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 on Persistent Organic Pollutants

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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, issued in January 2017, 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. The experts nominated by Parties and others to be consulted in the process for review and update of the guidelines and guidance on BAT and BEP are part of the joint Toolkit and BAT and BEP expert roster (UNEP/POPS/COP.8/INF/14).

Abbreviations and Acronyms

AFFF	aqueous film-forming foam
AR-AFF	alcohol resistant aqueous film-forming foam
ARC	anti-reflective coating
AR-FFFP	alcohol-resistant film-forming fluoroprotein
AR-FP	alcohol-resistant fluoroprotein foam
BARC	bottom anti-reflective coating
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
DWR	durable water-repellent
ECF	electrochemical fluorination
EMS	environmental management system
ETFE	ethylene tetrafluoroethylene, a fluorine-based plastic
EtFOSA	N-Ethyl perfluorooctanesulfonamide
EtFOSE	N-Ethyl perfluorooctanesulfonamidoethanol
FFFP	film-forming fluoroprotein foam
FOSA	N-Alkylperfluorooctanesulfonamide
FOSE	N-Alkylperfluorooctanesulfonamidoethanol
FP	Fluoroprotein foam
GHS	Global Harmonization System
LCD	liquid crystal display
PASF	Perfluoroalkanesulfonyl fluoride
PBT	persistent, bioaccumulative and toxic
PFAS	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutane sulfonic acid ($F\text{-}(CF_2)_4\text{-}SO_3H$) /potassium perfluorobutane sulfonate ($F\text{-}(CF_2)_4\text{-}SO_3^- K^+$)
PFOS	Perfluorooctanesulfonate
PFOSF	Perfluorooctanesulfonyl fluoride
PFSA	Perfluoroalkane sulfonic acid
POPRC	Persistent Organic Pollutant Review Committee
POPs	persistent organic pollutants
SDS	safety data sheet
TARC	top anti-reflective coating
VOC	volatile organic compounds

1 Introduction

1.1 Purpose

The concept of best available techniques (BAT) is not aimed at the prescription of any specific technique or technology. BAT 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 practical, generally to reduce releases of chemicals and their impact on the environment as a whole. Best environmental practices (BEP) describe the application of the most appropriate combination of environmental control measures and strategies (Article 5, f (i) and (v) of the Stockholm Convention on Persistent Organic Pollutants (POPs)).

Article 3, paragraph 6 of the Stockholm Convention, requests Parties that have a specific exemption and/or acceptable purpose in accordance with Annex 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 (i.e. applying BAT and BEP).

This guidance document has been developed to guide Parties in their actions to prevent or reduce releases of perfluorooctane sulfonic acid (PFOS), its salts and PFOS-related substances from production and use under the specific exemptions and acceptable purposes listed in the Convention at its 4th meeting in 2009 (COP-4, SC-4/17). This document includes most up-to-date information and knowledge and supersedes the previous version published as UNEP/POPS/COP.7/INF21.

1.2 Structure and use of this document

Chapter 1 outlines the purpose and structure of this document. It also includes a brief overview of characteristics and uses of PFOS, its salts and PFOS-related substances, the relevant provisions under the Stockholm Convention and a summary of required measures under these provisions. Furthermore, Tables 3 and 4 summarize whether or not alternatives are available and in use for each “acceptable purpose” and “specific exemption”. Tables 5 and 6 provide a comprehensive summary of BAT and BEP for each “acceptable purpose” and “specific exemption”.

Chapter 2 includes high level BAT and BEP principles for general chemical management, general pesticide management and guidance for the management of PFOS and PFOS-related substances in particular.

Chapters 3 and 4 provide specific guidance for the processes/applications listed as acceptable purposes and specific exemptions under the Convention. Each section within these chapters provides a general description (Background) of the process/application in which PFOS, its salts and/or PFOS-related substances were/are used, including information on available alternatives for that use, and specific BAT and BEP guidance for management of PFOS and related substances and their alternatives in the respective process/application.

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

1.3.1 Chemicals listed in Part III of Annex B of the Convention

Perfluorooctyl sulfonate ($F\text{-}(CF_2)_8\text{-}SO_3^-$) 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 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, N-alkyl perfluorooctanesulfonamides (FOSAs, F-$(CF_2)_8$-SO_2-NH(alkyl)) or N-alkyl perfluorooctanesulfonamidoethanols (FOSEs, F-$(CF_2)_8$-SO_2-N(alkyl)(CH_2CH_2OH)). 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-$(CF_2)_8$-SO_2-N(C_2H_5)(CH_2CH_2OH))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 Table 1 below.

All these substances belong to different subgroups in the large family of per- or poly-fluoroalkyl substances (PFAS). PFOS belongs to the subgroup of perfluoroalkane sulfonic acids (PFSA) and PFOSF and its derivatives belong to the PASF (perfluoroalkanesulfonyl fluoride) subgroup (Buck *et al.* 2011). In this document, PFOS, its salts and PFOSF and products made there from are often referred to as ''PFOS and PFOS-related substances''. This term is restricted to compounds having the C_8F_{17}-SO_2- or C_8F_{17}-SO_3-group, i.e., fully fluorinated at the eight carbon atoms followed by a leaving group such as sulfonyl (-SO_2) or sulfonate (-SO_3). PFOS and PFOS-related substances as referred to in this document are characterized by the C_8F_{17}-moiety; they contain only C and F atoms in the PFOS-moiety and do not contain any hydrogen (H) or oxygen (O).

1.3.2 Characteristics

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).

1.3.3 Risks

At its second meeting, the POPs Review Committee has developed and adopted the risk profile for PFOS contained in document UNEP/POPS/POPRC.2/17/Add.5. The Committee concluded, in accordance with paragraph 7 (a) of Article 8 of the Convention, that PFOS is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted. At its third meeting, the Committee adopted the risk management evaluation for PFOS, which is set out in document UNEP/POPS/POPRC.3/20/Add.5. Detailed information on the risks posed by PFOS and PFOS-related substances can be found in the above-mentioned documents.

1.3.4 Production and use

In 2009, PFOS, its salts and related substances 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 notified the secretariat of the intention to produce and/or use them for the specific exemptions and acceptable purposes listed in Part I of Annex B. The list of uses for acceptable purposes or specific exemptions pursuant to Part I of Annex B is given in Table2 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/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx

Table 1: Identity of PFOS and some key PFOS-related substances

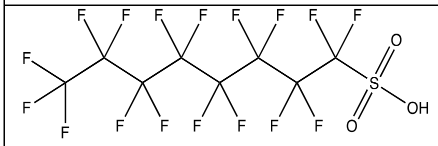
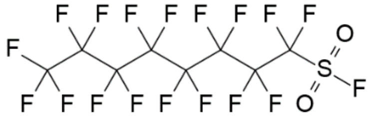
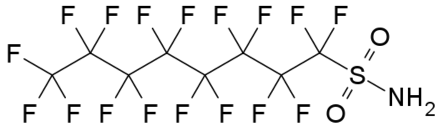
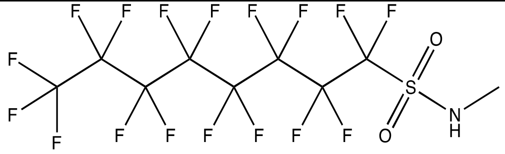
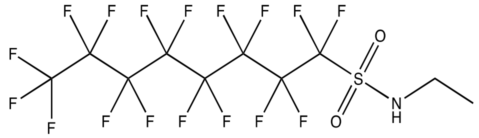
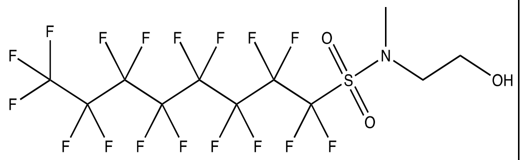
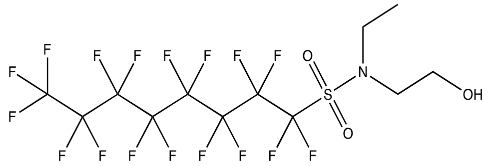
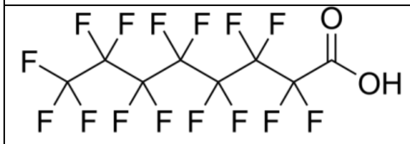
Structural formula	Substance name and abbreviation	Formula
PFOS, its salts and PFOSF		
	Perfluorooctyl sulfonate PFOS	$F-(CF_2)_8-SO_3^-$ $C_8F_{17}-SO_3^-$
	Perfluorooctanesulfonylfluoride PFOSF	$F-(CF_2)_8-SO_2F$ $C_8F_{17}-SO_2F$
PFOS-related substances (e.g., precursors)		
	Perfluorooctanesulfonamide FOSA	$F-(CF_2)_8-SO_2-NH_2$ $C_8F_{17}-SO_2- NH_2$
	N-methyl perfluorooctanesulfonamide MeFOSA	$F-(CF_2)_8-SO_2-NH-CH_3$ $C_8F_{17}-SO_2-NHCH_3$
	N-ethylperfluorooctanesulfon-amide EtFOSA Also: sulfluramid	$F-(CF_2)_8-SO_2-NH-CH_2CH_3$ $C_8F_{17}-SO_2-N(H)C_2H_5$
	N-methyl perfluorooctancesulfonamido ethanol MeFOSE	$F-(CF_2)_8-SO_2-N(CH_3)(CH_2CH_2OH$ $C_8F_{17}-SO_2-N(CH_3)(C_2H_4)-OH$
	N-ethyl perfluorooctanesulfonamido ethanol EtFOSE	$F-(CF_2)_8-SO_2-N(C_2H_5)(CH_2CH_2OH$ $C_8F_{17}-SO_2-N(C_2H_5)C_2H_4-OH$
Not PFOS-related		
	Perfluorooctanoic acid PFOA	$F-(CF_2)_7-COOH$ $C_7F_{15}-COOH$

Table 2: 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.

Acceptable purposes	Specific exemptions
1. Photo-imaging **2.** Photoresist and anti-reflective coatings for semiconductors **3.** Etching agent for compound semiconductors and ceramic filters **4.** Aviation hydraulic fluids **5.** Metal plating (hard metal plating) only in closed-loop systems **6.** Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters) **7.** Fire fighting foam **8.** Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*	**1.** Photo masks in the semiconductor and liquid crystal display (LCD) industries **2.** Metal plating (hard metal plating) **3.** Metal plating (decorative plating) **4.** Electric and electronic parts for some colour printers and colour copy machines **5.** Insecticides for control of red imported fire ants and termites **6.** Chemically driven oil production ***Expired exemptions**** ***7. Carpets*** ***8. Leather and apparel*** ***9. Textiles and upholstery*** ***10. Paper and packaging*** ***11. Coatings and coating additives*** ***12. Rubber and plastics***

* Expired exemptions are highlighted in italic red colour throughout this document

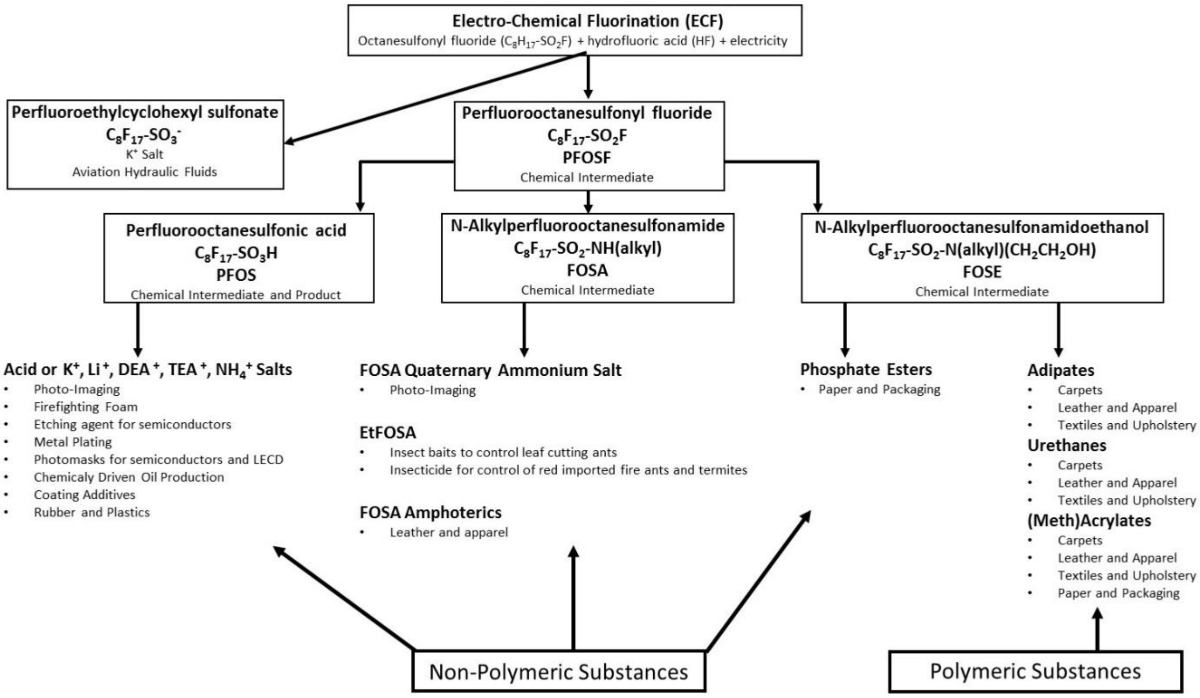
Acceptable purposes have no limited time frame, unless specified otherwise by the Conference of the Parties. Specific exemptions expire five (5) years after the date of entry into force of the chemical under the Convention unless the party indicates an earlier date when registering for an exemption. The amendments to list PFOS, its salts and PFOSF entered into force for most of the parties on 26 August 2010. In 2015, by decision SC-7/1, the Conference of the Parties decided that “specific exemptions for the production and use of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride for carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives and rubber and plastics, no new registrations may be made with respect to them”. These expired specific exemptions are highlighted in red in the table above and throughout this document.

Over the last decade, many Parties have implemented national regulations addressing these substances. A good overview has recently been also published by the OECD/UNEP Global PFC Group (OECD 2015).

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).

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). This is an important aspect to consider in applying BAT and BEP in the case of industries using these materials and having emissions to the environment. Furthermore, these products may also contain PFOA as an impurity (Jiang *et al.* 2015). In 2015, PFOA has been proposed for listing and is under review by the POPs Review Committee (UNEP/POPS/POPRC.11/5).

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.



1.4 Consideration of alternatives to PFOS, its salts and PFOS-related substances

1.4.1 General considerations

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. Guidance for consideration of alternatives has been developed by the POPs Review Committee (for the most recent document see UNEP/POPS/POPRC.12/INF/15). More detailed information on the availability and suitability of the alternatives are available in the source documents used for the development of the guidance.

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 or not 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. It is 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.

Tables 3 and 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 the specific Chapters 3 and 4.

