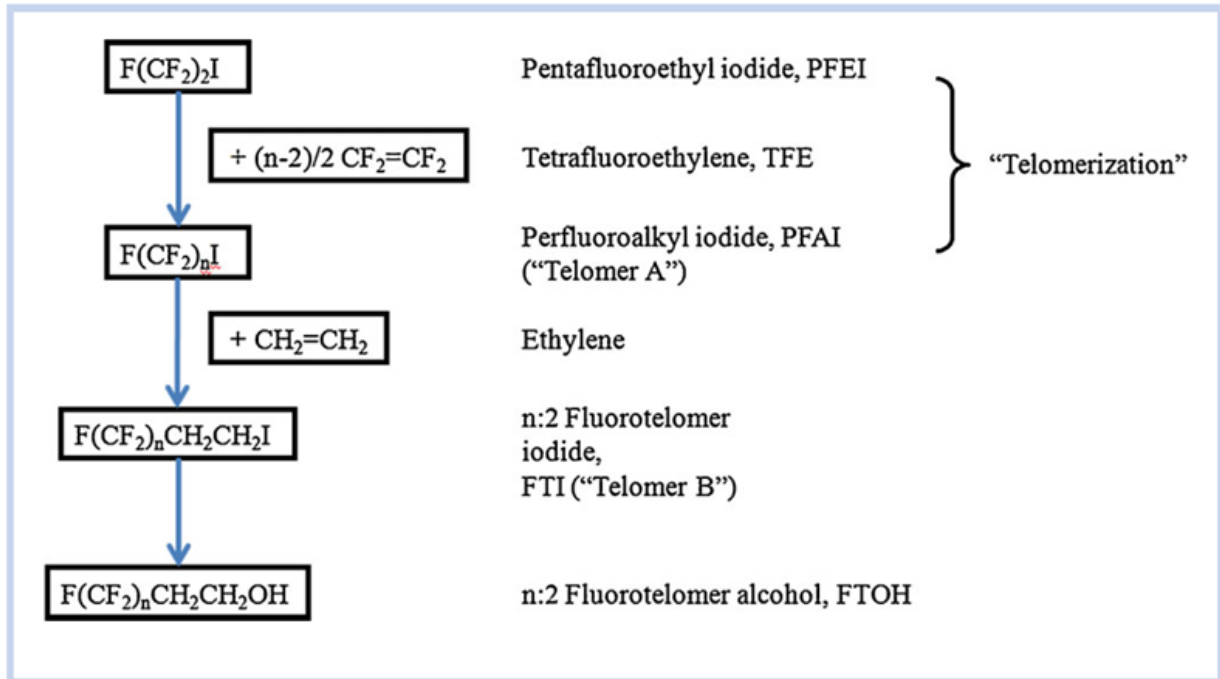


Figure 3: Synthesis, by telomerization, of building blocks leading to fluorotelomer alcohols (Buck et al. 2011)

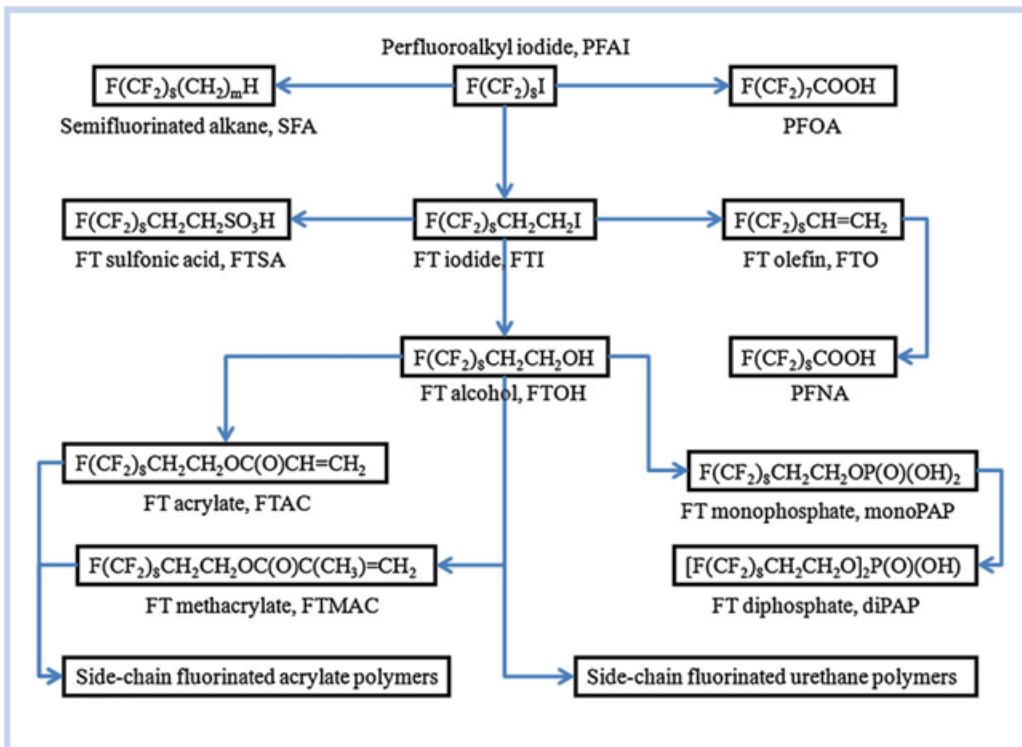


Figure 4: Perfluoroalkyl carboxylic acids and fluorotelomer derivatives synthesized from perfluoroalkyl iodides (here, example with eight fluorinated C atoms (Buck et al. 2011))

## 2.4 Consideration of alternatives

### 2.4.1 General considerations for PFOS, its salts and PFOSF

According to paragraph 4 of Part III of Annex B to the Convention, to reduce and ultimately eliminate the production and use of PFOS, its salts and PFOS-related chemicals, Parties are encouraged to phase out uses when suitable alternative substances or methods are available. In 2019, the assessment on further needs for PFOS and related substances presented information from Parties as to production, use and alternatives (UNEP/POPS/COP.9/INF/12). More detailed information on the availability and suitability of the alternatives are available in the source documents used for the development of the guidance. A summary table of expired acceptable purposes and specific exemptions is contained in the previous BAT/BEP guidance document dated 2017 UNEP (2017).

The present document includes information on available alternatives for the uses listed as specific exemptions and acceptable purposes under the Convention, but sometimes refrains from assessing their technical suitability for specific processes due to incomplete information. Whenever possible, trade names and names of manufacturers of potential alternatives are provided assuming that market presence of such products indicate technical suitability as substitutes. A hazard-based assessment for some of the alternatives has been conducted by the POPs Review Committee, based on an analysis as to whether the identified alternative substances meet the numerical thresholds in Annex D of the Convention (UNEP/POPS/POPRC.10/INF/7/Rev.1).

Parties may use these reports as a source of information when choosing alternatives to PFOS, its salts and PFOS-related substances. It should be noted that for alternatives which are listed in these reports:

- it is not always clear if these are drop-in replacements and/or whether process changes and/or product loadings would need to be modified. Suppliers of these chemicals may be able to provide additional information.
- their suitability to meet performance specification could not always be validated.
- Parties need to ensure those are registered for their intended use in their jurisdiction.
- for those considered not likely to exhibit POP characteristics, hazardous characteristics (e.g. mutagenicity, carcinogenicity, reproductive and developmental toxicity, endocrine disruption, immune suppression or neurotoxicity) may still be exhibited. Parties should assess these hazardous characteristics before considering such substances as a suitable alternative. It is also recommended to carefully review the Safety Data Sheet (SDS) in GHS format for each substance and to avoid using substances for which no, or an incomplete, SDS is provided by a supplier.
- it is unknown whether or not such alternatives are produced deploying best practices and to minimize unintended product content (such as unreacted raw material and other impurities). Suppliers of these chemicals may be able to provide additional information.

In summary, all potential alternatives and their suppliers should be carefully assessed by Parties before being considered as suitable alternatives.

Table 3 and

Table 4 below summarize information on the nature of incumbent products along with typical use rates, information on the availability of alternatives to PFOS and PFOS-related substances for the uses listed as acceptable purposes and specific exemptions under the Convention according to the annex to decision

POPRC-8/8 and the previously mentioned POPRC documents. Further details are available in Chapters 3 and 4.

## 2.4.2 General considerations for PFOA, its salts and PFOA-related compounds

Information on the nature of commercially available products along with typical use rates and information on the availability of alternatives to PFOA and PFOA-related substances for the uses listed as specific exemptions under the Convention needs to be prepared.

## 2.5 Chemical alternatives

### 2.5.1 PFOS, its salts and PFOSF

Chemical alternatives may include the following chemicals:

- Perfluorinated alkyl substances; mostly considered shorter chain perfluorinated sulfonic and carboxylic acids;
- Polyfluorinated alkyl substances; such as fluorotelomer-based polymeric or non-polymeric substances, PFBS-based polymeric or non-polymeric substances or fluoropolyether;
- Fluorine-free substances; based on a variety of chemical classes. These are specified throughout the text wherever possible.

Table 5: Availability of alternatives to PFOS for acceptable purpose and specific exemption applications (based on UNEP/POPS/COP.7/INF/26, DEFRA 2004, Willand 2020).

Acceptable Purpose or specific exemption	Incumbent PFOS or PFOS-related Substance	Typical Use Rate	Alternatives		
			Existence of Alternatives	Chemical Identity	Trade Names and/or Producers
<b>Acceptable purpose</b>					
1. Insect baits with sulfluramid (CAS No: 4151-50-2) as an active ingredient for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. for agricultural use only	EtFOSA (N-ethyl perfluorooctane sulfonamide (CAS No. 4151-50-2))	0.3%	No (alternative technologies are available but seem not viable to replace insect baits)	Known	Known
<b>Specific exemptions</b>					
2. Metal plating (hard metal plating) only in closed-loop systems	PFOS-salts: TEA* (CAS No. 56773-42-3), K (CAS No. 2795-39-3), Li (CAS No. 29457-72-5), 2,2'-iminodiethanol salt (CAS No. 70225-14-8)	0.03% to 0.08%	Yes	Known	Known



3. Fire-fighting foam	PFOS (CAS No. 1763-23-1)	0.5% to 6%	Yes	Known	Known
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\*TEA = tetraethylammonium heptadecafluorooctanesulfonate

### 2.5.2 PFOA, its salts and PFOA-related substances

The sequence follows the listing in Annex A (SC-9/12) and information is mainly based on (UNEP/POPS/POPRC.14/6/Add.2; ECHA, 2015; Wood-Ramboll-Cowi 2020).

Table 6: Availability of alternatives to PFOA for specific exemption applications (to be completed).

