Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants

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Draft
July 2012

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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
BOD_5	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	tetrafluoroethylene
EtFOSA	N-Ethyl perfluorooctane sulfonamide
FFFP	film-forming fluoroprotein foam
FOSA	N-Alkylperfluorooctanesulphonamide
FOSE	N-Alkylperfluorooctanesulphonamidoethanol
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	persistence, bioaccumulation and toxicity
PFAS	perflouroalkyl sulphonate
PFBS	perfluorobutane sulphonate
PFC	perfluorinated compound
PFOS	perfluorooctane sulfonic acid
PFOSA	perfluorooctanesulphonic acid
PFOSF	perfluorooctanesulphonyl fluoride
POPRC	Persistent Organic Pollutant Review Committee
POPs	persistent organic pollutants
PPE	personal protective equipment
PVD	physical vapour deposition

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R&D	research & development
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

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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 techniques available in addition to the practical suitability of particular techniques. Best environmental practices (BEP) describe the application of the most appropriate combination of environmental control measures and strategies (Article 5, f (v) of the Stockholm Convention.

Article 3 para. 6 of the Stockholm Convention requests Parties that have a specific exemption and or acceptable purpose 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. This guidance document has been developed to guide Parties in adequately addressing the risks of perfluorooctane sulfonic acid (PFOS) and its related substances.

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, directly relevant provisions of the Stockholm Convention (Article 5, Annexes B and C) and a summary of required measures under these provisions.

Chapter 2 provides a description of the various processes in which PFOS is used and guidance on the consideration of alternatives for these processes.

Chapter 3 includes general guidance, applicable principles and descriptions of considerations that cut across multiple process categories.

Chapter 4 contains specific guidance for the process categories listed in chapter 2.

Chapter 5 provides general guidance on best environmental practices for the management of PFOS.

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 that can result in PFOS, are members of the large family of perfluoroalkyl sulfonate (PFAS) substances.

1.3.2 Characteristics

PFOS is very persistent and has substantial bioaccumulations and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues;

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instead, it binds to proteins in the blood and liver. It has a capacity to undergo long-range transport and also fulfils the toxicity criteria of the Convention.

1.3.3 Risks

At its second meeting, the Persistent Organic Pollutants Review Committee (POPRC) adopted the "risk profile" on perfluorooctane sulfonate. At its third meeting, the POPRC adopted the "risk management evaluation" on perfluorooctane sulfonate. For more information on the risks posed by PFOS, these documents can be found in the "New POPs" section at www.pops.int.

1.3.4 Production and uses

PFOS and PFOS-related substances are listed under Part I of Annex B of the Convention and Part III specifically addresses issues related to these chemicals. Production and use shall be eliminated by all Parties except Parties that have notified the secretariat to produce/or use them according to the possible specific exemptions and acceptable purposes described in Annex B, Part I. So, PFOS is still produced and used in several countries.

The list of uses for acceptable purposes or specific exemptions in the Convention is given below in the table. The use categories not listed in the Convention are banned uses, and were identified and described in the *Guideline on Alternatives to Perfluorooctane Sulfonate and its Derivatives* developed under the POPs Review Committee (UNEP/POPS/POPRC.6/13/Add.3, 2010). In its decision SC-5/5, the Conference of the Parties to the Stockholm Convention requested the Persistent Organic Pollutants Review Committee to develop a technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid (PFOS) in open applications. The technical paper will be considered by the Committee at its eighth meeting, October 2012. The information provided in the technical paper on the identification and assessment of alternatives to the use of PFOS in open applications is set out in document UNEP/POPS/POPRC.8/INF/17.

Acceptable purposes	Specific exemptions
• 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*	• 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

Although alternatives to PFOS are available for some applications, as described in the chapter 2, this is not always the case in developing countries, where they still need to be phased in.

Some applications like photo imaging, use for semiconductors or aviation hydraulic fluids are considered as acceptable purposes, partly because technically feasible alternatives to PFOS have not been well established to date.

For an illustration of major product categories and applications of PFOS, see the *Guidance for the Inventory of Perfluorooctane Sulfonic Acid (PFOS) and Related Chemicals Listed under the Stockholm Convention on Persistent Organic Pollutants* (*PFOS Inventory Guidance*; Secretariat of the Stockholm Convention, 2012).

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2. Process descriptions of current and alternative chemistry and processes

This chapter provides brief descriptions of the different processes involving PFOS and related substances and the viable alternative chemistry to PFOS for each described process. The processes described are for those where production and use is allowed. Information on alternative processes is also given under each process description.

Many processes using PFOS are no longer needed and alternatives have been identified. More specific chemical information on alternatives to PFOS can be found in the *Guidance on Alternatives to Perfluorooctane Sulphonate and its Derivatives* (UNEP/POPS/POPRC.6/13/Add.3, 2010) and in the Technical Paper

2.1 Coated and impregnated items

2.1.1 Introduction

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.

PFOS and 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 –$(CF_2)_6F$ or "C6" technology. 3M has moved to a "C4" technology based on -$(CF_2)_4F$. OMNOVA Solutions has attempted to distance itself further from the mainstream with "C1" (-CF_3) and "C2" (-CF_2CF_3)-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). 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.

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

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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. As discussed above, there are PBT concerns with long perfluoroalkyl chain surfactants. In summary, environmental exposure and contamination from fluorosurfactants can be minimized or eliminated using short-chain surfactants.

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).

