

UNEP/POPS/COP.7/INF/21

Distr.: General 5 February 2015

English only



Stockholm Convention on Persistent Organic Pollutants

Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants Seventh meeting Geneva, 4–15 May 2015 Item 5 (b) of the provisional agenda*

Matters related to the implementation of the Convention: measures to reduce or eliminate releases from unintentional production

Revised draft guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid and related chemicals listed under the Stockholm Convention

Note by the Secretariat

- 1. At its sixth meeting, the Conference of the Parties considered the draft guidance on best available techniques (BAT) and best environmental practices (BEP) for the use of perfluorooctane sulfonic acid and related chemicals listed under the Stockholm Convention and the draft guidance on BAT and BEP for the recycling and waste disposal of articles containing polybrominated diphenyl ethers listed under the Stockholm Convention which were developed by the Secretariat, in collaboration with UNIDO and UNITAR.¹
- 2. As referred to in the note by the Secretariat on the guidelines on best available techniques and provisional guidance on best environmental practices (UNEP/POPS/COP.7/14), the Conference of the Parties requested the Secretariat to revise the above-mentioned draft guidance according to the comments from parties and the appropriate bodies of the Basel Convention.
- 3. In response to this request, the Secretariat has collected and compiled comments from parties and others on the above-mentioned draft guidance, facilitated the review of the waste content of the draft guidance by the Basel Convention small intersessional working group on the development of technical guidelines on persistent organic pollutants wastes,² and supported the experts on BAT and BEP in their work to review and update the guidelines and guidance.
- 4. At their meeting, held in Geneva on 24 and 25 November 2014, the experts on BAT and BEP have evaluated the information and addressed the comments submitted on the above-mentioned draft guidance. The compilation of comments and responses is included in annex III to the meeting report.³ The Secretariat has integrated the comments as agreed at the expert meeting and prepared revised draft guidance for consideration by the Conference of the Parties. The revised draft guidance on BAT and BEP for the use of perfluorooctane sulfonic acid and related chemicals listed under the Stockholm Convention is set out in the annex to the present note. The revised draft guidance on BAT and BEP for

^{*} UNEP/POPS/COP.7/1.

¹ UNEP/POPS/COP.6/15.

² UNEP/CHW/OEWG.9/INF/30/Rev.1.

³ UNEP/POPS/COP.7/INF/19.

the recycling and waste disposal of articles containing polybrominated diphenyl ethers listed under the Stockholm Convention is set out in document UNEP/POPS/COP.7/INF/22.

5. The present note, including its annex, has not been formally edited.

Annex

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

Draft
Revised January 2015













Disclaimer

The designations employed and the presentations in this publication are possible options, based on expert judgment, for the purpose of assisting countries in their actions to reduce or eliminate releases of perfluorooctane sulfonic acid (PFOS) and related chemicals listed in the Stockholm Convention. UNEP or contributory organizations cannot be liable for misuse of the information contained in this publication.

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Abbreviations and Acronyms

ABS acrylonitrile butadiene styrene
AFFF aqueous film-forming foam
APEO alkylphenoletoxylates

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
BOD₅ 5-Day biochemical oxygen demand

BPM barrels per minute

BREF BAT Reference Document

CCD charge-coupled device (technology for capturing digital images)

CMC critical micelle concentration
COD chemical oxygen demand
COP Conference of Parties
DUV deep ultra violet

DWR durable water-repellent ECF electrochemical fluorination

EMS environmental management system

ETFE ethylene tetrafluoroethylene
EtFOSA N-Ethyl perflurooctane sulfonamide
film forming fluoroprotoin form

FFFP film-forming fluoroprotein foam FOSA N-Alkylperfluorooctanesulfonamide

FOSE N-Alkylperfluorooctanesultonamidoethanol

FP fluoroprotein foam

IBC intermediate bulk container

INPEV National Institute for Processing of Empty Packages

LCD liquid crystal display
MSDS material safety data sheet

PBT persistent, bioaccumulative and toxic

PFAS perflourinated alkyl sulfonates

PFBS perfluorobutane sulfonic acid/potassium perfluorobutane sulfonate

PFC perfluorinated compound
PFOS perfluorooctane sulfonic acid
PFOSA perfluorooctanesulfonic acid
PFOSF perfluorooctanesulfonyl fluoride

POPRC Persistent Organic Pollutant Review Committee

POPs persistent organic pollutants
PPE personal protective equipment
PVD physical vapour deposition
R&D research & development

SDS safety data sheet

STMP surface treatment of metals and plastics

TARC top anti-reflective coating

THPFOS tetrahydro PFOS

TLV threshold limit value

UNEP United Nations Environment Programme

US EPA United States Environmental Protection Agency

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).

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) and PFOS-related substances from production and use under the specific exemptions and acceptable purposes listed in the Convention. The document has been developed based on currently available information and knowledge and is continuously updated as new relevant information and data become available.

1.2 Structure and use of this document

Chapter 1 outlines the purpose and structure of this document. It also includes a brief description of the characteristics and uses of PFOS and PFOS-related substances, the relevant provisions under the Stockholm Convention and a summary of required measures under these provisions.

Chapter 2 includes general BAT and BEP principles and guidance for the management of PFOS and PFOS-related substances that cut across multiple process categories.

Chapter 3 provides specific guidance for the processes/applications listed as specific exemptions and acceptable purposes under the Convention. Each section within the chapter provides a general description of the process/application in which PFOS and/or PFOS-related substances are used including information on available alternatives for that use, and specific BAT and BEP guidance for management of PFOS in the respective process/application.

Technologies that are currently under investigation with respect to their efficacy and commercial availability are considered as emerging and are listed the annex to this document.

1.3 Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride

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

PFOS is a fully fluorinated anionic substance, which is commonly used as a salt in some applications or incorporated into larger polymers. PFOS and its closely related compounds, which may contain PFOS impurities or substances which can give rise to PFOS, are members of the large family of perfluoroalkyl sulfonate (PFAS) substances (UNEP/POPS/POPRC.2/17/Add.5, UNEP/POPS/POPRC.3/20/Add.5)¹. In this document, PFOS, its salts and PFOSF are referred to as "PFOS and PFOS-related substances". The term "PFOS-related substances" (also known as precursors) refers to any substance that contains the structural element PFOS in their molecular structure as they are and were produced with PFOS, its salts or PFOSF as an intermediate or starting material (UNEP/POPS/POPRC.8/INF/17/Rev.1).

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¹ Specifically, PFOS belongs to the class of perfluoroalkane sulfonic acids or PFSAs (OECD, 2013).

1.3.2 Characteristics

PFOS is extremely 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

PFOS and PFOS-related substances are 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. Therefore, PFOS and PFOS-related substances are still produced and/or used in a number of countries. The list of uses for acceptable purposes or specific exemptions pursuant to Part I of Annex B is given in Table 1 below. The register of specific exemptions and the register of acceptable purposes for PFOS and PFOS-related substances are available on the Convention's website.²

Table 1. 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

- Photo-imaging
- Photoresist and anti-reflective coatings for semiconductors
- Etching agent for compound semiconductors and ceramic filters
- Aviation hydraulic fluids
- Metal plating (hard metal plating) only in closed-loop systems
- Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)
- Fire fighting foam
- Insect baits for control of leaf-cutting ants from Atta spp. and Acromyrmex spp

Specific exemptions

- Photo masks in the semiconductor and liquid crystal display (LCD) industries
- Metal plating (hard metal plating)
- Metal plating (decorative plating)
- Electric and electronic parts for some colour printers and colour copy machines
- Insecticides for control of red imported fire ants and termites
- Chemically driven oil production
- Carpets
- Leather and apparel
- Textiles and upholstery
- Paper and packaging
- Coatings and coating additives
- Rubber and plastics

² http://chm.pops.int/Implementation/Exemptions/RegisterofSpecificExemptions/tabid/1133/Default.aspx and

http://chm.pops.int/Implementation/Exemptions/Acceptable Purposes PFOS and PFOSF/tabid/794/Default. as px

1.4 Consideration of alternatives to PFOS and PFOS-related substances

According to paragraph 4 of Part III of Annex B to the Convention, to reduce and ultimately eliminate the production and use of PFOS and PFOS-related chemicals, parties are encouraged to phase out uses when suitable alternatives or methods are available. Guidance for consideration of alternatives has been developed by the POPs Review Committee. This includes the Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications (UNEP/POPS/POPRC.8/INF/17/Rev.1), Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals (UNEP/POPS/POPRC.9/INF/11/Rev.1), the Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (UNEP/POPS/POPRC.10/INF/7/Rev.1) and Factsheets on alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (UNEP/POPS/POPRC.10/INF/8/Rev.1).

The present document includes information on available alternatives for the uses listed as specific exemptions and acceptable purposes under the Convention, but refrains from assessing their suitability. A hazard-based assessment of the alternatives has been conducted by the POPs Review Committee, based on an analysis as to whether or not the identified chemical alternatives meet the numerical thresholds in Annex D of the Convention (UNEP/POPS/POPRC.10/INF/7/Rev.1). Parties may use that report as a source of information when choosing alternatives to PFOS and PFOS-related substances. It should be noted that for the substances which the Committee 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 and such substances should be assessed by parties before being considered as suitable alternatives. Further details are available in the above mentioned set of guidance documents.

Tables 2 and 3 below summarize 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.

Table 2. Availability of alternatives to PFOS for "Acceptable Purpose" applications.

Acceptable Purpose	Existence of Alternatives	Chemical Identity and Properties	Trade Names and Producers
Photo-imaging	Commercially available	Available	Unknown
Photoresist and anti-reflective coatings for semiconductors	No information	No information	No information
Etching agent for compound semiconductors and ceramic filters	No information	No information	No information
Aviation hydraulic fluids	No information	No information	Available
Metal plating (hard metal plating) only in closed-loop systems	At trial phase prior to scale up	Scarce information on input substances	Available
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)	Available for some applications	Available	Unknown
Fire fighting foam	Commercially available	Scarce information on input substances owing to CBI	Available

Insect baits for control of leaf- cutting ants from genus Atta spp. and Acromyrmex spp.	Undergoing evaluation	Available	Available
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Table 3. Availability of alternatives to PFOS for "Specific Exemption" applications.

Specific Exemption	Existence of Alternatives	Chemical Identity and Properties	Trade Names and Producers
Photo masks in the semiconductor and liquid crystal display (LCD) industries	No information	No information	No information
Metal plating (hard metal plating)	At trial phase prior to scale up	Scarce information on input substances	Available
Metal plating (decorative plating)	Commercially available	Available	Available
Electric and electronic parts for some colour printers and colour copy machines	No information	No information	No information
Insecticides for control of red imported fire ants and termites	Commercially available	Available	Available
Chemically driven oil production	Scarce information	Available	No information
Carpets	Commercially available	Available	Available
Leather and apparel	Commercially available	Available	Available
Textiles and upholstery	Commercially available	Available	Available
Paper and packaging	Commercially available	Available	Available
Coatings and coating additives	Commercially available	Available	Available
Rubber and plastics	Commercially available	Available	Unknown

1.5 Relationship to the Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal was adopted in 1989 and entered into force in 1992. The Basel Convention is the one other global agreement, besides the Stockholm Convention, directly relevant to the application of best available techniques (BAT) and best environmental practices (BEP) to the control of chemicals listed in the Stockholm Convention. The Convention places obligations on countries that are Parties to, inter alia: minimize generation of hazardous waste; ensure that adequate disposal facilities are available; and ensure environmentally sound management of wastes.

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)."

The Conference of the Parties to the Basel Convention, at its eleventh meeting in May 2013, decided to update the general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants, which were adopted at its eighth meeting in December 2006, with regard to the chemicals listed in the Stockholm Convention in 2009, 2011, and 2013. The general technical guidelines developed under the Basel Convention address matters related to all three of the outstanding definitional issues raised in paragraph 2 of Article 6 of the Stockholm Convention. The eleventh meeting of the Conference of the Parties to the Basel Convention also decided to prepare or update specific technical guidelines with regard to the newly listed POPs.

The draft updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with POPs and the technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with PFOS, its salts and PFOSF are available on the Convention's website³.

In addition, regarding the use of PFOS in pesticides, the technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with the pesticides aldrin, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordane, chlordecone, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), lindane, mirex, pentachlorobenzene, perfluorooctane sulfonic acid, technical endosulfan and its related isomers, toxaphene or with HCB as an industrial chemical are relevant.

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³ http://www.basel.int/Implementation/POPsWastes/TechnicalGuidelines/tabid/2381/Default.aspx

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 environmental control measures and strategies, which includes practices that relate to the continuous improvement of environmental performance. BEP provides the framework for ensuring the identification, adoption and adherence to management options that can play an important role in improving the environmental performance of the installation. These good housekeeping/management techniques/tools often prevent releases. As an example of general good international industry practice see IFC (2007a).

The main ecological advantages achieved through the use of BEP management methods include savings in consumption of chemicals/auxiliaries, fresh water and energy; and minimizing the amount of solid waste and ecological loads in wastewater and off-gas. Another advantage is an improved workplace situation. Well-trained employees are a prerequisite for implementing BEP system 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 (automated dosing systems, etc.). These applicability factors can be limited due to the fact that the measures may be too cost-intensive or due to technological/logistics or a space problem (Schönberger et al., 2005).

