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Use of PFOS in chromium plating – Characterisation of closed-loop systems, Use of alternative substances

by

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Abstract

The Öko-Institut e.V. in cooperation with IUW-Integrierte Umweltberatung and POPs Environmental Consulting have prepared an expert opinion on behalf of the German Federal Environment Agency (Umweltbundesamt). The aim of this document is to provide missing information related to the use of PFOS (perfluorooctane sulfonic acid) in electroplating and to compile it as a basis for reporting to the European Commission in line with article 12 of the EU POP regulation. The use of PFOS is allowed in the EU “for non-decorative hard chrome plating in closed loop systems”.

In the current document, examples from five existing electroplating facilities are used to show the distinctive features characterizing a closed loop system and the measures that can be applied to extend the closed system. The data of five reference electroplating facilities have been collected based on an interview guide agreed with the Federal Environment Agency and incorporated into the report anonymously. Additionally, the term "non-decorative hard metal plating" is critically reviewed, and compared with the alternative terms, "functional chrome plating" and "functional chrome plating with decorative character".

In addition, an overview of possible substitutes for PFOS is provided. The risks relating to persistence, biodegradability and ecotoxicity of using these materials cannot yet be assessed as these aspects are still insufficiently tested. Raising awareness about available fluorine-free surfactant alternatives (e.g. in the form of stakeholder consultations) would advance the current dawdling debate and transparency on the replacement of PFOS. It is also assumed that a forced public promotion of the subject would greatly accelerate the process of substitution of PFOS in the plating sector.

In this document, a number of supplementary results and conclusions are presented and an initial recommendation to update the EU POP regulation is presented.

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Abbreviations

ABS	Acrylonitrile butadiene styrene copolymer
CETAC	Chromium Trioxide Authorization Consortium CTAC
ECHA	European Chemicals Agency
EU POP regulation	European POP Regulation (EC) No. 850/2004
CrO ₃	Chromium trioxide
(BAT/BEP)	Best Available Techniques / Best Environmental Practices
H4PFOS	1H,1H,2H,2H-perfluorooctane sulfonate; 6:2 FTS
PFBS	Perfluorobutanesulfonic acid
PFC	Perfluorinated and polyfluorinated chemicals
PFOS	Perfluorooctane sulfonate
PFS	Perfluorinated surfactants
POP	Persistent organic pollutant
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SDS	Safety data sheet
UNEP	United Nations Environment Programme
ZVO	Zentralverband Oberflächentechnik e.V. (German central association for surface technology)

1 Aim and background

The European POP Regulation (EC) No. 850/2004 (EU POP Regulation) on persistent organic pollutants (POPs) serves the implementation of the Stockholm Convention and the POP Protocol (Aarhus-Protocol)¹. In addition to rules concerning the production and use, also provisions applying to waste management are included in the EU POP Regulation.

Since 27 June 2008, the use of perfluorooctane sulfonates/perfluorooctane sulfonic acid (PFOS) has been banned in the EU (under Directive 2006/122/EC) due to its high persistence, its carcinogenic and reprotoxic effects (toxicity) and its potential to accumulate along the food chain (bioaccumulation), in addition to a high potential for long range environmental transport and poor biodegradability of PFOS-containing wetting agents. Since 24 August 2010, Regulation (EU) No. 757/2010 amending the EU POP Regulation has been in effect.

The Regulation also provides that the uses of PFOS will be phased out as soon as the use of safer alternatives is technically and economically feasible and releases of PFOS into the environment have been minimized by applying best available techniques. Hence, the necessity of exemptions is intended to be reviewed at regular intervals. After expiration of the derogation for wetting agents for use in controlled electroplating systems on 26 August 2015, the only specific exemption on the use of PFOS in electroplating will apply to

- ▶ "mist suppressants for non-decorative hard chromium (VI) plating in closed loop systems".

In their Status Report „Ersatz von PFOS in der Galvanik durch halogenfreie Ersatzstoffe“ [Substitution of PFOS in the metal-plating sector with halogen-free alternatives] (Blepp et al, 2013), the authors have arrived at the following conclusions:

1. A clear technical definition is required of the term, "controlled electroplating system", and what it means to "minimize releases of PFOS into the environment".
2. In case the derogation for hard chrome plating should further be extended, it is required for the POP Regulation to provide a clear technical definition of the term, "closed loop system" in order to ensure equal treatment of companies.

Furthermore, the Status Report has described alkyl sulfonates to be available as a substitute for PFOS. In the field of bright chrome plating, this substitute has already been used successfully for several years in an electroplating company. Hard chrome plating is extremely important for industry and currently, can rarely be replaced by other methods. So far, halogen-free alternatives are still used only rarely in hard chrome plating.

Based on the Status Report (Blepp et al. 2013), it is intended to compile more information on the use of PFOS in electroplating in order to address existing gaps in knowledge. This expert opinion is intended to contribute to this aim.

2 Methodological approach and determinations

To prepare this expert opinion, a literature search and review of scientific studies and journals was performed. Legal texts and recent publications by associations as well as information provided by the electroplating industry were evaluated. In addition, relevant stakeholders were contacted and interviewed (see Chapter 5).

For research on the internet, the keywords listed in the Table below were used for the individual work steps.

¹ http://www.unece.org/env/lrtap/pops_h1.html

Table 1: Keywords used for internet research

Keywords, German	Keywords, English
Hartverchromung <ul style="list-style-type: none"> ▶ dekorative Hartverchromung ▶ nicht dekorative Hartverchromung ▶ Funktionelles Verchromen 	Hard chrome plating / hard chromium plating <ul style="list-style-type: none"> ▶ Decorative hard chrome plating ▶ Non-decorative hard chrome plating
Kreislaufführung <ul style="list-style-type: none"> ▶ PFOS Galvanik ▶ Netzmittel für Chrombäder ▶ Schließung des Materialkreislaufs ▶ Geschlossenes Kreislaufsystem ▶ Chrom VI ▶ Antischleiermittel, Mittel zur Sprühnebelunterdrückung 	Closed loop circulation <ul style="list-style-type: none"> ▶ PFOS metal plating ▶ Wetting agent for chrome baths ▶ Closed material loop ▶ Closed loop system ▶ Chromium VI ▶ Mist suppressant / fume suppressant
Substitute / Ersatzstoffe <ul style="list-style-type: none"> ▶ PFOS-freies/ PFOS-frei / ohne PFOS ▶ halogenfrei 	Substitutes / Alternatives <ul style="list-style-type: none"> ▶ PFOS free
Stand der Technik <ul style="list-style-type: none"> ▶ Verdunster / Verdampfer ▶ Adsorption ▶ Absorption ▶ Verfahrenstechnik 	Best available Technology (BAT) <ul style="list-style-type: none"> ▶ Evaporator ▶ Adsorption ▶ Absorption ▶ Process technology