2.1.2 Textiles, paper and leather

Fluorosurfactants and polymers have been used to treat textiles and leather to provide oil and water repellence and soil and stain release properties, and to provide oil, grease and water repellence for paper. 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.

The earliest applications used fluorosurfactants. These were quickly replaced, however, with high molecular weight fluorinated polymers, most commonly fluorinated poly(meth)acrylates. The 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. For textiles and leather, the polymers are designed to perform after multiple cleanings/washings and last the lifetime of the treated article.

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.)

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• 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

Current 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 market, 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

Current impregnation processes

Fluorochemical repellents are usually applied in combination with other finishing auxiliaries by a pad-dry-cure process, as shown in figure 2-1.

Figure 2-1: General principle for the pad dry cure process (IPPC, 2003)
Note: Baking is sometimes called curing or fixation.

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).

Textiles, paper and leather chemistry

PFOS and alternative chemistry

Fluorinated finishes are the only technology known to deliver durable and effective oil and water repellence and release properties. Historically, fluorinated polymers based on perfluorooctane sulfonyl (PFOS-based) electrochemical fluorination chemistry have been used. PFOS-related substances were used to treat textiles but PFOS as such was present at up to 2 wt % in articles. In addition, fluorotelomer-based polymers have also been used. As stated earlier, major manufacturers in conjunction with global regulators have agreed to discontinue the manufacture of "long-chain" fluorinated products and move to "short-chain" fluorinated products. New short-chain products, currently defined as BAT to achieve the needed performance effects, have been approved for manufacture, sale and use, and have been demonstrated to deliver the desired performance in textiles, leather and paper applications.

Alternative hydrophobic finishes for textiles

For most of the applications, such as outdoor clothing, tents, awnings etc., the durable water-repellent effect (DWR) of the fabric is the main property requested by the users. For these applications, there are several existing alternatives to fluorocarbons that are not based on persistent molecules:

- Wax-based repellents consisting of paraffin-metal salt formulations
- Hydrophobic modified polyurethanes (hydrophobic modified hyperbranched polyurethanes called dendrimers)
- Silicone repellents
- Resin-based repellents consisting of fatty modified melamine resins

Non-fluorinated alternative technologies such as hydrocarbon waxes and silicones can provide durable water repellence (DWR; aka hydrophobic properties) but not oil repellence or oil and soil release. If oil, blood or soil repellence is required, fluorinated polymers are the state of the art.

With fully capable and acceptable alternative technologies commercially available worldwide, there is no need to use PFOS-derived, -containing or -releasing chemistry in treating textiles, leather or paper. Since these alternatives have their own special profiles, the textile industry needs to be very selective about BAT and BEP depending on for which purpose which kind of chemistry is used.

2.1.3 Carpets

Fluorinated polymers may 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 situation regarding past and current chemistry is the same for carpets as described for textiles, leather and paper (see section 2.1.2). Since there are fully capable and acceptable alternative technologies commercially available worldwide, there is no need to use PFOS-derived, -containing or -releasing chemistry in treating carpets.

2.1.4 Paper and packaging

Fluorinated compounds are used to render paper and cardboard grease- and waterproof and 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).

As stated in section 2.1.2, there is no need to use PFOS-derived, -containing or -releasing chemistry in treating paper. There are fully capable and acceptable alternative technologies commercially available worldwide.

2.2 Insecticides

2.2.1 Introduction

N-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS No. 4151-50-2), also called sulfluramid, is both a surfactant and a pesticide used against termites, cockroaches, and ants.

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 (US). 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.

2.2.2 Current insecticides for control of red imported fire ants and termites

Sulfluramid is a PFOS-related substance that was used in insecticides at a concentration of 0.01-0.1% at an annual volume of up to 17 tonnes (OECD, 2006).

According to information submitted to the Secretariat of the Stockholm Convention, sulfluramid is used for pest control (to control cockroaches, white ants, and fire ants) in China (UNEP/POPS/POPRC.6/13/Add.3, 2010).

2.2.3 PFOS-related substances and alternative pesticides for the control of leaf-cutting ants

Sulfluramid is still used in Brazil as an active ingredient in the manufacturing of ant baits for the control of leaf-cutting ants belonging to the genus Atta (saúvas) and Acromyrmex (quenquéns), which are the insects that cause the most damage to the agriculture sector of the country:

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. In sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose. Sulfluramid is the only active ingredient with all the properties necessary for effective functioning as ant bait, which makes it the only effective option for controlling leaf-cutting ants.

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. An adequate insecticide used to formulate baits for the control of leaf-cutting ants should be lethal at low concentrations, act by ingestion and present a delayed toxic action. Since 1958, over 7,500 chemical compounds for ant control have been studied in many countries. Less than 1% of those 7,500 compounds have shown promise. *(UNEP/POPS/POPRC.6/13/Add.3, 2010)*

2.3 Aviation hydraulic fluids

2.3.1 PFOS and alternative chemistry

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% (UNEP/POPS/POPRC.6/13/Add.3, 2010), to prevent evaporation, fires, and corrosion.

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) is not a PFOS precursor, and has been used in hydraulic oils instead of PFOS. 3M, however, which formerly produced this chemical, has ceased to do so, probably because of lack of demand (UNEP/POPS/POPRC.6/13/Add.3, 2010).

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2.4 Fire fighting foams

2.4.1 Finishing processes

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 enable it to be extremely effective in preventing and extinguishing fires, especially Class B flammable liquid events. 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.