1.4.2 Chemical alternatives

Chemical alternatives may include the following classes of chemicals:

a) Perfluorinated alkylsulfonyl substances; mostly considered shorter chain substances such as PFBS or perfluorinated carboxylic acids
b) Polyfluorinated alkyl substances; such as short-chain fluorotelomer-based polymeric or non-polymeric substances or fluoro-polyethers
c) Fluorine-free substances; based on a variety of chemical platforms. These are specified throughout the text wherever possible

Table 3: Availability of alternatives to PFOS for "Acceptable Purpose" applications (UNEP/POPS/COP.7/INF/26, DEFRA 2004, Blepp 2015).

			Alternatives		
Acceptable Purpose	**Incumbent PFOS or PFOS-related Substance**	**Typical Use Rate**	**Existence of Alternatives**	**Chemical Identity**	**Trade Names and/or Producers**
1. 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
2. Photoresist and anti-reflective coatings for semiconductors	Inconsistent Information	0.02% to 0.1% ~ 0.1%	Yes Yes	Inconsistent Information Incon-	Known Known

				sistent Information	
3. Etching agent for compound semiconductors and ceramic filters	PFOS (CAS No. 1763-23-1)	Inconsistent Information	Yes	Known	Inconsistent Information
4. Aviation hydraulic fluids	Perfluoroethylcyclohexyl sulfonate (CAS No. 67584-42-3)	<0.05%	Inconsistent Information	Inconsistent Information	Inconsistent Information
5. 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), DEA* (CAS No. 70225-14-8))	0.03% to 0.08%	Yes	Known	Known
6. 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 150ng for CCD Filter	Inconsistent Information	Inconsistent Information	Inconsistent Information
7. Fire fighting foam	PFOS (CAS No. 1763-23-1)	0.5% to 6%	Yes	Known	Known
8. Insect baits for control of leaf-cutting ants from genus *Atta spp.* and *Acromyrmex spp.*	EtFOSA (N-ethyl perfluorooctane sulfonamide (CAS No. 4151-50-2)	0.3%	Yes (but not for all needs)	Known	Known

*TEA = tetraethylammonium, DEA = diethanolamine

Table 4: Availability of alternatives to PFOS for “Specific Exemption” applications (UNEP/POPS/COP.7/INF/26, DEFRA 2004, Blepp 2015, U.S. FDA database).

			Alternatives		
Specific Exemption	**Incumbent PFOS or PFOS-related Substance**	**Typical Use Rate**	**Existence of Alternatives**	**Chemical Identity**	**Trade Names and/or Producers**
1. Photo masks in the semiconductor and liquid crystal display (LCD) industries	PFOS (CAS No. 1763-23-1)	Inconsistent Information	Yes	Inconsistent Information	Inconsistent Information
2. Metal plating (hard metal plating)	PFOS-Salts (TEA* (CAS No. 56773-42-3), K (CAS No. 2795-39-3),	0.03% to 0.08%	Yes	Known	Known

	Li (CAS No. 29457-72-5), DEA* (CAS No. 70225-14-8))				
3. Metal plating (decorative plating)	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
4. Electric and electronic parts for some colour printers and colour copy machines	Inconsistent Information	Inconsistent Information	Inconsistent Information	Inconsistent Information	Inconsistent Information
5. 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
6. Chemically driven oil production	PFOS (CAS No. 1763-23-1) and non-specified PFOS-related substances	Inconsistent Information	Yes	Known	Known

Table 4 continued:

Specific Exemption	**Incumbent PFOS or PFOS-related Substance**	**Typical Use Rate**	**Existence of Alternatives**	**Chemical Identity**	**Trade Names and/or Producers**
Expired exemptions					
7. 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	Yes	Known	Known
8. Leather and apparel	Acrylate or methacrylate or adipate or urethane copolymers with EtFOSE (N-ethyl perfluorooctane sulfonamide ethanol) as raw material FOSA Amphoterics (not further specified)	Inconsistent Information	Yes	Known	Known
9. Textiles and upholstery	Acrylate or methacrylate or adipate or urethane copolymers with EtFOSE (N-ethyl perfluorooctane	2% to 3% of weight of fiber	Yes	Known	Known

	sulfonamide ethanol) as raw material				
10. 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	Yes	Known	Known
11. 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_4 (CAS No. 29081-56-9) potassium N-ethyl-N-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS No. 2991-51-7)	0.01% to 0.05%	Yes Yes	Known Known	Data Gap Known
12. Rubber and plastics	PFOS (CAS No. 1763-23-1)	Inconsistent Information	Inconsistent Information	Inconsistent Information	Inconsistent Information

1.5 Summary of Best Available Techniques (BAT) and Best Environmental Practices (BEP) by process category

Tables 5 and 6 below summarize information on BAT and BEP 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 the specific Chapters3 and 4; general principles on BAT and BEP are laid out in Chapter 2.

Table 5: Summary of BAT and BEP for each “Acceptable Purpose” application. *General BEP guidance is provided in Chapter 2.

Acceptable Purpose	BAT	BEP*
1. Photo-imaging	Non-PFOS-based, non-PFOS-related and Non-PFOA-related substances	Collect all waste, recover valuable raw materials (such as silver and PET) followed by incineration at high enough temperatures to thermally mineralize the fluorinated substances
2. Photoresist and anti-reflective coatings for semiconductors	PFOS and PFOS-related substances for formulations commercialized before 2011 non PFOS-related substances (incl. PFOS) for all other formulations	Collect all waste followed by waste incineration operating at high enough temperatures to thermally mineralize the fluorinated alternatives
3. Etching agent for compound semiconductors and ceramic filters	Non-PFOS-based surfactants	Collect spent etching solution for recovery and re-use or be sent to a waste incineration facility that operates at high enough temperatures to thermally mineralize the etchant

Acceptable Purpose	BAT	BEP*
4. Aviation hydraulic fluids	Perfluoroethylcyclohexyl sulfonate potassium salt	Collect all spent hydraulic fluids to be sent to oil recycling companies for proper handling followed by waste incineration operating at high enough temperatures to thermally mineralize the fluorinated substance
5. Metal plating (hard metal plating) only in closed-loop systems	Non-PFOS-based mist suppressant PFOS-based mist suppressant in a "closed-loop system" that fulfills the criteria summarized in respective Chapter 3.5	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the mist suppressant
6. Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)	Insufficient information	Insufficient information
7. Fire fighting foam	Surrogate, non-fluorinated foams for training purposes, for testing and commissioning of fixed systems and vehicle proportioning systems Short-chain fluorotelomer-based substances for Class B fire fighting foam concentrates	Follow best practices outlined in chapter 3.7 to minimize releases to the environment and to collect all waste with following incineration at high enough temperatures to thermally mineralize the firefighting foam ingredients
8. Insect baits for control of leaf-cutting ants from genus *Atta spp.* and *Acromyrmex spp.*	The following techniques (1. through 4.) stand on their own but are often considered to be complimentary to the use of toxic baits (5.) for controlling infestation. 1. Thermo-nebulization with permethrin: For initial large area land preparation and high infestation rate on mature *Atta* nests 2. Mechanical Control: Excavation of the young nests and capturing the ant queens 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 4. Dried-powder dusting with deltamethrin (see "Caution" on page 43): To control nests no larger than 5m^2 To control young *Atta* colonies To control certain *Acromyrmex* species 5. Baits containing sulfluramid (EtFOSA): For all other suitable uses	Determine which ant genus is present to select the appropriate BAT. Consider an integrated pest management system to minimize the use of pesticides. When using sulfluramid containing baits, collect all leftover baits after treatment and send for incineration at high enough temperature to mineralize the sulfluramid (EtFOSA)

Table 6: Summary of BAT and BEP for each "Specific Exemption" application. *General BEP guidance is provided in Chapter 2.

Specific Exemption	BAT	BEP*
1. Photo masks in the semiconductor and liquid crystal display (LCD) industries	Non-PFOS-based surfactants	Collect spent etching solution for recovery and re-use or be sent to a waste incineration facility that operates at high enough temperatures to thermally mineralize the fluorinated surfactant
2. Metal plating (hard metal plating)	Non-PFOS-based mist suppressants and to implement all measures of a "closed loop" system	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the mist suppressant
3. Metal plating (decorative plating)	Non-PFOS-based mist suppressants and to implement all measures of a "closed loop" system	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the mist suppressant
4. Electric and electronic parts for some colour printers and colour copy machines	Insufficient information	Insufficient information
5. Insecticides for control of red imported fire ants and termites	Non-sulfluramid-based substances allowed for pesticide use (see "Caution" on page 43), natural enemies or biological control agents In addition, to control termites: to properly prepare the construction site, to utilize a proper building design and to utilize termite resistant building material for new construction and during repairs	Hire a professional pest control operator who will identify the pest and adheres to the 2-Step Method
6. Chemically driven oil production	Non-PFOS-related substances	Insufficient information

Expired exemptions		
7. Carpets	Side-chain fluorinated polymers based on short-chain fluorotelomers	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymer
8. Leather and apparel	Side-chain fluorinated polymers based on short-chain fluorotelomers	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymer
9. Textiles and upholstery	Side-chain fluorinated polymers based on short-chain fluorotelomers	Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymer
10. Paper and packaging	Non-PFOS-related short-chain fluorinated polymeric substances	Collect all waste followed by incineration at high enough temperatures to thermally mineralize

		the fluorinated polymer
11. Coatings and coating additives	Non-PFOS based fluorinated polymers (for coatings) Non-PFOS and non-PFOS-related fluorinated substances based on short-chain technology (for Coatings Additives)	Insufficient information Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated substances
12. Rubber and plastics	Insufficient information	Insufficient information

1.6 Relationship to the Basel Convention

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" and the "Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride" are available on the Convention´s website:

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

The Basel Convention COP.12 has adopted a low POP content of 50 mg/kg for PFOS, its salts, and PFOSF in waste (2015).

2 General principles and guidance on BAT and BEP for managing PFOS and PFOS-related substances

2.1 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.

2.1.1 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 ISO9001 andISO14000).

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

2.1.2 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
- The drain is never an appropriate disposal system for chemicals

2.1.3 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.

2.2 General BAT and BEP measures applicable to handling all 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 on-line 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.

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
- Dosing and dispensing without spilling in automated dosing systems

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

- Cleaning and recycling of process water – where possible

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
- 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.

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

Emissions Reductions and Waste Management

- Follow all procedures as outlined above
- Adhere to waste disposal methods given in the SDS
- For guidance on sound management of waste, guidance is provided by the Basel Convention (see above).
- Incinerate waste at an approved facility that operates under conditions that completely mineralize the fluorinated substances

2.3 BEP Measures for Manufacturing of PFOS Containing or PFOS-Related Substances Containing Products

- 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 2of this document is applicable and should be followed
- Technology should be deployed to minimize unreacted raw material and impurity content in products sold
- 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 PFOS-related substances from waste water

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). For example, in Germany metal plating facilities may have to comply with maximum concentrations of 10 µg/l for the sum of PFOS and PFOA or 30 µg/l for ten different PFCAs and PFSAs (incl. PFOS and PFOA) in waste water.

Activated carbon may be used to remove PFOS from water via adsorption. The environmentally sound management of the spent activated carbon adsorbent involves high temperature treatment of the adsorbent. The activated carbon may be incinerated to destroy both the PFOS and the activated carbon or may be thermally regenerated to destroy the PFOS and recover useful activated carbon for subsequent use. Either way, the operating conditions of the afterburner (downstream of the chamber where the activated carbon is introduced) dictate destruction of the PFOS evolved off the carbon in the primary chamber of the thermal treatment unit.

In starved air laboratory-scale thermal reactor studies, Yamada and Taylor (Yamada and Taylor 2003) demonstrated 99.5% destruction of PFOS at 600 ^{o}C and 99.93% destruction of PFOS at 900 ^{o}C, in each case with a nominal gas-phase residence time of 2 seconds.

For full-scale incineration (rotary kiln plus afterburner chamber), the Japanese Ministry of the Environment (METI) reports >99.999% destruction (METI 2013). The METI report notes the afterburner (secondary) chamber temperature for this testing is 900oC and that the total gas residence time for the primary and secondary chambers is 8 seconds. Since the full-scale unit for this testing was a commercial waste incineration facility in Japan with a rotary kiln, the gas-phase residence time in the afterburner (secondary) chamber is expected to be 2 seconds and the oxygen concentration is expected to be greater than 5%. The 1100 ^{o}C temperature reported by METI for the rotary kiln (primary chamber) has a larger impact on the physical form of the solid residuals from the incineration facility than on the destruction performance of PFOS. While carbon reactivation furnaces generally have afterburner chambers operating at 900 ^{o}C, their primary chambers are generally run at temperatures well below 1100 ^{o}C to assure recovery of the activated carbon as solid activated carbon since higher temperatures would burn the carbon itself.

Environmentally sound management of PFOS-laden adsorbent is assured by treating the adsorbent in a well-operated thermal treatment unit with an afterburner (secondary) chamber operating at 900 ^{o}C, a gas-phase residence time of at least 2 seconds, and sufficient oxygen. 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.

2.4 General BEP Measures when Using PFOS and PFOS–Related Substances

- When using PFOS or a PFOS-related substance, 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.
- Have dedicated equipment in your facility that only runs processes with PFOS and/or PFOS-related substances

2.5 BEP Measures for Manufacturing of Alternatives to PFOS and PFOS–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

2.6 General BEP measures when using Alternatives to PFOS and PFOS–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 long-chain fluorinated substances (for a definition, see http://www.oecd.org/ehs/pfc/), including 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
- 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.

3 BAT and BEP measures for PFOS and PFOS-related substances for acceptable purpose applications

3.1 Photo-imaging

3.1.1. Background

The use of PFOS and PFOS-related substances in this industry included film (negative (both b/w and colour), colour reversal, cine and television and b/w diagnostic X-ray), paper (colour reversal and positive (incl. b/w)) and b/w reprographic plate (ESWI 2011).

In the photographic industry, PFOS and PFOS-related substances such as tetraethylammonium perfluorooctanesulfonate, FOSA quaternary ammonium iodide and others have been used in manufacturing of film, paper and plates. These chemicals lack photo-activity and provide critical functionality enabling to continually produce high quality material, lowering output of off-spec material (DEFRA 2004). The substances function to:

- Control surface tension
- Control electrostatic charge
- Control friction
- Repel dirt
- Control adhesion

Imaging materials are coated with multiple (up to 18) thin layers of light sensitive materials at high speed. Any irregularity in coating thickness makes imaging materials useless and increases manufacturing waste. The right surface tension is critical for these steps. Controlling the static charge of imaging materials during handling and transport is very important as light produced by a static discharge during processing will have an effect of the sensitivity of the medium. Furthermore, the film (or paper) is moving rapidly across metal surfaces and the developed static charge may be discharged either on a metal surface or on a worker. The use of PFOS or PFOS-related substances was preventing such occurrences ensuring operational and employee safety. PFOS and PFOS-related substances improve camera, projector and printer transport by eliminating unwanted photographic effects; excessive friction during the transport of imaging materials and contamination of imaging materials by dirt or clogging the magnetic strip readers with debris that can lead to significant waste of imaging materials during manufacture and use. Adhesion control of various types of tapes to imaging material is important because tape is the primary way in which imaging materials are attached to spools and to each other during processing. The strength of the bond between the tape and the imaging materials must be controlled so that imaging devices (cameras, photo-processors) and imaging materials are not damaged during transport (the adhesive bond between tape and imaging material must be broken by a force that will not damage devices or materials being transported).