The following sections provide information on environmental management systems that could improve environmental performance of an installation including increased awareness of the workers/employees.

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 installation, and the range of environmental impacts it may have.

BEP is to implement and adhere to an EMS that incorporates the following features, as appropriate, for individual circumstances:

- Definition of an environmental policy for installation by top management (its commitment is regarded as a precondition for a successful application of other features of the EMS).
- Planning and establishing of the necessary procedures.
- Implementation of the procedures, paying particular attention to:
 - 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
- Checking of performance and taking of corrective action, paying particular attention to:
 - Monitoring and measurement
 - Corrective and preventive action

- Maintenance of records
- Perform independent (where feasible) internal auditing to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained.

Three additional features are considered as supporting 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 (and possibly external validation) of a regular environmental statement
 describing all the significant environmental aspects of the installation, allowing for year-by-year
 comparison against environmental objectives and targets as well as with sector benchmarks as
 appropriate.
- Consideration of applicable industry-specific standards, when available.
- Implementation and adherence to an internationally accepted EMS.

This last voluntary step could give higher credibility to the EMS, particularly internationally accepted and transparent standards, such as ISO9001 and ISO14001⁴. Non-standardized systems can in principle be equally effective provided that they are properly designed and implemented.

2.1.2 Education and training of employees

The following specific training and education opportunities could be beneficial for raising awareness at work for sound chemicals management in general:

- Process- and machinery-specific training to increase the level of environmental awareness.
- Appropriate education of workers concerning handling of chemicals and auxiliaries, especially in case of hazardous substances.
- Maintenance of technical equipment (machines in production as well as abatement and recovery devices); machinery checking (e.g. pumps, valves, level switches); general maintenance by specialized companies at regular intervals; and checking of the burner air inlet at regular intervals.
- Leak control of chemicals when stored and during processing.
- Filter maintenance (periodically cleaning and controlling).
- Calibration of equipment for chemicals measuring and dispensing devices.

2.1.3 Industrial considerations

It is also important for industry to consider the following potential 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, consumption of water and generation of waste.
- Ensure the provision of full details of the activities carried out on-site. A good deal of that is contained in the following documentation:
 - Descriptions of the waste treatment methods and procedures in the place of installation.

⁴ http://www.iso.org/iso/home/standards/management-standards/iso14000.htm

- 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 the environmental monitoring information.
- Details on how protection is provided during abnormal operating conditions such as momentary stoppages, start-ups, and shutdowns.
- Instruction manual.
- Operational diary.
- 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 good housekeeping procedures in place, which will also cover the maintenance procedure, and an adequate training programme, covering the preventive actions that workers need to take on health and safety issues and environmental risks.
- Have a close relationship with the waste producer/holder so that the customers' sites implement
 measures to produce the required quality of waste necessary for the waste treatment process to
 be carried out.
- 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

This section describes general principles, measures and safety precautions related to PFOS that apply to all types of products and industries in the following areas:

- Storage, handling, dosing, dispensing and transport
- Improved knowledge of the raw materials used
- Minimization/optimization of the chemicals used
- Equipment

Guidelines that apply to specific process categories / applications are described in the following chapter.

2.2.1 Storage, handling, dosing, dispensing and transport

When storing and handling PFOS and PFOS-related substances, indicate that such substance(s) is being stored in a defined location. In storing, handling, dosing, dispensing, and transporting PFOS-containing products, caution should be used to ensure:

- Proper storage according to the instruction of the safety data sheet (SDS).
- Proper labelling of containers and equipment 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.
- Use of only as much PFOS or PFOS-related substances as essentially needed for the process, by measuring and recording the PFOS and/or PFOS-related substances consumption.

2.2.2 Improved knowledge of the raw materials used

When handling products and preparations containing PFOS or PFOS-related substances, the following relevant information should be collected and analyzed to plan proper handling:

- Consult and follow instructions given on the product SDS. If a SDS is not available, the product should not be used due to missing information of safe handling. Preferably the SDS should adhere to GHS format and be provided in a local language version.
- Auxiliaries and basic chemicals information from the supplier concerning proper storage and handling; and environmental characteristics (COD, BOD₅, aquatic toxicity, degree of biodegradation/bioelimination, content of nitrogen, phosphorous, sulphur, adsorbable organic halogens (AOX)-relevant compounds, kind and amount of volatile compounds, emission factor, health and safety aspects).
- Information from the supplier concerning types of preparation agents, amounts of residual monomer and solvent contents of the raw materials.
- Chemical and physical characteristics to be considered for proper handling.
- Technology should be deployed to minimize un-reacted raw material and by-product content in the products sold.
- Avoid alternative products that contain an unknown amount or high levels of un-reacted raw materials and by-products.
- Information on un-reacted raw material and by-product content in products sold should be made public to all customers and interested parties.

2.2.3 Minimization/optimization of the chemicals used

Minimization and optimization of PFOS or PFOS-related substances may be achieved by taking the following into consideration:

- Avoiding any kind of applied fluorinated chemicals and auxiliaries that may have a potential to transform into and/or emit PFOS or PFOS-related substances.
- Using fluorinated chemicals that do not transform and emit PFOS, and performing regular revising
 of the recipes that include auxiliaries and chemicals with a high degree of
 biodegradation/bioelimination. Low human and ecological toxicity, low volatility and low odour
 intensity are preferred.
- Avoiding surpluses of applied chemicals and auxiliaries and consider application equipment that
 uses the least amount of chemical products needed.
- Avoiding, if possible, add-on devices (spraying, foam application, special padding devices).
- Decreasing the use of PFOS or PFOS-related substances to the lowest possible level if unable to replace them.

2.2.4 Equipment

When choosing and using equipment, the following could be considered:

- Employing technology to minimize exposure to workers and to minimize releases to the environment (water, air and soil).
- Using equipment made of materials that sustain corrosion.
- Limiting the use of the equipment to PFOS or its salts only.
- Installing ventilation where scattering is expected and, to prevent releases into the environment, installing a dust collector, scrubber or similar devices.
- Using material that is not likely to corrode for piping from equipment as well as for wastewater.

2.3 General considerations for water, off-gas and solid waste management

The following measures could be considered for water management, off-gas and solid waste management:

- Avoidance of leaks and spills.
- Substitution of overflow rinsing or minimization of water consumption in overflow rinsing by means of optimized process control.
- Reuse of rinsing baths, especially final rinsing baths.
- Reversing of current flows in continuous washing.
- Cleaning and recycling of process water in selected low charged wastewater streams.
- Operational safety in place to avoid unnecessary exposure and accidents.
- Use of low emission preparation agents through the total supply chain where possible.
- Use of low emission options.
- Separate collection of solid waste consisting of, containing or contaminated with PFOS or PFOSrelated substances.
- Storing of this waste in a controlled landfill (i.e. a landfill with no leakage to the surrounding environment).
- Reuse and recycling of known "PFC-free" product wastes (RPA and BRE Env., 2004).
- Destruction of PFOS and/or PFOS-related substances contained in waste at a minimum of 1100 °C (RPA and BRE Env., 2004; Ministry of Environment of Japan, 2013).
- Avoidance of mixing PFOS-free solutions or wash water with solutions containing PFOS.

2.4 Handling and knowledge of the waste flow

The following know-how needs to be taken into account for the management of waste flows: i) the treatments to be carried out, ii) the types and origins of waste to be accepted and treated, and iii) the handling procedures under consideration and their associated risks.

The monitoring of waste flow involves implementation of the following procedures:

- Pre-acceptance procedure
- Acceptance procedure
- Different sampling procedures
- Reception facility

BAT and BEP for each of these areas are discussed in the next four sections. Further details are available in the technical guidelines under the Basel Convention referred to in section 1.5.

2.4.1 Pre-acceptance procedure

Implementing the pre-acceptance procedure could consider at least the following items:

- Tests for the incoming waste with respect to the planned treatment.
- All necessary information received on the nature of the processes producing the waste, including the variability of the process. Personnel dealing with the pre-acceptance procedure need to be able to deal with all guestions relevant to waste treatment in the waste treatment facility.
- A system for providing and analyzing representative samples of the waste from the production process producing such waste from the current holder.

- A system for carefully verifying, if not dealing directly with the waste producer, the information received at the pre-acceptance stage, including the contact details of the waste producers and an appropriate description of waste composition and its hazardousness.
- An existing national waste code, provided or developed.
- Appropriate treatment for each waste to be received at the installation by identifying a suitable
 treatment method for each new waste enquiry and a clear methodology in place to assess the
 treatment of waste, which considers the physico-chemical properties of the individual waste and
 the specifications for the treated waste.
- Waste characterization laboratory testing necessary to establish the concentration of PFOS or PFOS-related substances, if required.
- The toxicological properties of the individual waste, where applicable, sometimes have also to be considered to assess proper characteristics of the treatment.

2.4.2 Acceptance procedure

The acceptance procedure involves implementing a clear and specified system that allows the operator to accept wastes at the receiving plant only if a defined treatment method and disposal/recovery route for the output of the treatment are determined. Waste containing PFOS and/or PFOS-related chemicals should be accepted only where environmentally sound management is implemented.

Planning for this procedure involves guaranteeing that the necessary storage treatment capacity and dispatch conditions (e.g. acceptance criteria of the output by the other installation) are also respected:

- Measures in place to fully document and deal with acceptable wastes arriving at the site, such as a pre-booking system, e.g. to ensure that sufficient capacity is available.
- Clear and unambiguous criteria for the rejection of wastes and the reporting of all non-conformances.
- A system for identifying the maximum capacity limit of waste that can be stored at the facility.
- Visual inspection of the waste IN to check compliance with the description received during the pre-acceptance procedure. For some liquid and hazardous waste, this may not be applicable.

2.4.3 Sampling procedures

Implementation of different sampling procedures for different incoming waste vessels delivered in bulk and/or containers could contain the following items:

- Sampling procedures based on a risk approach, which could consider the type of waste (e.g. hazardous or non-hazardous) and the knowledge of the customer (e.g. waste producer).
- Relevant physico-chemical parameters of all registered waste materials.
- Different sampling procedures for bulk (liquid and solids), large and small containers, and laboratory samplers. The number of samples to be taken should increase with the number of containers. In extreme situations, all small containers must be checked against the accompanying paperwork. The procedure should contain a system for recording the number of samples and degree of consolidation.
- Details of the sampling of wastes in drums within designated storage, e.g. the time scale after receipt.
- Samples prior to acceptance.
- Maintenance of a record at the installation of the sampling regime for each load, together with a record of the justification for the selection of each option. Includes a system for determining and recording.
- A suitable location for the sampling points.

- The capacity of the vessel sampled (for samples from drums, an additional parameter would be the total number of drums).
- The number of samples and degree of consolidation.
- Operating conditions at the time of sampling.
- A system to ensure that the waste samples are analyzed.
- A temporary storage, in case of cold ambient temperatures, to allow sampling after defrosting. This may affect the applicability of some of the above items.
- For additional details on sampling techniques, see the Guidance on sampling, screening and analysis of persistent organic pollutants in products and articles relevant to the substances listed in Annexes A, B and C to the Stockholm Convention on Persistent Organic Pollutants in 2009 and 2011⁵.

2.4.4 Reception facility

The reception facility could cover at least the following issues:

- A laboratory to analyze all the samples. Particularly for hazardous wastes, this often means that the laboratory needs to be on site.
- A dedicated waste storage area as well as written procedures to manage non-accepted waste.
 Wastes can be temporarily stored safely if the inspection or analysis indicates that they fail to
 meet the acceptance criteria (including, e.g. damaged, corroded or unlabelled drums). Such
 storage and procedures could be designed and managed to promote rapid management (typically
 a matter of days or less) to find a solution for that waste.
- A clear procedure to deal with wastes when inspection and/or analysis prove that they do not
 fulfil the acceptance criteria of the plant or do not fit with the waste description received during
 the pre-acceptance procedure. The procedure includes all measures, as required by the permit or
 national/international legislation, to: inform competent authorities and safely store the delivery
 for any transition period or reject the waste and send it back to the waste producer or to any
 other authorized destination.
- Waste in the storage area only after acceptance of the waste.
- Clearly marked inspection, unloading and sampling areas on a site plan.
- Sealed drainage system.
- Qualification and regular training of the personnel involved in the sampling, checking and analysis procedures.
- Application of a waste tracking system unique identifier (label/code) to each container at this stage. The identifier will contain at least the date of arrival on site and the waste code.

2.5 Occupational health and safety measures

This section describes procedures, equipment and measures related to handling PFOS and PFOS-related substances, special and personal protection when working with PFOS and PFOS-related substances and first aid procedures. Before storing, handling, dosing, dispensing, and transporting PFOS or any PFOS-related chemical, it is necessary to review the latest available SDS. In case a complete SDS is not available from the supplier, the product should not be used..

2.5.1 Handling precautions

Leak and spill detection procedures:

• Shut off source of spill if possible to do so without hazard.