2.4.2 Types of foams

Foams have been developed for both Class A (solid combustibles) 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 (but not fluorochemical) surfactants. AR-AFFFs are designed to be effective in the presence of alcohols and other water miscible compounds.

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-FP), and alcohol-resistant film-forming fluoroprotein (AR-FFFP).

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 within developed countries. The primary supply of

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AFFF then became fluorotelomer-based. Over the last several years, manufacturers of fluorotelomer AFFF have been replacing long-chain fluorosurfactants with shorter-chain fluorosurfactants. The perfluorinated compounds (PFCs) in current fluorotelomer-based AFFF are shorter-chain molecules, generally 6:2 telomer-based, and tend to be less bioaccumulative and less toxic. Telomer-based AFFF does not contain PFOS but may contain constituents that can be degraded to PFOA or shorter-chain perfluorinated carboxylic acids.

2.4.3 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.

One reference that identifies alternatives for use can be found in the "*Guidance on Alternatives to Perfluorooctane Sulphonate and its Derivatives* (UNEP/POPS/POPRC.6/Add.3, 2010). As stated previously, it is critically important that the tremendous effectiveness of AFFF products in protecting life and property be considered in making use and system design decisions. The expertise of fire protection personnel is imperative in such matters.

2.5 Decorative and hard metal plating processes

2.5.1 PFOS and alternative chemistry

PFOS is useful as a surfactant or wetting agent in the electroplating industry to achieve uniform thickness of the plating or uniform chemical attack (Zhou et al., 2003). It also serves as a mist-suppressing agent so as not to contaminate nearby baths and to reduce the losses by drag-out (UNEP/POPS/POPRC.3/20/Add.5, 2007). In chrome plating it decreases aerosol emissions and improves the work environment.

PFOS was previously used for decorative chrome plating, but new technology using chromium-III instead of chromium-VI has made this use mostly obsolete. Although the use of chromium-III does not work for hard chrome plating, some kinds of non-PFOS agents are being used in both

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decorative and hard chrome plating. Non-fluorinated alternatives for decorative chromium plating and hard chromium are available on the European market. 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. In the meantime telomer-based surfactants, too, are used as a bridge technology.

2.5.2 Electroplating of plastics

PFOS is used as a wetting agent in the pre-treatment (etching) of plastics, which is essential before the electroplating process. It provides the wettability of the surface and uniform chemical attack of the chromic and sulphuric acid used for etching.

2.5.3 Rubber and plastic products

Perfluorobutane sulphonate (PFBS) derivatives or various C4-perfluorocompounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics. More information on alternatives to PFOS can be found in the "*Guidance on Alternatives to Perfluorooctane Sulphonate and its Derivatives* (UNEP/POPS/POPRC.6/13/Add.3, 2010).

2.6 Chemically driven oil and gas production

2.6.1 PFOS and alternative chemistry

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.

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.

2.7 Electronics industry

2.7.1 PFOS and alternative chemistry

Electrical and electronic equipment often requires hundreds of components 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 2-2). PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners,

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satellite communication systems, radar systems and the like. The PFOS-related compounds are process chemicals, and the final articles are mostly PFOS-free.

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 processes smooth the surface of a through-hole in printed circuit boards. PFOS can be used as a surfactant in the desmear agent, i.e. etching agent. PFOS is added into a desmear agent, and rinsed out during the washing treatment. The other processes involved are described in the discussions on the semiconductor industry (section 2.7.2) and metal plating (section 2.5).

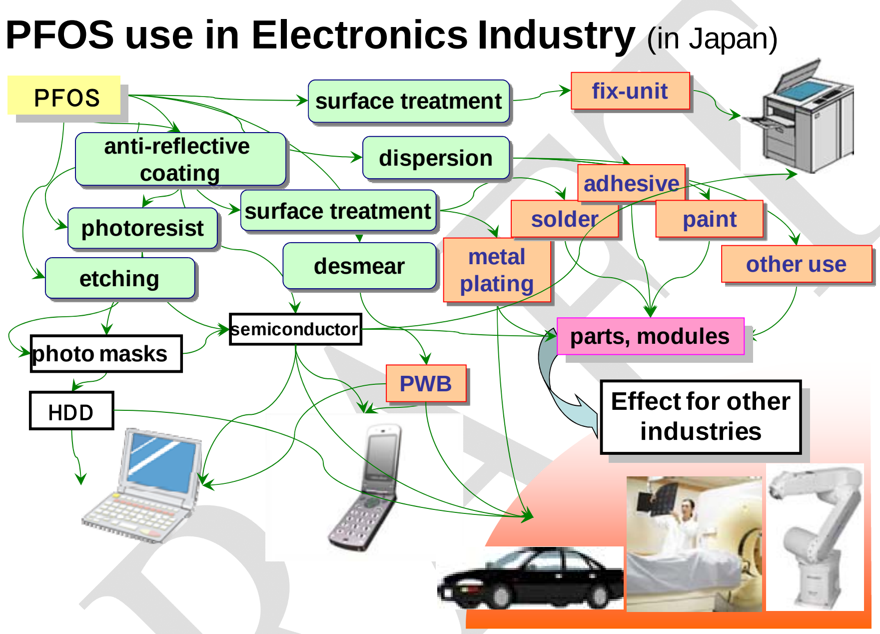

Figure 2-2: PFOS use in electronics industry supply chain (Japan Electronics and Information Technology Industries Association Semiconductor Board)

2.7.2 Semiconductor industry

PFOS and PFOS-based substances are chemicals required by the semiconductor industry for formulation of resists and anti-reflective coatings in high-end lithography. 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 2-3), involving four fundamental physical processes:

- Implant
- Deposition
- Etch
- Photolithography

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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 association, 2004).