The platforms searched included:

- ▶ Google Scholar +
- ▶ Advanced Google Search
- ▶ Elsevier
- ▶ Plasma + Oberfläche
- ▶ Umwelttechnik
- ▶ Galvanotechnik
- ▶ Leuze Verlag
- ▶ Zentralverband Oberflächentechnik e.V. (ZVO)
- ▶ Stockholm Convention / UNEP / EU POP Regulation / ECHA

The work steps taken to prepare the expert opinion included:

- ▶ Description of decorative and non-decorative hard chrome plating as well as (new) functional chrome plating;
- ▶ Proposal for a definition of the term “closed loop circulation”, based on existing experience of the contractor, expert interviews by Mr. Willand (IUW-Integrierte Umweltberatung) and relevant literature;

- ▶ Screening of possible substitutes based on existing literature and the Status Report: „Ersatz von PFOS in der Galvanik durch halogenfreie Ersatzstoffe“ [Substitution of PFOS in the metal-plating sector with halogen-free alternatives) (Blepp et al, 2013);
- ▶ Qualitative expert interviews are carried out with the help of an interview guide with strategically selected stakeholders from the electroplating sector.

Suitable studies and information for this expert opinion have been listed in the List of references (see Chapter 10). The findings made and information obtained were completed with the help of interviews and examined for topicality in order to develop a statement on the issues concerned.

3 Chromium electroplating

With regard to the use of PFOS, chromium electroplating means the electrochemical deposition of chromium from aqueous electrolytes onto surfaces. So far, the different types of chromium plating have been distinguished mainly from the technical and optical perspective, i.e. bright chrome plating, hard chrome plating, soft chrome plating, matt chrome plating, pearl gloss chrome plating, black chrome plating, precision hard chrome plating, chrome plating for repair operations, etc.

However, for legal provisions such as the EU POP Regulation, it is required to define generic terms. Below, reference is made to the terms currently used.

3.1 *Hard chrome plating*

There is a great variety of techniques referred to as hard chrome plating based on different electrolyte compositions. The thicknesses of the functional hard chrome coating layers will mostly vary between 10 µm and 100 µm. However, they can also be as thin as 2 µm for precision hard chrome plating and up to 5000 µm for hard chrome plating for repair operations.

For standard sulfuric acid electrolytes, the anodes mostly consist of lead. However, today, mixed acid high-performance electrolytes containing methanesulfonic acid or methanedisulfonic acid are used most frequently. In these hard chrome electrolytes, platinized titanium electrodes or mixed oxide electrodes are used. There are also mixed acid hard chrome electrolytes that contain hydrofluoric acid, fluorides or silicofluorides. PFOS is used in chrome plating electrolytes, as a rule, in a concentration range of 30-80 mg/L in order to reduce the surface tension of the process solution.

Technical hard chrome layers have a number of high-technology properties which, above all in their sum, are difficult to replace, such as

- ▶ Extremely high hardness;
- ▶ Excellent wear resistance;
- ▶ High adhesion strength on the base materials;
- ▶ Very good tribological properties (low friction coefficient, good lubrication, minimal wear);
- ▶ High temperature resistance (up to 400°C);
- ▶ High resistance against chemicals;
- ▶ Low wettability;
- ▶ High corrosion resistance, above all on previously nickel-plated metal surfaces;
- ▶ The components are exposed to only very low temperatures so that warping of components is avoided;
- ▶ High abrasion resistance;
- ▶ Hard chromium layers are anti-adhesive;
- ▶ Wide range of minimum and maximum layer thicknesses;

- ▶ Good decorating properties for repair operations, i.e. the hard chromium layer can easily be removed in most cases;

Typical uses include highly stressed components in the automotive industry, in aircraft construction, ship-building and engineering, such as

- ▶ pulleys and application rollers in the paper industry;
- ▶ cylinders and piston rings as well as shock absorbers in the automotive industry;
- ▶ cylinders in the printing industry;
- ▶ pumps and pipes in the cement industry;
- ▶ cooling and drying drums in the food industry;
- ▶ pistons and piston rods for hydraulics and pneumatics, e.g. in medical technology;
- ▶ tools in mould construction.

3.2 “Decorative hard chrome plating”

The terms used in some legal texts and their translations with regard to the different chrome plating techniques in electroplating are in part misleading and/or obsolete. Thus, in the EU POP Regulation (Commission Regulation (EU) No 757/2010 of 24 August 2010 amending Regulation (EC) No 850/2004), the use of PFOS as mist suppressants for “non-decorative hard chromium (VI) plating” in closed loop systems is allowed as a specific exemption (see Chapter 1). Such wording suggests a „decorative hard chromium plating” to exist as well, where consequently, the use of PFOS would be banned.

However, according to the concordant opinion of almost all experts, “decorative hard chromium plating” does not exist in practical use. This is why the distinction used in the above Regulation is misleading. All variants of “**hard chromium plating**” are “**non-decorative hard chromium plating**”.

This is why it is suggested by the authors to introduce the term of “functional chromium/chrome plating” in general for all types of hard chrome plating (see Chapter 3.4).

3.3 Decorative chrome plating

Decorative chrome plating represents the preferred surface finish for a majority of electroplated consumer products and equipment goods. The economic benefit consists in an optically attractive surface combining a high hardness, chemical resistance and toxicological safety, which are all achieved with comparatively low costs/efforts. This guarantees a long usable lifetime of the coated goods, which contributes to the sustainability of a product. An example is chromium plating of furniture components such as swivel chair feet. In addition to decorative reasons, corrosion protection and wear resistance play an important role.