⁵ http://chm.pops.int/Implementation/NIPs/Guidance/tabid/2882/Default.aspx

- Contain the spill by diking.
- Absorb spillage with clay, sawdust, or other absorbent material.
- Place all spilled material, contaminated dirt, and other contaminated materials in approved drums for disposal.

Waste disposal:

Always dispose of according to local/national regulations.

Handling and special equipment:

- Do not get PFOS-containing products in eyes, on skin or clothing.
- Do not take it internally.
- Do not breathe vapours.
- Keep away from heat, sparks, and open flames.

Refill:

- Wear proper personal protective equipment.
- Handle the product indoors.
- Minimize number refills necessary.
- Avoid spills and overflows, use secondary containers to catch any spilled material.
- Prevent the product from remaining in equipment and take measures to recover it as much as possible.

Storage requirements:

- Store in a cool dry place away from heat, sparks, and open flames.
- Store in a well-ventilated area.

2.5.2 Special and personal protection

- An up-to-date product SDS should be consulted.
- Mechanical ventilation: the use of mechanical ventilation is recommended whenever the PFOScontaining product is used in a confined space. Otherwise, assure use in an area where there is natural air movement.
- Respiratory protection: in operations where the vapour can be released, wear a respirator with organic vapour canister or cartridge.
- Protective gloves: rubber or neoprene.
- Eye protection: goggles.
- Additional protective equipment: eyewash bottles or other rinsing equipment should be accessible.

2.5.3 First aid procedures

For eyes:

- Immediately flush with plenty of water for at least 15 minutes.
- Contact a physician if irritation persists.

For skin:

- Flush skin with water or wash with mild soap and water if available.
- Remove contaminated clothing.

• Contact a physician if irritation persists.

For inhalation:

- Remove to fresh air.
- If breathing has stopped, give artificial respiration.
- Keep body warm and quiet and get medical attention.

For ingestion:

- If conscious, immediately induce vomiting by giving two glasses of water and sticking finger down the throat.
- Get immediate medical attention.
- After patient has vomited, give milk, water or sodium bicarbonate in water to drink. Never give anything by mouth to an unconscious or convulsing person.



3. Specific guidance on BAT and BEP for managing PFOS and PFOS-related substances by process category

3.1 Photo-imaging

3.1.1. Process description

In the photographic industry, PFOS-related substances have been used in manufacturing film, paper and plates. These chemicals function as dirt rejecters and friction control agents to reduce surface tension and static electricity. Imaging materials that are very sensitive to light (e.g., high-speed films) benefit particularly from these properties. PFOS-related substances such as tetraethylammonium perfluorooctane sulfonate and perfluorooctyl sulfonamidopropyl quaternary ammonium iodide have been used in the range of 0.1–0.8 $\mu g/cm^2$ for the following purposes in mixtures for coatings (RPA and BRE Env., 2004):

- Surfactants
- Electrostatic charge control agents
- Friction control agents
- Dirt-repellent agents
- Adhesion control agents

PFOS is still used (probably in small quantities) in X-ray film for photo imaging for medical and industrial uses (inspection by non-destructive testing). It is also used in film for other industries, such as the movie industry (UNEP/POPS/POPRC.9/INF/11/Rev.1).

3.1.1.1. Alternative chemistry

The spread of digital techniques as an alternative technology has substantively reduced photographic film use. The possible chemical alternatives identified for the photographic industry are (UNEP/POPS/POPRC.9/INF/11/Rev.1):

- Telomer-based products of various perfluoroalkyl chain length;
- C3- and C4-perfluorinated compounds;
- Hydrocarbon surfactants;
- Silicone products⁶.

3.1.2. BAT and BEP measures

As the spread of digital cameras has reduced film use, the use of PFOS in this area is not expected to grow. PFOS or its salts used in photographic film for industry (photographic developing work) are not likely to undergo chemical transformation through natural processes and bioaccumulate, posing risks to human health. Part of BAT and BEP in this sector is to endeavour to reduce releases of PFOS or its salts by recovery of developing solution and fixing solution.

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

The same measures as described below for the semiconductor industry would also be effective for the photographic industry.

⁶ There are considerable data gaps of siloxane compounds used on the market for photographic applications, see reference UNEP/POPS/POPRC.8/INF/17/Rev.1

3.2. Semiconductor industry

3.2.1. Process description

PFOS and PFOS-based substances are chemicals required by the semiconductor industry for formulation of resists and anti-reflective coatings in high-end lithography. PFOS can also be used as a surfactant in etching processes in the manufacture of compound semiconductors. PFOS is then added as part of an etching agent, and rinsed out during the subsequent washing treatment.

The manufacture of advanced semiconductor devices is not currently possible without the use of PFOS in critical applications such as photo resistant and anti-reflective coatings. PFOS is a process chemical; it does not remain in the final article – the semiconductor device.

Semiconductor manufacturing comprises up to 500 steps (see figure 3.2.1). The technology primarily involves four fundamental physical processes:

- Implant
- Deposition
- Etch/polish
- Photolithography

Photolithography is the most important of the four processes. It is essential for the successful implementation of the other three processes and, indeed, the overall production process. It shapes and isolates the junctions and transistors; it defines the metallic interconnects; it delineates the electrical paths that form the transistors; and it joins them together. Photolithography reportedly represents 150 of the total 500 steps. Photolithography is also integral to the miniaturization of semiconductors (RPA and BRE Env., 2004).

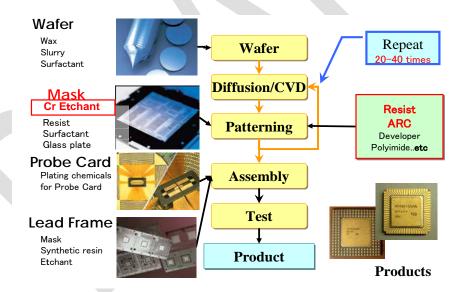


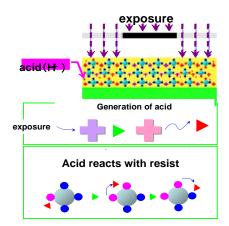
Figure 3.2.1: Different steps in semiconductor manufacturing where PFOS is used as an intermediate (The process in red is related to PFOS related substances. Source: Japan Electronics and Information Technology Industries Association Semiconductor Board)

PFOS reduces the surface tension and reflection of etching solutions, properties that are important for precise photolithography in the semiconductor industry (photo resists and photo masks). Small amounts of PFOS-based compounds are required during the following critical photolithography applications, which are crucial for achieving the accuracy and precision required to manufacture miniaturized high-performance semiconductor chips (UNEP/POPS/POPRC.9/INF/11/Rev.1):

- Ultra-fine patterning/photo resists as photo-acid generators and/or surfactants
- Anti-reflective coatings as uniquely performing surfactants

Wave length of Laser light for exposure device is very short.

Then light can not attain to the bottom of resist. PAG can resolve this problem



- 1. Low surface tension
- 2. Low reflection
- 3. High acid durability
- 4. Thermal stability
- 5. High UV durability



No substitution of PFOS

Figure 3.2.2: Description of photo resist critical use of PFOS and PFOS-related substances in photolithography processes (Japan Electronics and Information Technology Industries Association Semiconductor Board)

Note: 1 to 6 describe the important functions of PFOS and PFOS-related substances when used as a component of a photoresist substance.

PFOS is used as a component of a photo resist substance (see figure 3.2.2), including photo acid generators or surfactants; or in anti-reflective coatings, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturized devices (see figure 3.2.3). Photo resist is a polymer material necessary to shape a circuit in the photolithographic process. PFOS is added to the photo resist agent to make photo resist soluble in water and to give surface activity. Since the photo resist agent is rinsed out during the photolithographic process, PFOS does not remain in semiconductors.

The manufacture of semiconductors includes a series of photolithography processes. Since diffused reflection would possibly disorder the shape of a circuit in design, anti-reflective coating is necessary to avoid disturbance during photolithographic processes. PFOS is used in anti-reflective coating agents to give surface activity and regulate reflective characteristics of the coating between the metal and resist layers (see figure 3.2.3). Since anti-reflective coating agents are rinsed out during the photolithographic process, PFOS does not remain in semiconductors. A number of resist suppliers sell top anti-reflective coating (TARC) and bottom anti-reflective coating (BARC), which are used in combination with deep ultra violet (DUV) photo resist. The process involves placing a thin, top coating on the resist to reduce reflective light, in much the same way and for the same purposes that eyeglasses and camera lenses are coated.

The estimated global annual PFOS use (2010 data) for the critical applications is as follows (WSC, 2011):

Photo resists: 46.4kg

BARC: 4.5kg

TARC: 893.5kg

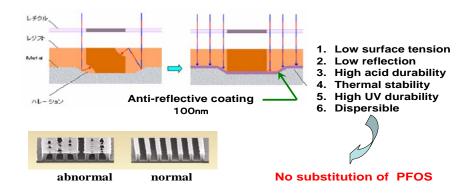


Figure 3.2.3: Description of anti-reflective coating critical use of PFOS and its related substances in photolithography processes (Japan Electronics and Information Technology Industries Association Semiconductor Board)

Note: 1 to 6 describe the important functions of PFOS and its related substances when used a anti-reflective coating agents.

3.2.1.1. Alternative chemistry

According to UNEP/POPS/POPRC.9/INF/11/Rev.1, no alternatives are currently available that would allow for the comprehensive substitution of PFOS in the critical applications described above. The World Semiconductor Council (WSC), an industry body, was committed to ending non-critical uses of PFOS in member countries of the United Nations Economic Commission for Europe by May 2007 and globally in May 2009. WSC, consisting of the Semiconductor Industry Associations in China, Chinese Taipei, Europe, Japan, Korea and the United States agreed to this voluntary agreement on PFOS in 2006 and subsequently implemented that agreement. Non-critical uses of PFOS are as edge bead removers, de-gluing agents and developing agents.

In 2011 the WSC also announced that the semiconductor industry has reduced global emissions of PFOS from semiconductor use to approximately 6kg/year which represents a 99% reduction from semiconductor emissions in 2005 (WSC, 2011). These emissions will continue to decrease as technology and feasibility permit replacement of critical uses.

New photolithography technologies, which in detail are trade secrets, use less photo resist per wafer, and the new photo resist formulations contain much lower concentrations of PFOS.

3.2.2. BAT and BEP measures

PFOS and PFOS-related substances are not likely to undergo chemical transformation through natural processes and bioaccumulate, posing risks to human health. Measures could be taken to reduce releases of by preventing mixing with water, and by the recovery (or the like) of wastewater.

In refill work, take measures to minimize the amount of scattering or run-off, and where scattering or runoff occurs, wipe it up immediately with a cloth (or the like).

For wastewater containing PFOS or PFOS-related substances, take measures to recover the wastewater, to the extent possible. Such measures prevent the release of PFOS in the environment, but the consequent increasing PFOS concentrations in the process water should be taken into account (this increase could also be reflected in the waste produced by wastewater treatment, e.g. sludge).

The majority of the photoresists and anti-reflectant 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 later neutralized in wastewater-treatment processes, any fluorinated material remaining in the aqueous phase should be removed before being discharged to the

aquatic environment. Process tools are implemented to reuse and recycle as well as to incinerate spent liquid (WSC, 2011). As an example of good industry practice in this sector, see IFC (2007b).

The product SDS should be consulted along with the information provided in the following sections.

3.2.2.1. Leakage recovery

Regarding waste such as waste liquid, the company should dispose of its own waste properly, or to dispose of it by entrusting it to a waste disposal operator, based on applicable acts and ordinances. Liquid and solid wastes from the manufacturing processes are collected and ultimately incinerated.

3.2.2.2. Storage of PFOS-containing product

- Store in a location where only the relevant persons can easily enter.
- Use a sealed container of solid design from which the PFOS-containing product is not likely to leak or spill, etc. and that is made using material that is not likely to allow seepage.
- To prevent the run-off of PFOS by rainwater (or the like), store containers containing PFOS indoors, and take measures to ensure the floor is concrete or coated with synthetic resin (or the like).

3.2.2.3. Indication of storage location

When handling PFOS storage and containers storing PFOS, it needs to be indicated that PFOS is being stored in the defined location.

3.2.2.4. Transport

When a business operator handling PFOS (excluding a transport operator to whom transport is entrusted) transports it, it is recommended that measures be taken to prevent a container that stores PFOS from overturning. The container must be able to withstand the physical impact.

3.2.2.5. Refill

When refilling the PFOS-containing agent:

- Handle PFOS indoors.
- Minimize refills of PFOS.
- Take measures to minimize the amount of scattering or run-off of PFOS.
- Prepare in case of scattering or run-off of PFOS.
- Prepare a cloth and, where necessary, provide a tray under the containers of PFOS- containing products.
- Minimize the amount of PFOS mixing with washing liquid.
- Prevent any PFOS from remaining in equipment that uses PFOS and take measures to recover it as much as possible.