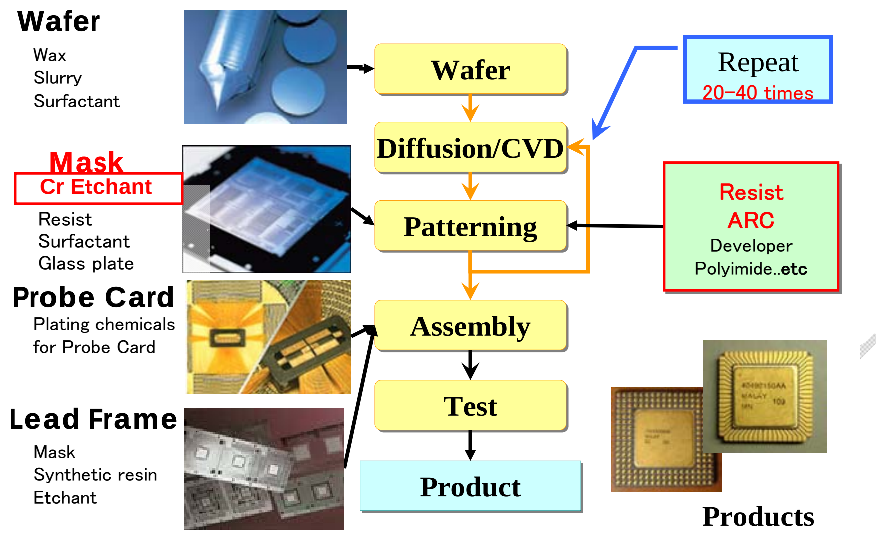

Figure 2-3: Different steps in semiconductor manufacturing where PFOS is used as an intermediate (The process in red is related to PFOS related substances. Source: Japan Electronics and Information Technology Industries Association Semiconductor Board)

PFOS reduces the surface tension and reflection of etching solutions, properties that are important for precise photolithography in the semiconductor industry (photoresists 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:

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

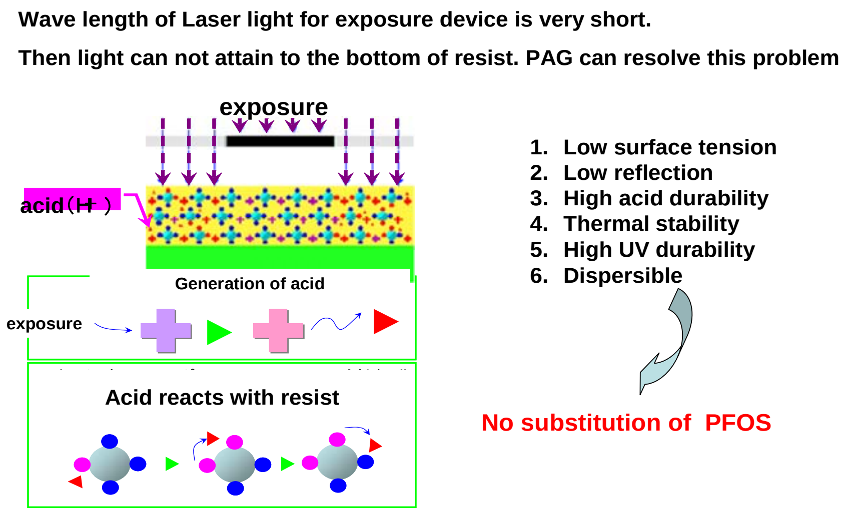

Figure 2-4**:** Description of photoresist critical use of PFOS and its related substances in photolithography processes (Japan Electronics and Information Technology Industries Association Semiconductor Board) Note*:* 1 to 6 describe the important functions of PFOS and its related substances when used as a component of a photoresist substance*.*

PFOS is used as a component of a photoresist substance (see figure 2-4), including a photo acid generator or surfactant; or of an anti-reflective coating, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturized devices (see figure 2-5). Photoresist is a polymer material necessary to shape a circuit in the photolithographic process. PFOS is added to the photoresist agent to make photoresist soluble in water and to give surface activity. Since the photoresist 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 2-5). 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) photoresist. 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.

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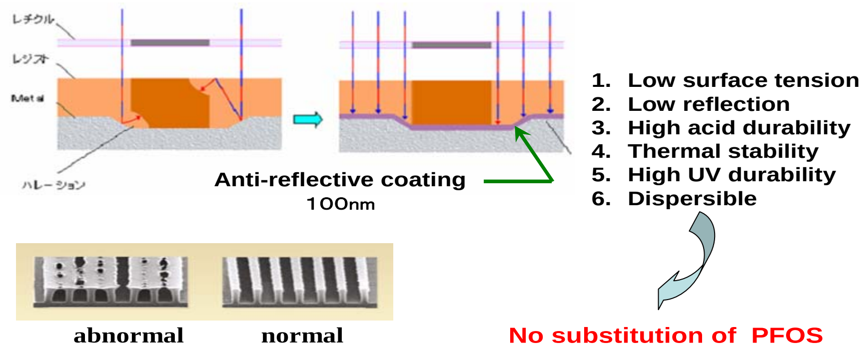

Figure 2-5 **:** Description of anti-reflective coating critical use of PFOS and its related substances in photolithography processes (Japan Electronics and Information Technology Industries Association Semiconductor Board)
Note*:* 1 to 6 describe the important functions of PFOS and its related substances when used as a component of a photoresist substance*.*

Despite significant R&D in recent years, currently there are no replacement substances, for some of the specific uses of PFOS, that provide the critical functionality and equal the performance required at these technology levels.