Present Uses			Alternatives		
Specific Exemption	Incumbent PFOA or PFOA-related Substance	Typical Use Rate	Existence of Alternatives	Chemical Identity	Trade Names and/or Producers
1. Photolithography or etch processes in semiconductor manufacturing	PFOA				
2. Photographic coatings applied to films	PFOA, APFO	Insufficient information			
3. Textiles for oil- and water-repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety	Side-chain fluorinated polymers that degrade to PFOA	Difficult to handle as focused on the textiles and not on the chemical providing the functionality  Not all oil- and water-repellent textiles have been treated with these substances.			
4. Invasive and implantable medical devices					
5. 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 this Annex	PFOA <sup>2</sup> , APFO APFO, ammonium salt of PFOA <sup>3</sup> PFOA-related substances	<3% in foam concentrate  0.02-0.08% in foam	Yes	Known	Known

<sup>2</sup> [https://echa.europa.eu/documents/10162/28801697/pfas\\_flourine-free\\_alternatives\\_fire\\_fighting\\_en.pdf/d5b24e2a-d027-0168-cdd8-f723c675fa98](https://echa.europa.eu/documents/10162/28801697/pfas_flourine-free_alternatives_fire_fighting_en.pdf/d5b24e2a-d027-0168-cdd8-f723c675fa98)

<sup>3</sup> (UNEP/POPS/POPRC.14/6/Add.2)

Present Uses			Alternatives		
6. 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 this Annex	perfluorooctyl iodide (PFOI) contamination in PFOB (perfluorooctyl bromide)	PFOB is used as a processing aid in the manufacture of certain porous particles in pressurized-metered dose inhaler medicines.			
7. Manufacture of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) for the production of: a. High-performance, corrosion-resistant gas filter membranes, water filter membranes and membranes for medical textiles b. Industrial waste heat exchanger equipment c. Industrial sealants capable of preventing leakage of volatile organic compounds and PM2.5 particulates	PFOA, APFO, PFOI	PFOA as processing aid in manufacture of fluoropolymers PFOI used in reprocessing tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)			
8. Manufacture of polyfluoroethylene propylene (FEP) for the production of high-voltage electrical wire and cables for power transmission	PFOA APFO				
9. Manufacture of fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors	<ul style="list-style-type: none"> <li>• Ammonium salt of PFOA</li> <li>• Potassium salt of PFOA</li> <li>• Silver salt of PFOA</li> <li>• Sodium salt of PFOA</li> <li>• PFOA, perfluorooctanoic acid</li> <li>• Ethylperfluorooctanoate</li> </ul>				

Present Uses		Alternatives			
	<ul style="list-style-type: none"> <li>• Methylperfluorooctanoate</li> <li>• Pentadecafluorooctyl fluoride</li> <li>• Poly(oxy-1,2-ethanediyl), <math>\alpha</math>-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl)-<math>\omega</math>-[(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl)oxy]-</li> <li>• 2-Propenoic acid, C<sub>16</sub>-C<sub>18</sub>-alkyl esters, polymers with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate</li> <li>• Cyclotetrasiloxane, 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-2,4,6,8-tetramethyl-, Si-[3-(oxiranylmethoxy)propyl] derivs</li> <li>• Trisiloxane, 3,3'-(3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-decanediyl)bis[3-[(dimethylsilyl)oxy]-1,1,5,5-tetramethyl-, reaction products with 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-1-undecene</li> </ul>				

## 2.6 Summary of best available techniques (BAT) and best environmental practices (BEP) by process category

### 2.6.1 PFOS, its salts and PFOSF

Table 7 below summarizes information on BAT and BEP for the PFOS uses listed as acceptable purposes and specific exemptions under the Convention according to the annex to decision POPRC-8/8 and the previously mentioned POPRC documents. For PFOS and PFOS-related substances, after becoming waste, should be managed following the Basel Technical guidelines (General Technical guideline, PFOS and PFOA Technical guideline, Pesticide POP Technical guidelines (UNEP 2021a,b,c in preparation).

Table 7: PFOS: Summary of BAT and BEP for acceptable purpose and specific exemption application.  
\*General BEP guidance is provided in Chapter 3.

Acceptable Purpose	BAT	BEP*
1. Insect baits with sulfluramid (CAS No: 4151-50-2) as an active ingredient for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. for agricultural use only	<p>The following techniques (1. through 4.) stand on their own but are often considered to be complimentary to the use of toxic baits for controlling infestation.</p> <ol style="list-style-type: none"> <li>1. Thermo-nebulization with permethrin: For initial large area land preparation and high infestation rate on mature <i>Atta</i> nests</li> <li>2. Mechanical Control: Excavation of the young nests and capturing the ant queens</li> <li>3. "Barriers" fastened around tree trunks, such as plastic tape coated with grease, plastic cylinders and strips of aluminum: For small areas, such as small orchards</li> <li>4. Dried-powder dusting with deltamethrin: To control nests no larger than 5 m<sup>2</sup>  To control young <i>Atta</i> colonies  To control certain <i>Acromyrmex</i> species</li> </ol>	When using sulfluramid containing baits, collect all leftover baits after treatment followed by environmentally sound management and disposal according to the Basel technical guidelines.
Specific exemption	BAT	BEP*
2. Metal plating (functional chromium plating) only in closed-loop systems	<p>Non-PFOS-based mist suppressant</p> <p>PFOS-based mist suppressant in a "closed-loop system" that fulfills the criteria summarized in respective Chapter 5.2.1</p> <p>Resin and activated carbon adsorption for removal or recover of the mist suppressants</p> <p>Note: Residues are considered hazardous waste and sent to landfill due to presence of Cr(VI). It is not known if PFAS are contained</p>	<p>Collect all waste followed by environmentally sound management and disposal according to the Basel technical guidelines.</p> <p>Recover the PFOS-based and non-PFOS-based mist suppressants and reuse in closed-loop systems</p>
3. Fire-fighting foam	<p>Surrogate, non-fluorinated foams for training purposes, for testing and commissioning of fixed systems and vehicle proportioning systems</p> <p>Fluorine-free foams for Class B fire-fighting foam concentrates (not yet for large storage tank facilities)</p>	Follow best practices outlined in chapter 0 to minimize releases to the environment and to collect all waste followed by environmentally sound management and disposal

	Short-chain fluorotelomer-based substances for Class B fire-fighting foam concentrates for large storage tanks only.	according to the Basel technical guidelines.
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## 2.6.2 PFOA, its salts and PFOA-related compounds

Table 8 summarizes the information on BAT and BEP for PFOA uses as specific exemptions under the Convention according to and general principles on BAT and BEP are laid out in Chapter 3. For PFOA and PFOA-related compounds, wastes should be managed following the Basel Technical guidelines (General Technical guideline, PFOS and PFOA Technical guideline (UNEP 2021a,b in preparation)).

Table 8: PFOA and PFOA-related substances: Summary of BAT and BEP for each “Specific Exemption” application. \*General BEP guidance is provided in Chapter 3.3

Acceptable Purpose	BAT	BEP*
Fire-fighting foam	<p>Surrogate, non-fluorinated foams for training purposes, for testing and commissioning of fixed systems and vehicle proportioning systems</p> <p>Fluorine-free foam concentrates for Class B fire-fighting foam meeting required standards and/or specifications (not yet for large storage tank facilities)</p> <p>Short-chain fluorotelomer-based substances for Class B fire-fighting foam concentrates for large storage tanks only.</p>	<p>Follow best practices outlined in chapter 0 to minimize releases to the environment and to collect all waste followed by environmentally sound management and disposal according to the Basel technical guidelines.</p>

## 2.7 Relationship to the Basel Convention

In addition to the provisions of the Stockholm Convention, those of the Basel Convention are directly relevant to the application of best available techniques and best environmental practices to address PFOS and PFOA releases from wastes as waste. Considering that specific waste streams might be major potential PFOS- and PFOA-containing material flows, synergies between the Stockholm Convention and Basel Convention are of high importance. The Basel Convention places obligations on countries that are Parties to, *inter alia*: minimize generation of hazardous waste; ensure that adequate disposal facilities are available; and ensure environmentally sound management of wastes.

Under the Stockholm Convention, POP-containing wastes are, in accordance with Article 6, paragraph 1 (d) (ii), to be disposed of in such a way that the POP content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of POPs or otherwise, they may be disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option, or the POP content is low, taking into account international rules, standards, and guidelines, including those that may be developed pursuant to paragraph 2, as well as relevant global and regional regimes governing the management of hazardous wastes.

To destroy the extraordinary stable C-F bonds in PFOS and PFOA-related substances, these substances must be exposed to very high temperatures for a sufficiently long time. The Japanese Ministry of the Environment issued a Technical Guideline for the Environmentally Sound Treatment of PFOS Wastes, in

which a destruction rate of more than 99.999% was proofed for PFOS by applying an incineration temperature of 1,100 °C for several seconds. (Japan, 2013)

These are conditions, which can be reached, e.g. by cement kiln co-incineration, where feasible, and advanced hazardous waste incinerators. For waste incinerators operating at temperatures lower than 1,100°C, robust full scale tests are pending. For further information see (General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. (UNEP/CHW/POP-SIWG.4/3).

Paragraph 2 of Article 6 of the Stockholm Convention, which addresses measures to reduce or eliminate releases from stockpiles and wastes, contains the following provisions:

“The Conference of the Parties shall cooperate closely with the appropriate bodies of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal to, inter alia:

- a) Establish levels of destruction and irreversible transformation necessary to ensure that the characteristics of persistent organic pollutants are not exhibited;
- b) Determine what they consider to be the methods that constitute environmentally sound disposal referred to above; and
- c) Work to establish, as appropriate, the concentration levels of the chemicals listed in Annexes A, B and C in order to define the low persistent organic pollutant content referred to in paragraph 1 (d) (ii).”

Following the invitation from the Stockholm COP to the Basel COP, under the Basel Convention a technical guideline on PFOS waste has been developed and adopted by the Conference of the Parties. The latest version of the “General technical guidelines on the environmentally sound management of wastes of wastes consisting of, containing or contaminated with persistent organic pollutants” (UNEP 2021c in preparation), the “Technical guidelines Addendum: 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 2021b in preparation), and the “Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with the pesticides aldrin, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordane, chlordecone, dicofol, dieldrin, endrin, heptachlor, hexachlorobenzene, hexachlorobutadiene, lindane, mirex, pentachlorobenzene, pentachlorophenol and its salts, perfluorooctane sulfonic acid, technical endosulfan and its related isomers or toxaphene or with hexachlorobenzene as an industrial chemical” (covers sulfluramid) (UNEP 2021c in preparation) are under development and will be available for consideration of adoption at Basel Convention COP.14 (for actual versions of the Basel POPs waste technical guidelines, see on the Convention’s website:

<http://www.basel.int/Implementation/POPsWastes/TechnicalGuidelines/tabid/5052/Default.aspx>

## 3 General principles and guidance on BAT and BEP for managing PFOS, PFOA and their related substances listed in annexes of the Stockholm Convention

### 3.1 Best environmental practices (BEP)

BEP describe the application of the most appropriate combination of chemical management strategies and environmental control measures, including best practices relating to the continuous improvement of environmental, health and safety performance. BEP provide the framework for ensuring the identification, adoption and adherence to management options that play an important role in improving the occupational and environmental performance of a facility. General good international industry practices (e.g. IFC 2007) and industry specific best practices (e.g. IPPC 2006, ZDHC 2015) are available.

Key ecological and economic advantages achieved through BEP implementation include protection of workers, the surrounding community and the environment. Specifically, worker and community health, savings in consumption of chemicals, fresh water and energy, and minimizing waste, and minimizing ecological loads in wastewater and off-gas. Committed senior level company executives are key to making BEP implementation and adherence a success. Well-trained employees are a prerequisite for implementing BEP measures. Limiting factors for improving existing equipment also need to be taken into consideration with the application of BEP, e.g. new equipment has to be rebuilt/modified or installed (for example, automated dosing systems, etc.). These applicability factors can be limiting measures because they may be too cost-intensive or technological/logistics or space problems exist (Schönberger and Schäfer 2005).

Environmentally sound management of waste is part of BEP. General technical guidelines have been developed under the Basel Convention (for further information, please see the Convention's website <http://www.basel.int/Implementation/POPsWastes/TechnicalGuidelines/tabid/5052/Default.aspx>).

The following sections provide basic information on environmental management systems. Their implementation will improve worker safety and environmental performance of the facility.

#### 3.1.1 Environmental management systems

A number of environmental management techniques are determined as BEP. The scope and nature of an environmental management system (EMS) will generally be related to the nature, scale and complexity of the facility, and the range of environmental impacts it may have. One example of a good overall chemical management guide has been published by ZDHC (ZDHC 2015), one for small and medium sized enterprises has been published by the German Federal Ministry for Economic Cooperation and Development (GTZ 2008), and internationally recognized standards exist (such as ISO 9001 and ISO14000).