Compatibility with photo-retouching materials is another benefit. The PFOS-based surfactant reduces the surface tension and allows uniform blending of the retouching solution with the existing emulsion so that it is not possible to distinguish the retouched areas from the virgin photograph.

In the past, FOSA quaternary ammonium salt (CAS No. 1652-63-7) and non-specified PFOS-related polymeric mixtures were used in the manufacture of photographic film, paper and plates. Tetraethylammonium perfluorooctanesulfonate (CAS No. 56773-42-3) was used in the manufacture of photographic film (DEFRA 2004). The use of these substances in the EU (for which data are available) decreased a) for film from 4.75 t in 2000 to 0.27 t in 2010, b) for paper from 0.73 t in 2000 to 0 t in 2005 and c) for plates from 0.40 t in 2000 to 0 t in 2010, indicating alternatives are available and in use (ESWI

2011). One report (DEFRA 2004) indicates 85% of the PFOS and PFOS-related substances used in the EU photo-imaging industry is in X-ray film. The industry aims to shift to alternatives. X-ray film is estimated to contain 0.8 µg/cm^2 or 13.45 ppm PFOS. All X-ray film produced in the EU in 2010 contained an estimated 187 kg of PFOS (reduced from 624 kg in 2000) – for more details see Table 6-18 (contained in products) and Table 6-19 in (ESWI 2011).

3.1.2. BAT and BEP for PFOS and PFOS-related substances

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all waste, recover valuable raw materials (such as silver and polyethylene terephthalate (PET)) followed by incineration at high enough temperatures to thermally mineralize the fluorinated substances.

Alternative Substances:

The possible alternative substances identified for the photographic industry are listed below (UNEP/POPS/POPRC.9/INF/11/Rev.1, Michiels 2010). No specific trade names or other product specific details have been reported.

- Fluorotelomer-based products of various perfluoroalkyl chain length
- PFOA and PFOA-related compounds (but reduced >90% since 2000)
- C3- and C4-perfluorinated compounds
- Hydrocarbon surfactants
- Silicone products

Alternative Technology:

Digital techniques have substantively reduced photographic and X-ray film use. Estimates for 2010 for Europe published in ESWI (2011) report a 70% decrease in demand for coating solutions because of that shift.

Best Environmental Practices for Manufacturing of Photographic Materials

- Coating formulations are formulated using common best practices and worker protection as described in the product Safety Data Sheets
- After preparation of the coating mixture, solutions are transferred via automatic piping to the production area where they are added to coating machines for application of the mixtures onto the media. Since these processes need to run in clean environments to avoid contamination of the product, human exposure is minimal.
- Waste from this operation is collected on site and then disposed of through high temperature incineration
- Unused/excess coating material is send to silver recovery before being sent to high temperature incineration. In case the coating material does not contain silver, it is send to high temperature incineration.

Best Environmental Practices for Finishing Operations

The finishing stage involves slitting the up to several meters wide film rolls into sizes appropriate for the product type. Waste from this process is solid waste and is either directly sent to incineration or is incinerated after recovery of silver, PET film base and other materials.

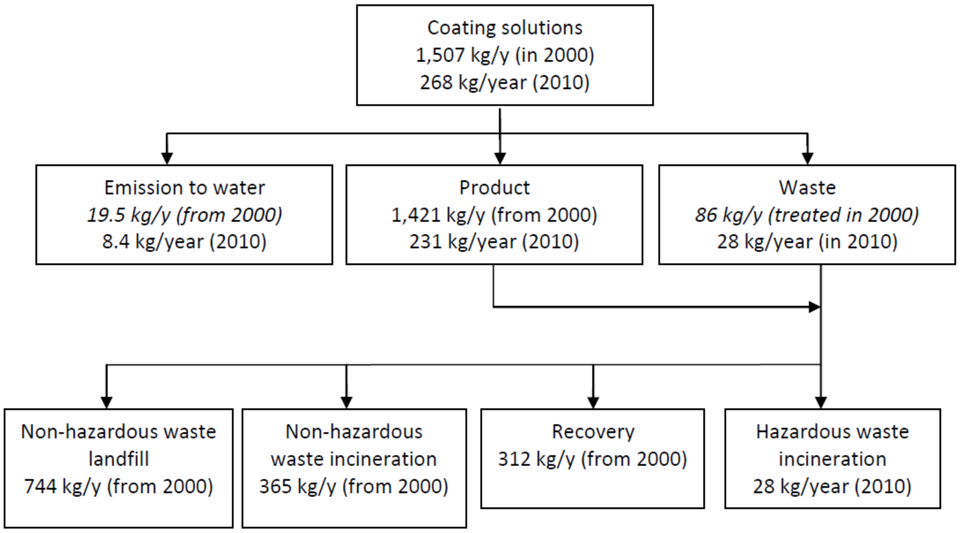
Best Environmental Practices for Photo-Processing Operations (wet film processing)

When conducting photographic developing work, a business operator handling photographic film for industry needs to consider the following measures:

- Recover used developing solution and fixing solution
- Prepare for spills and leaks where developing solution and fixing solution are used

By applying the above BAT and BEP measures, it was estimated that about 13.6% of the total PFOS amount used (here assumed to translate to PFOS, its salt and PFOS-related substances) is not contained in the products (film, paper and plate) but is emitted to water (8.4kg/year) and waste (28 kg/year) that is most likely being incinerated; see Figure 2 below (ESWI 2011). From the numbers it is apparent that the EU industry applies practices that limit emissions to water. The solid waste is handled by waste management companies and is transformed in incineration processes (NO_x reduction) in cement plants.

Figure 2: Substance flow of PFOS from the photographic industry. The diagram shows the PFOS substance flow for years 2000 and 2010.



Best Environmental Practices for the Recycling of X-Ray Pictures

In Europe, an estimated 50% of all X-ray pictures kept at hospitals or similar institutions will be collected by recycling companies after ten years (ESWI 2011). Therefore, in 2010 ca. 50% of the x-ray pictures made in 2000 were handed to recycling companies. There are two recycling processes (ESWI 2011):

1. For film recycling the film surface is removed and the PET carrier material is recovered (~23,000 t). The collected chemicals from the film surface contain, silver, other chemicals and ca. 312 kg PFOS. The liquid is de-silvered electrochemically and the remaining waste is used as fuel in cement plants helping to reduce NO_x emissions from those operations. No emission to water ways is expected from this process. It is not known whether PFOS will be fully mineralized in this process.
2. The film surface is removed and results in sludge and some emissions to water. The report was unclear as to how the sludge will be further processed but stated that recycling facilities should be equipped with waste water treatment (activated carbon) to remove the majority of the PFOS contained in the waste water.

3.2 Photoresist and Anti-Reflective Coatings for Semiconductors

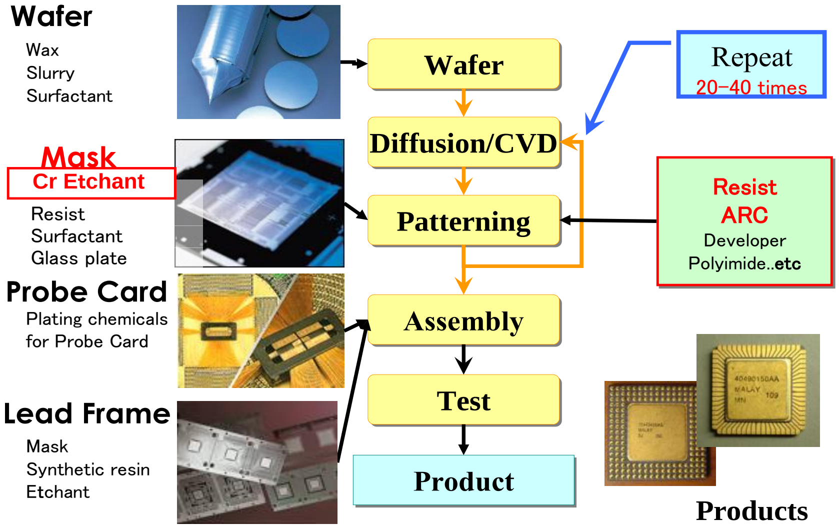
3.2.1. Background

The semiconductor industry is utilizing fluorinated surfactants and fluorinated polymers in different manufacturing processes. The chemical nature of these substances has not been disclosed. Fluorinated surfactants find applications in various etching processes, such as for compound semiconductors and ceramic filters, photomasks and liquid crystal displays. Fluorinated surfactants and/or fluorinated polymers are needed in formulations for photoresists and anti-reflective coatings in high-end photolithography.

Semiconductor manufacturing comprises up to 500 steps (see Figure 3 below). The technology primarily involves four fundamental physical processes:

- Implant
- Deposition
- Etch/polish
- Photolithography

Figure 3: Different steps in semiconductor manufacturing where PFOS and PFOS-related substances are/were used. Source: Japan Electronics and Information Technology Industries Association Semiconductor Board



Photolithography is one of the most important processes in semiconductor manufacturing, as it enables and defines the level of sophistication and performance of devices. The most critical need in photolithography is to be able to develop increasingly smaller features on the surface of a silicon wafer (i.e., patterning). Formation of such small circuit features are enabled by so called photoresists which are light sensitive polymer coatings on the silicon wafer. Light exposure changes the solubility of the photoresist enabling to develop (etch) the small circuit features. Photoresists require the use of so called photo-acid generators (PAGs) to increase their sensitivity to allow etching images smaller than the wavelength of visible light. In addition, anti-reflective coatings (ARCs) are often used to help reduce blurred images associated with reflections off of the substrate surface, the resist surface and the resist/ARC interface. Two types of ARCs are being used, so called TARCs (top anti-reflective coating) – applied after the photoresist - and BARCs (bottom anti-reflective coating) – applied before the photoresist.

Typical polar ionic PAGs consist of a photosensitive cation and an acidic counter-ion which releases when exposed to light. Historically, the acidic counter-ion was PFOS or a PFOS-related substance. The PFOS or PFOS-related substance concentration was in the range of 0.02 wt% to 0.1 wt% for photoresists. It is not clear whether PFOS directly or a PFOS-related substance was used in older ARC formulations but the typical concentration of PFOS and/or PFOS-related substances was ~0.1 wt% for ARC formulations (DEFRA 2004).

Approximately 97% of the applied product will be spinning off the wafer and should be captured as waste for off-site incineration. The product remaining on the wafer undergoes heat treatment (baking step) and converts to a film (solvents are evaporated). The dry film may consist of non-volatile acrylic polymers, cross-linkers, surfactant, stabilizers and other additives. Ca. 50% of the dried film may dissolve during the development step. It is unclear whether or not the remaining approximately 3% of PFOS and PFOS-related substances are heat cured and therefore fixed in a polymer matrix.

The estimated global annual "PFOS use" (2010 data) for the three remaining applications is as follows (WSC 2011):

Application	2010 estimated global annual PFOS consumption (kg)
Photoresists	46.4
Bottom Anti-Reflective Coating	4.5
Top Anti-Reflective Coating	893.5

Furthermore, the World Semiconductor Council (WSC) states in the 2011 joint statement: "The industry continues to work towards developing comprehensive PFOS substitutes for current and future semiconductor manufacturing. From discussions with suppliers we know that the manufacturers who synthesize and supply PFOS to the photolithography chemical suppliers have terminated production of these PFOS materials. The WSC SC manufacturers have agreed not to seek new uses of photolithography chemicals containing PFOS and the suppliers have publically stated that they will not provide PFOS-containing chemicals for any new uses. Additionally, semiconductor companies are replacing remaining use of PFOS as the feasibility and capability are proven. A few semiconductor companies will be required to continue to use PFOS blends until these feasibility issues are overcome. The amount left in use is highly controlled."

Photoresist and anti-reflectant products are either water-based or solvent-based solutions. For example, DOW™ Photoresists and Anti-Reflectants contain up to 80% solvents with the remaining components being acrylic or other polymer resins, PFOS-derived cross-linking agents, stabilizers and/or PFOS-derived surfactants. The EMD AZ® Aquatar® VIII is a water-based formula that contains a polymeric hydrolysed fluoroalkyl acid ester.

3.2.2. BAT and BEP for PFOS and PFOS-related substances

The use of PFOS and PFOS-related substances for formulations that were introduced into the market before 2011 should be phased out and alternative/non PFOS-based and non PFOS-related substances should be used for formulations that were introduced into the market after 2011.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all waste followed by waste incineration operating at high enough temperatures to thermally mineralize the fluorinated alternatives.

Alternative Substances:

Photoresists and anti-reflective products without the use of PFOS are commercially available but information on the type and chemical class of alternatives has not been disclosed in detail. Information on some of the alternative substances disclosed the use of fluorinated compounds; most other information was not that specific.

Table 7: Information on alternatives based on internet searches conducted in May/June 2016.

Use/Product	Producer	Web reference
Photoresists		
GKR Series KrF	Fujifilm Holdings America	http://www.fujifilmusa.com/products/semiconductor_materials/photoresists/krf/index.html
Various Product Names	TOKYA OHKA KOGYO	http://tok-pr.com/catarog/Deep-UV_Resists/#page=1)
ARCs		
ARC® Coatings	Brewer Science Inc.	http://www.brewerscience.com/arc
AZ® Aquatar®-VIII Coating	EMD Performance Materials	http://signupmonkey.ece.ucsb.edu/wiki/images/b/bb/AZ_Aquatar_VIII-A_45_MSDS.pdf
Photoresist and ARCs		
Dow™ Photoresists and Anti-Reflectants (non-PFOS)	The Dow Chemical Company	http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb120.pdf?filepath=productsafety/pdfs/noreg/233-00827.pdf&fromPage=GetDo

Alternative Technology: No information

Best Environmental Practices:

- See Chapter 2 for general best practices information
- For general environmental, health, and safety guidelines for semiconductors & other electronics manufacturing, see for example the IFC guidelines (IFC 2007b). Product Safety Assessment documents exists for at least one supplier (see above link for Dow™ Photoresists and Anti-Reflectants).
- Incinerate solvent waste containing PFOS at high enough temperatures to thermally mineralize the fluorinated substances.
- The industry has implemented process tools to reuse and recycle as well as to incinerate spent liquid along other measures and reports global emissions of PFOS to waste water of approximately 6kg/year (WSC 2011). In that report, no information on emission quantities of the alternative products was provided.
- When photoresists and anti-reflective coating products are applied to silicon wafers approximately 97% of the applied product will be spinning off the wafer and should be captured as waste for off-site incineration. The product remaining on the wafer undergoes heat treatment (baking step) and converts to a film (solvents are evaporated). The dry film may consist of non-volatile acrylic polymers, cross-linkers, surfactant, stabilizers and other additives. Ca. 50% of the dried film may dissolve during the development step. The dissolved ingredients should be neutralized and any

other material remaining in the aqueous phase should be removed before discharging to the wastewater-treatment processes.