In the photolithography industry, few alternatives are available that would allow for the comprehensive substitution of PFOS in critical applications. Thus the new photolithography technologies, which in detail are trade secrets, use less photoresist per wafer, and the new photoresist formulations contain much lower concentrations of PFOS. Non-critical uses of PFOS are as edge bead removers, de-gluing agents and developing agents.

2.7.3 Photographic industry

PFOS-based chemicals are used for the following purposes in mixtures, in coatings applied to photographic films, papers, and printing plates (RPA association, 2004):

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

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The uses of PFOS in this industry include coatings for surface tension, static discharge, adhesion control for analogue and digital imaging films, papers, and printing plates; and as a surfactant in mixtures used to process imaging films.

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3. BAT/BEP principles for chemicals management of PFOS

3.1 General BAT/BEP measures

This section describes principles, measures and safety precautions that apply to all types of products and industries related to PFOS 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 only to specific process categories are described in chapter 4.

3.1.1 Storage, handling, dosing, dispensing and transport of PFOS

In storing, handling, dosing, dispensing, and transporting PFOS containing-products, caution should be used to ensure:

- Proper storage according to the instruction of the material safety data sheet (MSDS).
- 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 as essentially needed for the process, by measuring and recording the PFOS consumption.

3.1.2 Improved knowledge of the raw materials used

When handling products and preparations containing PFOS, the following relevant information could be collected and analyzed to plan proper handling:

- Auxiliaries and basic chemicals information from the supplier concerning proper storage and handling; and environmental characteristics (COD, BOD_5, 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.

3.1.3 Minimization/optimization of the chemicals used

Minimization and optimization of PFOS-containing chemicals may be achieved by taking the following into consideration:

- Avoiding any kind of applied fluorochemicals and auxiliaries that may have a potential to transform into and emit PFOS.
- Using fluorochemicals 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 smell intensity are preferred.

- Avoiding surpluses of applied chemicals and auxiliaries.
- 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.

3.1.4 Equipment

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

- 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.

3.1.5 Summary

General BAT/BEP measures for PFOS can be summarized as follows:

- Perform proper storage of products containing PFOS.
- Operate manufacturing processes in a closed system at limited sites.
- Maintain the reactors, containers and pipes containing PFOS-related feedstock in a well-sealed condition without leakage.
- Collect and dispose of the waste acid and solvent at the end of the manufacturing process in an environmentally sound manner; where applicable, high temperature incineration could be a reliable way to treat such PFOS-contained waste.
- Use sealed containers for products containing PFOS to guarantee there is no leakage or scattering.
- Label with the concentration and attach the MSDS of PFOS and PFOS-related substances or precursor with any commercial products containing it.
- Recover wastewater containing PFOS; if possible separate the PFOS, reduce the volume of the wastewater, and treat it properly.

3.2 Water management, 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.

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- 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 that has an unknown quantity of PFOS and related 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 association with BRE ENV., 2004).
- Irreversible destruction of waste with an unknown quantity of PFOS and related substances at a minimum of 1100 °C.
- Avoidance of mixing PFOS-free solutions or wash water with solutions containing PFOS.

3.3 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.

3.3.1 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 questions 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, if required.

3.3.2 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.

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.

3.3.3 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.

3.3.4 Reception facility

The reception facility could cover at least the following issues:

- A laboratory to analyze all the samples at the speed required by BAT. Typically this requires a robust quality assurance system, quality control methods and the maintenance of suitable records for storing the analysis results. Particularly for hazardous wastes, this often means that the laboratory needs to be on site.
- A dedicated quarantine waste storage area as well as written procedures to manage non-accepted waste. Wastes can be temporarily stored there 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.

3.4 Occupational health and safety measures

This section describes procedures, equipment and measures related to PFOS handling, special and personal protection when working with PFOS and first aid procedures.

3.4.1 PFOS Handling precautions

Leak and spill detection procedures:

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

Storage requirements:

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

3.4.2 Special and personal protection: PFOS

- Mechanical ventilation: the use of mechanical ventilation is recommended whenever the PFOS-containing 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.

3.4.3 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.

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4. Specific BAT/BEP measures by process category

4.1 Coated and impregnated Items

BAT and BEP for soil- and water-repellent textile and upholstery applications 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 behaviour of the degradation products in the wastewater-treatment that result in PFOS.

4.1.1 Minimization/optimization of chemicals used

Perfluoroalkyl-based water-and oil-repellent chemicals are not biodegradable. In the past products with a 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:

- 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 self-organization of the fluorocarbon, such as detergents or rewetting agents.
- Avoid spray application if possible.

4.1.2 Application of hydrophobic finish of textiles and upholstery

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. The product is transported and delivered by truck.

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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.

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.

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.

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, either be released directly into the environment via an exhaust air unit or passed on to an exhaust air washer.

Winding up of the fabric

Behind the stenter the fabric is winded up.

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.

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.