BEP is to implement and adhere to an EMS that incorporates the following features:

- Definition of an environmental policy for implementation led by top management (senior corporate leadership commitment is regarded as a precondition for a successful application of the EMS).
- Planning and establishing of the necessary procedures.
- Implementation of the procedures, paying particular attention to:
  - Organizational structure and responsibility
  - Training, awareness and competence
  - Communication
  - Employee involvement



- Documentation
- Efficient process control
- Maintenance programme
- Emergency preparedness and response
- Safeguarding compliance with environmental legislation
- Performance checks and taking corrective action
- Monitoring and measurement
- Records maintenance
- Perform independent (where feasible) internal auditing to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained.

Four additional features are considered as progressive measures; their absence, however, is generally not inconsistent with BEP:

- Examination and validation of the management system and audit procedure by an accredited certification body or an external EMS verifier.
- Preparation and publication of a regular environmental statement describing all the significant environmental aspects of the facility, allowing for year-by-year comparison against environmental objectives and targets as well as with sector benchmarks as appropriate (i.e., continuous improvement plan and annual progress report).
- Consideration of applicable industry-specific standards, when available.
- Implementation and adherence to an internationally accepted EMS, such as ISO 9001 and ISO 14001

### 3.1.2 Specific education and training of employees

The following basic training and education opportunities are beneficial for raising awareness for sound chemicals management; the guide developed ZDHC provides easy to use tools or references them (ZDHC 2015):

- Appropriate education of workers concerning handling, storing, using and disposing of chemicals and auxiliaries, especially in case of hazardous substances;
- Process- and machinery-specific training to increase the level of environmental awareness;
- Regular maintenance of technical equipment (machines in production as well as abatement and recovery devices such as filters and scrubbers); general maintenance (e.g. pumps, valves, level switches);
- Calibration of equipment for measuring and dispensing chemicals; and
- The drain is never an appropriate disposal system for chemicals.

### 3.1.3 Additional considerations for BAT and BEP

It is also important to consider the following forward looking features of the EMS:

- At the plant design stage, give consideration to the environmental impact of the eventual decommissioning of the unit;
- Give consideration to the development of cleaner technologies;
- Where practicable, conduct sectoral benchmarking on a regular basis, including energy efficiency and energy conservation activities, choice of input materials, emissions to air, discharges to water, water consumption and generation of waste;

- Ensure full details provision for activities carried out on-site, such as
  - Descriptions of the waste treatment methods and procedures in the place of installation
  - Diagrams of the main plant items that have some environmental relevance, together with process flow diagrams (schematics)
  - Details on the control system philosophy and how the control system incorporates environmental monitoring information
  - Details on how protection is provided during abnormal operating conditions such as momentary stoppages, start-ups, and shutdowns
  - Annual survey of the activities carried out and the waste treated, which contains a quarterly balance sheet of the waste and residue streams, including the auxiliary materials used for each site.
- Have sufficient staff available on duty with the requisite qualifications at all times. All personnel should undergo specific job training and further education.

## 3.2 General BAT and BEP measures applicable to handling chemicals

This section describes general principles, measures and safety precautions that apply to all types of chemicals and industries handling them (ZDHC 2015, GTZ 2008). Further, an online information system on hazardous substances has been developed by the German Social Accident Insurance (DGUV) and is available in English – the GESTIS Substance Database (Gestis Database).

General best practices for handling pesticides are closely related to principles outlined in the previous and the following chapters.

### 3.2.1 Chemical knowledge, storage, handling, dosing, dispensing and transport

- When storing, handling, dosing, dispensing, and transporting any chemical, caution should be used, necessary protective measures implemented and proper personal protective equipment worn;
- Before ordering/receiving any chemical review the local language Safety Data Sheet (SDS). If possible, avoid CMR (carcinogenic, mutagenic, reproductive toxin) and PBT (persistent, bioaccumulative and toxic) substances, and substances that can degrade to CMR or PBT substances (see SDS Section 2, 11, and 12). Resources such as the GESTIS Substance Database (Gestis Database) can also be used;
- In case a complete SDS is not available from one supplier, order the product from an alternative supplier that provides a complete SDS;
- Before handling any chemical, review the SDS carefully (and/or check resources, such as the GESTIS Substance Database);
- Gather information from your supplier on amounts of residual raw materials, by-products and potential degradation products in the product you intend to order;
- Reject leaking or dented containers upon receiving;
- Proper storage according to the instruction of the most up to date safety data sheet (SDS), preferably in Global Harmonization Standard (GHS) format;
- Proper labelling of containers and equipment; storage in special compartments, containers or locations for toxic and explosive chemicals to avoid leakage and spill; and
- Dosing and dispensing without spilling in automated dosing systems.

### 3.2.2 Minimization/optimization of the chemicals used

- Minimize the use of all chemicals and auxiliary materials;
- Measure, mix and dose chemicals carefully to avoid losses;
- Minimize residual, left-over chemicals, by calculating exactly how much is needed for the process step;
- Substitution of overflow rinsing or minimization of water consumption in overflow rinsing by means of optimized process control;
- Reuse of rinsing baths, including final rinsing baths – where possible;
- Reversing of current flows in continuous washing; and
- Cleaning and recycling of process water – where possible.

### 3.2.3 Equipment

- Use equipment, pipes, valves, etc. that are suited to handle the material (e.g., corrosion resistance) to ensure a long equipment life and to avoid equipment breakdown and leaks;
- To prevent releases to the environment via air, install dust collectors, scrubbers or similar devices; and
- Collect all waste and leftover chemicals from all processes and dispose of them in accordance to guidance provided in the product SDS and in compliance with local rules and regulations. In general, the drain is not an appropriate outlet for liquid waste and a community landfill is not an appropriate outlet for solid waste.

### 3.2.4 Leak and spill procedure

- Follow instructions according to information provided on the SDS;
- Make such a procedure part of the operator training to enhance preparedness.

### 3.2.5 Emissions reductions and waste management

- Follow all procedures as outlined above;
- Adhere to waste disposal methods given in the SDS;
- For guidance on environmentally sound management of waste, guidance is provided by the Basel Convention (see above).

## 3.3 BEP measures for manufacturing of PFOS, its salts and PFOSF and PFOA, its salts and PFOA-related compounds

### 3.3.1 BEP measures for manufacturing of PFOS, its salts and PFOSF

- In case such products still need to be manufactured, the manufacturer should employ technology to minimize worker exposure and to minimize emissions to the environment, which includes water, air and soil;
- Information provided in Chapter 3 of this document is applicable and should be followed;
- Technology should be deployed to minimize unreacted raw material and impurity content in products sold; and
- Information on unreacted raw material and impurity content in products sold should be made public to all customers and interested parties.

### **Removal of PFOS and PFOA and their related substances from waste water (from production plants)**

The recommendations of the Stockholm Convention's COP-5 must be taken into account when using any adsorption method that requires a final destruction of the adsorbent that contains PFOS or PFOS-related substances at the end-of-life so as not to deposit such wastes improperly (SC-5/5, POPRC-6/2).

Activated carbon or basic ion exchangers may be used to remove PFOS from water via adsorption.

The Basel Convention technical guidelines contain more detailed information on the environmentally sound management of wastes consisting of, containing or contaminated with PFOS, its salts and PFOSF and PFOA, its salts and PFOA-related compounds.

#### **3.3.2 BEP measures for manufacturing of PFOA, its salts and PFOA-related compounds**

### **3.4 General BEP measures when using PFOS, its salts and PFOSF and PFOA, its salts and PFOA-related compounds**

- When using PFOS, PFOA or related substances, select a product that has a verified lowest possible amount of unreacted raw materials, impurities and potential degradation products present;
- Apply all BEP principles from above and adhere to BEP principles for the particular process outlined in the following chapters;
- Follow instructions given on the most recent SDS, preferably the SDS should adhere to GHS format and be provided in a local language version. Resources such as the GESTIS Substance Database (Gestis Database) can be consulted for further information; and
- Have dedicated equipment in your facility that only runs processes with PFOS, PFOA and/or related substances.

### **3.5 BEP measures for manufacturing of alternatives to PFOS and PFOA and their related substances**

- The manufacturer should employ technology to minimize exposure to workers and minimize emissions to the environment which includes water, air and soil;
- The content of all previous chapters on BEP apply and should be utilized;
- Technology should be deployed to minimize unreacted raw material and impurity content in the products sold;
- Information on unreacted raw material and impurity content in products sold should be made public to all customers and interested parties

### **3.6 General BEP measures when using alternatives to PFOS and PFOA and their-related substances**

- Avoid any material that may contain PFOS and/or PFOS-related substances as impurities or that can potentially degrade to form them;
- Avoid any material that may contain PFOA and/or PFOA-related substances as impurities or that can potentially degrade to form them;
- Avoid – if possible – alternative products that contain an unknown amount or high levels of unreacted raw materials and impurities;
- Apply all BEP principles from above and adhere to BEP principles for your particular process outlined in the following chapters; and

- Follow instructions given on the most recent SDS, preferably the SDS should adhere to GHS format and be provided in a local language version. Resources such as the GESTIS Substance Database (<https://gestis-database.dguv.de/>) can be consulted for further information.

## 4 BAT and BEP measures for PFOS, its salts and PFOSF for acceptable purpose applications

### 4.1 Insect baits with sulfluramid as an active ingredient for control of leaf-cutting ants from [genus] *Atta spp.* and *Acromyrmex spp.* for agricultural use only

#### 4.1.1 Background

N-Ethyl perfluorooctane sulfonamide (EtFOSA; CAS No. 4151-50-2), called sulfluramid, is a pesticide to control leaf-cutting ants of the genus *Atta* and the genus *Acromyrmex* and their species. Ingested sulfluramid is being metabolized to form perfluorooctanesulfonamide (FOSA) that interrupts ATP production in the mitochondria causing death of the animal. These leaf-cutting ant species are only found on the American continent from central Argentina to the southern United States of America and represent the main pests of Brazilian forest plantations (eucalyptus and pine), agricultural production (corn, sugar cane, cassava and others) and to pastures in all affected regions with associated annual economic losses estimated to be in the order of several hundred million USD (Britto *et al.* 2016, Brazil submission as follow-up to POPRC-11, Zanetti *et al.* 2014, Fowler *et al.* 1986).

Nesting and food habits differ by species and therefore treatment technique and/or dosage may vary and need to be considered for this guidance (Zanetti *et al.* 2014; for a detailed species overview and their occurrence in Brazil, see Britto *et al.* 2016).

For example, for *Atta*:

- Nests are loose soil mounds with chambers extending into the ground;
- Specialize primarily on tree leaves; some *Atta* species are considered grass-cutting ants.

For example, for *Acromyrmex*:

- Nests are typically smaller than *Atta* nests, more inconspicuous and are sometimes covered with plant debris or straw.
- Nests are shallow in colder regions, deeper in warmer regions (up to 7 m deep).
- Focus mainly on collecting grass, flowers and herbal leaves. However, sulfluramid was introduced in Brazil to replace the active ingredient dechlorane (mirex) which use was banned in 1993 (and is listed in Annex A of the Stockholm Convention).

Quantitative production and use data are available from Brazil for the year 2017 (Table 9: Brazil: Sulfluramid-related production, imports, exports, uses (reference year 2017, source: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOInfoSubmission/tabid/6176/Default.aspx>). ) and for Costa Rica for the period 2017-2019 (Table 10:

Costa Rica: Amounts of sulfluramid as active ingredient in pesticides (reference period: 2017-2019, amounts in kg per year. Source: Servicio Fitosanitario del Estado 2020; <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOInfoSubmission/tabid/6176/Default.aspx>).

Table 9: Brazil: Sulfluramid-related production, imports, exports, uses (reference year 2017, source: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOInfoSubmission/tabid/6176/Default.aspx>).