3.2.2.6. Measures for equipment that uses PFOS

A business operator handling PFOS needs to consider the following measures

- Equipment that uses PFOS: use material that is not likely to corrode or take effective measures to prevent corrosion; and try to limit the use of the equipment to only work that uses PFOS.
- Floor on which equipment that uses PFOS is placed: to prevent underground leakage of PFOS, take measures to coat the surface with concrete or synthetic resin.
- Ground and bond all containers and handling equipment.
- Solvents used in these processes will evaporate during the production process. Where scattering of PFOS is expected: install local ventilation equipment and, to prevent releases into the atmosphere, install a dust collector, scrubber or equipment with a similar function.

- Piping from equipment that uses PFOS: use material that is not likely to corrode or take effective measures to prevent corrosion.
- Wastewater that contains PFOS: use discharge pipes or drainage ditches made of material that can prevent underground leakage.

Inspection of containers that store PFOS and equipment that uses PFOS

A business operator handling PFOS needs to regularly inspect the following items:

- Any leakage or scattering of PFOS from a container, equipment, or piping.
- Any damage or corrosion that has occurred to a container, equipment, or piping.
- Any crack or fissure in the floor.

A business operator handling PFOS who, as a result of an inspection, has identified an irregularity in a container containing PFOS, or in equipment that uses PFOS, needs to promptly make repairs and take other necessary measures.

3.2.2.7. Measures to deal with leakage of a container storing PFOS or during refill

A business operator handling PFOS needs to consider the following measures in the event of a leakage of PFOS:

- Notify the proper regulatory agencies about the leakage of PFOS and promptly take emergency measures to prevent its spread.
- Recover leaked PFOS.
- Wear respiratory protection during spill clean-up, remove all ignition sources.
- In case of a small spill, absorb with inert material such as sand or soil. Collect that material and dispose of it appropriately as chemical waste
- Large spills can be prevented by only using the material in small containers (1 gallon or less). In the event of a spill, the product should be captured, collected, and reprocessed or disposed of according to applicable governmental requirements
- Place and store recovered PFOS in a sealable container along with the cloth (or the like) used to wipe up PFOS.

3.2.2.8. Confirmation of release amounts of PFOS

A business operator handling PFOS could consider the following measures:

- Confirm the amount of release of PFOS or its salts by conducting sampling and analysis suitable for confirmation of the amount of discharge water from the place of business.
- If confirmation of release amounts through sampling and analysis is technically difficult, it can be estimated using the usage amount of PFOS.
- If PFOS could be released during refilling, take measures to reduce of release amount of PFOS based on the results of sampling and analysis.

Record the results of the estimated PFOS release.

3.3. Aviation hydraulic fluids

3.3.1. Process description

In the manufacturing process of aviation hydraulic fluids, PFOS-related substances or precursors, such as potassium perfluorooctane sulphonate, were used as an additive, with a content of about 0.1%, to prevent evaporation, fires, and corrosion (UNEP/POPS/POPRC.8/INF/17/Rev.1). 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 kilograms/year in 2009 (Carloni, 2009).

3.3.1.1. Alternative chemistry

There is uncertainty about alternative substances in this area. Aviation hydraulic fluids without fluorinated chemicals but based on, for example phosphate esters, exist, and fluorinated chemicals other than PFOS can be used. A search for alternatives is said to have been going on for the past 30 years. While several different compounds are said to have been tested, neither the fluorotelomers nor the non-fluorinated chemicals have met the performance requirements or the high safety standards of this industry. The potassium salt of perfluoroethylcyclohexyl sulphonate (CAS No. 67584-42-3)⁷ is not a PFOS precursor, and has been used in hydraulic oils instead of PFOS. 3M, which formerly produced this chemical, has ceased its production (UNEP/POPS/POPRC.8/INF/17/Rev.1)⁸.

3.3.2. BAT and BEP measures

- The measures indicated in the previous general chapter on BAT and BEP should be applied.
- Aviation hydraulic fluids should be disposed of by approved disposal methods in accordance with national, federal, state and local guidelines. Presently, the most universally accepted disposal method is incineration in an approved facility.
- Partial reclamation of phosphate ester base stock of spent aviation hydraulic fluids is being practiced. There is no approved reclamation system or known practical technology to completely reclaim spent aviation hydraulic fluids for return to aircraft hydraulic system usage.

3.4. Metal plating

3.4.1. Process description

PFOS is used as a surfactant and wetting agent in order to achieve uniform thickness of the plating or uniform chemical attack of the chromic and sulphuric acid used for etching. Further, it serves as a mist suppressing agent for chrome plating to create a protective foam and decrease aerosol emissions and improve the work environment (UNEP/POPS/POPRC.3/20/Add.5). It was previously used for both decorative chrome plating and hard chrome plating processes, but new technology using chromium-III instead of chromium-VI for certain decorative chrome plating has made PFOS use in decorative chrome plating obsolete. Chromium-III does not work for hard chrome plating, however.

The plating process is an electrolytic process that causes mist and bubbles to be ejected from the plating bath containing plating bath solution. This mist is released to the work place environment and will eventually be dispersed into outdoor ambient air unless controlled with add-on air pollution control equipment or chemical fume (mist) suppressants. Chemical fume (mist) suppressants are surfactants that lower the surface tension of the plating solution. While they reduce bubble formation, they also allow for better wetting of the electrolyte at the electrode and allow for better plating bath penetration into patterned articles. The bubbles can cause defects on the plated articles and also cause mist formation. 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 onto the plating bath surface.

Hard Metal Plating

Hard metal plating, also known as functional hard metal plating, usually refers to the process of electrodepositing a thick layer (0.2mm or more) of certain types of metal directly onto substrates.

⁷ In the U.S. this chemical is considered a C8 PFOS equivalent and its use in hydraulic fluids is regulated under a Significant New Use Rule:https://www.federalregister.gov/articles/2002/12/09/02-31011/perfluoroalkyl-sulfonates-significant-new-use-rule

⁸ Note that uncertainties exist about aviation hydraulic fluids, their composition and additives, and the properties these additives provide.

However, due to new technologies, like thin dense chrome plating, a functional chrome layer can also be considerably thinner. Therefore, the thickness of the layer cannot serve as the sole distinguishing feature. The deposited chrome layer provides the following desirable properties:

- Hardness (in general above the following hardness numbers: 850 Vickers (HV30) or 65 Rockwell (HRC))
- Wearability
- Corrosion resistance
- Lubricity
- Low coefficient of friction

Examples of hard chrome plated parts are:

- Hydraulic cylinders and rods
- Railroad wheel bearings and couplers
- Molds for the plastic and rubber industry
- Tool and die parts

Decorative metal plating

Decorative metal plating, or more precise, plating for decorative applications with functional aspects, refers to a different process than described above, whereby only a thin layer (0.05 to 0.5 μ m) of metal is deposited onto substrates. In terms of decorative chrome plating, for example, the deposited chrome layer provides the following desirable properties:

- Appearance (aesthetically pleasing)
- Non-tarnishing

Examples of decorative chrome plated parts are:

- Car and truck pumpers
- Motorcycle parts
- Kitchen appliances
- Smart phones and tablets

In hard and decorative chrome plating, PFOS is still used because other wetting agents degrade more or less rapidly under the prevailing, strongly acidic and oxidizing conditions. In hard chrome plating and Cr(VI) anodizing tank operations, the plating bath consists of Cr(VI) acid. This acid is a highly oxidative, strong acid that decomposes most types of surfactants. In addition, 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. Emissions to the atmosphere can be reduced by either limiting the amount of Cr(VI) through use of add-on air pollution control devices or utilizing a chemical mist suppressant. PFOS works by lowering surface tension and forming a single foamy barrier on the surface of the chromic acid bath, (see figure 3.4.1), which maintains its aerosol (fog) formation, thus reducing airborne loss of chromium-VI from the bath and decreasing exposure to this carcinogenic agent.



Figure 3.4.1: Foamy barrier on the surface of a chromium bath

The aerosol can also be reduced through optimized covering of the chromic acid bath and optimized exhaustion, or enclosure of the baths.

Electroplating of plastics

In this application, the most commonly used plastic is acrylonitrile butadiene styrene (ABS). It is etched in a first treatment step to partly remove the butadiene from the surface. Currently a highly concentrated solution of chromic and sulphuric acid is used for that. PFOS is used to enable the acids to make wetting of the water-repellent plastic surface possible. Non-fluorinated surfactants, which are not toxic and easily biodegradable, can be used successfully in the etching process if the production line is very constant. As a precondition, the plastic goods have to be dipped into the surfactant liquid before the etching process.

If demands on corrosion resistance and hardness of the surface are low, the physical vapour deposition (PVD) method can replace electroplating processes for decorative applications.

Further electroplating systems

Other uses of PFOS are the alkaline zinc and zinc alloy plating, the electroless nickel dispersion coating and strong acid electrolytes with insoluble anodes, such as precious metal electrolytes (e.g. gold, palladium and rhodium).

It must be taken into account that, due to its high ability to absorb to the surface of most materials, PFOS has a "memory effect" and can be found in the wastewater stream of electroplating plants months (or, in some cases, more than a year) after being substituted (Breidenbach, 2009). Ion exchangers, washing water from exhausters and every contact surface must be purified or exchanged as well as the electrolyte liquid itself.

3.4.1.1. Alternative chemistry

Non-fluorinated alternatives for decorative chromium plating and hard chromium are available on the European market, such as TIB Suract CR-H (UNEP/POPS/POPRC.9/INF/11/Rev.1). They are quite new, and some are still being tested. These biodegradable alternatives seem to work, but require continually adding to and stirring the chromium bath along with some technical changes before these substitutes can be used. Information is currently lacking regarding the processes for which these alternatives can be used and when and why they cannot be used. In the meantime telomer-based surfactants, too, are used as a bridge technology. One of the most common alternatives in electroplating is 1H,1H,2H,2H-perfluoroctane sulfonic acid. Other names are 6:2-Fluorotelomer sulfonate or (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate). It is not fully fluorinated, but the perfluorinated tail is persistent and

can be a precursor of perfluorinated carboxylic acids (Wang et al., 2011, UNEP/POPS/POPRC.8/INF/17/Rev.1). Because it is structurally related to PFOS, its common name is THPFOS (tetrahydro PFOS). In the environment a decrease in the stable perfluorohexane acid (PFHxA) is found. In Canada ATOTECH markets Fumetrol® 140 with PFOS and Fumetrol® 21 without PFOS but with the fluorotelomer derivatives 1H,1H,2H,2H-perfluorooctane sulfonic acid.

In China the available PFOS alternatives used for chrome plating are F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate, CAS no. 756426-58-1), F-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate, CAS RN 73606-19-6), which belong to the class of perfluorohexane sulfonyl fluorides (PFHxSF) (UNEP/POPS/POPRC.9/INF/11/Rev.1).

There is little independent and reliable information available on the toxicological and ecotoxicological characteristics of these polyfluorinated substitutes or their persistence and degradation products. Nevertheless, these substitutes, and in particular their degradation products, are likely persistent in the environment.

According to UNEP/POPS/POPRC.9/INF/11/Rev.1, currently, no other surfactant can match the low surface tension of PFOS. Therefore, the quantity required for substitution of PFOS by polyfluorinated surfactants increases considerably, about 3 to 10 times (Pabon, 2002). On the output side it must be taken into account that it is much more difficult to remove THPFOS or PFBS from the wastewater by adsorption. These alternatives tend to adsorb less to sewage sludge in wastewater treatment plants (e.g. Wang et al., 2011), which could translate into higher releases to the environment than when using PFOS. Therefore, deposits to soil and in particular groundwater, as well as surface water could occur and contaminate sources of drinking water.

Substitution of PFOS by biologically degradable, non-toxic substances would likely be the final solution. Non-fluorinated surfactants are successfully used during the production process for hard chrome plating and decorative chrome plating (Bresselschmidt, 2009). They are not toxic and easily biodegradable. Although they are degraded in the chromium electrolyte or etching bath and must be constantly dosed, the costs are not higher than using fluorosurfactants. Trivalent chromium is formed by chemical degradation in the bath, which has to be oxidized to hexavalent chromium by membrane electrolysis. This is BAT and commonly used for chromium solution maintenance (IPPC, 2006).

3.4.2. BAT and BEP measures

Current BAT and BEP means either using PFOS in closed loop so that hardly any emissions take place (Schwarz, 2011) or using non-fluorinated readily degradable surfactants. The use of polyfluorinated alternatives could only be considered as BAT and BEP if the removal by adsorption technologies or other means were to be considerably improved or the degradation in the environment and/or the ecotoxicological harmlessness was demonstrated.

A current research project is investigating adsorbents with the aim of regeneration so that adsorbed PFOS from process water might be recycled back to the process (Schuricht et al., 2014a, b).

Conclusively, BAT and BEP are as follows:

Chromium-VI-electrolytes in decorative and hard metal plating:

- Provide additional extraction ventilation and/or greater tank enclosure to reduce the exposure of chromium-VI emission to acceptable levels when using chromium-VI both for decorative and hard metal plating.
- Apply new technology using chromium-III instead of chromium-VI in decorative metal plating processes.

Hard chromium plating:

- Apply a closed loop system to replace the traditional open system in hard metal plating processes.
- Substitute PFOS mist suppressing agent with available non-PFOS agent in hard metal plating processes.