For some uses, there is no clear distinction between decorative chrome plating, so far mostly referred to as bright chrome plating, and hard chrome plating for technical reasons. Therefore, it makes sense to refer to the purpose and function of the deposited chromium layer.

As an example, the use of chromium plating of fittings in the sanitary industry is mentioned in this context. Even under conditions of intensive industrial use and contact with abrasive or acid-containing cleaning agents, such chromium surface will protect high-quality water taps and similar goods for decades. Thus, decorative chromium surfaces contribute to saving natural resources. In order to develop the envisaged properties, the chromium coatings need an even structure. Such structure is expressed in the form of a cracks network or porosity that can be electrochemically produced by hexavalent chromium processes only.

In terms of quality, the properties required are not achieved by alternative surfaces in many cases. For surfaces coated by means of alternative techniques, e.g. from trivalent chromium plating processes, or lacquers, the usable lifetime is a mere fraction of that achieved by hexavalent chromium processes.

However, chrome plating is also applied to consumer goods where only optical properties are important. For example, chrome plating of plastic articles (such as perfume bottle caps) for merely optical reasons can clearly be considered as “decorative”.

3.4 Functional chrome plating

In an application for authorization of chromium trioxide (CrO₃) filed with ECHA, the term of “functional chrome plating” has been defined by the CTAC Consortium, an association of more than 150 companies (CTAC 2015):

“An industrial use, meaning the electrochemical treatment of surfaces (typically metal) to deposit metallic chromium using a solution containing chromium trioxide (amongst other chemicals), to enhance wear resistance, tribological properties, anti-stick properties, corrosion resistance in combination with other important functional characteristics. Such secondary functional characteristics are chemical resistance, able to strip, unlimited in thickness, paramagnetic, deposit not toxic or allergic, micro-cracked brightness. Process characteristics are closed loop processing, high speed, flexibility in size, plating of inner surfaces, low process temperature, surface can be machined, assemblability.”

Functional chrome plating may include use of chromium trioxide in pre-treatment and surface deposits unlimited in thickness but typically between 2 µm and 5,000 µm. Functional chrome coatings are widely used in many industry sectors.”

In this application for authorization, the term of “functional chrome plating with decorative character” has also been defined:

„The electrochemical treatment of metal, plastic or composite surfaces to deposit metallic chromium to achieve an improvement in the surface appearance, level of corrosion protection and to enhance durability. In functional plating with decorative character, chromium trioxide is used to deposit a coating of typically 0.1- 2.0 µm, or, where increased corrosion resistance is required, a ‘micro cracked’ chromium deposit at thicknesses of typically 0.5 - 2.0 µm, over a nickel undercoat. Functional plating with decorative character may include use of chromium trioxide in a series of pre-treatments and surface deposits. Functional plating with decorative character is used widely in automotive, plumbing, household appliances and bathroom, furniture and homeware applications. Functional plating with decorative character includes black chrome plating provided that there is no residual Cr(VI) on the surface of the article at the detection limit¹, which has been used, for example, in solar panel manufacture, where deposits are porous and <1 µm in thickness.”

There are a number of approaches to a suggested definition by other stakeholders in the field of surface technology:

- Opinion of the Austrian “Fachverband der Metallwaren” (national representation of all enterprises active in mechanical and plant engineering, steel construction and metalware production)²
- Extract definition from T.W. Jenlink (2015): Branchenführer Galvanotechnik 2015/16. Nachschlagewerk für galvanische Betriebe und Anwender galvanischer Überzüge (14. Auflage). Bad Saulgau: Eugen G. Leuze Verlag, page 619:

„Functional electroplated coating is a term used if the coatings or combination of coatings are intended to confer properties to the surface that are not characteristic of the base material but are indispensable for the function of the component, enhance or optimize its functional behaviour or extend its working life. Functional electroplated coatings are of particular importance in cases where at the same time several

² http://www.fmmi.at/uploads/media/Stellungnahme_PFOS_FMMI_06_2014.pdf

surface properties or a certain combination of these are required. In English usage, the probably more accurate term of “surface engineering” is used to describe such functional coatings.

The properties referred to as “functional properties” include, among others, hardness, abrasiveness, lubricating qualities, solderability, electrical and thermal conductivity. A property commonly (but incorrectly) not included is corrosion behaviour, although the latter is of particular importance in almost any case, in addition to all other properties. Another property not considered as belonging to this group is appearance, although in certain cases (e.g. mirrors), it will also determine the function.

The uses of functional electroplating also include repair operations of components worn out in use or manufactured undersize. During maintenance operations, the coatings applied by electroplating are used to restore measurements and/or confer to the surface certain properties such as hardness, abrasion resistance etc. Also the manufacture of components by electroforming is included in functional electroplating.”

Thus, the terms of “functional chrome plating” and “functional chrome plating with decorative character” appear to be more appropriate for a differentiation than the terms of “decorative hard chrome plating” and “non-decorative hard chrome plating” hitherto used.

4 PFOS in electroplating

4.1 General use of PFOS

Perfluorinated and polyfluorinated chemicals (PFC)³ are used as wetting agents for numerous wet-chemical processes of surface finishing due to their properties with regard to process safety (e.g. chemical resistance, good and even wetting of the surface).

In electroplating, a field of surface technology, PFOS is of particular importance. PFOS is used due to its very high chemical stability (resistance) to the very strong oxidizer, chromium (VI), and to sulfuric acid/chromosulfuric acid. PFOS and PFOS compounds, respectively, are toxic, persistent and carcinogenic industrial chemicals not found in nature originally. They are anthropogenic, i.e. originate in human activity. In electroplating systems, PFOS serves to decrease the surface tension of treatment baths, where the components to be treated are immersed (good wetting properties), and to reduce the amount of process solution carried over into subsequent tanks by means of more rapid draining. A complete removal of process solutions from the surface is a prerequisite for the quality and uniformity of coatings.