Import of PFOSF from China:	63.8 t
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Use of PFOSF in the production of sulfluramid:	56.1 t
Production of sulfluramid:	35.1 t
Use of sulfluramid for the production of insect baits:	33.2 t
Export of sulfluramid (formulated in insect baits):	1.4 t
Export of insect baits (containing 0.3% sulfluramid):	350 t

Sulfluramid-containing pellet bait represents 95% of the formicide bait market in Brazil. The pellets consist of a mixture of an attractive substrate (vehicle) (usually dehydrated citric pulp from the orange juice industry and vegetable oil) that the ants identify as food and the active ingredient (insecticide). Baits are “ready to use” (0.3% active ingredient, see e.g. MIREX 0.3 GB ([http://www.ramac.com.ni/?page\\_id=370](http://www.ramac.com.ni/?page_id=370))) to be directly applied from their packaging close to active nest entrance holes or anthill trails and carried into the colony by the ants themselves. The suggested dosage is 6 g -10 g insecticide/m<sup>2</sup> of loose soil anthill (to control *Atta*) and 6 g-50 g insecticide/m<sup>2</sup> of loose soil mound to control *Acromyrmex*. After the pellets have been carried into the nest, multiple ants lick the pellet fragments to prepare them for cultivation by the symbiotic fungus. This takes place, ca. 6 h to 18 h after the bait was transported into the nest.

Table 10: Costa Rica: Amounts of sulfluramid as active ingredient in pesticides (reference period: 2017-2019, amounts in kg per year. Source: Servicio Fitosanitario del Estado 2020; <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOSInfoSubmission/tabid/6176/Default.aspx>)

Activity	Quantity in kg for year		
	2017	2018	2019
Import	90.00	86.25	97.50
Export	0	0	0
Apparent use	90.00	86.25	97.50

#### 4.1.2 BAT and BEP for PFOS and PFOS-related substances

Assessment of BAT and BEP poses a challenge because the two genera of ants affect so many different agribusinesses of all sizes and a distinction between controlling leaf-cutting ant species and other grass-cutting ant species is not clear. Although several publications and submissions by Parties are available, their focus is mainly on ways to control the genus *Atta* whereas little information is available on ways to controlling the genus *Acromyrmex*. It is known that toxic baits containing sulfluramid are sufficient, viable and effective (>80% colony control under field conditions) and that all other techniques should be considered as complementary to the use of toxic baits. It is important to note that alternative technologies are only effective and efficient in specific situations and require specific equipment and different labor skills than those needed to apply toxic bait. The combination of technologies overall seems more labor intensive and may be more expensive.

Pesticides usually require a country-specific registration process and therefore it is important to ensure that the alternative substances listed below are registered for use before applying them. Furthermore, it is important to ensure the safety and health of the workers applying the chemicals in the fields. Proper personal protective equipment and other safety measures need to be adhered to as outlined in the safe handling instructions for each specific substance. This information should be available to all workers and should be reviewed with them prior to them handling the pesticides.

From the available data, the following is BAT:

For initial large area land preparation and high infestation rate on mature *Atta* nests:

- Thermo-nebulization with permethrin or with fenitrothion

For small areas, such as small orchards:

- Mechanical control: Excavation of the young nests and capturing the ant queens
- “Barriers” fastened around tree trunks, such as plastic tape coated with grease, plastic cylinders and strips of aluminum

To control nests no larger than 5 m<sup>2</sup>:

- Dried-powder dusting with deltamethrin

To control young *Atta* colonies:

- Dried-powder dusting with deltamethrin

To control certain *Acromyrmex species* (not further specified which species):

- Dried-powder dusting with deltamethrin
- Baits containing sulfluramid

In general, chemical control with toxic baits containing sulfluramid seems often more practical, economical and operational to control the pests. This technique seems to be mostly used to control the genus *Atta*.

According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose.

Advantages:

- No specialized equipment needed for localized application

Disadvantages:

- Labour intensive; well-trained manpower needed;
- Required dosage per colony needs to be calculated. Potential for under-dosing and over-dosing;
- Cannot be applied during rain and when moisture is present (unless bait holders are used).

BEP is, in addition to the general best practices for pesticides outlined in Chapter 2, to determine which ant genus is present to select the appropriate BAT. Where possible, consider an integrated pest management system to minimize the use of pesticides. When using sulfluramid containing baits, collect all leftover baits after treatment.

Once becoming waste, sulfluramid containing baits, should be managed according to the Basel General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants and the pesticides technical guidelines.

#### **Alternative substances:**

Fipronil (CAS No. 120068-37-3): In Brazil, it is only registered for use in baits to control certain *Atta* species (i.e., dicotyledonous leaf-cutting ants). It might not be as efficient and seems to display broader toxicity to other animals. Insufficient data to determine whether this alternative substance is BAT.

#### **Alternative technology:**



Deploying alternative technology alone is likely not be sufficient to effectively control infestation of leaf cutting ants of the genus *Atta* and the genus *Acromyrmex* and their species.

### **1. Dried-powder dusting with deltamethrin:**

The insecticide deltamethrin (CAS No. 52918-63-5) is mixed in a talcum powder vehicle and manually applied via hand-held equipment (called “dusters”) into the ant hill holes (see Brazil submission as follow-up to POPRC-11). Before application, loose soil needs to be removed from the ant hill. This method is not effective in controlling large nests because the powder will not reach into the depth of all the tunnels.

The technology is recommended for complimentary use to control initial nests of *Atta* species and some *Acromyrmex* species (Britto *et al.*, 2016)

Disadvantage:

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

### **2. Thermo-nebulization, also called Thermal Fogging Technique (TFT):**

Thermal fogging is the generation of ultra-fine droplets in a range of 1 µm – 50 µm using thermo-pneumatic energy (see Brazil submission as follow-up to POPRC-11). Units consist of an engine (a simple motor or a more sophisticated small pulse jet engine) that burns fuel in a combustion chamber which opens into a long exhaust pipe of smaller diameter (called a resonator) and a pressurized pesticide tank (e.g., <http://www.pulsfog.de/sources/downloads/pulsFOG%20thermal%20fogging.pdf>). Via controlled flow through a nozzle, the pesticide solution is injected into the hot exhaust gas stream near the outlet of the resonator causing it to be atomized forming ultra-fine fog droplets. This technique requires special equipment and up to 3 operators per nebulizer (when using large equipment). The active ingredient permethrin (CAS No. 52645-53-1) or fenitrothion (CAS No. 122-14-5) is mixed with diesel or kerosene as a vehicle.

This technique can be applied to control *Atta* in mature nests but cannot be used to control *Acromyrmex*. It is being utilized in specific situations, such as very high infestation rates and initial land preparation for cultivation (ABRAISCA submission; <http://chm.pops.int/TheConvention/POPsReview-Committee/Meetings/POPRC13/POPRC13Followup/PFOInfoSubmission/tabid/6176/Default.aspx>).

### **3. Mechanical control:**

Excavation of the young nests and capturing the ant queens is an effective way to control the leaf-cutting ants in smaller areas. Excavation is recommended only during the third and fourth months after the nuptial flight, when the queens are about 20 cm deep in the soil (Zanetti *et al.* 2014).

### **4. “Barriers”:**

Barriers are one of the oldest and most cost effective control methods used for these ants, but only in small orchards (Zanetti *et al.* 2014). Plastic tape coated with grease, plastic cylinders and strips of aluminum, plastic or metal are fastened around the trunks. However, constant inspections and repairs are necessary to protect the trees. This control mechanism may not be feasible for agricultural and forest crops because of the high maintenance requirements.

An excellent overview over other potential alternative substances and alternative technology, such as biological control methods is provided by Britto *et al.* (2016).

**Best environmental practices:**

Utilize an integrated pest management system by utilizing as many techniques as possible to control the pests and to minimize pesticide usage. Note, utilization of an integrated pest management system cannot be practiced in Brazil (ABRAISCA <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOInfoSubmission/tabid/6176/Default.aspx>).

For dried-powder dusting with deltamethrin:

- Calculate the required dosage to prevent under-dosing (inefficient pest control) and over-dosing (unnecessary environmental burden)
- Avoid clogging tunnels
- Apply to dry soil only
- Collect left-over material and dispose of according to information of the manufacturer.

For Thermo-nebulization with fenitrothion or permethrin:

- Use of the equipment should be restricted to professional use by persons of age and qualified operators duly instructed
- The hot exhaust gas of the engine of thermal foggers is a potential source of ignition. For this reason: Make a risk analysis and develop a strategy to prevent risks. Accordingly, strictly observe the safety instructions.
- Operate the unit with the built-in automatic shut-off function active. Keep a fire extinguisher near at the unit readily available. For further details, see e.g., <http://www.pulsfog.de/sources/downloads/pulsFOG%20safety%20instructions%20Thermal%20Fogger%20-Quer-%204-SEPT-2012.pdf>.

For baits with sulfluramid:

- Qualification and periodical training of control teams;
- Have experts recommend the most efficient method and period of application;
- Calculate the required dosage to prevent under-dosing (inefficient pest control) and over-dosing (unnecessary environmental burden);
  - Place baits in proper location
  - Place baits in dry weather periods only (or use bait stations to keep the baits dry);
- Do not use baits in rainy weather or on moist/wet soil unless bait stations are properly used;
- Assess bait consumptions and control efficiency; and
- Collect and dispose left-over bait pellets according to information of the manufacturer. Send collected waste to incinerator that operates at temperatures mineralizing the sulfluramid.

## 5 BAT and BEP measures for PFOS, PFOA and their related substances for specific exemption applications

Fire-fighting foams for liquid fires (see section 0) is an application where a specific exemption is listed for PFOS, its salts and PFOSF and for PFOA, its salts and PFOA-related substances.

### 5.1 PFOS and PFOA: Fire-fighting foams for liquid fuel fires

Fire-fighting foams for liquid fuel fires is an application where a specific exemption is listed for PFOS, its salts and PFOSF and for PFOA, its salts and PFOA-related substances.

#### 5.1.1 Background

Aqueous film-forming foam (AFFF), sometimes referred to as aqueous firefighting foam, is a generic term for firefighting and/or vapour suppression products used globally to protect both lives and property. It is important to point out that the majority of products used are so called foam concentrates while the foam that extinguishes the fire will be generated on-site in real time. AFFFs are unique among other firefighting foams in that they contain a small percentage of fluorinated surfactant. This key ingredient brings performance attributes to the product, which enables it to be extremely effective in extinguishing and preventing fires, especially Class B flammable liquid events. For a definition of classes of fire, see for example the European standard EN 2, “Classification of fires” (EN 2:1992/A1:2004). AFFF agents are formulated by combining synthetic hydrocarbon surfactants with fluorinated surfactants. When mixed with water, the resulting solution achieves extremely low surface tension allowing the solution to produce an aqueous film that spreads across a hydrocarbon fuel surface. Alcohol-resistant AFFF (AR-AFFF) products are designed to be also effective at extinguishing flammable liquid fires containing alcohols and other water miscible flammable organic substances. More information on types and composition of fire-fighting foams can be found e.g. in Korzeniowski et al. (2018).

AFFF products can be used in fixed and portable systems (e.g. sprinkler systems, handheld fire extinguishers, portable cylinders, fire-fighting vehicles (fire trucks), etc.). In most situations, AFFF is purchased as a concentrate, typically referred to as “3%” or “6%” depending on its mixing ratio (during use) with water.

Prior to 2000, fluorinated substances used in AFFFs concentrates were often PFOS- or PFOA-related substances based, which resulted in AFFFs that contained 0.5 wt% to 6 wt% PFOS or PFOS precursors or PFOA-related substances in concentrations of 1 wt% to 3 wt% (ECHA 2014). At the same time, AFFFs concentrates based on long-chain fluorotelomers were also available for certain products and uses. Shortly after the phase-out announcement by 3M in 2000, PFOS-based AFFFs concentrates were generally no longer available in many industrialized countries and generally substitution of long chain PFAS<sup>4</sup> with shorter-chained PFAS has taken place. The primary supply of fluorinated surfactants for AFFF then became fluorotelomer-based. Over the last several years, manufacturers of fluorotelomer-based AFFF have been replacing long-chain fluorinated surfactants with shorter-chain fluorinated surfactants based often on C<sub>6</sub> chemistry (Fire Fighting Foam Coalition, 2017). A recent study on fire-fighting foam concentrates used in Europe indicated that used fluorinated substances differ in chain length and head groups and only a relatively small amount of these substances could be identified by CAS/EC number (Wood-Ramboll- Cowi

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<sup>4</sup> “Long-chain PFAS” are non-polymeric PFASs that include PFCA  $\geq 7$  perfluorinated carbons, PFSA  $\geq 6$  perfluorinated carbons, and their precursors (modified from OECD, 2013).