- Any waste generated in these processes should be sent to an incineration facility that operates at high enough temperatures to thermally mineralize the fluorinated substances.

3.3 Etching Agent for Compound Semiconductors and Ceramic Filters

3.3.1 Background

PFOS has been used as a surfactant in etching processes in the manufacture of compound semiconductors. PFOS was part of an etching agent, and rinsed out during the subsequent washing treatment.

PFOS has been used in the etching process of piezoelectric ceramic filters which are used as a bandpass filter at intermediate frequency in two-way radios for police radios, FM radios, TV, Remote Keyless Entry Systems for Cars, etc. (Japan, 2007, Annex F submission). For deciding on the bandwidth of piezoelectric ceramic filters, the gap dimension of vibrating electrodes on both sides of the ceramic element is the important indicator. The gap dimension must be controlled within several hundred □ m. To prevent bubble creation during the etching process a surfactant needs to be added.

3.3.2 BAT and BEP for PFOS and PFOS-related substances

Etching Agent for Compound Semiconductors

Non PFOS-based surfactants are in use for etching application (WSC 2011).

In addition to the general BEP measures outlined in Chapter 2 that should be followed, spent etching solution needs to be collected for recovery and re-use or be sent to a waste incineration facility that operates at high enough temperatures to thermally mineralize the etchant.

According to information provided by the Chemical Management Policy Division, Manufacturing Industries Bureau, Ministry of Economy, Trade and Industry of Japan the use of PFOS has been eliminated for this application (Japan, 2007 Annex F submission).

Alternative Substances:

According to information provided by the World Semiconductor Council short-chain perfluoroalkyl sulfonates are alternatives in use today (WSC 2011).

Alternative Technology: No information

Etching Agent for Ceramic Filters

Non PFOS-based surfactants are in use for etching application (WSC 2011).

In addition to the general BEP measures outlined in Chapter 2 that should be followed, spent etching solution needs to be collected for recovery and re-use or be sent to a waste incineration facility that operates at high enough temperatures to thermally mineralize the etchant.

According to information provided by the Chemical Management Policy Division, Manufacturing Industries Bureau, Ministry of Economy, Trade and Industry of Japan (Japan, 2007 Annex F submission), the use of PFOS has been eliminated for this application. However, the type of alternative substances in use has not been disclosed.

Alternative Substances: No information

Alternative Technology: No information

3.4 Aviation hydraulic fluids

3.4.1 Background

Aviation hydraulic fluids based on fire resistant alkyl and/or aryl phenyl phosphate esters may contain additives such as cyclohexanesulfonic acid, decafluoro(pentafluoroethyl), potassium salt (CAS No. 67584-42-3) and different chain-length homologs (SDS Hyjet®) in concentrations of about 0.05% (DEFRA 2004):

Chemical Name	CAS Number
Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt	67584-42-3
Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt	68156-07-0
Cylohexanesulfonic acid, nonafluorobis(trifluoromethyl)-, potassium salt	68156-01-4
Cyclohexanesulfonic acid, undecafluoro-, potassium salt	3107-18-4

According to Norway's submission as follow-up to POPRC-11, PFOS itself does not seem to be used in this application.

Phosphate-ester based fluids have been used in civil and military airplanes since the 1970s (United States Patent 3,679,587 dates from 1972). These fluids are used in applications with performance demands that "oil-based" hydraulic fluids cannot match (e.g., fire resistance and very good low temperature properties). Hydraulic fluids actuate moving parts of the aircraft such as wing flaps, ailerons, the rudder and landing gear. It was discovered that localized corrosion (referred to as erosion) occurs in the valves of the hydraulic system over time affecting their efficiency causing premature overhaul of mechanical parts. Presence of the fluorinated surfactant inhibits corrosion of mechanical parts of the hydraulic system by altering the electrical potential at the metal surface, thereby preventing the electrochemical oxidation of the metal surface under high pressure. For further information, see DEFRA 2004.

The total global market for fluorinated compounds in aircraft hydraulic fluids is estimated to be about 2 tonnes per year. Annual fluorinated compound consumption in the European Union for this use was about 730 kilogram/year in 2000 (Carloni 2009).

3.4.2 BAT and BEP for PFOS and PFOS-related substances

There is uncertainty about alternative substances in this area. In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all spent hydraulic fluids to be sent to oil recycling companies for proper handling followed by waste incineration operating at high enough temperatures to thermally mineralize the fluorinated substances.

Alternative Substances:	No Information
Alternative Technology:	No Information

Best Environmental Practices (BEP):

Suppliers to this industry as well as users of aviation hydraulic fluids should adhere to BEP practices outlined in the safety data sheets so that emissions to the environment are minimized.

Spent aviation hydraulic fluids are down-cycled and handled by oil recycling companies with physical chemical treatment to generate (unspecified) new products or are incinerated in specialized treatment facilities (DEFRA 2004, ESWI 2011). Any waste generated in these processes should be sent to an incineration facility that operates at high enough temperatures to thermally mineralize the fluorinated substances.

3.5 Metal Plating (hard metal plating) Only in Closed-Loop Systems

3.5.1 Background

Metal plating refers to the process of electrodepositing a layer of certain types of metal directly onto substrates. In terms of chrome plating the deposited chrome layer provides very different optical and physical properties as function of deposited thickness (see Table 8).

Table 8: Parameter and properties of hard chrome plating and decorative chrome plating (based on Blepp 2015, CTAC 2015, and Netherlands' submission as follow-up to POPRC-11).

Parameter/Properties	Hard Chrome Plating	Decorative Chrome 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^2)	>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^2)	~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

The 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_2) 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 no longer desirable because they cause higher carryover of mist suppressants into the rinsing process (see BEP guidance) and might pose a deflagration hazard of the hydrogen gas emitted from the electrolyte solution (Wiethölter2014).

In chrome plating, the plating bath consists of chromic acid (H_2CrO_4, often referred to as Cr(VI) acid). Cr(VI) is a known human carcinogen and therefore Cr(VI) emissions are regulated to protect workers from occupational exposure and to protect the environment. Amounts of Cr(VI) in the ambient air of plating facilities need to be controlled by utilizing a chemical mist suppressant and add-on air handling and air scrubbing devices. Recent experiments demonstrated that add-on air handling devices alone are not able to sufficiently reduce Cr(VI) amounts in air to comply with the proposed limit of 1μg/m^3 under EU-REACH making the use of mist suppressants essential (Wiethölter 2014). Examples of permissible Cr(VI) amounts in air for different countries are summarized in Figure 8 (see Wiethölter 2014). They range from 50 μg/m^3 in Austria and Switzerland, 30 μg/m^3 in Canada, 20 μg/m^3 in Germany, 10μg/m^3 in the USA, and 1 μg/m^3 in the Czech Republic and France. In addition, the US State of California maintains a list of approved fume suppressants which have undergone testing to meet hexavalent chromium emission standards (CA EPA 2016).

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 used since the 1930s because of their ability to withstand the highly oxidative plating bath conditions (Wiethölter 2014). Thus, introduction of PFOS-salts as mist suppressant helped solving occupational safety concerns relating to Cr(VI) in the hard chrome 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 ranged from 0.41 years to 0.7 years.

50% of PFOS-salts used in the German plating industry was used for hard chrome plating (Zangl *et al.* 2012). Germany reports that estimated annual use of PFOS-salts in Germany in the metal plating industry was 3400 kg (UNEP/POPS/COP.7/INF/12). Furthermore, it was estimated that 3187 kg (94%) PFOS-salts enter a waste stream that is thermally treated at temperatures at which PFOS decomposes. The remaining 207 kg (6%) PFOS-salts enter waste water streams that are treated in waste water treatment plants. Air emissions of PFOS have been estimated in 2010 to be 0.36 kg/year (0.01%) from such processes (Zangl *et al.* 2012).

Other, no longer permitted, uses of PFOS-salts were the alkaline zinc and zinc alloy plating, sulfuric acid anodising of aluminium, the electro-less nickel dispersion coating and strong acid electrolytes with insoluble anodes, such as precious metal electrolytes (e.g. gold, palladium and rhodium) (IPPC 2006).

3.5.2 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 recent 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 processes to manufacture for different end uses and that there is not a “one fits all” closed loop system for metal plating (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) 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 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).

The criteria to achieve "closed loop" performance can be summarized as follows and most of them are graphically summarized in Figure 4:

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 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
    a. Measuring surface tension of the electrolyte
    b. Measuring ampere hour rate
    c. Determining a defined surface throughput
    d. Measuring foam stability

    These measures indicate the necessity to re-dose the mist suppressant into the plating bath. Controlling the electroplating process this way can lead to up to 50% reduced mist suppressant use (IPPC 2006)

3. Transport exhaust air and aerosols above the plating bath via an exhaust air handling system to an evaporator to condense the evaporated bath contents to be recirculated into the plating bath
4. Treat the remaining exhaust air further in a 2-stage wet air scrubber with a) rinse water from the first rinsing cascade that is being recirculated into the plating bath (yellow line) and with b) deionised water in the second step that is recirculated into the rinsing cascade (green line). These processes remove water from the process and therefore help keeping the water balance in the plating bath
5. Utilize multi-step counter-current rinse cascades to further clean the finished parts and recycle the electrolyte solution
6. Utilize evaporators to concentrate the rinse solution to be recirculated into the plating bath
7. Remove contamination of Cr(III) and other metal ions in the plating bath by circulating the most diluted rinsing cascade through a double cation exchange resin
8. Pass any waste water through ion exchange resins to remove metal ions and through granulated activated carbon filters to remove mist suppressant residues. (Regenerate spent resin and incinerate waste from the regeneration process. Incinerate activated carbon filters 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. Land-filling the chromium hydroxide sludge cannot be considered as BEP.

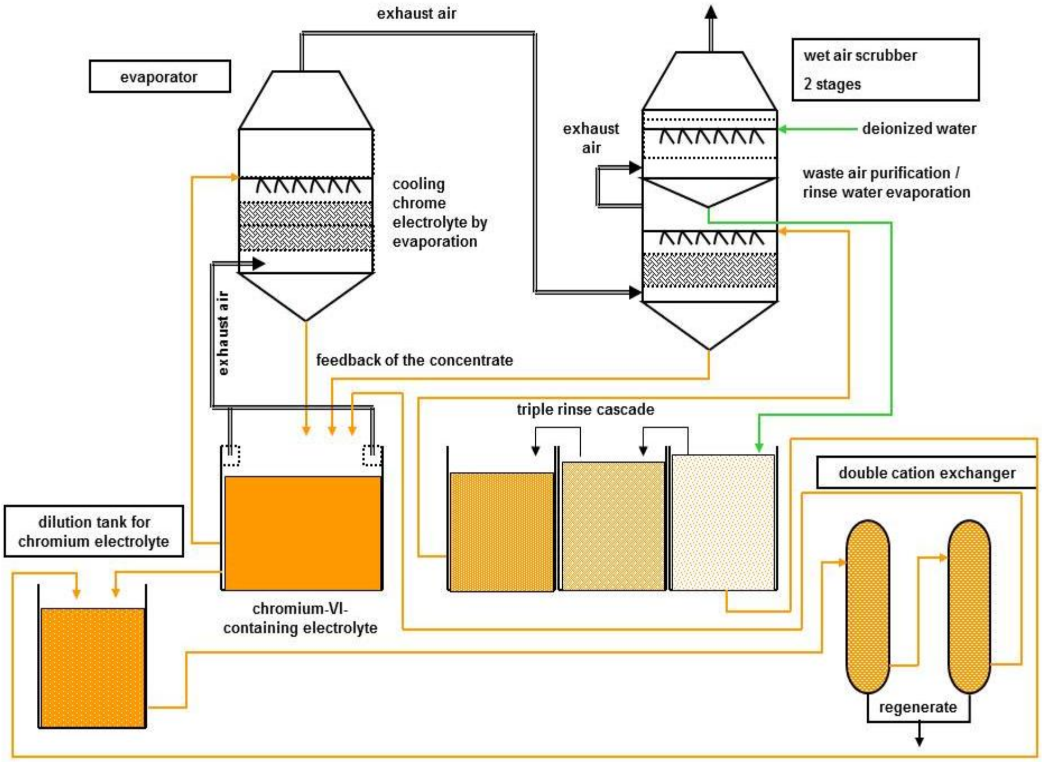
Following process steps 1 through 9 leads to a ca. 98% efficiency to recover chromic acid (Blepp *et al.* 2015). However, no information is available on mist suppressant recovery efficiency.

Due to the space requirements of such processing equipment, it is most likely not suited to retrofit all existing plating operations. In addition, cost considerations and affordability factors may play important roles as well.

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 2 that should be followed, it is needed to collect all waste with following incineration at high enough temperatures to thermally mineralize the mist suppressant.

Figure 4: Graphical summary of a "closed loop" metal plating system (Hauser 2011).



3.6 Certain medical devices

3.6.1 Background

Video endoscopes contain(ed) a charge-coupled device (CCD) colour filter containing 150ng of PFOS. The CCD is part of technology enabling capturing digital images. Another use of PFOS described is as a dispersant of contrast agents that are incorporated into an ethylene-tetrafluoroethylene (ETFE) copolymer layer that is used in radio-opaque catheters.

3.6.2 BAT and BEP for PFOS and PFOS-related substances

An information gap exists as to BAT and BEP for this application. For a general best practices overview see Chapter 2.

Use in ethylene-tetrafluoroethylene (ETFE) copolymer layers

Alternative Substances:

PFBS may have replaced PFOS as a dispersant of contrast agents in EFTE layers for radio-opaque catheters.

Alternative Technology: No information

Use in production of radio-opaque ETFE

Alternative Substances: No information

Alternative Technology: No information

Use in certain in-vitro diagnostic devices

Alternative Substances: No information

Alternative Technology: No information

Use in charge-coupled device (CCD) colour filters

Alternative Substances: No information

Alternative Technology: PFOS-free CCD filters seem to be in use

Best Environmental Practices: No information

3.7 Firefighting foam

3.7.1 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. AFFFs are unique among other firefighting foams in that they contain a small percentage of fluorinated surfactant. This key ingredient brings unique 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 Scottish Classification Authority, "Classes of Fire" (http://www.sqa.org.uk/e-learning/FirstLine02CD/page_06.htm). 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 effective extinguishing flammable liquid fires containing alcohols and other water miscible flammable organic substances.

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 surfactants used in AFFFs were often PFOS-based, which resulted in AFFFs that contained 0.5wt% to 6wt% PFOS or PFOS precursors. At the same time, AFFFs 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 were generally no longer available in industrialized countries. 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. Some countries and/or regions have implemented regulations addressing PFOS containing AFFF. For example, in the European Union, PFOS containing AFFF were ultimately phased out by 2011 and stockpiles had to be properly disposed.

3.7.2 Types of foams

AFFF are divided into two major categories: synthetic foams and protein foams. Synthetic foams 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 hydrocarbon surfactants and synthetic fluorinated surfactants
- 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
- other foam concentrates derived from synthetic and hydrocarbon surfactants such as fluorine-free foams

Protein-based foams 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).