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4.2 Insecticides

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 1993, after verification of its efficiency with many leaf-cutting ant species, replacing the active ingredient dodecachlor. Currently, the active ingredients used in ant baits are sulfluramid, fipronil and chlorpyrifos. Fipronil and chlorpyrifos are more acutely toxic to mammals, aquatic organisms, fish and bees than sulfluramid. Comparative studies also demonstrate the low efficiency of ant baits with chlorpyrifos and fipronil.

Sulfluramid is the active ingredient in the manufacturing of ant baits in ready-to-use formulations (3 g/kg). Sulfluramid is used as an active ingredient in the manufacturing of ant baits for the control of leaf-cutting ants such as the genus *Atta* (saúvas) and *Acromyrmex* (quenquéns), which are the insects that cause the most damage to agriculture.

The baits are presented in granular form (pellets), and used in local application next to the holes of the anthill. The ants carry the baits into the nest, incorporating them into the fungus garden. Sulfluramid will stay strongly adsorbed or bounded to the organic matter.

An adequate insecticide used to formulate ant baits is lethal at low concentrations and, by ingestion, causes a delayed toxic action. Additionally, it should be odourless and non-repellent, so as to be dispersed by trophallaxis to most workers in the colony. Quick-action products will kill many ants in the first hours following their application, hindering or impairing insecticide distribution throughout the colony. They cause a certain disorder in the anthill and even temporarily stop some of its activities, such as leaf cutting.

Granulated baits represent the most widely used method for leaf-cutting ants control, consisting of a mixture of an attractive (usually orange pulp and vegetable oil) and an active ingredient (insecticide), presented in the form of pellets. This method features some significant advantages over other methods. It is a low-cost method that delivers high efficiency with reduced health hazards to humans and the environment during application, and it is specific to the pest target. Its formulation is developed with low concentrations of active ingredients, and its localized application does not require application equipment. Baits are directly applied from their packaging, with no dermal contact, close to active nest entrance holes or anthill trails and carried into the colony by the ants themselves. The utilization of ready-to-use formulations should reduce or impede exposure to humans.

BEP for ant baits application could consider the following actions:

- Assessment of infestation in the areas
- Estimation of bait consumption
- Qualification and periodical training of control teams
- Recommendation of method and period for application
- Assessment of bait consumption and control efficiency
- 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

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overalls, as specified in the product label. Additionally, periodical examinations are adopted, which are included in local or national labour safety rules.

4.3 Fire fighting foam

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. Finally, residual materials could be appropriately managed.

4.3.1 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.

4.3.2 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.

4.3.3 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.

4.3.4 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.

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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

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requirements and procedures could be clearly outlined in facility emergency response plans and be reviewed as part of routine training.

4.3.5 Management of residual (waste) materials

Specific actions relative to the management of waste are determined on a case-by-case basis.

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.

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.

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).

4.4 Decorative and hard metal plating process

Current BAT and BEP means either using PFOS when closing the loop very closely so that hardly any emissions take place (Schwarz, 2011) or using non-fluorinated readily degradable surfactants. Other 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.

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.

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- 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.

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

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, PFOS works by lowering surface tension and forming a single foamy barrier on the surface of the chromic acid bath, (see figure 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” (UNEP/POPS/POPRC.6/13/Add.3, 2010). The same applies for decorative chrome plating.

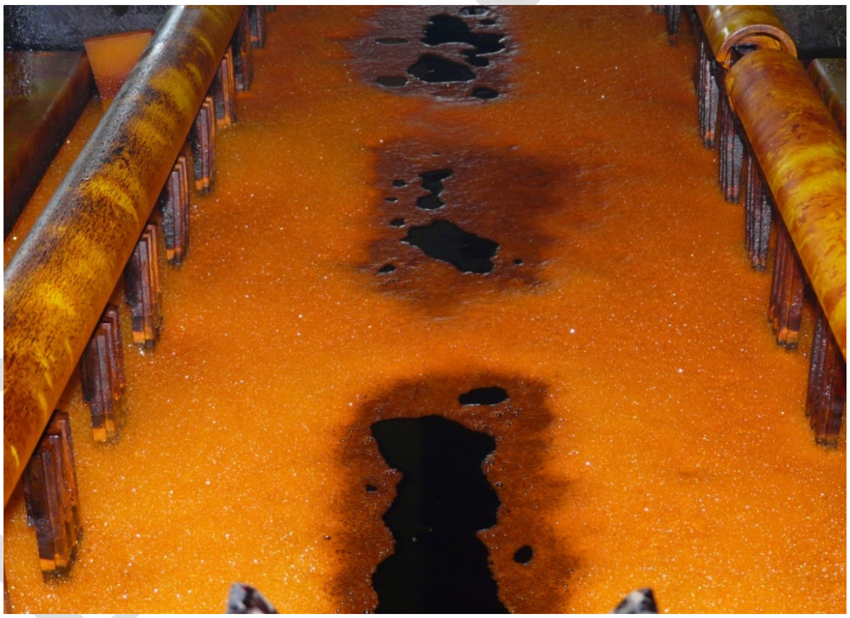

Figure 4-1: Foamy barrier on the surface of a chromium bath

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

4.4.2 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.

4.4.3 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).

4.4.4 Measures to avoid or reduce emissions of PFOS into the environment

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 in controlled electroplating systems

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 as a function of 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).

Hard chromium plating

BAT is to close the material loop for hexavalent hard chromium by using suitable combinations of techniques such as cascade rinsing, ion exchange and evaporation. When hot electrolytes with high evaporation rates are used, closing of the material loop can sometimes already be achieved by simple methods such as using a single static rinse in combination with seven rinsing

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steps in a pumped, very slowly flowing, rinse cascade. But in most cases, an evaporator is required to regain the electrolyte from the rinse water.