Removal of PFOS from the wastewater:

• Collect and dispose of the waste from the metal plating process using PFOS in an environmentally sound manner (UNEP, 2014a and b).

3.4.2.1. Measures to avoid or reduce releases

Prevention of PFOS by changing the production technology

Wherever possible, PFOS-free alternative processes should be used, such as the substitution of chromium-VI electrolytes by chromium-III electrolytes in decorative chromium plating. In some applications the PVD method can replace electroplating processes.

Minimizing input of PFOS by implementing controlled electroplating systems

In the European Union, the specific exemption to use PFOS as a wetting agent applies only to controlled electroplating systems. Such a system can only be considered as controlled if PFOS is dosed as a function of a measured value for a certain purpose. This is often not the case in practice. Although great efforts are often undertaken to reduce the PFOS output, the input side is often considered much less accurately. In some cases, the output can be reduced by up to 50%, only by detailed investigation of PFOS inputs and optimized dosage of PFOS (IPPC, 2006).

BAT to optimize dosage of PFOS includes:

- Measured surface tension of the electrolyte (not in etching plastics)
- The measured ampere hour rate (not electroless nickel and etching plastics)
- A certain defined surface throughput
- The measured foam stability (only in chromium-VI electrolytes)

Closing the material loop

Maximum water-reduced rinsing, extensive material recycling and low carry-over losses by transportation, as well as the reduction of material losses due to process-integrated measures, are the precondition for the next steps (IPPC, 2006).

For hexavalent hard chromium, BAT is to close the material loop by using suitable combinations of techniques such as cascade rinsing, ion exchange and evaporation. When hot electrolytes with high evaporation rates are used, closing the material loop can sometimes be achieved by simple methods such as using a single static rinse in combination with seven rinsing steps in a pumped, very slowly flowing rinsing cascade. But in most cases, an evaporator is required to regain the electrolyte from the rinse water.

In decorative chromium plating, BAT is to close the loop using evaporation for drag-out recovery. An example of this technology, which has been used commercially in decorative plating processes is given below in figure 3.4.2.

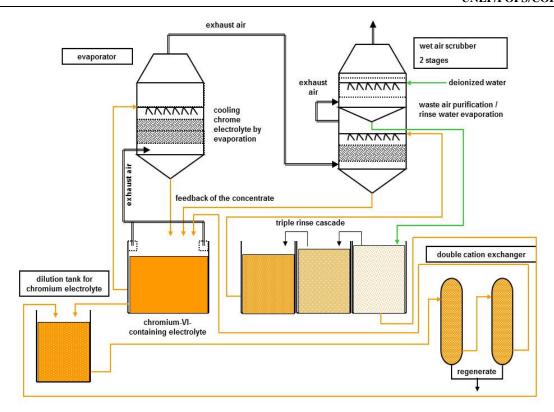


Figure 3.4.2: Closed loop in chromium plating (Hauser, 2011)

Regional weather patterns may affect applicability of evaporation. Cation exchanger resins with high resistance to strong oxidants are used to selectively remove unwanted metal ions. Closing the loop for process chemicals does not mean being free of wastewater. In fact no loop can be held completely closed all the time. Losses of 10–20% of the applied PFOS amount into the wastewater cannot be avoided. Sources for PFOS can be regeneration of ion exchangers, air scrubber effluents, floor water of the plating plant and carry-over effects.

3.4.2.2. Removal of PFOS from wastewater

Removal by adsorption

By selecting suitable activated carbon and optimized flow rates, up to 99% of PFOS can be removed from wastewater by adsorption onto activated carbon (Fath, 2008).

When using special basic ion exchange resins, a reduction of more than 99% of the initial PFOS concentration can be achieved (Zentralverband Oberflächentechnik, 2011). A combination of weak base and strong base anion exchangers is able to reduce the PFOS concentration to <10μg/l (Neumann, 2011).

The recommendations of the Stockholm Convention's COP5, as set out in the annex to decision POPRC-6/2 on risk reduction for PFOS, its salts and PFOSF, to use BAT and BEP destruction technologies for wastes containing PFOS, must be taken into account when using any adsorption method that requires a final destruction of PFOS contained in the adsorbent at the end-of-life so as not to deposit such PFOS-containing wastes improperly. The destruction could for example be done in a BAT hazardous waste incineration plant at temperatures of at least 1100 °C and with a residence time of 8 seconds (Ministry of Environment of Japan, 2013). The technical guidelines under the Basel Convention as referred to in section 1.5 should be taken into account (UNEP, 2014a and b).

Figure 3.4.3 shows a flow diagram of an almost closed system with optimized PFOS adsorption, which is used in plastic plating processes. The use of evaporators is a costly investment but is amortized over a few years.

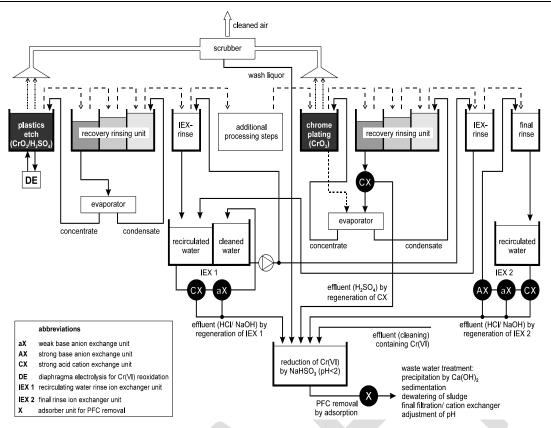


Figure 3.4.3: Process and systems engineering for chromium plating on ABS plastics (Schwarz, 2011)

With this combination of recycling of rinse water, ion exchangers, evaporators, air scrubber, and finally a two-step adsorption unit, a return or elimination of PFOS by > 99% can be permanently achieved. The separation of PFOS using activated carbon or ion exchangers is realized at a central point in the conventional process of chromium (VI) reduction (Schwarz, 2011).

Photochemical decomposition in the wastewater stream

Photochemical degradation of PFASs seems to be useful technique because significant photodegradation of PFASs, including PFOS and some alternatives (perfluoroalkyl sulfonates and perfluoroalkyl calboxylates) in the environment was observed recently. Fifteen to sixty percent of PFASs in test solution were decomposed under irradiation period (106 days) of natural sunlight at high altitude mountain. Degradation potency was higher in longer chains PFASs compared to shorter chains (Taniyasu et al., 2013).

Furthermore, efficient decomposition of perfluorocarboxylic acids (PFCAs) in water by use of persulphate ion $(S_2O_8^{2^-})$ was reported. Photolysis of $S_2O_8^{2^-}$ produced highly oxidative sulphate radical anions (SO^{4^-}), which efficiently decomposed perfluorocatanoic acid (PFOA) and other PFCAs including C4-C8 perfluoroalkyl groups. PFOA at a concentration of 1.35 mM (typical of that in untreated wastewater after an emulsifying process in fluoropolymer manufacture) was completely decomposed by a photochemical system with 50 mM $S_2O_8^{2^-}$ after 4 hours of irradiation from a xenonmercury lamp (200W). The major products were F- and CO_2 and nearly complete decomposition can be expected (Hori et al., 2005). Further, Jin et al. 2014 found that photodecomposition of PFOS under UV was greatly accelerated by addition of ferric ions.

Decomposition using subcritical water

Subcritical water with zerovalent metals revealed significant degradation of PFOS in test solution of wastewater. Among tested metals (Al, Cu, Zn, Fe), use of iron led to the most efficient PFOS decomposition. Concentration of PFOS in test solution with iron powder decreased to the less than 2% of original solution after heating at 350 °C for 6hrs. Spectroscopic measurements indicated that PFOS in water markedly adsorbed on the iron surface even at room temperature, and the adsorbed fluorinated

species on the iron surface decomposed with rising temperature, with prominent release of F- ions to the solution phase above 250 °C (Hori et al., 2006).

This method was also effective in decomposing other perfluoroalkylsulfonates including shorter chain (C2-C6) perfluoroalkyl groups and was successfully applied to the decomposition of PFOS contained in an antireflective coating agent used in semiconductor manufacturing (Hori et al., 2006). Further details on subcritical water oxidation are found in UNEP (2014a).

Other techniques

Emerging technologies that have not fully proven their efficiency in removing PFOS and PFOS-related substances from wastewater are listed in the annex to the present document.

3.5. Certain medical devices

3.5.1. Process description

PFOS and PFOS-related substances have been used in critical parts of certain medical devices. Video endoscopes contained 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.

3.5.1.1. Alternative chemistry

It is technically possible to produce PFOS-free CCD filters for use in new equipment. For use in EFTE copolymer layers, PFBS replaced PFOS as a dispersant of contrast agents in EFTE layers for radio-opaque catheters.

3.5.2. BAT and BEP measures

The general measures indicated in Chapter 2 should be applied.

3.6. Fire fighting foam

3.6.1. Process description

Aqueous film-forming foam (AFFF), sometimes referred to as aqueous fire fighting foam, is a generic term for fire fighting and/or vapour suppression products used globally to protect both lives and property. AFFFs are unique among other fire fighting foams in that they contain a small percentage of fluorinated surfactant (fluorosurfactant). This key ingredient brings unique performance attributes to the product, which enables it to be extremely effective in preventing and extinguishing fires, especially Class B flammable liquid events. AFFF agents are formulated by combining synthetic hydrocarbon surfactants with perfluorinated 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. 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 mixture ratio (during use) with water.

Not every situation will necessarily require the use of fire fighting foams. Selection of the correct product can only be determined by a careful consideration of the specific situation at hand (emergency incident or design of life/property protection system) and review of local building codes and other regulations. It is important to remember that foams have proven to be highly effective for their intended purpose.

3.6.1.1. Types of foams

Foams have been developed for both Class A (solid combustibles such as paper and wood) and Class B (flammable liquids) fires. AFFFs were designed to be especially effective in dealing with Class B incidents.

Class B foams have two major categories: synthetic foams and protein foams.

Synthetic foams

AFFFs and alcohol-resistant AFFFs (AR-AFFFs) are synthetic foams based on synthetic hydrocarbon and fluorinated surfactants. AR-AFFFs are designed to be effective in the presence of alcohols and other water miscible compounds. This category also encompasses training foams that are used as AFFF and AR-AFFF substitutes in training and system commissioning tests, Class A foams used primarily as wetting agents for Class A fire protection and wildland/forestry protection, and other foam concentrates derived from synthetic and hydrocarbon surfactants such as fluorine-free foams..

Protein foams

Protein foams contain natural proteins as foaming agents and, as such, are not more or less biodegradable than synthetic foams. Types of protein foams include regular protein foam (P), fluoroprotein foam (FP), film-forming fluoroprotein foam (FFFP), alcohol-resistant fluoroprotein foam (AR-FFP), and alcohol-resistant film-forming fluoroprotein (AR-FFFP).

3.6.1.2. Alternative chemistry

The chemicals used to make the fluorosurfactants that are a key ingredient in AFFF have been manufactured by different processes and have different chemical structures.

Prior to 2000, fluorosurfactants used in AFFFs were often PFOS-based, which resulted in AFFFs that contained 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 manufacturing phase-out announcement by 3M of PFOS-based products in 2000, PFOS-based AFFFs were generally no longer available in industrialized countries. The primary supply of AFFF then became fluorotelomer-based. Over the last several years, manufacturers of fluorotelomer AFFF have been replacing long-chain fluorosurfactants with shorter-chain fluorosurfactants. In the European Union, PFOS containing AFFF were ultimately phased out by 2011.

The alternatives to the use of PFOS fluorosurfactants in fire-fighting foams are (UNEP/POPS/POPRC.9/INF/11/Rev.1):

Non-PFOS-based fluorosurfactants with shorter chain length such as:

- C6-fluorotelomers such as perfluorohexane ethyl sulfonyl betaine, often used in combination with hydrocarbons such as Capstone® products (DuPont);
- Dodecafluoro-2-methylpentan-3-one (3M);

A return to the previously used technology, which employed fluorine-free fire fighting foams. Examples include:

- Silicone-based surfactants, often used in combination with fluorosurfactants;
- Hydrocarbon-based surfactants, often used in combination with fluorosurfactants;
- Synthetic detergent foams, often used for forestry and high-expansion applications and for training ("Trainol"); new products with glycols (Hi Combat ATM from AngusFire);
- Protein-based foams (e.g. Sthamex F-15), which are less effective for flammable liquid fuel fires and are mainly used for training but also have some marine uses.

3.6.1.3. Choosing an AFFF

The choice of foam to be used in any specific situation needs to be carefully made, taking into consideration numerous factors. Fire protection experts clearly need to have a lead role in making these decisions. When evaluating foam for use in preventing or fighting a fire, several factors could be considered:

• Is any type of foam actually needed? For example, in a Class A incident, it may not be necessary to use any foam to control the situation.