The use of PFOS in chromium electrolytes reduces the formation of toxic chromium (VI) aerosols by evaporation of hydrogen and oxygen on the electrodes and thus, makes an important contribution for occupational safety. In addition, PFOS is not to be expected to form sludge from degradation products in the tanks, which could also impair the quality of component surfaces. From time to time, PFOS has to be replenished because its partial drag-out into subsequent electroplating tanks cannot be completely prevented. The precise amount of PFOS to be replenished is determined for example by measuring the surface tension. Under such chemically extremely aggressive conditions, conventional, biodegradable surfactants would rapidly degrade.

Prior to the general ban on the use of PFOS by the EU POP Regulation, PFOS was used in the electroplating sector in Germany in hard and bright chrome electrolytes, in chromic acid plastic etchants, in alkaline zinc and zinc alloy electrolytes, in precious metal plating, e.g. in strongly acidic gold-palladium and rhodium baths, and

³ Another term frequently used instead of PFC is PFAS (perfluorinated and polyfluorinated alkyl substances).

in electroless nickel plating. Already in 2005, the use of PFOS-free surfactants in aluminium anodizing was described as the state of the art in the BAT (UBA BVT St2005)⁴.

The drawback of the extreme chemical resistance of PFOS consists in the fact that PFOS is almost indestructible also in the cycles of nature. It accumulates in the organisms of the food chain and, at the top of the food chain, returns to man as its originator.

The quantitatively largest share of PFOS is used in hard chrome plating, amounting to about 50% of the total PFOS quantity used in surface technology processes in Germany (Zangl et al. 2012).

Below, a number of wetting agents containing PFOS have been listed.

- ▶ „FUMETROL 140“ by Atotech, 43 g/L PFOS
- ▶ „Bayowet FT 248“ by Lanxess: Analysis in 2008: 580 g/L PFOS + 64 g/L PFBS
- ▶ Proquel Z Fa.Kiesow: 50 g/L PFOS Ammoniumsals
- ▶ Silken Wet 302 : 45 g/L PFOS
- ▶ Ankor SRK: 69 g/L
- ▶ PFOS without PFBS: Surfactant NCR by Blasberg-Werra-Chemie: ca. 50 g/L PFOS ; PFBS-free

4.2 Use of PFOS in plastic electroplating

Electroplating of plastic materials such as acrylonitrile butadiene styrene copolymers (ABS) requires making them electrically conductive in a first step. To this aim, microscopic pores of about 1 µm in size are etched into the plastic surface initially by treatment with very strong oxidizing etchants. In this process, it is only the butadiene component that is chemically attacked.

In the vast majority of cases, the etchant is a highly concentrated chromo-sulfuric acid solution used at high temperatures. In order to achieve wettability of the hydrophobic plastic surfaces, a stable surfactant has to be added to the chromo-sulfuric acid. PFOS is used for this purpose.

Palladium ions are then introduced into the microscopic pores (“activation”), which subsequently are reduced to elemental palladium by means of a catalyst. Alternatively, a colloidal seeding process is applied where colloidal palladium in a tin hydroxide protective colloid is used, and the palladium seeds are exposed by treatment with an acid mixture. Subsequently, the plastic components are immersed in a stabilized electroless nickel electrolyte. The palladium seeds will catalyze the reductive deposition of nickel. Similar to the palladium, the deposited nickel will, in turn, act as a catalyst for further nickel deposition, resulting in the formation of a closed conductive nickel-metal layer.

Subsequently, other metals can be deposited onto the surface that has become electrically conductive in this way. Frequently, the plastic component is chrome plated subsequently, where again, PFOS may be used.

Alternative immersion techniques for etching of plastic materials that have, in principle, been successfully tested so far include acid permanganate solutions, nitric acid and trichloroacetic acid mixtures. Disadvantages that have become apparent included: Problems with wastewater treatment due to organohalogen compounds contained, problems when searching for suitable rack insulation, risk of formation of nitrous gases during the use of nitric acid, and problems with the formation of manganese dioxide and fire safety issues when using permanganate solutions.

⁴ under Chapter 5.2.5.2, the BAT for surface treatment of metals and plastic materials.

5 Interviews

The qualitative expert interviews with strategically selected stakeholders from the electroplating sector were carried out based on an interview guide and questionnaire, respectively. They were used for an in-depth analysis of the situation of the current state of the art in technology and cross-check the information obtained with that from existing literature. The knowledge gained in this way is used to review the definition of closed loop circulation and to screen possible alternative substances. Originally, it was intended to address three or four strategically important stakeholders involved in the value chain. However, in order to take better account of the above-mentioned great variety of electroplating systems despite a tight budget, a fifth company and the ZVO (German central association for surface technology) as an important stakeholder were also included. Each of the interviews was documented in writing in a final protocol / questionnaire.

The data compiled were integrated and anonymized. They were included in Chapters 6 and 7 and are documented in Chapter 11.

The stakeholders involved in the value chain that were available for interviews and onsite visits are listed below in Table 2.

Table 2: Overview of interview partners

COMPANY	Type of chrome plating
Company A	Functional chrome plating Electroplating subcontractor (“jobbing shop”), hard chromium ⁵
Company B	Functional chrome plating In-house electroplating plant, hard chromium
Company C	Functional chrome plating Electroplating subcontractor, hard chromium
Company D	Functional chrome plating Electroplating subcontractor, hard chromium
Company F	Functional chrome plating In-house electroplating plant, rack electroplating
ZVO	German central association for surface technology; ZVO cooperated in revising Chapter 3.

The names of the companies are known to the Federal Environment Agency.

Immediately after the project had been launched, the German central association for surface technology (ZVO) was requested to communicate the names of a number of member companies willing to cooperate in the project. Regrettably, this approach remained unsuccessful. Due to these fruitless efforts, the company interviews started with a delay of eight weeks. The companies involved could only be found for collaboration owing to the existing contacts of the contractors/authors of this expert opinion. The interviews were predominantly carried out on site.

⁵ An electroplating subcontractor (“jobbing shop”) is a company exclusively treating components of other companies. An in-house electroplating plant is a facility treating the company’s own products. This is why for in-house electroplating plants, the order inflow, the workflow and the operating conditions are much more constant. Electroplating subcontractors have to handle a much wider range of base materials, processes and customer requirements.