2020). Some countries and/or regions have implemented regulations addressing the phase-out of foam concentrates containing PFOS or PFOA-related substances, for example, the European Union, Canada, Norway or Sweden (UNEP/POPS/POPRC.14/6/Add.2) or in several airports in Costa Rica.

### 5.1.2 Types of fire-fighting foam concentrates

Fire-fighting foams are divided into two major categories: synthetic foams (such as AFFF) and protein foams. Synthetic foam concentrates are formulated with manufactured surfactants. The category encompasses both fluorinated and non-fluorinated surfactant based foam concentrates:

- AFFF and AR-AFFF foam concentrates based on synthetic hydrocarbons and synthetic fluorinated substances;
- training foams that are used as AFFF and AR-AFFF substitutes in training and system testing and commissioning tests;
- Class A foams used primarily as wetting agents for Class A fire protection and wildland/forestry protection; and
- Fluorine-free fire-fighting foam concentrates derived from protein or synthetic foams are based on hydrocarbons and/or surfactants. Siloxane based foam concentrates are currently under development though are not currently a viable alternative.

Protein-based foam concentrates contain natural proteins as foaming agents. Types of protein foams include regular protein foam (P), fluoroprotein foam (FP), film-forming fluoroprotein foam (FFFP), alcohol-resistant fluoroprotein foam (AR-FP), and alcohol-resistant film-forming fluoroprotein (AR-FFFP).

### 5.1.3 BAT and BEP for PFOS and PFOA and their related substances

It is important to select the correct type of foam concentrate to be used according to the flammable liquid and application. Foam concentrates are tested by manufacturers to meet internationally or national recognised performance standards.

Non-fluorinated foam concentrates are available and technically feasible for almost all applications of class B fires including aviation, upstream petrochemical sector (e.g. offshore installations) and marine applications (Wood-Ramboll-Cowi 2020). Successful replacements of military applications in Denmark and Norway indicate the suitability of viable alternatives, however military approvals can be a time-limiting step in substitution. At present The US Department of Defence, while facilitating research and funding for fluorine-free foams, stated that no fluorine-free foam, including foam that does not contain PFAS, meets the safety standards in the Military Specification considering also fluorine-free foams (US Department of Defence, 2020). While non-fluorinated alternatives for most training scenarios in the petrochemical industry and large tank farms can be applied, the technical feasibility of fluorine-free alternatives for large tanks above 500m<sup>2</sup> surface area are not fully proven yet (DGMK Project 230-01 1985; Wood-Ramboll-Cowi 2020). Research and development of suitable test criteria for large storage tanks (50 m x 6 m) and the capability of fluorine-free foams will be tested by the Lastfire project (LASTFire 2020, 2021).

In addition to the general BEP measures outlined in Chapter 2 that should be followed, best practices should be applied as outlined below and in alignment with the Basel technical guidelines to minimize releases to the environment and to collect all waste. New provisions for training and containment of fire-fighting foam and firewater in live incidents are now proposed for in the Stockholm Convention.

### **Alternative substances:**

In general, usage of fluorine-free alternatives is recommended as outlined in part II of SC-9/13, where available, feasible and efficient because fluorine-based fire-fighting foams could have negative environmental, human health and socioeconomic impacts due to their persistence and mobility (SC-9/13, 2019).

### **Fluorinated alternatives**

According to a recent study on the use of fluorinated and fluorine-free alternatives in fire-fighting foam concentrates several **short-chain based fluorotelomers** with different charged head groups were identified by CAS numbers. 6:2 Fluorotelomer sulfonamide betaine (CAS N°34455-29-3) and N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonamide N-oxide (CAS N°80475-32-7) are fluorinated compounds with minor market share estimates for Europe. In addition, other non-polymeric PFAS are used as replacements, e.g. dodecafluoro-2-methylpentan-3-one (CAS N°756-13-8) (Wood-Ramboll-Cowi 2020).

Additionally, the majority of fluorinated substances in fire-fighting foam concentrates were only described by name/structure in the scientific literature. A 2018 Eurofeu survey among five foam manufacturers representing 60%-70% of the EU market found, that three non-polymeric PFAS compounds that accounted for 87% share of the EU fire-fighting foam concentrate market were not known due to confidentiality claims (Wood-Ramboll-Cowi 2020). Details on AFFF surfactant structures, supplier and product names can be found in the reports by Wood-Ramboll-Cowi (2020) and Backe et al. (2013).

Examples of fire-fighting foam concentrates containing fluorotelomers can be found in the annex in

Table 13 and suppliers for short-chain fluorotelomer based surfactants in

Designation (synonyms)	Acronym	CAS	EC	Supplier and Product Name
Fluorotelomer sulfonates	4:2 FTS	757124-72-4	816-391-3	Angus Fire, 2004 Tridol S 3%; Ansul 2002 Anslite 3% AFFF-DC-6; Hazard Control Tech 1197 F-500; National Foam
4:2 Fluorotelomer thioamido sulfonates	4:2 FtTAoS	1432486-88-8	N/a	Ansul AFFF formulations; Angus Fire, 2004 Tridol S; Ansul, 2002 Anslite 3% AFFF DC-3; Ansul, 2006 Ansl Anulite ARC; Hazard Control Tech., 1997 F-500; Chemguard; Ansul; Angus
5:1:2 Fluorotelomer betaine	5:1:2 FTB	171184-02-4	N/a	3M; Ansul, 2002 Anslite 3% AFFF DC-3; Buckeye 2009; Buckeye AFFF 2004
5:3 Fluorotelomer betaine	5:3 FTB	171184-14-8	N/a	3M; Buckeye
6:2 Fluorotelomer sulfonamide betaine	6:2 FTAB	34455-29-3	252-046-8	Chemours, STHAMEX® -AFFF 3% F-15 #4341; Dr. Sthamer; 3M; National Foam; F-500, Hazard Control Tech., 1997 (Foam 1); Angus Fire, 2004 Tridol S; Angus Fire, 2000 Niagara 1-3
6:2 Fluorotelomer alcohol	6:2 FTOH	647-42-7	211-477-1	No product/supplier is mentioned; Publications are based on environmental samples
6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2	248-580-6	Dr. Richard Sthamer GmbH & Co. KG STHMEX-AFFF 3%; Hazard Control Tech., 1997 F-500; Angus Fire, 2004 Tridol S 3 %; Angus Fire, 2000; Niagara 1-3; Angus Fire, 1997; Forexpan; Angus Fire, 2004 Tridol S 3 %; Ansul, 2002 Anslite 3 % AFFF -DC-4; Ansul, 2006; Ansul Anulite ARC; National Foam 2005; National Foam 2007; National Foam 2008;
6:2 Fluorotelomer sulfonamide amine	6:2 FtSaAm	1383438-86-5	N/a	3M,; National Foam 2005; National Foam 2007; National Foam 2008;

Designation (synonyms)	Acronym	CAS	EC	Supplier and Product Name
6:2 Fluorotelomer thioether amido sulfonic acid	6:2 FtTAoS	88992-47-6	N/a	Angus Fire, 2004 Tridol S; Ansul 1986; Ansul 1987; Angus Fire, 2000 Niagara 1-3; Ansul, 2002 Ansulite 3% AFFF DC-3; Ansul 2009; Ansul 2010; Chemguard 2008; F-500, Hazard Control Tech., 1997
6:2 Fluorotelomer thio hydroxy ammonium	6:2 FtTHN+	88992-46-5	N/a	3M

Table 14. Also of note, many of the fire-fighting foam concentrate producers have introduced fluorine-free alternatives in recent years and are offering both types.

Further information concerning the assessment of hazards of fluorine-free foams as well as a socio-economic analysis of substitution including costs for the European Union can be found in Wood-Ramboll-Cowi (2020).

#### Non-fluorinated alternatives

Ingredients to formulate fire-fighting foam concentrates include alcohols, detergents, siloxanes and protein foams.

A compilation of identified substances can be found in the report by Wood-Ramboll-Cowi (2020) with examples of substances used in most commonly named products (based on market analysis and stakeholder engagement) listed in

Table 15. However, it is unclear whether the substances listed are the key ingredients that provide the key properties of the foam to work and to fulfill the performance requirements. Also this analysis was done for Europe and does not reflect the global market.

Several international standards are available with distinct compliance criteria e.g. UL/ICAO/EN standards. The European Standards EN 1568 Part 1-3 (EN Standards 2018) specify requirements for chemical and physical properties as well as minimum performance requirements for different expansion foam concentrates for surface application to water-immiscible liquids. Part 4 deals with low expansion foam concentrates used for water-miscible liquids. The standards measure extinguishing performance and burnback resistance. Fluorine free foams can meet the highest grade (A1) for both Part 3 and Part 4 (Wood-Ramboll-Cowi 2020).

#### Alternative technology:

Currently, no information is available.

#### Best environmental practices:

The Fire Fighting Foam Coalition published best practice guidance for use of Class B fire-fighting foams (FFFC 2016). Key points representing BEP are:

- **Training Foams:** Use foams that **do not contain fluorinated surfactants;**

- Testing and Commissioning of **Fixed Systems** and **Vehicle Proportioning Systems**: Use surrogate liquid test methods that **do not contain fluorinated surfactants**;
- Provide for containment, treatment, and proper disposal of any foam solution – do not release directly to the environment;
- Develop firewater runoff plans;
- Collect and contain firewater runoff;
- Treat firewater runoff with a combination of coagulation, flocculation, electro-flocculation, reverse osmosis, and adsorption on activated carbon (GAC) and incinerate the activated carbon or
- Incinerate firewater runoff in appropriate equipment
- Disposal of Class B foam concentrate: send for thermal destruction (high temperature incineration) to a facility permitted for handling halogenated waste or the equivalent

Foam concentrates based on PFOS and PFOA-related substances including their impurities and (pre-treated) firewater runoff should be disposed according to disposal methods as per the Basel convention technical guidelines. According to the recent study on use of specific PFAS and fluorine-free alternative in fire-fighting foam concentrates some countries have local or national regulations in place to prevent release of fire-fighting foam or firewater run-off. Also, for infrastructure like airports or petrochemical facilities or fire-fighter training sites the location should be engineered to allow capture of fire-fighting water (followed by appropriate disposal). However, for live incidents the releases of fire-fighting foams are situation and site specific and it may not be possible to retain all runoff from fire-fighting (Wood-Ramboll-Cowi 2020).

Based on historic accidents and pollution of rivers from fire-fighting waters, recognizing that this is a transboundary issue, the UNECE developed safety guidelines and good practices for fire-water retention with recommendation for fire-water retention to governments, competent authorities and operators. Technical and organizational measures are outlined including fire-fighting water retention dimensions, planning and design of retention systems and disposal. The design of the retention system is key and systems can be installed permanently with pre-installed water barriers or permanent retention basins (including pumping installations) or be provided as mobile facilities like fire-fighting water barriers, hoods and sealing pads, and mobile storage tanks (UNECE 2019).

## 5.2 PFOS

### 5.2.1 Metal plating (hard metal plating) only in closed-loop systems

#### 5.2.1.1 Background

Metal plating as hard metal plating refers to functional chromium plating; a process of electrodepositing a layer of chromium directly onto substrates. In terms of chromium plating the deposited chromium layer provides very different optical and physical properties as a function of deposited thickness (see Table 11). Previously, according to the BREF on Surface treatment of metals (IPPC 2007) and Blepp (2015) PFOS had also been used in alkaline cyanide-free zinc and zinc alloy electrolytes, in electroless nickel plating as well as in acidic gold-palladium and rhodium processes. The chapter discusses only chromium plating and the use of PFOS due to Cr(VI) containing electrolytes. Cr(VI) containing electrolytes are used in functional chromium plating, which has higher corrosion protection than decorative chromium plating.