- If use of a foam is deemed appropriate and/or necessary, does it need to be a Class B foam? While Class B foams may be quite effective on Class A fires, other techniques may be equally effective and more appropriate.
- If a Class B (flammable liquids) situation presents itself, which type of Class B foam would be most appropriate and most effective?
- For situations calling for the use of AFFF or AR-AFFF, has consideration been given to using the latest products available on the market? This question may also surface as the inventory of existing AFFF ages and routine performance evaluations may point to the need to replace a product.

3.6.2. BAT and BEP measures

AFFF products are extremely effective in protecting lives and property, and this guidance is not intended to discourage the use of AFFF for fire protection services. There are numerous available techniques and environmental practices, however, that can be employed to minimize the possibility of unintended or unnecessary releases and mitigate impacts in the event that an incident occurs (see for instance Industrial Fire Journal, 2014). Finally, residual materials could be appropriately managed.

3.6.2.1. Inventory management

Inventory identification

A list of fire protection systems and associated types and amounts of AFFF used in each system or piece of equipment may be developed and maintained. When product identification is uncertain, the services of an analytical laboratory may be helpful. Product information sheets (i.e. MDSD) could be available at a facility where AFFF is in use. This information could be vital in the event of an incident. It is practical that containers or vessels (tanks) used to store AFFF concentrate are clearly marked concerning their contents.

Inventory review

It is important to periodically review the inventory of fixed and portable systems that contain AFFF in order to determine the ongoing need for use of these products in each specific location. Over time, use and fire protection classification of areas can change significantly. As appropriate, fire protection personnel would be involved in these determinations. AFFF that is no longer needed at any given facility or location could be removed and appropriately disposed of. As part of this review, the age of products in the inventory could be considered along with the possibility of replacement by newer products.

3.6.2.2. Training with foams

Training of emergency response personnel is a critical step to ensure that timely and appropriate actions can be taken in the event of an emergency. Relative to practice exercises on extinguishing fires, practice foams that do not contain fluorosurfactants can be readily available and used, unless special circumstances warrant otherwise.

3.6.2.3. Prevention of unintended releases

It is important that unintended or unnecessary releases to the environment be minimized as much as possible. Towards this end, this section includes a list of actions that can be applied to help prevent an unintended release at a facility and/or mitigate the impacts of such a release to the environment.

Secondary containment

- Review adequacy and integrity of secondary containment systems that may be utilized in the event of a potential release.
- Upgrade these systems, as necessary, based on the assessment performed.

Testing of fire protection systems

- Review procedures to test fire protection systems and modify as needed to ensure containment or capture of any AFFF-containing solution.
- Avoid releases to sewers or soils need in testing activities.

Evaluation of sprinkler systems

- Survey sprinkler systems to identify the potential for accidental discharge. Consider areas where sprinkler heads could be physically damaged (e.g. vehicular traffic). Evaluate the potential for ambient air temperature or system pressure excursions to trigger a discharge.
- Evaluate options and make changes as deemed necessary.

Preventative maintenance

 Regularly perform preventative maintenance on sprinkler systems, including backflow prevention valves.

Emergency procedures

• Establish/modify site-specific emergency procedures to incorporate the options proposed in this guidance (see also section 4.3.4).

Training

• Conduct training, especially for plant maintenance and emergency response personnel, on this guidance (see also section 4.3.4).

Container integrity

- Regular inspection of containers and vessels (tanks) used to store AFFF concentrate. Integrity of related secondary containment areas could also be included in this procedure.
- Record inspection results.

3.6.2.4. Response to a release

Response actions

The following guiding principles could be used for responses to an AFFF release:

- Minimize intentional release of material or rinse water onto soil.
- Avoid discharge of released material or rinse water into a sanitary or storm sewer.
- Minimize the volume of impacted materials to the greatest extent possible.

These principles could also be incorporated into a facility's emergency response plans and procedures. Again, execution of this guidance should not compromise protection of life or property in the event of an emergency.

The initial response to a release can be critical in terms of minimizing possible impacts. Possible immediate actions that could be taken following a release to prevent/mitigate the migration of the release into the environment include:

- Use close containment or isolation valves
- Use secondary containment
- Place released material into secure containers as soon as possible (if plausible)
- Build a dam to contain/control run-off
- Block a trench
- Install a sewer plug

- Divert released material into a containment pond
- Pump released material into a septic system pumper truck or vacuum truck
- Use a defoamer to reduce foam volumes
- Place impacted soils on plastic and cover to prevent run-on and run-off
- Add adsorbent

The above list is only intended to suggest possible actions that could be taken and is not necessarily exhaustive. It would be beneficial that each facility has a site-specific response plan that appropriately considers and incorporates relevant actions and procedures, some of which may be listed above.

Documenting a release

It is also important to quantify and document any release that occurs including estimations of the amount of AFFF released, the nature of the release (i.e. concentrate or dilute), and the amount of materials impacted (i.e. soil, water, etc.). Two ways to quantify a release from fire protection systems are to:

- Calculate the amount based on how long the fire suppression system operated
- Measure the amount of AFFF concentrate remaining in the system following the incident and compare it to the inventory before the release

Release notification

Prompt and appropriate notification concerning a release is another critical element. Notification requirements and procedures would vary depending on where the AFFF release occurred, the nature of the release and governmental reporting requirements (considerations could include potential impacts to drinking water supplies, release to a sensitive environmental area, magnitude of the release, involvement of outside parties, etc.). Site-specific notification requirements and procedures could be clearly outlined in facility emergency response plans and be reviewed as part of routine training.

3.6.2.5. Management of residual (waste) materials

Specific actions relative to the management of waste are determined on a case-by-case basis. Technical guidelines for the environmentally sound management of POPs wastes have been adopted or are under development under the Basel Convention as referred to in section 1.5. For the general technical guidelines, see UNEP (2014a) and for detailed guidelines on the environmentally sound management of PFOS-containing waste see UNEP (2014b).

BAT in dealing with AFFF concentrate and concentrated rinse water is high temperature incineration at a facility designed to handle halogenated waste streams. Small volumes of solid materials (soils, absorbent materials, etc.) that contain higher levels of AFFF can be handled in a similar fashion.

According to experiments on destruction of PFOS contained in wastes conducted by the Ministry of Environment, Japan, destruction could be done in an incinerator which consists of a primary furnace (a rotary kiln) at temperature of 1100 °C and secondary furnace at temperatures of 900° C, with the combined gas retention time of approximately 8 seconds (Ministry of Environment of Japan, 2013).

When AFFF exists in a dilute solution (e.g. collection of water resulting from an accidental triggering of a sprinkler system), treatment using granular activated carbon may be an option. Carbon vendors can be contacted for assistance if the treatment is to occur on site, or off-site wastewater treatment facilities with tertiary treatment can be considered (Chaudhary et al., 2003; RPA and BRE Env., 2004; Herrera, 2008; Qu et al., 2010). The exhausted granular activated carbon used to remove PFOS and PFOS-related substances in dilute AFFF solutions should be treated in an environmentally sound manner (see UNEP, 2014a and b).

In situations where dilute AFFF has been applied on top of fuel to prevent or extinguish a fire, the analysis of potential residual management options can become quite complex. Treatment using granular activated carbon may be a viable option although pre-treatment steps may be required to extend the life of the carbon in removing perfluorochemicals. Use of reverse osmosis coupled to electrocoagulation-

filtration has also recently been reported as a possible means to treat fire fighting water (Baudequin et. al., 2011).

There is ongoing research to develop innovative treatment technologies to remove PFCs from wastewater streams (see Herrera, 2008; Senevirathna, 2010).

3.7. Insecticides

3.7.1. Process description

N-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2) is both a surfactant and a pesticide used in tropical areas against termites, cockroaches and other insects and in Brazil for control of leaf-cutting ants from the species of Atta spp. and Acromyrmex spp. According to UNEP/POPS/POPRC.3/20/Add.5., sulfluramid had been used for pest control (to control cockroaches, white ants and fire ants) in China, and is used in Brazil in more than 95% of baits for the control of leaf-cutting ants, although the amount of PFOS used was not reported. Since 10% of sulfluramid is degraded to PFOS, its use represents a direct release of PFOS to the environment. PFOS is no longer used to manufacture ant bait or insecticides against beetles and ants in the European Union, and the United States Environmental Protection Agency cancelled the registration of sulfluramid in May 2008.

The production of sulfluramid is often carried out in a closed system, with no releases (discharges, losses, or emissions). The best available process results in a product with purity of at least 98%. Sulfluramid was introduced in Brazil in 1992, after verification of its efficiency with many leaf-cutting ant species, replacing the active ingredient dodecachlor. In addition, the following active ingredients are registered and in use in Brazil for the control of leaf-cutting ants: fenitrothion (in the form of thermo-nebulization) and deltamethrin (in powder form).

Sulfluramid is the active ingredient in the manufacturing of ant baits in ready-to-use formulations (3g/kg) for the control of leaf-cutting ants from the species of *Atta spp.* and *Acromyrmex spp.* The active ingredient is effective after ingestion and presents a so called retarded action. The baits are presented in granular form (pellets), and used in local application next to the holes of the anthill.

Granulated baits represent the most widely used method for leaf-cutting ants control, consisting of a mixture of an attractive substrate (vehicle) (usually dehydrated citric pulp from the orange juice industry and vegetable oil) and an active ingredient (insecticide), presented in the form of pellets. This method seems to be low-cost that delivers high efficiency with reduced acute health hazards to humans and the environment during application, and it is specific to the pest target. Its localized application does not require application equipment. Baits are "ready to use" 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.

In addition to their function as pesticides, fluorosurfactants may be used as "inert" surfactants (enhancers) in pesticide products. The two PFOS-related substances, potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS No. 2991-51-7) and 3-[[(heptadecafluorooctyl)sulfonyl]amino]-*N*,*N*,*N*-trimethyl 1-propanaminium iodide (CAS No. 1652-63-7), have been approved in pesticide formulations in the United States in the past. Both chemicals have other uses, for example as cleaning agents. PFOS derivatives were used in pesticides because they were considered rather inert and non-toxic to humans.

3.7.1.1. Alternative chemistry

Currently, the active ingredients registered in Brazil for producing baits to control leaf-cutting ants are sulfluramid, fipronil and chlorpyrifos. The latter two, however, are considered more acutely toxic to humans and the environment than sulfluramid. Furthermore, the effectiveness of these substances has been questioned; thus new alternatives are being studied in Brazil. According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose (UNEP/POPS/POPRC.9/INF/11/Rev.1).

There are many differences between leaf-cutting ants and exotic ants (urban ants), including in alimentary behaviour. Such differences explain why certain active ingredients are effective for controlling urban ants

and not for controlling leaf-cutting ants. Fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone and methoprene had been tested for leaf-cutting ants, but they were not effective.

There are a number of chemical alternatives to sulfluramid, with a multitude of uses: Chlorpyrifos, Cypermethrin, mixture of Chlorpyrifos and Cypermethrin, Fipronil, Imidacloprid, Abamectin, Deltamethrin, Fenitrothion, mixture of Fenitrothion and Deltamethrin.

3.7.2. BAT and BEP measures

Several non-chemical control methods for red imported fire ants (RIFA) and termites have been evaluated for effectiveness (UNEP/POPS/POPRC.8/INF/17/Rev.1). Biological controls for RIFA include a group of decapitating phorid flies (*Pseudacteon spp*) which parasitize the ants. The microsporidian protozoan *Thelohania solenopsae* and the fungus *Beauveria bassiana* are also promising controls for RIFA. Three viruses, SINV-1, SINV-2, SINV-3, have been found infecting fire ants in the field, and two of these, SINV1 and 3 appear to be associated with significant mortality, indicating their potential as biological control agents. Other potential biological controls include the endoparasitic fungi *Myrmecomyces annellisae* and *Myrmicinosporidium durum*, and the parasite *Mattesia sp*. Biological control options for termites include Beauvaria bassiana and Metarhizium anisopliae.

As for sulfluramid-based ant baits application, BEP could consider the following actions:

- 1. Assessment of infestation in the areas
- 2. Estimation of bait consumption
- 3. Qualification and periodical training of control teams
- 4. Recommendation of method and period for application
- 5. Placement of granular pellets in proper location (avoid overdose)
- 6. Assessment of bait consumption and control efficiency
- 7. Disposal of left-over granular pellets according to information provided by the manufacturer
- 8. Elaboration of a database for constant improvement of monitoring

Precautions taken to ensure the safety of appliers concerning health hazards include the use of personal protection equipment, such as boots, gloves, protective masks and long-sleeve overalls, as specified in the product label. Additionally, periodical examinations are adopted, which are included in local or national labour safety rules.

3.8. Electric and Electronic Parts for Some Colour Printers and Colour Copy Machines

3.8.1. Process description

Electrical and electronic equipment often requires hundreds of parts and thousands of processes. PFOS has many different uses in the electronics industry and is involved in many of the production processes needed for electric and electronic parts (see figure 3.8.1). PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, radar systems and the like. The PFOS-related compounds are used as process chemicals, and the final products are considered as mostly PFOS-free. 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. Industry groups reported that alternatives are currently not available for those applications (UNEP/POPS/POPRC.9/INF/11/Rev.1).