3.7.3 BAT and BEP for PFOS and PFOS-related substances

Surrogate, non-fluorinated foams should be used for training purposes as well as for testing and commissioning of fixed systems and vehicle proportioning systems. Non-PFOS fluorinated surfactants based on short-chain fluorotelomers should be used for Class B firefighting foam concentrates.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to follow best practices as outlined below to minimize releases to the environment and to collect all waste with following incineration at high enough temperatures to thermally mineralize the firefighting foam ingredients.

Alternative Substances:

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

Producer	Web Reference
Chemguard	http://www.chemguard.com/specialty-chemicals/catalog/fire-fighting-foam-surfactants/
Chemours	https://www.chemours.com/Capstone/en_US/tech_info/Index.html
Dynax	http://dynaxcorp.com/products/fire-fighting-foam-applications/

Each supplier offers a portfolio of products. Details on AFFF surfactant structures can be found in the report by (Backe *et al.* 2013).

- Non-fluorinated alternatives exist and are in use but often cannot achieve the stringent performance requirements. The chemical nature of these alternative surfactants is not known except that they are either hydrocarbon-based or silicone-based.

Alternative Technology: No information

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 capable of handling halogenated waste or the equivalent

3.8 Insect Baits for Control of Leaf-Cutting Ants from genus *Atta spp.* and *Acromyrmex spp.*

3.8.1 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. These 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).

The leaf-cutting ants *Atta* and *Acromyrmex* and their species differ in their nesting habits and food habits. For example, *Atta* nests are loose soil mounds with chambers extending into the ground, whereas *Acromyrmex* nests are smaller than *Atta* nests, more inconspicuous and are sometimes covered with plant debris or straw. *Acromyrmex* build shallow nests in colder regions, deeper nests in warmer regions (up to 7m deep). For both genera, big nests can cover an area of up to 200m^2 and host up to about 6 million ants (Zanetti *et al.* 2014). *Atta* specialize primarily on tree leaves whereas *Acromyrmex* focus mainly on collecting grass, flowers and herbal leaves. However, some *Atta* species are considered grass-cutting ants (for a detailed species overview and their occurrence in Brazil, see Britto *et al.* 2016).

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). From 2009 to 2014 Brazil reported an estimated use of 50 t/year of PFOSF to produce sulfluramid for the production of insect bait, which corresponds to 30 t of sulfluramid per year (see UNEP/POPS/COP.7/INF/11). Seven companies manufacture ten sulfluramid-based products registered in Brazil (Ministry of Environment of Brazil 2015).

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)) 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^2 of loose soil anthill (to control *Atta*) and 6 g-50 g insecticide/m^2 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. 6h to 18h after the bait was transported into the nest. Ingested sulfluramid is being metabolized to form perfluorooctancesulfonamide (FOSA) that interrupts ATP production in the mitochondria causing death of the animal.

3.8.2 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 (acceptable purpose exemption) and grass-cutting ant species is not made clearly. Although quite a number of publications and submissions by Parties are available, their focus is mainly on ways to control the genus *Atta* whereas little information is available on the need of and ways to controlling the genus *Acromyrmex*. In those publications it is emphasized that using toxic baits containing sulfluramid is 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 that those needed to apply toxic bait. The combination of technologies overall is more labor intensive and costly.

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 save handling instructions for the particular 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

For small areas, such as small orchards and residential uses:

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

To control nests no larger than 5m^2:

- Dried-powder dusting with deltamethrin (see “Caution” on p. 43)

To control young *Atta* colonies:

- Dried-powder dusting with deltamethrin

For all other:

- Baits containing sulfluramid

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

- Dried-powder dusting with deltamethrin

For all other:

- 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.*

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. Consider an integrated pest management system to minimize the use of pesticides. When using sulfluramid containing baits, collect all left over baits after treatment and send for incineration at high enough temperature to mineralize the sulfluramid.

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., dicotyledonuous leaf-cutting ants). It might not be as efficient and seems to display broader toxicity to other animals. Insufficient data to determine whether or not this alternative substance is BAT.

Hydramethylnon (CAS No. 67485-29-4): A special formulation of hydramethylnon, sold under the trade name Amdro® Ant Block, is currently the only widely available bait product labeled for control of leaf cutting ants in the USA. Ant activity in the treated colony will decline over a 4 to 6 week period. (For further information, see for example, http://www.cdpr.ca.gov/docs/risk/rcd/hydrameth.pdf and http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/hydmthn.pdf). However, about half the time activity will return in 4 to 6 months, requiring a second treatment.

Advantage: This product can be used on most sites

Disadvantage: This product may not be used in agricultural sites (e.g., livestock pastures, gardens, cropland)

Alternative Technology:

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.

For issues related to resistance to pyrethroids, see "caution" on page 43.

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

Thermal fogging is the generation of ultra-fine droplets in a range of 1µm - 50µm 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 burn 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) 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.

a. Caution:

Given the fact that pyrethroids are widely used in malaria vector control and are reported to have the highest rate of resistance among all chemical classes used, the use of deltamethrin (or other pyrethroids) may not be considered BAT). Especially in view that alternatives to pyrethroids have to be found for public health sector; therefore, opening up new applications for pyrethroids does not seem to be a viable alternative.

The 2016 World Malaria report states "Of 73 malaria endemic countries that provided monitoring data for 2010 onwards, 60 reported resistance to at least one insecticide, and 50 reported resistance to two or more insecticide classes. Resistance to pyrethroids – the only class currently used in ITNs –is the most commonly reported. A WHO-coordinated five-country evaluation showed that ITNs still remained effective but there is still a need for new vector control tools" (WHO 2016).

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 is not applicable to 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 in (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.

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 issues related to resistance to pyrethroids, see page 43.

For Thermo-nebulization with fenitrothion, chlorpyrifos, 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 recommendation 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
- 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.

4 BAT and BEP measures for PFOS and PFOS-related substances for specific exemption applications

4.1 Photo Masks in the Semiconductor and Liquid Crystal Display (LCD) Industries

4.1.1 Background

Photomasks are an essential part of the photolithography process of semiconductor and LCD production. Photomasks are used to transfer the desired geometric pattern via light to the photoresist carrying silicon wafer. The pattern on the photomask that will be transferred to the photoresist on the silicon wafer is being created by an etching process that requires the use of a surfactant to reduce patterning defects. For further details on the photomask production process, see (Japan, 2007 Annex F submission). In this wet etching process, PFOS was used as a surfactant in the etching solution to enhance surface wettability by reducing the surface tension of the solution. The WSC reported in 2011 that the use of PFOS in etchants has been eliminated (WSC 2011).

4.1.2 BAT and BEP for PFOS and PFOS-related substances

Non PFOS-based surfactants are in use for etching application (WSC 2011).

In addition to the general BEP measures outlined in Chapter 2 that should be followed, spent etching solution needs to be collected for recovery and re-use or be sent to a waste incineration facility that operates at high enough temperatures to thermally mineralize the fluorinated surfactant.

Alternative Substances: No information

Alternative Technology: A dry process exists and is practiced for some specific cases for photo masks for the semiconductor industry (Japan, 2007 Annex F submission).

4.2 Metal Plating (hard metal plating)

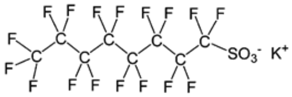
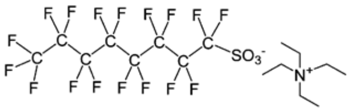
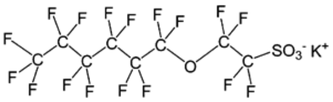
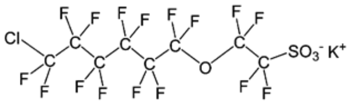
4.2.1 Background

For a comprehensive background chapter on metal plating, please see Chapter 3.5.1.

In China, the following two products are being offered as potential alternatives to PFOS:

- F-53 2-[1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl]oxy]-1,1,2,2-tetrafluoroethanesulfonic acid potassium salt
- F-53B (Potassium 2-[6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy]-1,1,2,2-tetraflouroethanesulfonic acid potassium salt

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 mono-chloro compound, which was marketed as F-53B (Wang *et al.* 2013). In a recent publication (Shi *et al.* 2016) the mean biological half-live 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.

Product Name	Chemical	CAS Number	Chemical Formula	Structure
FC-80	Potassium perfluorooctane sulfonate	2795-39-3	$C_8F_{17}O_3SK$	
FC-248	Tetraethylammonium perfluorooctane sulfonate	56773-42-3	$C_{16}H_{20}F_{17}O_3NS$	
F-53	2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)oxy]-1,1,2,2-tetrafluoroethanesulfonic acid potassium salt	Not available	$C_8F_{17}O_4SK$	
F-53B	2-[(6-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)oxy]-1,1,2,2-tetrafluoroethanesulfonic acid potassium salt	73606-19-6	$C_8ClF_{16}O_4SK$	

4.2.2 BAT and BEP for PFOS and PFOS-related substances

Non PFOS-based mist suppressants should be used for this application and all measures of a “closed loop” system (see chapter 3.5) should be implemented in the plating process.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all waste with following incineration at high enough temperatures to thermally mineralize the mist suppressant (IPPC 2006).

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.

Alternative Substances (Blepp 2015)**:**

- 6:2 Fluorotelomer sulfonate (6:2 FTS; CAS No. 27619-97-2)-based products and producers (Blepp 2015):
    - ANKOR® Dyne 30 MS (Enthone)
    - ANKOR® Hydraulics (Enthone)
    - ANKOR® PF1 (Enthone)
    - Fumetrol® 21 (Atotech)
    - Fumetrol® 21 LF 2 (Atotech)
    - HelioChrome® Wetting Agent FF (Kaspar Walter Maschinenfabrik GmbH & Co. KG)
    - PROQUEL OF (Kiesow Dr. Brinkmann)
    - Wetting Agent CR (Atotech)
- Other fluorinated alternatives, no information on chemical nature is known:
    - Chromnetzmittel LF (CL Technology GmbH)
    - Netzmittel LF (Atotech)
    - Non Mist-L (Uyemura)
    - RIAG Cr Wetting Agent (RIAG Oberflächentechnik AG)
- Alkylsulfonate (trade name: TIB Suract CR-H (TIB Chemicals AG))

- Other non-fluorinated alternatives, no information on chemical nature - Trade names (and producers):
    - CL-Chromeprotector BA (CL Technology GmbH)
    - Antifog V4 (Chemisol GmbH & Co. KG)

The available fluorinated alternatives may need to be dosed at higher concentrations than the PFOS-salts to meet specific surface tension requirements and might be less stable and therefore may have to be replenished more frequently. For example, the calculated process lifetime for 6:2 fluorotelomer sulfonate was 0.21 years for one facility (Blepp *et al.* 2015).

Non-fluorinated surfactants are rapidly oxidized in the plating bath and must be constantly dosed (Wienand *et al.* 2013). Those products are not considered equally effective. In addition, such products can reduce Cr-VI to Cr-III in the chromium electrolyte which can lead to serious faults in the chromium coating.

Alternative Technology:

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)

Novel plating processes:

- The company Topocrom offers an alternative process (www.topocrom.com).
- HVOF (High Velocity Oxygen Fuel) Process

However, no further details on the processes themselves, chemicals used along with best practices in these processes are known. Details on market acceptance of these technologies as an alternative to hard chrome plating are not known either.

Best Environmental Practices:

BEP is to adhere to the general BEP measures outlined in Chapter 2 and in Chapter 3.5 and to collect all waste with following incineration at high enough temperatures to thermally mineralize the mist suppressant.

4.3 Metal Plating (decorative plating)

4.3.1 Background

For a comprehensive background chapter on metal plating, please see Chapter 3.5.1.

4.3.2 BAT and BEP for PFOS and PFOS-related substances

Non PFOS-based mist suppressants should be used and all measures of a “closed loop” system (see chapter 3.5) should be implemented in the plating process. For some applications, the alternative technology “Cr(III) Plating” represents the BAT. This alternative process does not require the use of mist suppressants.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed tocollect all waste with following incineration at high enough temperatures to thermally mineralize the mist suppressant.

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

Alternative Substances (Blepp 2015):

- 6:2 Fluorotelomer sulfonate (6:2 FTS; CAS No. 27619-97-2)-based products:
    - ANKOR® Dyne 30 MS (Enthone)
    - Cancel ST-45 (Plating Resources, Inc.)
    - FS-600 High Foam (Plating Resources, Inc.)
    - FS-750 Low Foam (Plating Resources, Inc.)
    - Fumetrol 21 (Atotech)
    - SLOTOCHROM CR 1271 (SchlötterGalvanotechnik)
    - UDIQUE® Wetting Agent PF2 (Enthone)
    - Wetting Agent CR (Atotech)
- Other fluorinated substances, but no information on chemical nature is known
    - Chromnetzmittel LF (CL Technology GmbH)
- Alkylsulfonate (trade name: TIB Suract CR-H (TIB Chemicals AG))
- Oleo amine ethoxylates (ANKOR® Wetting Agent FF (Enthone))
- Other, non-fluorinated substances, no information on chemical nature is known
    - Antifog CR (Chemisol GmbH & Co. KG)
    - CL-Chromeprotector BA (CL Technology GmbH)

Non-fluorinated surfactants are rapidly oxidized in the plating bath and must be constantly dosed (Wienand *et al.* 2013). Those products are not considered equally effective. In addition, such products can reduce Cr-VI to Cr-III in the chromium electrolyte which can lead to serious faults in the chromium coating. Furthermore, it was reported that one non-fluorinated alternative (Wienand *et al.* 2013, Wienand 2014/15) caused corrosion of the lead anodes that then needed to be replaced in shorter and shorter intervals. Lead was detected in the sludge.

Alternative Technology:

Parts of the decorative chrome plating industry have adopted trivalent chromium or Cr(III) plating. Cr(III) is intrinsically less toxic than Cr(VI). This alternative technology represents the BAT for the applications in which it is feasible. However, the German industry group FKG "Fachverband Galvanisierte Kunststoffe" has published findings of a comparison field trial with 3000 samples (Fachverband Galvanisierte Kunststoffe). The Cr-III derived samples were less colour-stable, more soil sensitive and displayed higher corrosion rates. FKG concluded that the BAT for decorative chrome plating for the automotive industry is based on Cr-VI plating.

Best Environmental Practices:

BEP is to adhere to the general BEP measures outlined in Chapter 2 and in Chapter 3.5 and to collect all waste with following incineration at high enough temperatures to thermally mineralize the mist suppressant.

4.4 Electric and Electronic Parts for Some Colour Printers and Colour Copy Machines

4.4.1 Background

Electric and electronic equipment often requires hundreds of parts and thousands of processes to make them. For example, parts from the semiconductor industry might find uses in colour printers and colour copy machines (for more details, see Chapters 3.2, 3.3 and 4.1). It has been reported that intermediate transfer belts of colour copiers and printers contain up to 100 ppm of PFOS, while an additive used in producing PFA (perfluoroalkoxy) rollers contains 8×10^{-4} ppm PFOS. In 2013 industry groups reported that alternatives are currently not available for those applications (UNEP/POPS/POPRC.9/INF/11/Rev.1).