6 Closed loop operation

6.1 Preliminary considerations regarding the definition of a closed loop for PFOS

The definition of a closed loop (operation/system) has been much discussed in recent years and plays an important role also at present in individual cases for authorizations of new projects and for change authorizations, and, with regard to chromium(VI), for the authorization under REACH.

So far, there is no uniform definition for a closed loop operation with regard to PFOS or chromium(VI). The chrome plating processes are highly diversified in electroplating. Therefore, it is impossible to describe a general and uniform process technology for all of the various uses and process combinations as the state-of-the-art technology binding for all companies and plant types.

This is why in the framework of the present expert opinion, the issues listed in the specification of services with regard to the definition of “closed loop systems” can only be addressed from the perspective of actually existing facilities.

6.2 Examples of state-of-the-art closed loop systems for PFOS

6.2.1 Minimizing PFOS use by means of measurement technology

This chapter was chosen to precede the examples of closed loop systems for PFOS because it applies to all possible uses of PFOS in electroplating technology.

Until 26 August 2015, it was allowed to use PFOS as „wetting agents for use in controlled electroplating systems“ under the EU POP Regulation. However, no details are given of what is actually meant by the term, “controlled”. In the past, PFOS was frequently used by electroplating operators under uncontrolled conditions without close examination and/or only on the basis of empirical values, with practitioners working in the field often following the maxim “A lot helps a lot”. When, in contrast, the dosage was determined as a function of a measured value, a reduction of the use of PFOS by 50% was possible in some cases.

Hence, it should be considered whether in an update of the EU POP Regulation, the use of PFOS should be confined not only to the condition of a “closed loop system”, but in addition, to a “controlled electroplating system” also for functional chrome plating.

In the current version of the draft „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” (UNEP/POPS/COP.7/INF/21 2015), Chapter “3.4.2.1 Measures to avoid or reduce releases” , refers to the BAT in the use of PFOS, reading as follows⁶:

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

BAT to optimize dosage of PFOS as a function of a measured value includes:

⁶ Chapter 4.4.4 of the draft BAT/BEP Guidance (UNEP/POPS/COP.7/INF/21 2015) (?)

- ▶ *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) “*

Hence, the dosage of PFOA has to be based on

- 1) Measured surface tension (e.g. ring or bubble tensiometer), or
- 2) The measured ampere hour rate after determination of reproducible empirical values, or
- 3) A certain defined and documented surface throughput, or
- 4) The measured foam stability in the Hull cell.

Indents 1), 2) and 4) cannot be applied for plastic etchants due to the missing electrochemical processes and/or the presence of interfering substances.

At any rate, the measuring results and PFOS consumption figures per PFOS usage site should be documented in writing so that they can be controlled.

Another description can be found in Schwarz et al. (2011)::

- ▶ *“Separation of waste water streams containing PFOS from those that are PFOS-free*
- ▶ *Merging those waste water streams that contain PFOS which cannot be avoided*
- ▶ *Integration of efficient additional technology for virtually complete elimination of PFOS*
- ▶ *Optimisation of enhanced systems solution to avoid emissions of PFOS, recognizing that additional technology for elimination of PFOS (e.g. adsorption facility) can be cost-intensive”*

6.2.2 Example: Closed loop by means of an eightfold cascade

In Chapter 3.4.2.1 of the draft BAT/BEP Guidance (UNEP/POPS/COP.7/INF/21 2015) it is stated that under conditions of high evaporation losses of hot chromium baths, a closed loop can be achieved already by using a very water-saving rinsing system with recirculation of the concentrated rinse water into the process bath.

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

In the background paper on Annex 40 to the German wastewater ordinance (Abwasserverordnung, AbwV), a minimum of at least 3 rinsing steps after process baths are required. In the field of bright chrome plating, a five-step rinsing system is widely used already today for quality reasons alone. In the field of functional chrome plating, a largely closed loop can be achieved by using eight rinsing steps. The principle is as simple as it is effective. By applying a sufficient number of rinsing steps, the amount of excess rinse water is minimized to such an extent that eventually, the entire amount of rinse water can be used to compensate for the evaporation losses of the hot chromium bath. In this way, both the dragged-out chromic acid and the PFOS used are fed back into the electrolyte.

In the case of company E, the components are initially rinsed above the process bath. Subsequently, the components are rinsed in a static rinse, which is continuously recirculated into the process bath to balance drag-out and evaporation losses. The first tank of the eight-stage cascade is connected to a buffer tank which, at the

weekend, is used to compensate for further evaporation losses of the electrolyte. No PFOS-containing wastewater is discharged from the rinsing area.

This process works in a way reducing the amounts of effluent, but not effluent-free. PFOS-containing drip losses, ground effluent and effluent from the exhaust air scrubber must still undergo treatment in the in-house effluent pre-treatment plant.

However, since considerable space is required, a rinse system of this type is hardly suitable to upgrade existing systems. Rather, it can be considered for newly planned systems.

6.2.3 Example: Closed loop by means of a combination of evaporation and ion exchanger technology

Before their further use, chromium-plated components must be rinsed absolutely free from chromium(VI) and PFOS. Even in water-saving rinsing technology, excess rinse water will be generated, as a rule, which can only be countered by evaporation or vaporization of the excess water. Vacuum evaporation technology is occasionally used, however, material resistance limits will restrict its use because of the chemical aggressivity of chromic acid at elevated temperatures. Such limits are still tightened by the fact that, for reasons of e.g. enhanced electricity yield and throwing power, modern mixed acid hard chrome electrolytes may contain hydrofluoric acid, fluorides or silicofluorides (Lausmann und Unruh 2006)⁷, which under the reaction conditions prevailing in the vacuum evaporator may release hydrofluoric acid. This is why durably resistant vacuum evaporators must consist of very cost-intensive materials such as titanium or polytetrafluoroethylene (PTFE) / polyvinylidene fluoride (PVDF) components.