PFOS and PFOS-related substances have many different uses in the electronic industry and are involved in a large part of the production processes needed for electric and electronic parts that include both open and close loop processes. Open processes are applied for solder, adhesives and paints. Closed loop processes mostly include etching, dispersions, desmear, surface treatments, photolithography and photomicrolitography. PFOS can be used as a surfactant in etching processes in the manufacture of compound semiconductors and ceramic filters. PFOS is then added as part of an etching agent, and rinsed out during the subsequent washing treatment. Desmear process smoothes the surface of a through-hole

in printed circuit boards. PFOS can be used as a surfactant in desmear agent, i.e. etching agent. PFOS is added in a desmear agent, and rinsed out during washing treatment

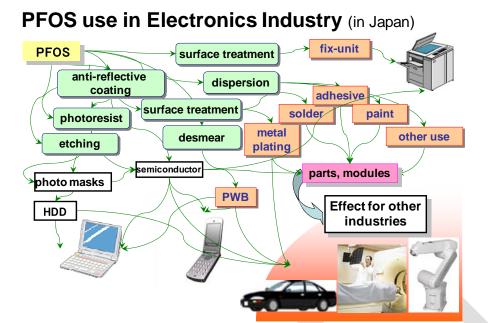


Figure 3.8.1: PFOS use in electronics industry supply chain (Japan Electronics and Information Technology Industries Association Semiconductor Board)

3.8.2. BAT and BEP measures

The measures specified in Chapter 2 and 3.2 are applicable to these processes.

3.9. Chemically driven oil and gas production

3.9.1. Process description

It is reported that PFOS is used in some parts of the world as surfactants in oil well stimulation to recover oil trapped in small pores between rock particles. Oil well stimulation is in general a variety of operations performed on a well to improve its productivity. The main two types of operations are acidization matrix and hydraulic fracturing.

3.9.1.1. Alternative chemistry

Alternatives to PFOS are PFBS, telomer-based fluorosurfactants or polymers, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids. In most parts of the world where oil exploration and production are taking place, oil service companies engaged in provision of well stimulation services predominantly use formulation of alcohols, alkyl phenols, ethers, aromatic hydrocarbons, inorganic salts, methylated alcohols, alipathic fluorocarbons for oil well stimulation. Oil well stimulation services also involve corrosion control, water blocks/blockage control, iron control, clay control, paraffin wax and asphaltene removal and prevention of fluid loss and diverting. Enhanced oil recovery operations have imbibed global best practices.

3.9.2. BAT and BEP measures

BAT measures include the following:

- **Step 1**: All arrangements put in place to avoid/prevent occupational health and safety hazards including ensuring the availability and use of personal protective equipment (PPE), review of checklist for spillage prevention and control and selection/use of relevant and applicable equipment and machinery.
- **Step 2:** All relevant equipment items including those for stimulation, coil tubing and nitrogen storage and circulation unit mobilized on site.

- **Step 3:** Stimulation equipment is connected to the wellhead and pressure testing is carried out at pressures of up to 4,500 psi for 15 minutes to ensure that system is leakproof. The system is bled off to zero.
- Step 4: The injectivity test is carried out by opening the lower master valve on well, 3% NH₄Cl is injected and the flow rates recorded against corresponding pressures. This is to ensure that the formation is open enough to accept the acid treated fluid. If injectivity is less than 0.5 barrels per minute (bpm) at less than fracture pressure, further assessment of the well will need to be made.
- **Step 5**: Mix the acid treatment as stipulated in the recipes once injectivity of well is established.
- **Step 6**: Acidize the formation intervals as follows:
 - Pump acid preflush (fresh water, corrosion inhibitor, hydrochloric acid, iron sequestering agent, surfactant, mutual solvent and phosphonic complex).
 - Follow with main treatment flush (fresh water, corrosion inhibitor, surfactant, clay stabilizing agent, iron sequestering agent, phosphonic acid, ammonium fluoride and hydrochloric acid).
 - Pump after-flush (fresh water, ammonium chloride, mutual solvent, surfactant, fine stabilizer and clay control).
 - Pump displacement fluid (3% ammonium chloride of tube volume amount) to top of perforation.
- **Step 7**: Open the upper master valve gradually and produce immediately the spent acid from the formation and neutralize with soda ash in the flow back tank. If the well does not flow naturally, run in the coil tubing to carry out gas lift with nitrogen gas.

3.10. Carpets, leather and apparel, textiles and upholstery

3.10.1. Process description

Fluorosurfactants and polymers have been used to treat textiles and leather to provide oil and water repellence and soil and stain release properties. Fluorinated polymers are used to render textiles stain-and waterproof when required, but they also have to keep their breathability (air and water-vapour permeability). They are mainly applied to home textiles like upholstery and to outdoor wear, especially work wear including uniforms and shoes.

Fluorinated polymers may also be applied during manufacturing of carpets made from both synthetic and natural fibres (e.g. wool) to provide stain and soil protection. Of paramount importance is the ability to repel oily soil. The products are typically aqueous dispersions of fluorinated polymers that are applied to the surface of a carpet by either spraying or applying by foam application an aqueous solution of the fluorinated polymer immediately followed by drying. The fluorinated polymer is designed to adhere strongly to the carpet fibres and withstand abrasive wear and cleaning.

The earliest applications used fluorosurfactants. These were quickly replaced, however, with high molecular weight fluorinated polymers, most commonly either PFOS-related or fluorinated poly(meth)acrylates based on fluorotelomer chemistry, also denoted as side-chain fluorinated polymers. The side-chain fluorinated polymers are typically aqueous polymer dispersions that are diluted and then applied to the textile, leather or paper, and then dried on. The polymers are designed to strongly adsorb and, in some cases, chemically bond to the textile, leather or paper fibre. For textiles and leather, the polymers are designed to perform after multiple cleanings/washings and last the lifetime of the treated article.

The main PFOS derivatives (normally 2–3% of the fibre weight for textiles but 15% for carpets) previously used for textile and carpet surface treatment applications were the acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE).

Finishing processes

Generally, finishing operations can be divided into a variety of mechanical finishing processes by applying a surface coat or through impregnation of a surface of paper, textile, leather or some other material.

The overall objective of finishing is to enhance the appearance of the finished product and to provide the performance characteristics expected of the finished product with respect to colour, gloss, handle, flex, adhesion, and rub fastness; as well as other properties including extensibility, break, light- and perspiration fastness, water vapour permeability and water resistance as required for the end use.

A wide range of mechanical finishing operations may be carried out to improve the appearance and feel of the finished articles (IPPC, 2003).

The purpose of applying a surface coat is to provide:

- Protection from contaminants (water, oil, soiling, etc.)
- Colour to modify dyed colour, reinforce colour provided by the dyes, even the colour or disguise defects
- Modifications to handle and gloss performance
- Attractive fashion or fancy effects
- Modifications to meet other customer requirements

Coating and printing processes

These processes involve the application of a thin film or paste of a functional material — in this case a fluorchemical product — to materials such as paper, fabric, film, foil or sheet stock.

There are various coating techniques on the market⁹, including:

- Gravure coating
- Reverse roll coating
- Knife over roll coating "gap coating"
- Metering rod coating
- Slot die (Slot, Extrusion) coating
- Immersion (Dip) coating
- Curtain coating
- Air knife coating

Impregnation processes

Fluorochemical repellents are usually applied in combination with other finishing auxiliaries by a pad-dry-cure process, as shown in figure 3.10.1.

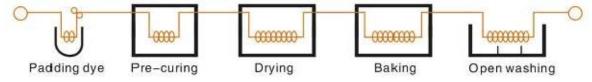


Figure 3.10.1: General principle for the pad dry cure process (IPPC, 2003)

Note: Baking is sometimes called curing or fixation.

⁹ For a description of the coating process see section 3.12.

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 fluorochemical, with a corresponding reduction in costs for this treatment. Finishing treatments with fluorochemical repellents produce emissions of VOCs in exhaust air. These emissions are attributable to the following:

- The solvents contained in the formulations (ketones, esters, alcohols, and diols).
- The "extenders", which under high-temperature conditions give rise to cracked by-products such as alcohols and ketones, but also oximes and in particular butanoxime (which is carcinogenic).
- The organofluoro components, which also release cracked fluororganic by-products.

With respect to water pollution, it has to be taken into account that polysiloxanes, melamine and fluorocarbon resins are all characterized by poor biodegradability and bioeliminability (IPPC, 2003).

3.10.1.1. Alternative chemistry

In these applications, PFOS has been replaced mainly with shorter-chain analogues and fluorotelomers but also with non-fluorinated chemicals.¹⁰ The alternative polymers for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles are (UNEP/POPS/POPRC.9/INF/11/Rev.1):

- a) Other polyfluorinated compounds with shorter alkyl chain length such as:
 - i. Substances based on PFBS (Scotchgard™ from 3M);
 - ii. fluorotelomer-based substances, including polymers (Capstone® from DuPont and similar products from Asahi, Daikin, Clariant, Rudolf Chemie and others);
- b) Hyperbranched hydrophobic polymers (dendritic i.e. highly branched polymers; e.g. Bionic Finish Eco® from Rudolf Chemie)
- c) Silicone-based products;
- d) Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins;
- e) Fluorotelomer silicones such as polyfluorooctyl triethoxy silane used in a bathroom floor spray product. This and similar substances were banned in Denmark in April 2010 because of toxic effects.

Non-fluorinated alternatives such as hydrocarbon waxes and silicones can provide durable water repellence but do not provide oil repellence or soil and stain release. Hyperbranched hydrophobic polymers (dendrimers) and specifically adjusted comb polymers as active components is one example of nonfluorinated alternative that can provide superhydrophobic surfaces (but does not provide oil repellency, soil and stain release).

As an alternative technology for stain protected residential carpets, inherently stain-resistant (but not soil resistant) polyester carpet fibres are offered for residential use.

3.10.2. BAT and BEP measures

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

- Use of applied fluorochemicals and auxiliaries with known and less hazardous characteristics that do not contain, transform into or emit PFOS and related substances.
- Elimination of the polymer, its side products (impurities) and degradation products in the wastewater treatment that result in PFOS.

¹⁰ In the European Union, the use of PFOS is not allowed for these applications.

- 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 reuse is possible.
- 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
 - o 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

For additional details on BAT and BEP for these applications see IPPC (2003), IPPC (2013), Carpet Institute of Australia Limited (2014) and FluoroCouncil (2014).

3.10.2.1. Minimization/optimization of chemicals used

Perfluoroalkyl-based water-and oil-repellent chemicals are not biodegradable. In the past products with high fluorine content (9-13% wt F) have been used to achieve good effects. These products and the FC-polymers are persistent and also might break down and/or release low-molecular perfluorinated chemicals.

Developments during the past years have shown that, with the improved affinity of the perfluorinated chemicals to the applied surfaces, the amount of fluorocarbon that contains the persistent fluorinated carbon chain with the potential of being degraded into PFOS could be significantly reduced without a significant loss of performance.

BAT and BEP for these applications are to:

• Use fluorine-free water-repellent agents, when oil and soil-repellency is not demanded at the same time, and the corresponding specification of requirements for the finish allow their use.

- Avoid surplus of applied chemicals and auxiliaries.
- Use crosslinking agents that help with the film formation and increase washing durability.
- Use extenders with the ability of improving the self-organization of the FC-polymer and safe fluorocarbon-polymer.
- Work with proper curing conditions to get an optimum orientation and cross-linking of the fluorocarbon finish on the textile.
- Make sure the fabric for the application is free of substances that could disturb the selforganization of the fluorocarbon, such as detergents or rewetting agents.
- Avoid spray application if possible.
- 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.

3.10.2.2.Application of hydrophobic finish of textiles and upholstery in impregnation processes

The following process could be used to minimize the impact on the environment and to secure a safe working environment.

Delivery and storage of the product

The aqueous emulsions are supplied in drums or intermediate bulk containers (IBCs) and stored in the warehouse of the mill. Each chemical is stored according to the instruction given by the manufacturer in the SDS. All areas where chemicals are stored or spillages are likely to occur are bunded and it is impossible for spillage to enter surface waters or sewers. Toxic and dangerous chemicals are stored separately. Reject dented or leaking containers upon delivery.

Preparation of the application liquor

The aqueous emulsion of the polymer is diluted with water in the preparing vessel. The typical concentration is 10–80 g/l. Measure, mix and dose chemicals carefully to avoid losses and minimize residual liquor by calculating exactly how much liquor has to be prepared.

The worker takes the required amount of product (according to the recipe instructions) from the IBC or container with a bucket and charges it into the preparing vessel. Protective gloves made of nitrile rubber, safety glasses and protective work clothing are recommended as personal protection equipment, without which the worker may be exposed to the PFOS-containing products. After use, the bucket is rinsed with water, which is added to the application liquor and diluted with the residual amount of water.

Transfer of the application liquor

The application liquor is transferred using a closed piping system. Transfer of chemicals from storage to machine is often prone to leakage or spillage. Pumps and pipework used for transfer must be regularly inspected and provisions should be made to ensure the safety of manual transfer (including appropriate training of workers, use of buckets with leak-proof lids, etc.)