Table 11: Parameter and properties of functional chromium plating and decorative chromium plating (based on Blepp 2015, CTAC 2015, and Netherlands' submission as follow-up to POPRC-11).

Parameter/Properties	Functional Chromium Plating	Decorative Chromium Plating
Thickness of deposited layer (µm)	10 to 5000	0.1 to 2
Hardness of deposited layer (µVickers)	>850	600 to 700
Hardness of deposited layer (kg/mm <sup>2</sup> )	>1000	800 to 1000
Surface Appearance	dull grey	shiny
Chromic Acid Concentration (g/l)	250	250
pH	<1	<1
Temperature (°C)	50 to 75	30 to 50
Current Density (A/m <sup>2</sup> )	~5400	~2000 to ~3000
Plating Time	5min to 24h	≤5min
Properties	Hardness Wear resistance Corrosion resistance Low coefficient of friction	Appearance Non-tarnishing Corrosion resistance
Application Examples	Hydraulic cylinders and rods Railroad wheel bearings and couplers Moulds for the plastic and rubber industry Tool and die parts	Kitchen appliances Bathroom/kitchen fixtures Smart phones/tablets Motorcycle parts

In functional chromium plating, the plating bath consists of chromic acid (H<sub>2</sub>CrO<sub>4</sub>, often referred to as Cr(VI) acid). PFOS or other fluorinated wetting agents are used to reduce surface tension of the liquid to reduce drag-out losses from the plating bath, to improve surface quality of the products and particularly to reduce the Cr(VI) concentration in the working air.

The functional chromium plating process is an electrolytic process that causes bubbles and mist to be ejected from the plating bath (sometimes referred to as “electrolyte”). This mist is released to the work environment and will eventually be dispersed into outdoor ambient air unless controlled with add-on air pollution control equipment and/or chemical fume (mist) suppressants. The plating baths cannot be completely closed because the process produces hydrogen gas (H<sub>2</sub>) that poses an explosion hazard. Chemical fume (mist) suppressants are surfactants that lower the surface tension of the plating solution. By reducing the surface tension, the created process gas bubbles become smaller and rise more slowly than larger bubbles. Slower bubbles have reduced kinetic energy so that when the bubbles burst at the surface, mist is less likely to be emitted into the air and the droplets fall back into the plating bath. Smaller bubbles in the plating bath and lower surface tension provide other process benefits that are well described (Blepp *et al.* 2015). In addition, if a foaming mist suppressant is used, the foam blanket over the electrolyte prevents formation of aerosols (Wiethölter2014). However, foam blankets are not always desirable because they may cause higher carryover of mist suppressants into the rinsing process and might pose a deflagration hazard of the hydrogen gas emitted from the electrolyte solution (Wiethölter2014).

Cr(VI) is a known human carcinogen and therefore Cr(VI) emissions are regulated in the EU and many other countries to protect workers from occupational exposure and to protect the environment. For a good overview, please see “Technical Rules for Hazardous Substances, Activities involving carcinogenic metals and their compounds, TRGS 561 ([https://www.baua.de/EN/Service/Legislative-texts-and-technical-rules/Rules/TRGS/pdf/TRGS-561.pdf?\\_\\_blob=publicationFile&v=2](https://www.baua.de/EN/Service/Legislative-texts-and-technical-rules/Rules/TRGS/pdf/TRGS-561.pdf?__blob=publicationFile&v=2)). Amounts of Cr(VI) in the

ambient air of plating facilities need to be controlled by utilizing add-on air handling and air scrubbing devices and in many cases by using a chemical mist suppressant. Recent experiments demonstrated that add-on air handling devices alone are in most cases not able to sufficiently reduce Cr(VI) amounts in air to comply with a limit of  $1 \mu\text{g}/\text{m}^3$  under EU-REACH making the use of mist suppressants essential in many cases (Wiethölter 2014).

Since chromic acid is a highly oxidative, strong acid, most types of surfactants are oxidised quickly. PFOS-salts such as the tetraethylammonium (CAS No. 56773-42-3) (DEFRA 2004), potassium (CAS No. 2795-39-3), lithium (CAS No. 29457-72-5), and diethanolamine (CAS No. 70225-14-8) were suitable surfactants due to their ability to withstand the highly oxidative plating bath conditions (Wiethölter 2014). Thus, introduction of PFOS-salts as mist suppressant helped solve occupational safety concerns relating to Cr(VI) in the hard chromium plating industry. The typical use rate of PFOS-salts in these applications was 30 mg/l-80 mg/l (0.03 wt% to 0.08 wt%) (Blepp *et al.* 2015). The calculated process lifetime for PFOS in the functional plating process ranged from five to eight months.

Recent report by Posner on Swedish hard chromium metal plating facilities (Posner, 2020) showed that the tetraethylammonium salt of PFOS (TEA; Trade name Candowet® 300) is still used as a mist suppressant.

#### 5.2.1.2 BAT and BEP for PFOS and PFOS-related substances

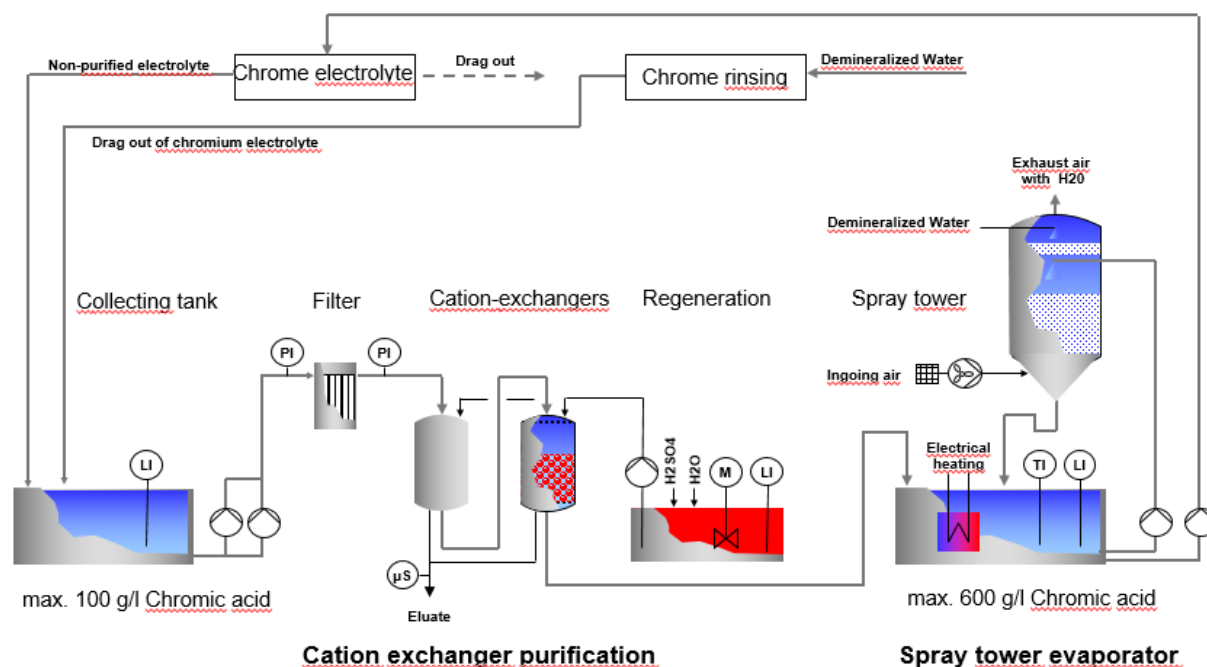
A closed loop system needs to be utilized when using PFOS or PFOS-related substances as mist suppressants. A industry survey commissioned by the German Environment Protection Agency (UBA for its acronym in German) documented, that there is a variety of processing equipment and many different manufacturing processes for different end uses and that there is not a single solution for all metal plating applications in close-looped systems (Blepp *et al.* 2015). The report provided a list of criteria that describe an “almost” closed loop system.

In the European Union, it is obligatory to apply a closed loop system when using PFOS-related substances as mist suppressants for non-decorative hard chromium (VI) plating. In addition, the European Industrial Emissions Directive (2010/75/EU, <https://ec.europa.eu/environment/industry/stationary/ied/legislation.htm>) is applicable to installations for surface treatment of metals or plastic materials using an electrolytic or chemical process where the volume of the treatment vats exceeds  $30 \text{ m}^3$ . These installations have to apply the best available techniques for the prevention and minimisation of emissions of PFOS described in the relevant European BAT reference document (IPPC 2007).

It is important to point out that functional chromium plating facilities might require adherence to various regulations (for example, see p. 35 in Schönberger 2016) and therefore the need to comply with the regulations takes precedence when modifying equipment and/or process steps.

However, there is still no clear definition or clear guideline on what constitutes a “closed loop system”. More research is necessary to determine a more precise definition.

Figure 5: Graphical summary of a typical closed loop system in functional chromium plating (Source: hauserwalz.ch/IUW Integrierte Umweltberatung)



The explanation of Figure 5 can be found below under point 4.

The criteria to achieve “closed loop” performance can be summarized as follows (some of them are graphically summarized in Figure 5):

1. Once the chrome-plated articles leave the plating bath, the remaining chromic acid and other residues, such as the mist suppressant need to be removed to allow for further processing. Rinse plated articles directly above the plating bath so that the main drag-out and rinsing water is directly recycled into the process.
2. Closely control the needed mass balance for the mist suppressant to be effective by means of either (please note not all measures might be applicable for all installations)
  - a. Measuring surface tension of the electrolyte
  - b. Measuring ampere hour rate
  - c. Determining a defined surface throughput (not applicable for subcontracted electroplating shops).

These measures indicate the necessity to re-dose the mist suppressant into the plating bath. Controlling the electroplating process this way can lead to more than 50% reduced mist suppressant use (ISWA 2016). However, throughput-based dosing can lead to inefficiencies, as functional chromium plating is usually not done continuously. Furthermore, a significant number of functional chromium plating installations are subcontracted electroplating shops, meaning that the shapes and requirements of the work pieces are varying considerably.

3. Utilize strong exhaust air systems for suction of the aerosols close to the bath surface (< 30 cm distance, (see p. 382-387 IPPC 2006) and clean the exhaust air with a wet exhaust air scrubber to return the dragged out PFOS to the chromium bath.

4. Evaporate rinsing water after removing Cr(III) and foreign metals, like iron and nickel by cation exchanger purification in a spray tower evaporator to regain chromic acid and PFOS (see Figure 5).
5. Do not expose the ion exchange resins to concentrations of more than 100 g/l chromic acid in the rinse water. Use only demineralised water to refill the rinses and wash solution in the spray tower. Utilize evaporators to concentrate the rinse solution to be recirculated into the plating bath. For higher, required evaporation rates, a heating medium, e.g. hot water instead of electric current, is used to heat the cleaned rinsing water. Heat required for evaporating has considerable cross-media effect. Using excess heat from Chromium plating (caused by low current efficiency) lowers cross-media effect. In functional chromium plating of individual parts with low rinsing water usage and high electrolyte concentration, no additional evaporation by means of atmospheric evaporator or vacuum evaporator for a closed circuit is required.
6. Additional activating baths enhance process bath life-span as well. These cleaning and evaporation processes remove water from the process, thus contributing to PFOS recycling and preventing excess rinse water.
7. When it is only seldom necessary to rinse workpieces: utilize multi-step (7-8 steps) counter-current rinse cascades to further clean the finished parts and recycle the electrolyte solution. For further details, such as equipment diagrams and pictures of exhaust air remediation equipment, see Marzinkowski (2016).
8. Pass any remaining waste water through ion exchange resins after reduction, neutralisation and sludge separation, to remove remaining metal ions and through granulated activated carbon filters or specialized ion exchangers to remove mist suppressant residues. Regenerate spent resin and incinerate waste from the regeneration process. Incinerate activated carbon filters and PFOS-containing ion exchange resins in a facility operating at temperatures at which the mist suppressant is mineralized.
9. Collect and reprocess chromium hydroxide sludge generated during the plating process to reclaim chromium. This process should operate at temperatures at which the mist suppressant is mineralized. Landfilling the chromium hydroxide sludge cannot be considered as BEP.