4.4.2 BAT and BEP for PFOS and PFOS-related substances

An information gap exists as to BAT and BEP for this application. For a general best practices overview see Chapter 2.

Alternative Substances:	No information
Alternative Technology:	No information
Best Environmental Practices:	No information

4.5 Insecticides for Control of Red Imported Fire Ants and Termites

4.5.1 Background

Red Imported Fire Ants

The red imported fire ant (*Solenopsisinvicta*), or simply RIFA, is one of over 280 species in the widespread genus *Solenopsis*. Although the red imported fire ant is native to South America, it has become a pest in the southern United States, Australia, the Caribbean, Taiwan, Hong Kong, and several southern Chinese provinces. RIFAs are known to give a painful, persistently irritating sting that often leaves a pustule on the skin. A common method to control RIFA is with baits consisting of pesticides on processed corn grits coated with soybean oil. Worker ants take the bait back to the colony, where it is shared with the queen, which then either dies or becomes infertile. Baits are slow-acting and require weeks to months to achieve 80% to 90% control. Bait products are used to treat large areas effectively. Other control methods are used as outlined below. *N*-Ethyl perfluorooctane sulfonamide (EtFOSA; CAS No. 4151-50-2), also called sulfluramid, has been used as a pesticide for this application.

Termites

The negative impact of termites is often cited in economic terms as expenditures for damage, repair, and preventative treatment costs. In the United States alone estimates range between $2-3 billion dollars annually. There are over 2,600 described species of termites, but fewer than 185 are considered pests. Termites become a problem when they damage structural timber and other materials in structures. Damage may extend to household furniture, paper products, many synthetic materials and food items. Each year hundreds of thousands of structures (bridges, dams, decks, homes, retaining walls, roads, utility poles, and underground cables and pipes) require treatment for the management of termites (UNEP 2000).Internationally important termite pests include species from subterranean, arboreal, dry and wet wood feeding ecologies.

4.5.2 BAT and BEP for PFOS and PFOS-related substances

Red Imported Fire Ants

Alternative substances to sulfluramid should be used to control RIFA effectively. It is important to note that 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.

A professional pest control operator should be hired to identify the pest and adhere to the 2-Step Method in addition to the general best practices applicable to pesticides as referred to in Chapter 2. Many alternative pesticides along with various treatment methods are being reported.

Alternative Substances: Products are formulated as dusts, granules, liquid drenches or baits (active ingredients are dissolved in a vehicle ants eat or drink). They are applied either to individual mounds or across the surface of the ground (broadcast). The various active ingredients affect ants in different ways, how quickly ants will be controlled and how long the effect will last (Alternative Substances RIFA). Examples of reported alternatives to sulfluramid are summarized in Table 9.

The "delayed action" pesticides are effective after a time period ranging from a few days to up to 6 months. Baits can be 80-90% effective in controlling RIFA because foraging ants carry the poison back to the colony. Granules containing contact insecticides might be less effective because they only control foraging ants but not the colony. Spraying ants or individual mounts might be less effective since this method does not control the colony but might cause the colony to disperse.

Some of the alternative chemistries have been part of the assessment of alternatives to endosulfan (UNEP/POPS/POPRC.8/INF/12). Conclusions from this document should be considered in the selection of suitable alternatives.

A list of product names available in the US for commercial and residential use along with basic use instructions can be found in Texas A&M AgriLife Extension:

http://fireant.tamu.edu/controlmethods/products/ and http://articles.extension.org/pages/68606/the-latest-broadcast-on-fire-ant-control-products.

Alternative Technology:

Several options have been evaluated for effectiveness (2-Step Method):

- Natural enemies, such as parasitic decapitating flies from South America have been successful in areas where they have been released but they are not available to the general public.
- Biological control agents available on the retail market, such as parasitic nematodes
- **2-Step Method**
  This method includes broadcasting a bait insecticide over a broad, infested area, and treating individual, problem mounds with an approved mound drench, granule, bait, or dust insecticide.
  Step One: Baits
    - Use fresh bait, preferably from an unopened container
    - Avoid applying in bright sunlight
    - Apply when the ground and grass are dry and no rain is expected for the next 24 to 48 hours
    - Apply when worker ants are actively looking for food, usually in late afternoon or in the evening. To test, put a small pile of bait next to a mound and see if the ants have found it within 30 minutes
    - Best applied at temperatures between 20 ˚C and 32 ˚C

  Step Two: Individual Mound Treatments

Treating ant mounds individually is more labor-intensive and may use more insecticide than other methods, it is a suitable approach for small areas with few fire ant mounds (fewer than 20 per acre) or where preservation of native ants is desired. Treatments are most effective when ants are nesting close to the mound surface (as they do when the temperature is mild). Colonies should not be disturbed during treatment.

Individual mounds can be treated in multiple ways:

- Dust Products, no water is needed and they act fast. However, they leave a surface residue
- Liquid drenches generally eliminate mounds within a few hours and leave little surface residue after application
- Granular products are relatively fast acting and usually require putting granules on and around the mound and then sprinkling 1 to 2 gallons of water on without disturbing the mound.

Table 9: Examples of reported alternatives to sulfluramid.

Active Ingredient	CAS No.	Pesticide Action	Application Method	Approved for Use (examples)
Abamectin	71751-41-2	Delayed Action	Baits for certain agricultural use and most urban areas	USA
Acephate	30560-19-1	Contact Insecticide	Mound treatment or broadcast treatment as aerosol, liquid, granules or dust	USA
Alpha-Cypermethrin	67375-30-8	No Information	No information	Australia, New Zealand, USA
Bifenthrin (Pyrethroid)[1]	82657-04-3	Contact Insecticide	Broadcast granules	Australia, USA
Carbaryl	63-25-2	Contact Insecticide	For pasture mound drench or as broadcast granules	USA
Chlorpyrifos	2921-88-2	Contact Insecticide	Being phased-out in USA; no longer available for consumer use	USA
Cyfluthrin (Pyrethroid)[1]	68359-37-5	Contact Insecticide	Broadcast granules	USA
Cypermethrin (Pyrethroid)[1]	52315-07-8	Contact Insecticide	Broadcast granules	USA
Deltamethrin (Pyrethroid)[1]	52918-63-5	Contact Insecticide	Broadcast granules	USA
D-Limonene (citrus oil extract)	5989-27-5	Contact Insecticide	Mound drenching - all areas or as broadcast granules	USA
Fipronil	120068-37-3	Delayed Action	Baits for most urban areas or as broadcast granules	Australia, China, USA
Hydramethylnon	67485-29-4	Delayed Action	Baits for urban and agricultural land	Australia, USA
Indoxacarb	144-171-61-9	Delayed Action	Baits for urban areas and non-food producing land	Australia, USA
Imidacloprid	138261-41-3, 105827-78-9	Contact Insecticide	Used in combination with Bifenthrin or Cyfluthrin	China, USA
Metaflumizone	139968-49-3	Delayed Action	Baits for certain orchards, most urban areas and animal holding areas	USA
Methoprene	40596-69-8	Delayed Action	Baits for broad use	USA
Permethrin (Pyrethroid)[1]	52645-53-1	Contact Insecticide	Broadcast granules	USA
Pyrethrin (natural product)	8003-34-7	Contact Insecticide	Broadcast granules	USA
Pyrethrins + Diatomaceous Earth	SeeAbove	Contact Insecticide	Applied as dry or wetted powder	USA
Pyrethroids	See Above	Contact Insecticide	Baits to kill foragers, but may not kill colony	USA
Pyriproxifen	95737-68-1	Delayed Action	Baits for agricultural use	Australia, New Zealand, USA
Spinosad (produced by soil microbe)	168316-95-8; 131929-60-7	Delayed Action	Baits for certain orchards, most urban areas or as mound drench	USA

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[1] For issues related to resistance to pyrethroids, see "Caution" on page 43

- Pouring 2 to 3 gallons (ca. 8 to 12 liter) of very hot or boiling water on the mound will kill ants about 60% of the time.

The "delayed action" pesticides are effective after a time period ranging from a few days to up to 6 months. Baits can be 80-90% effective in controlling RIFA because foraging ants carry the poison back to the colony. Granules containing contact insecticides might be less effective because they only control foraging ants but not the colony. Spraying ants or individual mounts might be less effective since this method does not control the colony but might cause the colony to disperse.

Some of the alternative chemistries have been part of the assessment of alternatives to endosulfan (UNEP/POPS/POPRC.8/INF/12). Conclusions from this document should be considered in the selection of suitable alternatives.

A list of product names available in the US for commercial and residential use along with basic use instructions can be found in Texas A&M AgriLife Extension:

http://fireant.tamu.edu/controlmethods/products/ and http://articles.extension.org/pages/68606/the-latest-broadcast-on-fire-ant-control-products.

Alternative Technology:

Several options have been evaluated for effectiveness (2-Step Method):

- Natural enemies, such as parasitic decapitating flies from South America have been successful in areas where they have been released but they are not available to the general public.
- Biological control agents available on the retail market, such as parasitic nematodes
- **2-Step Method**
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  Step One: Baits
  - Use fresh bait, preferably from an unopened container
  - Avoid applying in bright sunlight
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  - Best applied at temperatures between 20 ˚C and 32 ˚C

  Step Two: Individual Mound Treatments

Treating ant mounds individually is more labor-intensive and may use more insecticide than other methods, it is a suitable approach for small areas with few fire ant mounds (fewer than 20 per acre) or where preservation of native ants is desired. Treatments are most effective when ants are nesting close to the mound surface (as they do when the temperature is mild). Colonies should not be disturbed during treatment.

Individual mounds can be treated in multiple ways:

- Dust Products, no water is needed and they act fast. However, they leave a surface residue
- Liquid drenches generally eliminate mounds within a few hours and leave little surface residue after application
- Granular products are relatively fast acting and usually require putting granules on and around the mound and then sprinkling 1 to 2 gallons of water on without disturbing the mound.
- Pouring 2 to 3 gallons (ca. 8 to 12 liter) of very hot or boiling water on the mound will kill ants about 60% of the time.

Best Environmental Practices:

Hiring a licensed pest control operator is highly recommended because these professionals have access to the most effective management products and experience in controlling this pest. They are also trained to adhere to best practices.

Instructions on labels should be followed for appropriate use of the pesticide.

Develop a Management Plan. Chemical control lasts only as long as the effects of the insecticide used, or until new ant colonies move in from untreated areas (2-Step Method). Ant infestation will return to its original level eventually. Thus, keeping RIFA controlled requires a commitment of time and money. To reduce cost and make control easier, consider making a property map. Divide the property into treatment areas and designate the most appropriate treatment approach for each area. Make and maintain a schedule for first treatment and any necessary re-treatments.

Because control lasts longer when large areas are treated, consider participating in a community- or neighborhood-wide treatment program. These have been shown to improve control and reduce cost. If everyone participates by making coordinated treatments, ant colonies will not be able to migrate from property to property.

Termites

Termite pests and their management vary by continent (UNEP 2000). Before proceeding with any management strategy it is necessary to determine the termite pest (subterranean, arboreal or dry wood).

For new construction and during repairs it is suitable to properly prepare the construction site, to have a proper building design and to utilize termite resistant building material. In case pesticides use is necessary, alternative substances to sulfluramid should be used to effectively control termites. It is important to note that 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.

A professional pest control operator should be hired who will identify the pest and adhere to the 2-Step Method in addition to the general best practices applicable to pesticides as referred to in Chapter 2.

Proper design of a building and building practices, installation of termite management systems at the time of construction and ongoing regular inspections for termite activity can greatly reduce the risk of termite damage to structures.

Alternative Substances (UNEP 2000):

- Termiticides for soil, topical and subsurface applications
- Baiting systems Space Fumigation
    - Sulfuryl fluoride (CAS No. 2699-79-8)
    - CO_2 (CAS No. 124-38-9)
- Biological Control
    - Fungus spores, mycelium
    - Nematodes, infective stage

Alternative Technology (UNEP 2000):

Subterranean, arboreal and drywood termites can be managed by

- Proper building design and site preparation

- Termite resistant construction and use of treated timber products
- Physical barriers
- Thermal control

Table 10: Examples of reported alternatives to sulfluramid.

Active Ingredient	CAS No.	Pesticide Action	Application Method
Bifenthrin (Pyrethroid)[1]	82657-04-3	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members
Chlorpyrifos	2921-88-2	Contact Insecticide	Chemical applied to soil or foam. Lethal effects may be passed among colony members
Cyfluthrin (Pyrethroid)[1]	68359-37-5	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members
Cypermethrin (Pyrethroid)[1]	52315-07-8	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members
Deltamethrin (Pyrethroid)[1]	52918-63-5	Contact Insecticide	Applied as food matrix
Fenitrothion	122-14-5	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members
Fenvalerate	51630-58-1	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members
Fipronil	120068-37-3	Delayed Action	Chemical applied to soil or foam. Lethal effects may be passed among colony members
Hydramethylnon	67485-29-4	Delayed Action	Applied as food matrix
Imidacloprid	138261-41-3, 105827-78-9	Contact Insecticide	Chemical applied to soil or foam. Lethal effects may be passed among colony members
Permethrin (Pyrethroid)[1]	52645-53-1	Contact Insecticide	Chemical applied to soil or foam. Lethal effects are not passed among colony members

[1] For issues related to resistance to pyrethroids, see “Caution” on page 43.

Best Environmental Practices:

Hiring a licensed pest control operator is highly recommended because these professionals have access to the most effective management products and experience in controlling this pest. They are also trained to adhere to best practices.

Instructions on labels should be followed for appropriate use of the pesticide.

4.6 Chemically driven oil production

4.6.1 Background

PFOS and its related substances may be used as surfactants in the oil and gas industries to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, such as jet fuel and hydrocarbon solvents. As late as 2009 and 2012, PFOS and PFOS-related substances were reportedly used as surfactants in old oil fields in some regions to recover oil trapped in small pores between rock particles (UNEP/POPS/COP.7/INF/26). Obtaining detailed information on this use proved to be challenging.

4.6.2 BAT and BEP for PFOS and PFOS-related substances

Non-PFOS-related compounds should be used for this application.

Alternative Substances:

Alternatives to PFOS identified in two previous reports are:

- PFBS-based substances, such as 3M Gas Well Stimulant WS 1200 (see SDS at: http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSuUn_zu8l00xmxtG58mvlv70k17zHvu9lxtD7SSSSSS--.).
- Short-chain fluorotelomer-based fluorinated surfactants or polymers

Alternative Technology:

Oil and gas production were reportedly carried out without the use of PFOS and its related substances in other countries, including developing countries, thus indicating the existence of alternative processes that did not require PFOS (UNEP/POPS/COP.7/INF/26).

Best Environmental Practices: No information

4.7 Expired Exemption - Carpets

4.7.1 Background

Fluorinated polymers may be applied during manufacturing of residential and commercial carpets made from both synthetic and natural fibres to provide stain and soil protection. There are three scenarios for the chemical application: a) application at a carpet or rug mill during the manufacturing process via foam or spray application or via dye-bath application (DEFRA 2004); b) application to carpet after the manufacturing process at a separate finishing facility; c) re-application by professionals or end consumers in the post manufacturing stage (e.g., in offices or residences) (USEPA 2012).