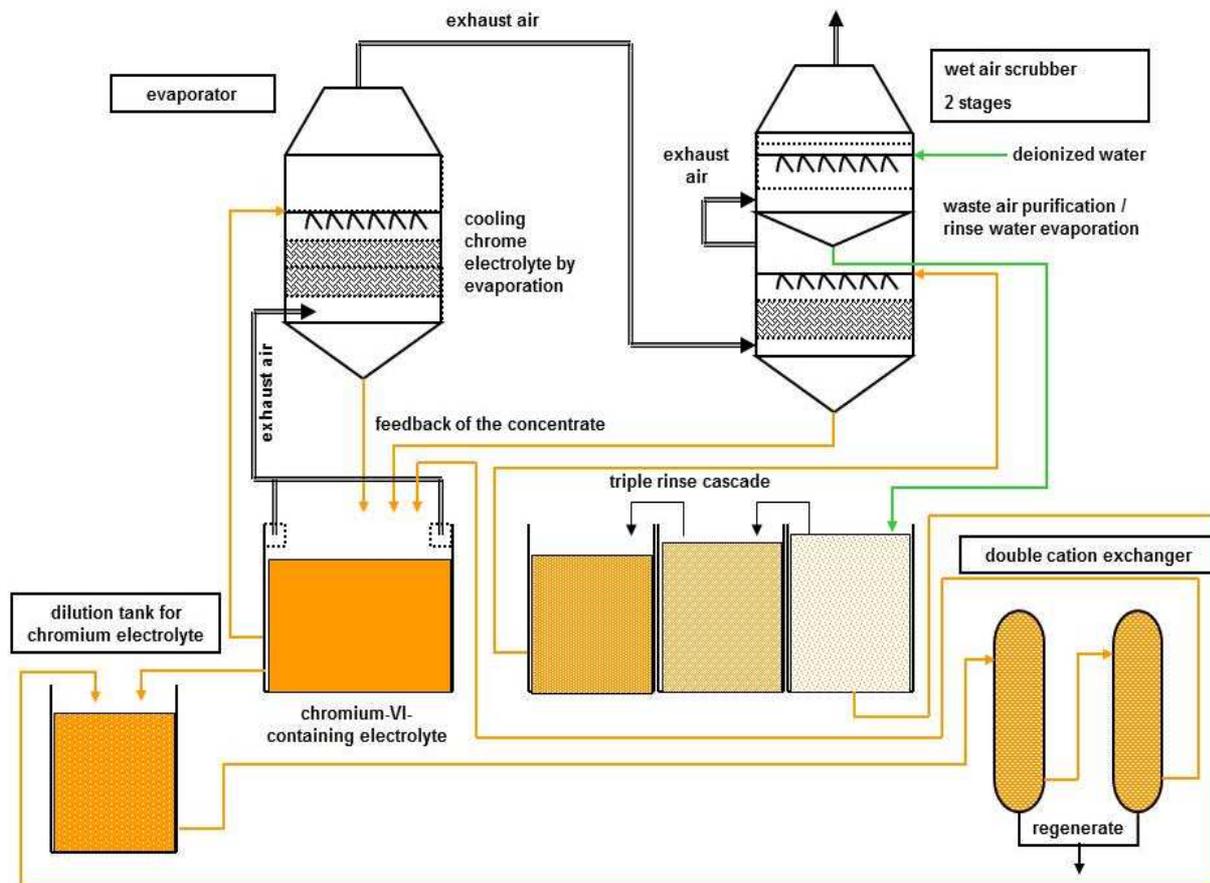
More frequently, water is therefore removed by evaporation technology operating at lower temperatures where chromo-sulfuric acid is less chemically aggressive. By means of an appropriate combination with an exhaust air scrubber, also the extracted chromic acid aerosols are recovered, which in decorative chrome plating can amount to up to 30% of the chromic acid used (Lausmann und Unruh 2006)⁸.

Chapter 4.4.4 of the draft BAT/BEP Guidance (UNEP/POPS/COP.7/INF/21 ?) contains a process flow chart demonstrating the combination of multiple rinse technique with evaporation technique, waste air scrubber and ion exchange for electrolyte purification.

⁷ P.116ff

⁸ P. 447

Fig. 1: Process flow chart: Multiple rinse technique with evaporation technique, waste air scrubber and ion exchange for electrolyte purification (UNEP/POPS/COP.7/INF/21 2015)



The route of PFOS-containing chromic acid aerosols shows that the latter are sucked off from the electrolyte surface, transported with the exhaust air and initially scrubbed and separated in an evaporator together with the chromium electrolyte proper. In two further exhaust air purification steps, the remaining aerosols are scrubbed in a 2-stage exhaust air scrubber initially with a relatively highly concentrated rinse water from the first cascade rinse and finally, with pure deionized water. Hence, the exhaust air is scrubbed three times in the counterflow and as a result, will safely comply with the provisions of the Technical Instructions on Air Quality Control. On its route through the different purification stages, the exhaust air will, at the same time, extract water from the chromic acid system and thus, will remove the excess rinse water mentioned above. In addition, heat will be extracted in the evaporator from the chromium electrolyte, which heats up due to the poor electrical efficiency of the process, resulting in a reduction of energy demand for cooling of the electrolyte.

The route of the water shows that essentially, the system is fed with deionized water only via the last step of the exhaust air scrubber (green arrow). The water is initially used for the final scrubbing of exhaust air and subsequently, led in the counterflow towards the components to be cleaned in a threefold cascade. During this procedure, it becomes more and more enriched with the dragged-out chromium electrolyte and thus, with PFOS. At last, the rinse water is further concentrated via the first step of the exhaust air scrubber and fed into the electrolyte. This will result in a largely closed loop for PFOS and chromium(VI). The recovery rate for chromic acid is up to 98%.

Company F operates largely according to the procedural principle described in the draft BAT/BEP Guidance. Instead of three, even five rinse tanks are used. In this procedure, deionized water is fed into the system via the last of the five rinsing steps instead of via the exhaust air scrubber.

Experience has shown that in the long run, a 100%-closed loop is impossible. Contaminants and impurities will accumulate and have to be removed from the system. In the process of chrome plating, foreign metals such as iron, copper, zinc, nickel, aluminium and chromium(III) ions accumulate in the chromium electrolyte, thus disturbing the deposition. The foreign metals originate from the metal surfaces to be treated, which initially, become partially dissolved in the chromic acid before the electrochemically deposited chromium layer will prevent a further etching attack. Also the copper bars used for power supply and the contact points of racks contribute to the contamination of the electrolyte by foreign metals. Such contamination requires a partial disposal of the electrolyte at regular intervals, resulting in an undesirable opening of the PFOS and chromic acid loop, thus incurring considerable costs. The working life of the chromium electrolyte can be extended considerably by removing the foreign metal ions. Depending on the plant where it is applied, the ion exchange technique for extension of the working life will pay off after 1 – 7 years (Moosbach 2015).