Following process steps 1 through 8 leads to a ca. 98% efficiency to recover chromic acid (Blepp *et al.* 2015). However, no information is available on mist suppressant recovery efficiency, but it is to be assumed in the same order of magnitude. Cost considerations and affordability factors may play important roles as well but are likely site-specific and are not in-scope for this document.

There might be additional BEP measures to consider related to chromium-VI which are important but outside the scope of this document.

In addition to the general BEP measures outlined in Chapter 3 that should be followed, all waste needs to be collected followed by environmentally sound management and disposal according to the Basel technical guidelines.

According to information from the European Union member states (Posner, 2020), waste from hard chromium plating has the residual chromium containing waste classified as hazardous waste due to its content of chromium. These wastes go to landfills for hazardous waste, no information (no investigation is undertaken) if they contain PFAS or not. There are no regulated landfill criteria for PFAS substances, neither at Swedish level nor at EU level.

**Alternative substances:**

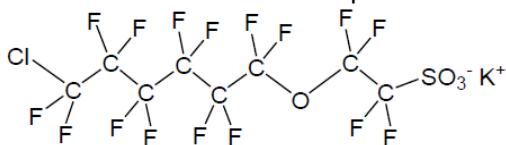
It is important to note that the use of mist suppressants enables to meet occupational health standard regulations and therefore each alternative needs to be assessed in those terms as well.

According to Posner (2020), the most commonly alternative in hard metal plating since 2016 is the 6:2 fluorotelomer sulfonate. It shall be noted and is recognized by the companies and the chemical's supplier that in addition, it has been shown that 6:2 FTS is less stable than PFOS during the hard chromium plating process, which means that a much higher amount is needed of 6:2 FTS relative to PFOS to achieve the same protective effect in chromium baths in the hard chromium plating process.

In the hard chromium plating process, 6:2 FTS can degrade to perfluorohexanoic acid (PFHxA) (Posner, 2020; Buck, personal communication).

In China, the following product is used as potential alternative to PFOS:

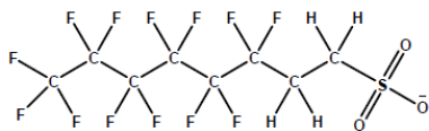
- F-53B (potassium 2-[6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy]-1,1,2,2-tetrafluoroethanesulfonic acid potassium salt ( $C_8HClF_{16}O_4SK$ ; CAS: 73606-19-6)



F-53 was tested in four electroplating companies with excellent performance but had high synthesis costs. Therefore, a simplified production process using chlorine in the last step was developed to produce the monochloro compound, which was marketed as F-53B (Wang *et al.* 2013). In a publication ((Shi *et al.* 2016) the mean biological half-life in humans via all routes of elimination was estimated to be 18.5 years for F-53B. Furthermore, F-53B can only be dissolved in boiling water, which makes handling much more difficult. Therefore, F-53 and F-53B should not be considered as viable alternatives to PFOS.

In Europe, the U.S. and most other countries the following product is used as potential alternative to PFOS:

- 6:2 FTS (6:2 Fluorotelomer sulfonate, 3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctanesulphonic acid, (1H,1H,2H,2H)-perfluorooctanesulfonic acid  $C_8H_5F_{13}O_3S$ ; CAS: 27619-97-2)



The available polyfluorinated alternatives need to be dosed at 2-10 times higher concentrations (Willand *et al.* 2020) than the PFOS-salts to meet specific surface tension requirements and might be less stable and therefore may have to be replenished more frequently. For example, the calculated process lifetime for 6:2 fluorotelomer sulfonate was 0.21 years for one facility (Blepp *et al.* 2015). 6:2 FTS is degraded in the environment to perfluorinated carboxylic acids like PFHxA, PFPeA and PFBA (Best available techniques for the substitution of PFOS in surface treatment of metals and plastics and analysis of alternative substances to PFOS for use in chromium plating and plastic etching (Willand *et al.* 2020).

#### Our research found (status: August 2020; non-exhaustive list)

- 6:2 Fluorotelomer sulfonate (6:2 FTS; CAS No. 27619-97-2)-based products and producers
  - ANKOR® Dyne 30 MS (McDermidEnthone)
  - Ankor PF1 (ENKE)
  - Fumetrol® 21 LF2 (Atotech)
  - HelioChrome® Wetting Agent FF (Kaspar Walter Maschinenfabrik GmbH & Co. KG)

- PK (Kampschulte)
- Proquel OF (Kiesow Dr.Brinkmann)
- riag Cr 320 (Riag)
- Slotochrom® CR1270 (Schlötter)
- Other fluorinated alternatives, no information on chemical nature is known - Trade names (and producers):
  - HCA-8.4 (Hunter Chemical LLC)
  - Non Mist-L (Uyemura)

Non-fluorinated alternatives are not known for functional plating.

The U.S. State of California maintains a list of approved fume suppressants which have undergone testing to meet hexavalent chromium emission standards (CA EPA 2016).

Closed reactor processes, for reference see Schönberger (2016):

The company Topocrom offers an alternative plating process without using mist suppressants in a closed reactor that is suitable for functional chromium plating of printing rollers or tubes achieving hardness values representative for hard chromium plating (<https://www.topocrom.com/en/services/plating-plants-from-topocrom-systems> and [https://www.topocrom.com/fileadmin/pdf/Artikel\\_Verfahren\\_k\\_muell.pdf](https://www.topocrom.com/fileadmin/pdf/Artikel_Verfahren_k_muell.pdf)). The chromium electrolyte circulates between the reactor and the storage tank while maintaining its concentration and temperature. After pumping back the chromium electrolyte, the component is rinsed via a triple cascade in a circulation process and the cascade is changed via valves after a pre-set time. In addition, a water spray system is installed in the reactor to clean the component as the last rinsing process. This supplied water serves to compensate for evaporation losses in the electrolyte reservoir. The process therefore works with low waste water and has been industrially tested for years. Due to the closed reactor technology, there is no need for the use of wetting agents. This alternative technology seems suitable for chromium plating of articles with a specific geometry only. For further details on operating see Willand *et al.* 2020. No information of equipment cost is available.

The company McDermidEnthone offers a closed system reactor for chromium plating of “piston or hollow rod of automotive shock absorbers” that is “OEM approved and meet the specification of the major Shock Absorber OEMs and Tier 1” suppliers, of hydraulics and rotors and engineering parts (<https://industrial.macdermidenthone.com/markets/automotive-solutions/suspension> and [https://www.pfonline.com/cdn/cms/1817\\_Cucuro.pdf](https://www.pfonline.com/cdn/cms/1817_Cucuro.pdf)). The system is described as a “horizontal continuous plating line” that is a closed system with “zero emission and exposure”. This alternative technology seems suitable for chromium plating of articles with a specific geometry only. No further details on operating and equipment cost are available.

The company Atotech offers DynaChrome® Plus, a “system for hard chrome plating of piston rods” (<https://www.atotech.com/products/general-metal-finishing/wear-resistance/dynachrome-plus/>).

According to a study conducted in 2018-2020 (Willand *et al.* 2020), the following alternatives to hard chromium plating with chromium (VI) are available on the German and European market on an industrial scale:

Wet chemical processes:

- Electroless nickel with embedded hard material particles (dispersion layers) in the textile machine industry and in mechanical engineering.

- Electroless nickel layers with embedded phosphorus or nanoparticles in the automotive and electrical industries and in mechanical engineering. However, the hardness of hard chromium layers can only be achieved by heat treatment, which is not always possible.
- Nickel alloy deposition (NiL35) with combination layer of two alloys of the metals copper, tin and nickel. This is a salt resistant coating. It is therefore used in wind power off-shore plants and hydraulic cylinders of harbour cranes.
- Nickel-tungsten alloy deposition (possibly with finely dispersed diamond-carbon inclusions). Due to the high cost of tungsten, this is a niche technology.

Physical processes:

- High velocity oxygen fuel (HVOF) process

HVOF is a high-speed flame spraying method. In this process, metal powder mixtures are applied in a burning gas jet at supersonic speed. For example, tungsten carbide and chromium carbide are used in a cobalt or nickel/chromium matrix to replace hard chromium. The HVOF process has already been used by 450 facilities in Germany in 2019.

- Physical Vapour Deposition (PVD)

In physical vapour deposition, the later deposited material is converted into the gas phase in a vacuum by evaporation or by laser bombardment. It is then accelerated by electrical fields, as a stream of particles at 160 - 500°C and precipitates again on the colder workpiece by condensation. In order to coat all surfaces as homogeneously as possible, the work pieces must be set in rotation during the coating process.

Hard material coatings based on titanium nitride (TiN), titanium carbonitride (TiCN), titanium aluminium nitride (TiAlN) or diamond (DLC) are mainly used as coatings. For die-cast parts made of aluminium and magnesium, chromium-based coating systems such as chromium nitride (CrN), chromium vanadium nitride (CrVN) and chromium aluminium nitride (CrAlN) are mainly used.

- Plasma Nitriding

Plasma nitriding works with a nitrogen-hydrogen mixture, which is ionized in a closed vacuum furnace at negative pressure by applying a voltage between the container wall and the charge. The ionized gas atmosphere diffuses into the peripheral zone of the metal components, increasing the surface hardness and improving the corrosion behaviour of castings and low- to high-alloy steels. The surface temperatures are 350 °C-600 °C.

- Extreme high speed laser metal deposition (EHLA)

Extreme high-speed laser deposition welding is a further development of laser metal deposition (LMD). In laser deposition welding, metal powder is applied to the surface of a base material and melted by laser. In the EHLA process, the powdered filler material already hits the laser light above the melting bath, which heats it up to close to the melting point on its way to the component.

Depending on the requirements for the wear layer, tungsten carbide, titanium and chromium carbides, but also iron, nickel and cobalt-based powders are used. The deposition rate is up to 1000 cm<sup>2</sup>/min, coating thicknesses are 10 µm-250 µm and the feed rate is >100 m/min.

None of the above-mentioned alternatives can cover all applications of functional chromium plating. Specific alternatives must be examined for each individual application. There are applications of functional chromium plating for which there is still no economic alternative.

- Test phase

There is ongoing pilot trial testing reported by one Swedish manufacturing metal plating company to use physical alternatives to PFOS in their hard chromium plating process, namely PTFE (polytetrafluoroethylene) coated balls. The tests are still in pilot scale and have not yet generated final results; neither have been scaled up to full production.

Further Alternative technologies are listed by Posner (2020):

- Case hardening: carburizing, carbonitriding, cyaniding, nitriding, boronizing
- Chemical vapour deposition (CVD)
- Nanocrystalline cobalt phosphorus alloy coating
- Trivalent chromium plating
- Plasma spraying
- Stainless steel & high-speed steel (HSS)

To further control mist and aerosol emissions from the plating bath:

- Mesh or blankets (Composite Mesh Pads) placed on top of bath
- Add-on air pollution control devices (Packed Bed Scrubbers)

**Best environmental practices:**

BEP is to adhere to the general BEP measures and collect all waste followed by environmentally sound management and disposal according to the Basel technical guidelines on POPs waste.

Waste management consideration

Beyond the provisions and recommendations given in the Basel technical guidelines on POPs waste, it shall be mentioned that in the European Union there is no regulation as to the handling

## 5.3 PFOA

This section shall be completed post 2026 when notifications will become available.