4.7.2 BAT and BEP for PFOS and PFOS-related substances

Substancesbased on acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) can no longer be used in this application. Alternative fluorinated substances such as side-chain fluorinated polymers based on short-chain fluorinated chemistry with known and less hazardous characteristics that do not contain, transform into or emit PFOS should be used when durable soil and stain resistance is desired.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed tocollect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymer.

Fluorinated finishes are the only technology known to deliver durable stain and soil resistance. Historically, fluorinated polymers based on acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) have been used of up to 15% of weight of fiber. Such polymer dispersions used to treat carpets contained PFOS as an impurity at levels of up to 2 wt%. In addition, long-chain fluorotelomer-based polymers have also been used. Major manufacturers, in conjunction with global regulators, have agreed to discontinue the manufacture of “long-chain” fluorinated products by the end of 2015 and move to “short-chain” fluorinated products (“PFOA Stewardship Program” (https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/and-polyfluoroalkyl-substances-pfass-under-tsca#tab-3)). Such “short-chain” polymeric alternatives have entered the commercial space over the last years and have undergone much higher regulatory rigor than their “long-chain” predecessors, for example in the USA (for example, see http://epa.gov/oppt/pfoa/pubs/altnewchems.html) . In the USA, the world largest producer of carpets, the transition to short-chain polymeric alternative products occurred around 2007 (OECD 2015).

Alternative Substances:

1. PFBS-based products
   Scotchgard™ from 3M http://www.3m.com/3M/en_US/company-us/
2. Short-chain fluorotelomer-based polymeric products, such as:

Product Name/Producer	Web Reference
Hexafor from Maflon	http://www.maflon.com/images/maflon.pdf
Thetaguard and Thetapel from ICT	http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/
Unidyne™ from Daikin	https://www.daikin.com/chm/pro/kasei/unidyne_multi/feature/
and others	

Alternative substances that provide water repellency: No supplier names, trade names or further details are available:

1. Wax-based repellents consisting of paraffin-metal salt formulations
2. Hydrophobic modified polyurethanes (hydrophobic modified hyper-branched polyurethanes called dendrimers)
3. Polysiloxane-based products
4. Resin-based repellents consisting of fatty modified melamine resins

Alternative Technology for stain protected residential carpet:

Inherently stain-resistant (but not soil resistant) polyester carpet fibers are offered as alternative technology to soil- and stain-protected for residential use.

Best Environmental Practices:

In addition to the general best practices of handling chemicals (See Chapter 2), these additional steps should be considered in commercial operations that treat carpet with soil and stain resists [For additional details on BAT and BEP for such applications see IPPC (2003), Carpet Institute of Australia Limited (2014) and FluoroCouncil (2014):

- Use of soil and stain resists and auxiliaries with known and less hazardous characteristics that do not contain, transform into or emit PFOS and related substances.
- Use of soil and stain resists containing validated high purity polymer, to avoid having to handle unreacted impurities and other impurities in the waste.
- Use the product only of necessary to obtain effects desired
- Calculate recipes for desired effect to avoid surplus of applied chemicals and auxiliaries.
- Use cross-linking agents and extenders that help with the film formation with the ability of improving the self-organization of the fluorinated polymer.
- Make sure the carpet for the application is free of substances that could disturb the self-organization of the fluorocarbon, such as detergents or rewetting agents.
- Check recipes regularly in order to identify and avoid unnecessary chemical volumes.
- Check water quality (e.g., pH, water hardness, suspended solids) to avoid loss in DWR performance.
- Minimize residual liquors by calculating exactly how much liquor has to be prepared.
- Optimize process sequences in production to minimize waste between runs.
- Re-using process liquors has to be done very carefully to avoid causing quality issues that could lead to off-quality goods production. The material supplier can be consulted to test whether re-use is possible.
- Dispose of chemicals appropriately

  - The wastewater drain is never an appropriate disposal system for chemicals such as residual bath liquor
  - Collect liquors containing fluorinated substances for separate treatment, including the rinsing bath from cleaning the application system. Consult SDS Section 13 for guidance.
  - Minimize waste water by minimizing changeover and collect all wash/rinse water before and after each run
- Maintain all equipment in excellent working condition and conduct periodic operations audits.
- Optimize drying and curing conditions in the stenter frame.
- Additional BAT opportunities to minimize waste and releases to the environment:
- Automated dosing systems with integrated self-learning systems minimize waste by:
  - Computing exact pick-up and liquor consumption
  - Mixing only what will be used in the scheduled run
  - Low add-on techniques minimize chemical consumption
- Where possible, use direct piping into the bath for each of the chemicals to be used so that the chemicals are not pre-mixed before being introduced into the applicator or machine, and there is no need to clean containers, pumps and pipes before the next step.
- Check the input and output flows of the individual processes. Determine the input and output mass flows for both the site as a whole and each individual production process. Implement a product input check that takes account of raw materials, chemicals, dyes and auxiliary materials, etc.
- Employ improved measurement and control equipment, for example for temperature, chemical addition, retention time, moisture (in dryers).
- Where possible, consider a combination of condensation and scrubbing followed by electrostatic precipitation (ESP) or the use of thermal combustion with energy recovery on the curing/drying frame/stenters used in processing the fabric.
- Where possible, consider treatment in wet scrubbers, absorbers, separation via low temperature condensation or combustion to reduce the release of volatile organic compounds from the framing/stenter process.
- Where possible, consider exhaust air treatment for emissions-relevant processes.
- Collect all waste with following incineration at high enough temperatures to thermally mineralize the fluorinated substances.

4.8 Expired exemption – Leather and Apparel

4.8.1 Background

Fluorinated polymers may be applied during the leather making process in the tannery, in the finishing step as a surface treatment or at home by the end consumer to provide water, stain and soil protection to leather substrates such as shoes, apparel and upholstery. In the past, aqueous dispersions of anionic PFOS-related polymers have been utilized in tanneries and in consumer products such as shoe care products. Solvent-borne PFOS-related polymers have been used in the finishing process of leather as well as in consumer shoe care aerosol sprays use under the Scotchgard® brand name. This type of chemistry has been replaced by either PFBS-based polymers or by short-chain fluorotelomer-based polymers.

4.8.2 BAT and BEP for PFOS and PFOS-related substances

Substancesbased on acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) can no longer be used in this application. Alternative fluorinated substances such as side-chain fluorinated polymers based on short-chain fluorinated chemistry with known and less hazardous characteristics that do not contain, transform into or emit PFOS should be used when durable soil and stain resistance is desired.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymers.

Alternative Substances:

Short-chain-based fluorinated polymeric products have been approved for manufacture, sale and use, and have been demonstrated to deliver the desired performance in leather applications. Examples of such products are:

1. PFBS-based products

PM-4800, Scotchgard™ from 3M marketed by TFL:
http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSuUn_zu8l00x48mGoYt1ov70k17zHvu9lxtD7SSSSSS--

2. Short-chain fluorotelomer-based polymeric products.

Product Name/Producer	Web Reference
Capstone™ from Chemours	https://www.chemours.com/Capstone/en_US/
Hexafor from Maflon	http://www.maflon.com/images/maflon.pdf
Ruco-Coat® from Rudolf Group	http://www.rudolf-duraner.com.tr/en/products/co-producer-b2b/10-water-oil-and-soil-repellent-agents/12-c6-based-fluorocarbon-polymers.html
Thetaguard and Thetapel from ICT	http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/
Unidyne™ from Daikin	https://www.daikin.com/chm/pro/kasei/unidyne_multi/feature/

Waterproofing agents (Water Repellency):

These offerings do not provide oil, soil and stain protection.

- Wax-based repellents consisting of paraffin-metal salt formulations
- Hydrophobic modified polyurethanes (hydrophobic modified hyper-branched polyurethanes called dendrimers)
- Polysiloxane-based products
- Resin-based repellents consisting of fatty modified melamine resins

No further information on suppliers, trade names and exact chemical nature is available.

Alternative Technology: No information

Best Environmental Practices:

In addition to the general best practices of handling chemicals (See Chapter 2) and adoption of industry specific best practices (IPPC 2013), these additional steps should be considered in commercial operations that finish leather:

Finishing Process

- The products are typically aqueous dispersions of fluorinated polymers that are being applied during the fat liquoring process in the tannery (but there might be other points of applications during the wet processing) or aqueous- or solvent-based formulations of fluorinated polymers being applied in an industrial spray coating process.
- Use of water and oil repellents and auxiliaries with known and less hazardous characteristics that do not contain, transform into or emit PFOS and related substances.
- Use of water and oil repellents containing validated high purity polymer, to avoid having to handle unreacted impurities and other impurities in the waste.
- Optimizing the process conditions to achieve high exhaust rates to minimize waste water contamination.
- Where possible, use direct piping into the bath for each of the chemicals to be used so that the chemicals are not pre-mixed before being introduced into the applicator or machine, and there is no need to clean containers, pumps and pipes before the next step.
- Check the input and output flows of the individual processes. Determine the input and output mass flows for both the site as a whole and each individual production process. Implement a product input check that takes account of raw materials, chemicals, dyes and auxiliary materials, etc.
- Employ improved measurement and control equipment, for example for temperature, chemical addition, retention time, moisture (in dryers)
- Dispose of chemicals appropriately
  - The wastewater drain is never an appropriate disposal system for chemicals such as residual fat liquor
    - Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymers

For a very detailed reference document on Best Environmental Practices for the tanning of hides and skins, see IPPC (2013).

Consumer Use

Formulations used by consumers are either leather care products in forms of creams, lotions or spray. Often spray applications are via aerosol spray (e.g., offered under the Scotchgard® brand and other companies' brands).

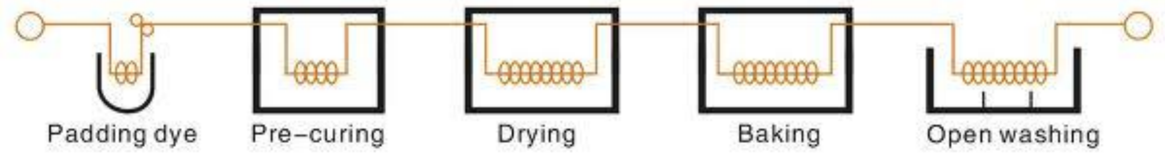
4.9 Expired exemption – Textiles and Upholstery

4.9.1 Background

Side-chain fluorinated polymers (Buck et al 2011, OECD 2013) are used by the textile industry for finishing fabric for a variety of end uses: Best known to consumers are the so called DWR finishes for all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, footwear, and the like to repel water, oil and dirt (stains) without impairing the breathability (air and water vapour permeability) of the fabric. In the commercial/industrial sector fabrics finished with this technology save lives because surgical gowns and other fabrics used in operating theatres repel blood, water/alcohol solutions and bodily fluids to prevent transfer of diseases. Chemical worker gear and fire fighter gear has been finished with this technology to protect people from aggressive chemicals, fuel and water. Furthermore, bullet proof vests protecting law enforcement and military personnel won't provide live saving protection without these finishes.

Fluorinated polymer repellents are usually applied in combination with other finishing auxiliaries by a pad-dry-cure process, as shown in Figure 5. In many cases, they are applied with "extenders", which can be other repellents themselves (e.g. melamine resins repellents or polyisocyanates). The use of these "extenders" allows a reduction in the required amount of fluorinated polymer, with a corresponding reduction in costs for this treatment.

Figure 5: General principle for the pad dry cure process (IPPC 2003)



Note: Baking is sometimes called "curing" or "fixation".

4.9.2 BAT and BEP for PFOS and PFOS-related substances

Substances based on acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) can no longer be used in this application. Alternative fluorinated substances such as side-chain fluorinated polymers based on short-chain fluorinated chemistry with known and less hazardous characteristics that do not contain, transform into or emit PFOS should be used when water and oil repellency and stain and soil protection is desired.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymers.

Fluorinated finishes are the only technology known to deliver durable and effective oil and water repellence and release properties. Historically, the acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) were one of the main PFOS derivatives used for textile surface applications at concentrations of 2-3% of weight of fiber (UNEP/POPS/COP.7/INF/26). Although PFOS-related substances were used to treat textiles, PFOS as such was present at up to 2wt% in articles. In addition, long-chain fluorotelomer-based polymers have also been used. Major manufacturers, in conjunction with global regulators, have agreed to discontinue the manufacture of "long-chain" fluorinated products by the end of 2015 and move to "short-chain" fluorinated products ("PFOA Stewardship Program"). Such "short-chain" polymeric alternatives have entered the commercial space over the last years and have undergone much higher regulatory rigor than their "long-chain" predecessors, for example in the USA (see references in chapter 4.7).

The side-chain fluorinated polymers are typically aqueous polymer dispersions that are diluted and then applied to the textile and then cured at a textile mill or industrial contract finisher. The polymers are designed to strongly adsorb and, in some cases, chemically bond to any kind of textile fiber. The polymers are designed to perform after multiple cleanings/washings and last the lifetime of the treated article.

Alternative Substances:

Short-chain-based polymeric products have been approved for manufacture, sale and use, and have been demonstrated to deliver the desired performance in textiles applications. Examples of well-known trademarked fluorinated durable water repellents are:

1. PFBS-based products:

Scotchgard™ from 3M http://www.scotchgard.com/3M/en_US/scotchgard/built-in-protection/carpet/

2. Fluorinated oxetane-based products:

Omnova https://www.omnova.com/en/products/chemicals/x-cape/2058

3. Short-chain fluorotelomer-based polymeric products:

Product/Producer	Web Reference
Nuva® from Archroma	http://textiles.archroma.com/products-services/finishing/repellency-soil-release/
Asahigaurd® from Asahi Glass	http://www.agcce.com/brochurespdfs/sales/AsahiGuard_6_pager.pdf
Capstone™ from Chemours	https://www.chemours.com/Capstone/en_US/
Unidyne® from Daikin	https://www.daikin.com/chm/pro/kasei/unidyne_multi/feature/
Thetaguard and Thetapel from ICT	http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/
Hexafor from Maflon	http://www.maflon.com/images/maflon.pdf
Products from Rudolf Chemie	http://www.rudolf-duraner.com.tr/en/products/co-producer-b2b/10-water-oil-and-soil-repellent-agents/12-c6-based-fluorocarbon-polymers.html
And others	

Non-fluorinated alternatives can provide durable water repellence (DWR; aka hydrophobic properties) but not oil repellence or oil and soil release. If oil, stain, blood or soil repellence is required, fluorinated polymers are the technology to deliver durable and effective oil repellence and/or oil and soil release. For most of the applications, such as outdoor clothing, tents, awnings etc., the durable water-repellent effect (DWR) of the fabric might be the main property requested by the users. For these applications several alternatives exist:

1. Wax-based repellents consisting of paraffin-metal salt formulations
2. Hydrophobic modified polyurethanes (hydrophobic modified hyperbranched polyurethanes called dendrimers; Bionic Finish Eco® from Rudolf Chemie[47])
3. Silicone repellents
4. Resin-based repellents consisting of fatty modified melamine resins

Over the last few years many new non-fluorinated alternative products entered the market. These are offered by companies such as Archroma, Chemours, C.H.T. Breitlich, HeiQ, Huntsman, Nano-Tex, OrganoClick, Schoeller, Tanatex and others. Often, the chemical nature of these products and associated hazards are not disclosed. In addition, these alternatives have not been assessed by POPRC as part of the alternatives assessment.