Before the chromium electrolyte can be purified from chromium(III) ions and foreign metal ions via cation exchanger, it has to be diluted to about 100 g/L CrO₃ because the organic cation exchange resins will be attacked too much by chromic acid at higher concentrations. The resins are regenerated by means of ca. 20% sulfuric acid since the entire process is carried out using sulfuric acid. The sulfuric acid used for regeneration is rich in iron, as a rule, and can be used as a flocculant in the electroplating wastewater treatment ⁹.

Limitations of the procedure

It is important for recycling of the evaporator and/or waste air scrubber solution that no foreign process baths, such as degreasing processes, are connected to the same waste air line, because the chromic acid may become contaminated with the aerosols of such process solutions, rendering its reuse impossible. Also in systems where different chromium electrolytes are used it may be required to apply separate waste air scrubber or evaporator systems, e.g. in order to avoid a mixing of mixed acid and sulfuric acid hard chrome electrolytes.

6.3 Characteristics of a largely closed loop for PFOS

A completely closed loop for PFOS would be characterized by the fact that any substance loss caused by aerosol extraction and drag-out of chromium electrolyte is compensated for by suitable recovery measures. However, recovery of components of waste air and rinse water will also recirculate foreign substances and impurities (above all foreign metals) that interfere with the process. Such foreign substances have to be eliminated from the chromium electrolyte by suitable purification measures (fine filtration and cation exchange). The regeneration process (back-flush water and ion exchanger regenerates) causes PFOS losses. Other substance losses of an unknown extent are caused by unintended side reactions such as the electrochemical degradation of PFOS (according to Fath 2008, to fluoride) or, in single cases, precipitation as barium salts during the so-called “blunting” (?) of hard chrome electrolytes (see Annex 11.1.4). Furthermore, the system undergoes unintentional and uncontrolled PFOS depletion due to adsorption on pipe and tank walls, waste air channels and other plant components and above all, alkaline ion exchange resins such as those applied in rinse water cycle systems. Finally, PFOS depletion from the cycle occurs as a result of discharge of PFOS-containing waste water and/or adsorption on the metal hydroxide sludge and/or a PFOS ion exchanger specifically applied for this purpose.

Note: There is a known case of a hard chrome electroplating plant where PFOS has no longer been used in the production since 2008. In this case, no PFOS was replenished into the hard chrome electrolyte. However, the existing process solution was not completely replaced. Nevertheless, today (in October 2015), the company concerned is still operating a PFOS-specific ion exchanger to remove PFOS from the waste water because oth-

⁹ The cation exchanger is used exclusively to extend the working life of the chromium electrolyte, which indirectly will considerably extend the usage duration of PFOS. The cation exchanger removes foreign metals present as cations. Being an anion, PFOS is not specifically captured.

erwise, it would be unable to comply with the PFOS limit value officially fixed for individual cases. This is caused by, in the case of PFOS, unusually long-lasting desorption processes involving all plant components that once came into contact with PFOS and the protracted drag-out of the remaining PFOS from the hard chrome electrolyte.

Characteristics of a largely closed loop for PFOS are

1. Process tanks with efficient extraction to minimize contamination of the environment with chromic acid aerosols; if required, encapsulated transporters with extraction system.
2. Exhaust air scrubber with recirculation of the wash solution into the process solution.
3. Exclusively documented PFOS dosage, related to throughput and demand, respectively;
4. Recovery of the PFOS-containing chromium electrolyte by rinsing of the components directly over the process bath;
5. Multi-stage cascade rinsing system for extensive recovery of dragged-out PFOS to achieve a high rinse criterion with a minimum amount of excess water;
6. Use of an evaporator for concentration of the rinse water and recovery of the dragged-out process solution with simultaneous use of excess heat - due to the poor electricity yield of the chrome plating process;
7. Recovery of rinse water concentrates to balance evaporation losses of the electrolyte;
8. Extension of the working life of the PFOS-containing chromium electrolytes by using cation exchange technique for separation of foreign metals and chromium(III) from rinse water concentrates; regeneration of cation exchanger resins with sulfuric acid and their reuse in the waste water treatment process;
9. Treatment of PFOS-containing waste water flow types by means of PFOS-specific ion exchangers;

In practice, only one company (Company F) was found to apply, on principle, all measures mentioned above. The other companies were found to apply the above measures only in part in an effort to close the loop for PFOS. To a vast extent, the economically reasonable options and measures to achieve a closed loop for PFOS and chromium(VI) depend on the actual conditions of the process stage on site.

7 The fate of PFOS from electroplating plants

Following the discussion of the options for closed loop systems for PFOS, we will have a look at possible leaks in the PFOS cycle.

In general, it is assumed that owing to the rinse process, there are no longer any traces of PFOS on the treated products of electroplating and surface technology (Buser und Morf 2009). This is why the treated components can be neglected as PFOS sources.

Substance flows (output) possibly involving PFOS losses (routes into the environment) include:

- ▶ Input into the environment via waste water and airborne emissions;
 - Emission via exhaust air within the legal limits (drag-out recovery after exhaust air scrubbing and droplet separator);
 - Discharge of the treated PFOS-containing electroplating waste water, unless zero discharge process;
- ▶ Wastes, via the residues from electroplating processes;

- Regenerates of the cation exchangers in the chromium(VI) cycle;
- Disposal of the chromium hydroxide sludge from waste water treatment;
- Disposal of ion exchange resins used to retain PFOS;
- Anion exchangers from rinse water cycles;
- Disposal of lead chromate sludge forming in the chromium electrolyte;
- Disposal of used porous lead anodes;
- Disposal of electroplating racks (ca. 1x/a);
- Disposal of tanks, pipes and waste air channels (at about 10-year intervals);
- Disposal of barium sulfate sludge from bath maintenance measures of the chromium electrolyte (note: applied to remove excess sulfate forming in some electrolytes);

An analysis of the barium chromate sludge from company F found high concentrations of H₄PFOS (1 600 mg/kg) and residual concentrations of 110 mg/kg of PFOS (no use of PFOS for years). It would be conceivable that in such cases, a poorly soluble barium salt of the perfluorinated and/or polyfluorinated sulfonic acids was formed during the treatment of the chromium electrolyte with barium carbonate (analogous to the formation of conventional calcium soaps). If this can be confirmed, the procedure could be suitable, on principle, to remove PFOS from water-based systems. In this respect, further research could possibly be required.