### 5.3.1 Photolithography or etch processes in semiconductor manufacturing

### 5.3.2 Photographic coatings applied to films

### 5.3.3 Textiles for oil- and water-repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety

### 5.3.4 Invasive and implantable medical devices

### 5.3.5 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 this Annex

### 5.3.6 Manufacture of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) for the production of...



- 5.3.7 Manufacture of polyfluoroethylene propylene (FEP) for the production of high-voltage electrical wire and cables for power transmission
- 5.3.8 Manufacture of fluoroelastomers for the production of O-rings, v-belts and plastic accessories for car interiors

## 6 Annex

Table 12: Former uses of PFOS and its salts that are expired according to decision SC-9/4 (adjusted from UNEP, 2017)

Use in former acceptable purposes or specific exemptions			Alternatives		
Acceptable Purpose	Incumbent PFOS or PFOS-related Substance	Typical Use Rate	Existence of Alternatives	Chemical Identity	Trade Names and/or Producers
Photo-imaging	FOSA quaternary ammonium salt (CAS No. 1652-63-7), PFOS-Salt (TEA* (CAS No. 56773-42-3)), Polymeric mixtures (not further specified)	Inconsistent Information	Yes	Known	Inconsistent Information
Photoresist and anti-reflective coatings for semiconductors	Inconsistent Information	0.02% to 0.1% ~ 0.1%	Yes Yes	Inconsistent Information	Known Known
Etching agent for compound semiconductors and ceramic filters	PFOS (CAS No. 1763-23-1)	Inconsistent Information	Yes	Known	Inconsistent Information
Aviation hydraulic fluids	Perfluoroethylcyclohexyl sulfonate (CAS No. 67584-42-3)	<0.05%	Inconsistent Information	Inconsistent Information	Inconsistent Information
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)	PFOS (CAS No. 1763-23-1)	Inconsistent Information 150 ng for CCD Filter	Inconsistent Information	Inconsistent Information	Inconsistent Information
Fire-fighting foam	PFOS (CAS No. 1763-23-1)	0.5% to 6%	Yes	Known	Known
<b>Specific Exemption</b>					
Photo masks in the semiconductor and liquid crystal display (LCD) industries	PFOS (CAS No. 1763-23-1)	Inconsistent Information	Yes	Inconsistent Information	Inconsistent Information
Metal plating (hard metal plating) except in closed loop cycles	PFOS-Salts (TEA* (CAS No. 56773-42-3), K (CAS No. 2795-39-3), Li (CAS No. 29457-72-5), DEA* (CAS No. 70225-14-8))	0.03% to 0.08%	Yes	Known	Known
Metal plating (decorative plating)	PFOS-Salts (TEA* (CAS No. 56773-42-3), K (CAS No. 2795-39-3), Li	0.03% to 0.08%	Yes	Known	Known

Use in former acceptable purposes or specific exemptions			Alternatives		
	(CAS No. 29457-72-5), 2,2'-iminodiethanol salt (CAS No. 70225-14-8))				
Electric and electronic parts for some colour printers and colour copy machines	Inconsistent Information	Inconsistent Information	Inconsistent Information	Inconsistent Information	Inconsistent Information
Insecticides for control of red imported fire ants and termites	EtFOSA (N-ethyl perfluorooctane sulfonamide (CAS No. 4151-50-2)	0.01% to 0.1%	Yes	Known	Known
Chemically driven oil production	PFOS (CAS No. 1763-23-1) and non-specified PFOS-related substances	Inconsistent Information	Yes	Known	Known
<b>Exemptions expired in 2015</b>					
Carpets	Acrylate or methacrylate or adipate or urethane copolymers with EtFOSE (N-ethyl perfluorooctane sulfonamide ethanol) as raw material	Up to 15% of weight of fiber	--	--	--
Leather and apparel	Acrylate or methacrylate or adipate or urethane copolymers with EtFOSE (N-ethyl perfluorooctane sulfonamide ethanol) as raw material; FOSA amphoteric (not further specified)	Inconsistent Information	--	--	--
Textiles and upholstery	Acrylate or methacrylate or adipate or urethane copolymers with EtFOSE (N-ethyl perfluorooctane sulfonamide ethanol) as raw material	2% to 3% of weight of fiber	--	--	--
Paper and packaging	Mono-, di- or triphosphate esters of N-ethyl perfluorooctane sulfonamide ethanol (EtFOSE), N-Methyl perfluorooctane sulfonamide ethanol acrylate (co)polymers	0.1% to 1.0% based on dry weight of paper	--	--	--
Coatings and coating additives	PFOS-salts: K (CAS No. 2795-39-3), Li (CAS No. 29457-72-5), DEA* (CAS No. 70225-14-8), NH <sub>4</sub> (CAS No. 29081-56-9) potassium N-ethyl-N-[(heptadecafluoro-octyl) sulfonyl] glycinate (CAS No. 2991-51-7)	0.01% to 0.05%	--	--	--

Use in former acceptable purposes or specific exemptions			Alternatives		
Rubber and plastics	PFOS (CAS No. 1763-23-1)	Inconsistent Information	--	--	--

\* TEA = tetraethylammonium,

Table 13: Examples of fluorinated telomer-based substances used in AFFF concentrates (Table modified from Wood-Ramboll-Cowi (2020)).

Designation (synonyms)	Acronym	CAS	EC	Supplier and Product Name
Fluorotelomer sulfonates	4:2 FTS	757124-72-4	816-391-3	Angus Fire, 2004 Tridol S 3%; Ansul 2002 Anslite 3% AFFF-DC-6; Hazard Control Tech 1197 F-500; National Foam
4:2 Fluorotelomer thioamido sulfonates	4:2 FtTAoS	1432486-88-8	N/a	Ansul AFFF formulations; Angus Fire, 2004 Tridol S; Ansul, 2002 Anslite 3% AFFF DC-3; Ansul, 2006 Ansl Anulite ARC; Hazard Control Tech., 1997 F-500; Chemguard; Ansul; Angus
5:1:2 Fluorotelomer betaine	5:1:2 FTB	171184-02-4	N/a	3M; Ansul, 2002 Anslite 3% AFFF DC-3; Buckeye 2009; Buckeye AFFF 2004
5:3 Fluorotelomer betaine	5:3 FTB	171184-14-8	N/a	3M; Buckeye
6:2 Fluorotelomer sulfonamide betaine	6:2 FTAB	34455-29-3	252-046-8	Chemours, STHAMEX® -AFFF 3% F-15 #4341; Dr. Sthamer; 3M; National Foam; F-500, Hazard Control Tech., 1997 (Foam 1); Angus Fire, 2004 Tridol S; Angus Fire, 2000 Niagara 1-3
6:2 Fluorotelomer alcohol	6:2 FTOH	647-42-7	211-477-1	No product/supplier is mentioned; Publications are based on environmental samples
6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2	248-580-6	Dr. Richard Sthamer GmbH & Co. KG STHMEX-AFFF 3%; Hazard Control Tech., 1997 F-500; Angus Fire, 2004 Tridol S 3 %; Angus Fire, 2000; Niagara 1-3; Angus Fire, 1997; Forexpan; Angus Fire, 2004 Tridol S 3 %; Ansul, 2002 Anslite 3 % AFFF -DC-4; Ansul, 2006; Ansul Anulite ARC; National Foam 2005; National Foam 2007; National Foam 2008;
6:2 Fluorotelomer sulfonamide amine	6:2 FtSaAm	1383438-86-5	N/a	3M,; National Foam 2005; National Foam 2007; National Foam 2008;

Designation (synonyms)	Acronym	CAS	EC	Supplier and Product Name
6:2 Fluorotelomer thioether amido sulfonic acid	6:2 FtTAoS	88992-47-6	N/a	Angus Fire, 2004 Tridol S; Ansul 1986; Ansul 1987; Angus Fire, 2000 Niagara 1-3; Ansul, 2002 Ansulite 3% AFFF DC-3; Ansul 2009; Ansul 2010; Chemguard 2008; F-500, Hazard Control Tech., 1997
6:2 Fluorotelomer thio hydroxy ammonium	6:2 FtTHN+	88992-46-5	N/a	3M

Table 14: Short-chain fluorotelomer-based surfactants from various suppliers such as:

Producer	Web Reference
Chemguard	<a href="http://www.chemguard.com/specialty-chemicals/catalog/fire-fighting-foam-surfactants/">http://www.chemguard.com/specialty-chemicals/catalog/fire-fighting-foam-surfactants/</a>
Chemours	<a href="https://www.chemours.com/Capstone/en_US/tech_info/Index.html">https://www.chemours.com/Capstone/en_US/tech_info/Index.html</a>
Dynax	<a href="http://dynaxcorp.com/products/fire-fighting-foam-applications/">http://dynaxcorp.com/products/fire-fighting-foam-applications/</a>
National Foam	<a href="https://nationalfoam.com/">https://nationalfoam.com/</a>

Table 15: Alternative fluorine-free fire-fighting foam concentrates with (partial) compositional information (Source: Wood-Ramboll-Cowi 2020)

Substance	CAS number	Concentration %	Product
1-dodecanol	112-53-8	0.1 - 1	Respondol ATF 3/6
1-tetradecanol	112-72-1	0.1 - 1	
1-butoxy-2-propanol	131-66-8	4 - 10	
Sulfuric acid, mono-C <sub>8</sub> -C <sub>10</sub> (even numbered)-alkyl esters, sodium salts	5338-42-7	1 - 4	
1,2-propanediol	57-55-6	4 - 10	
Sodium lauryl sulphate	8891-38-3	- 4	
Alkylamidobetaine	61789-40-0	< 5	Moussol FF3x6
1,2-ethandiol	107-21-1	< 10	
2-(2-butoxyethoxy)ethanol	112-34-5	< 10	
Alkylamidobetaine	147170-44-3	< 5	
Sulfuric acid, mono-C <sub>8</sub> -C <sub>14</sub> (even numbered)-alkyl esters, compds. with triethanolamine	85665-45-8	< 10	
Ethane-1,2-diol	107-21-1	< 10	Orchidex BlueFoam 3x6
D-Glucopyranose, oligomeric, C10-16-alkyl glycosides	110615-47-9	5 - < 10	
2-(2-butoxyethoxy)ethanol	112-34-5	1 - < 5	
Ammonium Lauryl Sulfate	32612-48-9	15 - < 20	

Substance	CAS number	Concentration %	Product
Sulfuric acid, mono-C <sub>10</sub> -C <sub>16</sub> -alkyl esters, ammonium salts	68081-96-9	1 - < 5	
Sucrose	57-50-1	> 1	Re-Healing Foam RF1 1%
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivatives, hydroxides, inner salts	61789-40-0	< 10	
2-(2-butoxyethoxy)ethanol	112-34-5	< 20	
Sodium octyl sulphate	142-31-4	< 10	
Sodium decyl sulphate	142-87-0	< 3	
1-Propanaminium, N-(3-aminopropyl)-2-hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts	68139-30-0	< 10	
Amides, coco, N-[3-(dimethylamino)propyl]	68140-01-2	< 0.2	
Amides, coco, N-[3-(dimethylamino)propyl], N-oxides	68155-09-9	< 1	
D-Glucopyranose, oligomers, decyl octyl glycosides	68515-73-1	< 3	
Sulfuric acid, mono-C <sub>12</sub> -C <sub>14</sub> -alkyl esters, compds. with triethanolamine [Alkyl-(C <sub>10</sub> -C <sub>16</sub> )-alcohol sulfuric acid ammonium salt]	90583-18-9 (EC number)	< 10	
Poly(oxy-1,2-ethanediyl), α-sulfo-ω-hydroxy-, C <sub>9</sub> -C <sub>11</sub> -alkyl ethers, sodium salts	96130-61-9	< 3	
Sucrose	57-50-1	> 1	Re-Healing Foam RF3x6 ATC
2-(2-butoxyethoxy)ethanol	112-34-5	< 20	
Starch	9005-25-8	> 1	
1-Propanaminium, N-(3-aminopropyl)-2-hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salts	68139-30-0	< 2.5	

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