Decorative chromium-VI plating

BAT is to close the loop in decorative chromium plating using evaporation for drag-out recovery. An example of this technology, which has been used successfully in ecological and economic terms for 20 years (Hauser, 2011), is shown in figure 4-2.

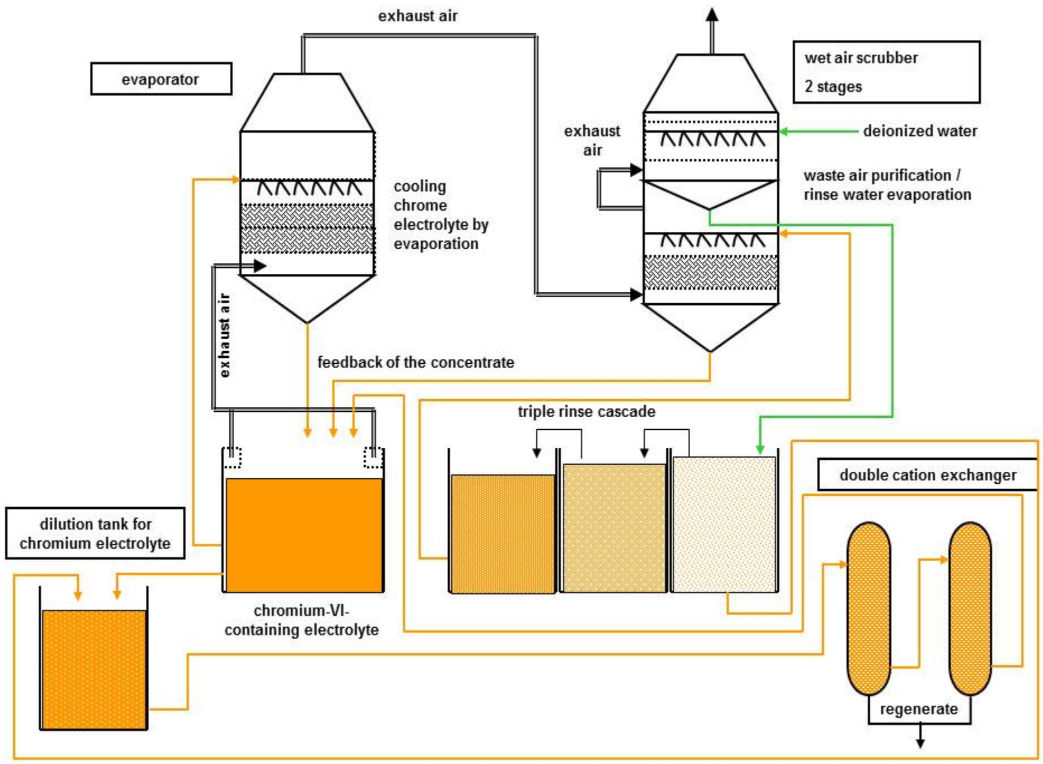

Figure 4-2: Closed loop in chromium plating (Hauser, 2011)

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.

4.4.5 Removal of PFOS from the wastewater

Removing PFOS from the wastewater stream 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 must be taken into account when using any adsorption method that requires a final destruction of the adsorbent that contains PFOS at the end-of-life so as not to deposit such PFOS-containing wastes improperly. The destruction could be done in a BAT hazardous waste incineration plant at temperatures of at least 1100° C and with a residence time of 2 seconds.

Figure 4-3 shows a flow diagram of an almost closed system with optimized PFOS adsorption. The use of evaporators is a costly investment but is amortized over a few years.