Finishing of the fabric

The fabric is immersed in the application liquor and then squeezed off with the padder rolls. The squeezed-off application liquor runs back into the padder (add-on application equipment).

Finishing time is approx. 2 to 8 hours, with one worker responsible for process control. Use of displacers in the padding device (Foulard) reduces required liquor volume. Use low add on techniques and optimize process sequences in production to minimize waste in between runs.

Drying and condensation

The fabric runs into the stenter (drying oven) where it is dried and cured. The typical drying and condensation temperature is between 150° C and 180° C. During this step all volatile components (water and organic solvents) evaporate. It is recommended that the exhaust air, which may contain PFOS-containing vapours, is passed on to an exhaust air treatment system (e.g. a combination of condensation and scrubbing followed by electrostatic precipitation (ESP) or the use of thermal combustion with energy recovery).

Cleaning of the equipment

The equipment (preparing vessel and padder) is rinsed with small quantities of water. The washing water is normally added to the residual application liquor.

BEP is to reuse the residual application liquor and save it for the next production batch. If this is not possible, it has to be disposed of according to the local or national regulations for industrial wastewater. Collect liquors containing fluorinated repellent for separate treatment, including the rinsing bath from cleaning the application system. Consult SDS section 13 for guidance.

The wearing of protective gloves made of nitrile rubber, safety glasses and protective work clothing as personal protection equipment is recommended during the cleaning of equipment.

3.11. Paper and packaging

3.11.1. Process description

Fluorinated chemicals are used in the paper industry to produce waterproof and greaseproof paper. 1.0–1.5% concentration of fluorochemical, based on the dry weight of the fibres, is typically used. Fluorinated compounds are thus applied only in a small part of the overall paper market (approximately 8%), targeted towards specialty papers for which grease protection is necessary. Such types of coated papers are of special importance in the food industry.

Similar to carpets, textiles and leather, PFOS itself is not directly applied but is part of a polymer. Again, some PFOS remains as impurity in the polymer, which gives rise to the residual PFOS content, typically in the range of 1% (Kara et al., 2010). For a description of finishing and impregnation processes, see section 3.10.1.

PFOS derivatives have been used both in food contact applications such as plates, food containers, popcorn bags, pizza boxes and wraps and in non-food contact applications such as folding cartons, containers, carbonless forms and masking papers. Paper protection by PFOS derivatives has been achieved by using one of the following:

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

Before 2000 about 32% of the total use of PFOS in the European Union was for paper coating; the use of PFOS for this purpose is no longer allowed and PFOS has been replaced mainly by other fluorinated chemicals.

Perfluorooctyl sulfonamido ethanol-based phosphates were the first substances used to provide grease repellence to food contact papers. Fluorotelomer thiol-based phosphates and polymers followed. Currently polyfluoroalkyl phosphonic acids (PAPs) are used in food-contact paper products and as eveling and wetting agents. Since paper fibers and phosphate-based fluorinated surfactants are both anionic, cationic bridge molecules need to be used in order to ensure the electrostatic adsorption of the surfactant onto the paper fiber. These surfactants are added to paper through the wet end press where cellulosic fibers are mixed with paper additives before entering the paper forming table of a paper machine. This treatment provides excellent coverage of the fiber with the surfactant and results in good folding resistance.

3.11.1.1. Alternative chemistry

In this application, PFOS has been replaced mainly with shorter-chain analogues and fluorotelomers but also with non-fluorinated chemicals. The known alternative surfactants for impregnation of paper and cardboard for use in packaging are short-chain telomer-based substances and perfluoropolyethers, and poly(dimethyl) siloxane (UNEP/POPS/POPRC.9/INF/11/Rev.1). Following are the main suppliers of fluorinated polymers in the paper industry:



¹¹ In the European Union, the use of PFOS is not allowed for these applications.

Short-chain fluorinated telomer-based polymers:

Archroma (formerly Clariant)

Asahi

Asahigard®

Ashland

ImPress®

Daikin

DuPont

Capstone®

Rudolf Chemie

Cartafluor®

Asahigard®

Asahigard®

Cartafluor®

Asahigard®

Asahigard®

Rundyne®

Ruco-guard®

Fluoro-polyethers:

Solvay Solvera®

An alternative treatment method involves application of a grease repellent at the size press and film press stage which consists of impregnating the formed paper sheet with a surface treatment. Fluorinated phosphate surfactants are not preferred for this mode of paper treatment. In this latter case, fluorinated polymers are used instead of surfactants. In terms of oil and water repellency, it is well recognized in the paper industry that phosphate-based fluorinated surfactants provide good oil repellency but have limited water repellency. Acrylate polymers with fluorinated side chains derived from sulfonamido alcohols and fluorotelomer alcohols are the most widely used polymers because they deliver oil, grease, and water repellence. Most recently, perfluoropolyether-based phosphates and polymers have become widely used treatments for food contact paper and paper packaging (UNEP/POPS/POPRC.8/INF/17/Rev.1).

3.11.2. BAT and BEP measures

At least one manufacturer has developed a non-chemical alternative for this use. 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).

The specific guidance described in the previous section for textile impregnation should be considered for this application as well. Additional details on BAT and BEP for this application can be found in IPPC (2001).

3.12. Coatings and coating additives

3.12.1. Process description

Fluorosurfactants have been used as additives in coatings for many years. For any coating to be applied successfully, it must first wet the substrate to which it is applied. If a high gloss is desired, the coating must flow and level over the substrate as well. Often, the coating has a higher surface tension than the substrate to be coated. This is an unfavourable situation for proper wetting. The solution is to reduce the surface tension of the coating, which can be done with a variety of surfactants. Fluorosurfactants are more effective and efficient than other similar hydrocarbon surfactants in lowering the surface tensions of coatings. This means that lower surface tensions can be achieved at lower surfactant addition levels. In many coating applications, increased effectiveness and efficiency in aiding wetting are critical for the successful application of a coating.

The same effectiveness and efficiency of surface tension reduction afforded by fluorosurfactants make this class of materials very useful, and often better than hydrocarbons, for providing increased flow and levelling attributes. The coatings industry is increasing production of water-borne systems to reduce volatile organic compounds (VOCs). This puts increased demand on coatings as water has a very high surface tension compared with organic coating solvents and lessens the ability to wet a substrate. Generically, coatings with lower surface tension produced by adding fluorosurfactants will function better in regard to wetting, flow and levelling.

Typical industries utilizing fluorinated surfactants to achieve these properties include:

- industrial and institutional floor polishes
- architectural paints and coatings

- varnishes
- printing inks
- adhesives

Current coating processes

Although fluorosurfactants are typically added early in the coating formulation process, they can be added at any time. All surfactants are delivered at high concentrations and usually beyond the critical micelle concentration (cmc). Since the utility of all surfactants at wetting, flow and levelling applications is at the molecular level, rather than as aggregates, time is required to disperse. Fluorosurfactants require more time than hydrocarbon surfactants to disperse from a concentrated state. This is true particularly if R&D testing will occur soon after a test formulation is prepared.

Defoamers are often required in tandem with fluorosurfactant use. The physicochemical properties of fluorosurfactants favour long-lived, voluminous foams and particularly under the vigorous conditions used to mix coatings properly. The propensity to foam and foam lifetime are dependent on surfactant type and perfluoroalkyl chain length ("C1" \leq "C2" < "C4" < "C6" < "C8"). Nonionic fluorosurfactants show little tendency to foam while ionics (both anionic and cationic) exhibit much more foam.

Use rates of fluorosurfactants tend to follow surface tension reduction and efficiency trends. The shorter perfluoroalkyl chain fluorosurfactants, the higher addition levels they require. The fluorosurfactant level required to achieve adequate wetting, flow and levelling will depend strongly on the coating formulation. For aqueous-based coatings, the fluorosurfactant use levels required are, generally, near the cmc and range from approximately 50 ppm to 500 ppm, based on the weight of the coating. Solvent-borne coatings, however, require much higher addition levels and can range from 500 ppm to 5000 ppm, based on the weight of the coating.

A typical coating application, and one of the largest consumers of fluorosurfactants, is floor polish. Every floor polish contains a fluorosurfactant. The floor polish must wet a floor that can be made of low surface tension material or contaminated with a low surface tension material. Proper wetting requires a surfactant (fluorosurfactant) that will ensure the coating has a sufficiently low surface tension to function. In addition, high gloss is very desirable with floor polish. Fluorosurfactants are excellent at mitigating surface tension gradients that can cause coating defects and reduce gloss. Any coating that has similar requirements could be formulated successfully with a fluorosurfactant.

Floor polishes form a somewhat unique subset of coatings in that they are applied, removed as required for another application and then disposed directly into wastewater. This procedure differs from a typical coating, such as paint, in that environmental exposure is direct as opposed to weathering and other forms of assault by which materials can leach into the environment either as original species or degraded by oxidative, light or acidic reactions. Disposing of removed floor polish into wastewater poses environmental concerns as the techniques and chemistry involved in most municipal wastewater treatment facilities cannot process all components properly. This is true particularly for fluorosurfactants. What remains of the fluorosurfactant after treatment depends on the nature of the fluorochemical; however, degradation is often of the oxidative type and perfluorocarboxylic acids can be produced and passed to the local aquifer.

Ultimately, the use and choice of a particular fluorosurfactant will depend on whether the material provides the necessary performance or benefits that cannot be attained with other surfactants. The conversion from PFOS to short-chain fluorosurfactants has been considered successful to date (OECD, 2010).

3.12.1.1. Alternative chemistry

It has been known for many years that the ability of a fluorosurfactant to reduce surface tension at a given concentration is superior to alternative surfactant substances (for detailed discussions of the important properties of and technology behind commercial fluorosurfactants, see Kissa 1994; Taylor 1999; Buck et al. 2011). Longer perfluoroalkyl chains ≈ lower surface tensions.

In the years following the commercial introduction of long perfluoroalkyl chain surfactants, evidence was mounting that long chain perfluoroalkyl chain-containing materials, including fluorosurfactants, could have substantial environmental impact with regard to persistence, bioaccumulation and toxicity (PBT). The magnitude and concern of PBT of this chemical group are directly related to perfluoroalkyl chain length; they are not just caused by fluorosurfactants themselves, but also by degraded forms of chemicals.

These observations have prompted a restructuring of the fluorosurfactant industry serving the coatings additives market. Large vendors (e.g. DuPont, Daikin, 3M, etc.) of long chain fluorosurfactants have discontinued, or are in the process of discontinuing, the manufacturing and marketing of fluorosurfactants in favour of short-chain alternatives. Currently, the target appears to be –(CF2)6F or "C6" technology. 3M has moved to a "C4" technology based on -(CF2)4F. OMNOVA Solutions has attempted to distance itself further from the mainstream with "C1" (-CF3) and "C2" (-CF2CF3)-based fluorosurfactants.

Concern over PBT issues has also resulted in global regulators pressing for the phase-out of "long-chain" fluorinated substances in favour of a move to "short-chain" fluorinated substances, which are currently considered to have a more favourable overall environmental profile (OECD, 2010). 12 Ongoing research, however, focuses on the environmental and health characteristics of the new short-chain chemistry, which is currently poorly described in recent scientific literature.

The possible alternatives identified for use as coating additives are as follows (UNEP/POPS/POPRC.9/INF/11/Rev.1):

- Short chain fluorotelomer-based surfactants (e.g. Capstone® products);
- C4-compounds based on perfluorobutane sulfonate, especially in the area of electronic coating;
- Fluorinated polyethers (PolyFox®);
- Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water, which is used as an alternative in wood primers and printing inks;
- Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di (2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd®);
- Propylated naphthalenes and propylated biphenyls, which can be used as water repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications;
- Fatty alcohol polyglycol ether sulfate, sometimes together with a sulfosuccinate.

3.12.2. BAT and BEP measures

The general guidance provided in Chapter 2 and the specific guidance described in the previous section should be considered for this application as well.

3.13. Rubber and plastic

PFOS and/or PFOS-related substances have been used as mold release agents in rubber and plastics moulding applications. Currently, PFBS derivatives or various C4-perfluorocompounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics.¹³

¹² In the European Union, the use of PFOS is not allowed for these applications.

¹³ In the European Union, the use of PFOS is not allowed for these applications.

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Annex

Other technologies for removing PFOS from wastewater

A number of technologies for removing PFOS and PFOS-related substances from wastewater are currently under investigation to prove their efficacy and applicability on a large scale. Such emerging technologies are listed below.

Electrochemical decomposition of PFOS in the wastewater stream

Strongly acidic wastewater streams with a high content of PFOS can be treated by an electrochemical process using lead electrodes in batch mode. PFOS is thereby destroyed by up to 99%. Fluorosurfactants are decomposed to hydrofluoric acid under the reaction conditions. Fluorinated organic degradation products were not detected. The short-chained perfluorobutane sulfonate can only be slightly reduced by electrochemical treatment. Because the efficiency of the electrochemical decomposition is strongly reduced with decreasing concentrations of PFOS, the combination with an adsorption step, as described earlier, is recommended for economic reasons (Fath, 2011). Although electrochemical treatment can be cheaper than adsorption, it is an emerging technology that cannot yet be regarded as general BAT.