Alternative technology: No information

Best Environmental Practices (For additional details on BAT and BEP for such applications see IPPC (2003), and FluoroCouncil (2014))**:**

Over the last several years, the entire value chain has been active to develop best practices guidance. Examples include voluntary initiatives and tools such as the Higg Index developed by the Sustainable Apparel Coalition (http://apparelcoalition.org/the-higg-index/) and the Chemical Management System Guidance Manual developed by the ZDHC (ZDHC 2015), for profit initiatives, such as the bluesign®system and SteP by Oeko-Tex®, political initiatives such as the Bündnis für nachhaltige Textilien (Bündnis für nachhaltige Textilien) as well as learning tools (for example, http://www.cpi2.org/home/) for continuous improvement in multiple languages.

BAT and BEP for soil- and water-repellent textile and upholstery applications in impregnations processes are:

- Use of water and oil repellents and auxiliaries with known and less hazardous characteristics that do not contain, transform into or emit PFOS and related substances.
- Use of water and oil repellents containing validated high purity polymer, to avoid having to handle unreacted impurities and other impurities in the waste.
- Use the product only of necessary to obtain effects desired
  - Calculate recipes for desired effect to avoid surplus of applied chemicals and auxiliaries.
  - Use cross-linking agents that help with the film formation and increase washing durability.
  - Use extenders with the ability of improving the self-organization of the fluorinated polymer.
  - Make sure the fabric for the application is free of substances that could disturb the self-organization of the fluorocarbon, such as detergents or rewetting agents.
  - Check recipes regularly in order to identify and avoid unnecessary chemical volumes.
  - Check water quality (e.g., pH, water hardness, suspended solids) to avoid loss in DWR performance.
  - Minimize residual liquors by calculating exactly how much liquor has to be prepared.
  - Optimize process sequences in production to minimize waste between runs.
  - Re-using process liquors has to be done very carefully to avoid causing quality issues that could lead to off-quality goods production. The material supplier can be consulted to test whether re-use is possible.
  - Dispose of chemicals appropriately
    - The wastewater drain is never an appropriate disposal system for chemicals such as residual bath liquor
    - Minimize waste water by minimizing change over and collect all wash/rinse water before and after each run
    - Collect liquors containing fluorinated substances for separate treatment, including the rinsing bath from cleaning the application system
    - Collect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated polymers
  - Maintain all equipment in excellent working condition and conduct periodic operations audits
  - Optimize drying and curing conditions in the stenter frame

Additional BAT opportunities to minimize waste and releases to the environment:

- Use of displacers in the padding device (Foulard) reduces required liquor volume
- Automated dosing systems with integrated self-learning systems minimize waste by:
  - Computing exact pick-up and liquor consumption
  - Mixing only what will be used in the scheduled run
  - Low add-on techniques minimize chemical consumption
- Where possible, use direct piping into the bath for each of the chemicals to be used so that the chemicals are not pre-mixed before being introduced into the applicator or machine, and there is no need to clean containers, pumps and pipes before the next step.
- Check the input and output flows of the individual processes. Determine the input and output mass flows for both the site as a whole and each individual production process. Implement a product input check that takes account of raw materials, chemicals, dyes and auxiliary materials, etc.
- Employ improved measurement and control equipment, for example for temperature, chemical addition, retention time, moisture (in dryers)

- Where possible, consider a combination of condensation and scrubbing followed by electrostatic precipitation (ESP) or the use of thermal combustion with energy recovery on the curing/drying frame/stenters used in processing the fabric
- Where possible, consider treatment in wet scrubbers, absorbers, separation via low temperature condensation or combustion to reduce the release of volatile organic compounds from the framing/stenter process

Where possible, consider exhaust air treatment for emissions-relevant processes.

4.10 Expired Exemption – Paper and packaging

4.10.1 Background

Fluorinated compounds are used to render paper, cardboard and molded pulp articles grease- and waterproof to, for example, keep packaging aesthetically pleasant, to extend shelf-life of food and to protect people from burns caused by hot oil and fluids and to protect valuable surfaces from stains. These are niche applications and represent only a small part of the overall paper market (approximately 8%). The specialty paper products may be found in food contact applications such as pizza boxes, fast food wraps, plates, food containers, (microwave) popcorn bags, and pet food packaging. Specific regulations exist in many countries that regulate and approve products for use in food contact applications. In addition, these specialty papers find uses in non-food contact applications, such as folding cartons, containers, carbonless copy forms and paint masking papers.

The oil- and grease repellents can be applied in various stages of the industrial paper making process, either in the pulp stage, in the so called wet-end or via size press application.

PFOS-related substances, such as mono-, di- or triphosphate esters of N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) (introduced in the 1960s) or N-Methyl perfluorooctanesulfonamidoethanol acrylate polymers were the first generation substances used to provide grease repellence for paper products. Ca. 1wt% of PFOS remained as impurity in the polymer (Kara *et al.* 2010). Second generation products included long-chain fluorotelomer thiol-based phosphates and polymers followed. Those were then followed by polyfluoroalkylphosphonic acids (PAPs) in 1970s which have been phased out by their major producers and for which the US FDA has amended the food additive regulation (see e.g. U.S. Fed. Reg. Vol. 81, No. 1, January 4, 2016 p. 5-8). Since then acrylate polymers with fluorinated side chains derived from sulfoamido alcohols and long-chain fluorotelomer-based alcohols had been the most widely used but are now discontinued products. Major manufacturers, in conjunction with global regulators, have agreed to discontinue the manufacture of “long-chain”-based fluorinated products and move to “short-chain”-based fluorinated products. The paper and packaging market seem to have moved mainly to polymeric substances. Such “short-chain” polymeric alternatives have entered the commercial space over the last years and have undergone much higher regulatory rigor than their “long-chain” predecessors, for example in the USA (see references in previous chapter).

4.10.2 BAT and BEP for PFOS and PFOS–related substances

PFOS-related substances can no longer be used in this application. Non PFOS-related and non-long-chain fluorotelomer-based substances should be used in this application.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed to minimize chemical usage and to minimize emissions to waste water and to adhere to general BEP considerations utilized in this industry, including collecting all waste to be sent to incineration at high enough temperatures to completely mineralize the fluorinated substances.

Most commonly used products today are side-chain fluorinated polymers based on short-chain fluorotelomer-based raw materials and perfluoropolyether-based phosphates and polymers (UNEP/POPS/POPRC.8/INF/17/Rev.1and USFDA database). Such products are used at 0.1-1.0wt% (based on dry weight of paper).

Alternative Substances:

1. Short-chain fluorotelomer-based polymers:

Product/Producer	Web Reference
Cartaguard® KST from Archroma	http://paper.archroma.com/wp-content/uploads/2016/03/Cartaguard-KST.pdf
Asahiguard® from Asahi	http://www.agcce.com/brochurespdfs/sales/AsahiGuard_6_pager.pdf
Capstone™ from Chemours	https://www.chemours.com/Capstone/en_US/
Unidyne™ from Daikin	https://www.daikin.com/chm/pro/kasei/unidyne_multi/feature/
Thetaproof from ICT	http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/
Rucoguard® from Rudolf Chemie	http://www.rudolf-duraner.com.tr/en/products/co-producer-b2b/10-water-oil-and-soil-repellent-agents/12-c6-based-fluorocarbon-polymers.html
ImPress® from Solenis	http://solenis.com/en/industries/packaging-paper-board/
Texfin C6-FCP from Texchem	http://www.texchem.co.uk/TexfinC6FCP.html

2. Fluorinated-polyethers:

Solvera® from Solvay: http://www.solvay.cn/en/binaries/Solvera-PT-5045-PG_EN-231085.pdf and http://www.solvay.com/en/markets-and-products/featured-products/solvera.html

Non-fluorinated alternatives cannot achieve the stringent performance requirements for oil and grease resistance but can achieve excellent water repellency.

Alternative Technology:

The Norwegian paper producer Nordic Paper is using mechanical processes to produce, without using any persistent chemical, extra-dense paper that inhibits leakage of grease through the paper (UNEP/POPS/POPRC.9/INF/11/Rev. 1).

Best Environmental Practices:

Additional details on BAT and BEP for this application can be found in IPPC (2001, 2015).

4.11 Expired exemption – Coatings and coating additives

4.11.1 Background

In the past, PFOS-related fluorinated polymers containing up to 4% of fluorinated residuals were sold as coating materials for e.g. printed circuit boards and hard disk drive components. Such coatings provide protection against corrosion, contamination and grime as well as repellent properties leading to an improved manufacturing efficiency.

The coatings industry is rapidly shifting to water-borne systems to reduce volatile organic compounds (VOCs). This puts increased demand on coatings as water has a higher surface tension than organic coating solvents and therefore wetting of substrates becomes a challenge. With utilizing fluorinated surfactants, the surface tension of liquid coatings is lower at lower surfactant concentration than when deploying hydrocarbon surfactants. In many coating applications, increased effectiveness and efficiency in aiding wetting are critical for the successful application of a coating. Fluorinated surfactants provide exceptional wetting, leveling and flow control for water-based, solvent-based and high-solids organic polymer coating systems when added in amounts of just 100 ppm–500ppm.These properties result in:

- improved anti-crater and improved surface appearance
- better flow and levelling
- reduced foaming
- decreased block
- extended open-time
- increased bond strength
- oil repellency
- better dirt pick-up resistance

Typical industries utilizing fluorinated surfactants to achieve these properties include:

- industrial and institutional floor polishes
- architectural paints and coatings
- varnishes
- printing inks
- adhesives

For detailed discussions of the important properties of and technology behind commercial fluorinated surfactants, see Kissa 1994, Taylor 1999, Buck, Murphy *et al.* 2011.

One of the largest consumers of PFOS and PFOS-related fluorinated surfactants, was floor polish for industrial and institutional flooring. The floor polish must wet a floor that might be made of low surface energy material or that may be contaminated with a low surface tension (hydrophobic) material. Proper surface wetting requires a surfactant that will ensure the polish has a sufficiently low surface tension to function. In addition, high gloss is very desirable with floor polish. Fluorinated surfactants are excellent at mitigating surface tension gradients that can cause coating defects and reduce gloss.

Ultimately, the use and choice of a specific fluorinated surfactant will depend on whether the material provides the necessary performance or benefits that cannot be attained with other surfactants. In the past, PFOS has been used in the described applications. The conversion from PFOS to short-chain fluorinated surfactants has been considered successful to date (OECD 2010).

4.11.2 BAT and BEP for PFOS and PFOS-related substances for Coatings

PFOS-related can no longer be used in this application. Non-PFOS-related fluorinated polymers should be used in this application.

For a general best practices overview see Chapter 2 and IPPC (2007).

Alternative Substances:

Perfluorobutane sulfonate (PFBS)-based polymeric substances (such as Novec® products from 3M; http://multimedia.3m.com/mws/media/842207O/3m-novec-2704-electronic-grade-coating.pdf)

Alternative Technology: No information

Best Environmental Practices: No information

4.11.3 BAT and BEP for PFOS and PFOS-related substances for Coatings Additives

PFOS and PFOS-related substances can no longer be used in this application. Non-PFOS and non-PFOS-related fluorinated substances based on short-chain technology should be used in this application.

In addition to the general BEP measures outlined in Chapter 2 that should be followed, it is needed tocollect all waste followed by incineration at high enough temperatures to thermally mineralize the fluorinated substances.

Alternative Substances:

1. Short chain fluorotelomer-based surfactants:
    a. Various products from Chemguard;
    http://www.chemguard.com/specialty-chemicals/catalog/wetting-leveling-fluorosurfactants/
    b. Capstone® from Chemours;
    https://www.chemours.com/Capstone/en_US/
    c. Flexiwet and Thetawet from ICT;
    http://www.ictchemicals.com/products/technical-platforms/fluorinated-surfactants/
    d. Hexafor from Maflon;
    http://www.maflon.com/images/maflon.pdf
2. Perfluorobutane sulfonate (PFBS)-based compounds (e.g., FC-4430, FC-4432 and FC-4434 products from 3M; http://multimedia.3m.com/mws/media/1028328O/3m-fluortenside-de-2015.pdf)
3. Fluorinated polyethers (e.g., PolyFox® products from Omnova; https://www.omnova.com/product-types/coating-resins-and-additives/for-floor-care)
4. Compounds based on two fluorinated carbons (e.g., Tivida® FL from EMD Performance Materials; http://www.emd-performance-materials.com/en/coatings/tivida/tivida_fl/tivida_fl_2300/tivida_fl_2300.html)
5. Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water (for wood primers and printing inks)
6. Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd® products from Worlée)
7. Propylated naphthalenes and propylated biphenyls (water repelling agents for rust protection systems, marine paints, resins, printing inks and coatings in electrical applications)
8. Fatty alcohol polyglycol ether telomers, sometimes blended with a sulfosuccinate

Alternative Technology: No information

Best Environmental Practices:

Coatings are often applied in an industrial setting with the exception of mainly architectural coatings at home (IPPC 2007). Coatings are permanent and stay with the substrate for long times, often until end of life. In industrial and institutional settings, floor polishes are applied and removed as required for another floor care application and may be disposed directly into wastewater. It is recommended to follow instructions provided on product safety data sheet for proper waste disposal.

4.12 Expired exemptions – Rubber and plastics

4.12.1 Background

PFOS and/or PFOS-related substances have been used as mould release agents in rubber and plastics moulding applications

4.12.2 BAT and BEP for PFOS and PFOS-related substances

The available documents and references do not give a clear picture on the exact use and applications and what BEP encompasses in this industry. For example, one report lists - UNEP/POPS/POPRC.6/13/Add.3/Rev.1 - "PFBS derivatives or various C4-perfluorocompounds …. as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics". Another report - UNEP/POPS/COP.7/INF/26 -states the following: "Because of good surfactant properties with extremely stable and non-reactive characteristics, perfluorocarbons (PFCs), including PFOS, are used in release agents for plastic and rubber products manufacture. A release agent is a chemical, often wax, silicone or fluorocarbon fluid, used in moulding and casting, that aids in the separation of a mould from the material being moulded. It reduces imperfections in the moulded surface; it is also known as a parting agent, mould lubricant, mould release lubricant and de-moulding agent. PFCs, however, were only used as a low concentration additive for a release agent, in which wax, hydrocarbons and organosilicons would be the basic ingredients. There is no survey on the use of PFCs/PFOS in industrial sectors using PFOS-containing release agents."

For a general best practices overview see Chapter 2.

Alternative Substances:	No information
Alternative Technology:	No information
Best Environmental Practices:	No information

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