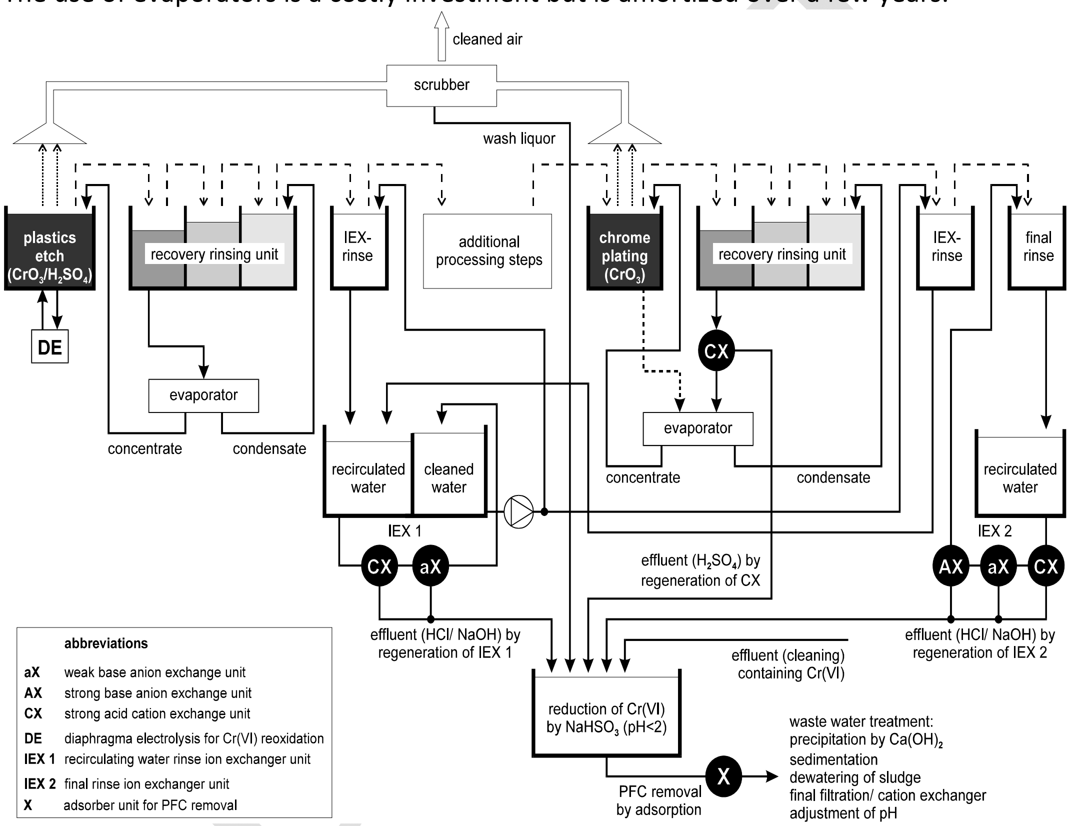

Figure 4-3: Process and systems engineering for chromium plating on ABS plastics (Schwarz, 2011)

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).

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.

4.4.6 PFOS and alternative chemistry

Polyfluorinated substitutes

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.

One of the most common substitutes 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). Because it is structurally very similar to PFOS, its common name is THPFOS (tetrahydro PFOS). In the environment a decrease in the stable perfluorohexane acid (PFHxA) is found.

PFOS alternatives[1] used for chrome plating available in China are:

- FC-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo)ethane sulfonate
- FC-53B (Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetraflouroethane sulfonate)
- Fumetrol®21 (1H,1H,2H,2H-perfluorooctane sulfonic acid)

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 the *Guidance on Alternatives to Perfluorooctane Sulfonate and its Derivatives*, currently, no other surfactant can match the low surface tension of PFOS (UNEP/POPS/POPRC.6/13/Add.3, 2010). 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.

In addition, these alternatives tend to adsorb less to the sewage sludge of wastewater treatment plants (e.g. Wang et al., 2011), which means there could be remarkably higher emissions to the environment than when using PFOS. Therefore deposits to soil and in particular groundwater, as well as surface water and related drinking water, could occur.

[1] UNEP/POPS/POPRC.6/13/Add.3, 2010

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Higher emissions, unknown toxicity and degradation to persistent substances highlight the necessity for a timely detailed assessment of environmental fate and the toxicity of the fluorinated alternatives to PFOS — to clarify as soon as possible to what extent the currently used fluorinated alternatives can contribute to a solution of the problem.

Non-fluorinated substitutes

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).

4.5 Chemically driven oil and gas production

It is reported that PFOS is being used as surfactants for enhanced oil recovery to recover oil trapped in small pores between rock particles. Oil production in some countries, however, has indicated that there are alternative processes that do not require the use of PFOS.

4.5.1 Well stimulation procedures

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% NH_4Cl 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.

4.6 Semiconductor industry

It is important to be aware that PFOS or its salts are not likely to undergo a chemical transformation through natural processes and they are bioaccumulative, which means they pose a risk of impairing human health if ingested continuously. Measures could be taken to reduce releases of PFOS or its salts 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 its salts, take measures to recover the wastewater, to the extent possible.

4.6.1 Leakage recovery

Regarding waste such as waste liquid, for the company to 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.

4.6.2 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).

4.6.3 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.

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4.6.4 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.

4.6.5 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.

4.6.6 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.
- 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.

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4.6.7 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.
- Place and store recovered PFOS in a sealable container along with the cloth (or the like) used to wipe up PFOS.

4.6.8 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.

4.7 Photographic industry

PFOS or its salts used in photographic film for industry (photographic developing work) are not likely to undergo a chemical transformation through natural processes. They are bioaccumulative and pose a risk towards impairing human health if ingested continuously. Part of BAT/BEP is to endeavour to reduce releases of PFOS or its salts by recovery of developing solution and fixing solution.

4.7.1 Measures pertaining to photographic developing work

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 for the semiconductor industry would also be effective for the photographic industry.

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5. Guidance/Guidelines on Best Environmental Practices

The following subchapters contain specific areas in relation to the environmental management systems that could improve environmental performance of an installation including the increased awareness of the workers/employees.

BEP describes the application of the most appropriate combination of environmental control measures and strategies, which includes a behaviour that relates to the continuous improvement of environmental performance. BEP provides the framework for ensuring the identification, adoption and adherence to management options that nevertheless remain important and can play a role in improving environmental performance of the installation. Indeed, these good housekeeping/management techniques/tools often prevent emissions.

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).

5.1 Environmental management systems

A number of environmental management techniques are determined as BEP. The scope and nature of an 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

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- 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.

5.2 Additional EMS considerations

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.
- 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 ISO14001. Non-standardized systems can in principle be equally effective provided that they are properly designed and implemented.

5.3 Specific education and training of employees

The following training and education opportunities could be beneficial for raising awareness at work for sound chemical 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.

5.4 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:

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    - Descriptions of the waste treatment methods and procedures in the place of installation.
    - Diagrams of the main plant items that have some environmental relevance, together with process flow diagrams (schematics).
    - Details on the control system philosophy and how the control system incorporates 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.

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