The distribution of the individual substance flows (emissions) depends on the site. This is why emissions will arise from spatially distributed sources instead of point sources. Furthermore, substance flows will depend to a considerable extent on the process technology used in production, recycling technologies and waste water treatment, the annual wastewater volume and the input concentration of PFOS.

The foremost part of the substance fed in will leave the process stage of the plant via the waste and waste water flows. The waste flow will end up in different waste treatment systems. Consequently, there will be different PFOS-containing waste fractions with different concentrations (also cf. the above list). In this regard, there are different situations of waste treatment to be considered in this industrial sector. Therefore, it is difficult to quantify the different amounts of the individual types of waste generated. According to the current state of knowledge, neither wastes from electroplating nor their waste waters are specifically treated for PFOS contained therein.

Because there are no natural sinks for PFOS, technical waste water treatment procedures for elimination of PFOS loads are of particular importance. In addition, many of the PFOS-containing waste waters¹⁰ are produced at first at the treatment facilities processing the waste flows from electroplating.

To a minor extent, input into the environment will also result from airborne emissions released to the atmosphere¹¹. However, the quantities of such substance flow are very small in proportion to the waste and waste water flows.

8 Substitutes and alternatives

8.1 General information

After expiry of the transitional rule on 26 August 2015 according to the EU POPs Regulation, PFOS may be used exclusively for “non-decorative hard chromium (VI) plating in closed loop systems” (see Chapter 1).

¹⁰ Depending on the process step, these may include complex-containing ammoniacal process waters, acid process waters containing copper and nickel as well as those containing chromium.

¹¹ According to Zangl et al. 2012, airborne emissions calculated for 2010 amounted to about 360 g.

Companies in the electroplating and surface technology sector have become aware of the risks and dangers from PFOS. In recent years, numerous methods for reducing PFOS consumption have been developed and PFOS-free wetting agents were examined with regard to their suitability for electroplating processes, in particular to minimize the PFOS load in waste water. In addition, the pressure to substitute PFOS as well as the dwindling economic importance (Seßler, B. (2014) also resulted in a considerable internal willingness to do without PFOS, regardless of the exemption mentioned above. Already now, ZVO has estimated that only a minority of companies have not yet found a way to do without PFOS. Also the ZVO generally supports the efforts to protect humans and the environment from the potential risks of dangerous substances. Substitution is a process that has begun and is being continued by the industry representatives concerned.

Surveys by the Öko-Institut that have been summarized in a Status Report for UBA (Blepp et al. 2013) have shown alkyl sulfonates to be available as a PFC-free substitute for PFOS. This alternative has been used successfully for several years in a few companies. In the field of bright chrome plating, this substitute could be used successfully in an electroplating plant. Also the technical specifications (such as chemical resistance at operating temperatures) required by customers were complied with. Partly fluorinated wetting agents remaining stable under the operating conditions and developing no harmful degradation products have clearly become established also in hard chrome plating, e.g. at temperatures between 50°C and 70°C (Wiethölter 2014) (see also Table 3).

On the other hand, a substantial point of criticism of the electroplating industry concerning the alternatives is that non-fluorinated or partially fluorinated surfactants become oxidatively decomposed very rapidly in process solutions for chromium electroplating and chromium(III) compounds are formed that impair the functional efficiency of process solutions.

8.1.1 Overview of substitutes

The perfluorinated surfactant most important for chrome plating processes is PFOS, whose technical formulations contain low amounts of perfluorobutanesulfonic acid (PFBS) in addition.

The alternative to PFOS used most frequently at present consists in the partially fluorinated substance H₄PFOS¹² CAS-No.: 276-19-97-2 (C₈F₁₃H₄SO₃-), also referred to as 6:2 fluorotelomer sulfonate (6:2 FTS) or 1H,1H,2H,2H-perfluorooctane sulfonic acid. By further transformation in the environment, this telomere-based alternative can degrade to become the stable perfluorohexanoic acid (PFHxA) and can be detected in water bodies.

As a rule, the surfactants are placed on the market in the form of mixtures rather than pure substances. Such mixtures are produced either by the manufacturer of the substance himself or a formulator. In the electroplating sector, many mixtures are not purchased directly by the electroplating company. Their use in the electroplating company is serviced by a specialized company. As a rule, the formulators will closely cooperate with these specialized companies (Blepp et al. 2013).

The following alternatives to PFOS are being discussed and/or used:

1. **Fluorinated substitutes:** As to their uses, these substances are comparable with PFOS, and they can be used in almost all processes including chromo-sulfuric acid etchant, bright chromium and hard chromium

¹² Other synonyms: (1H,1H,2H,2H)-Perfluorooctanesulfonic; 2-(Perfluorohexyl)ethane-1-sulfonic acid; 1H,1H,2H,2H-PERFLUOROOCETANESULFONIC ACID; 2-(Tridecafluorohexyl)ethanesulfonic acid; 1H,1H,2H,2H-PERFLUOROOCETANESULPHONIC ACID; 1H,1H,2H,2H-Perfluorooctanesulphonic acid 98%; 1H,1H,2H,2H-Perfluorooctanesulphonic acid 98%; 1H,1H,2H,2H-Tridecafluorooctane-1-sulphonic acid 98%; 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanesulfonic acid; 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonic acid

electrolytes.

The fluorinated substitutes can be divided into three sub-groups:

- i) short-chain fluorinated surfactants;
- ii) polyfluorinated surfactants; and
- iii) polyfluorinated compounds.

2. **Fluorine-free substances:** These have already been partially used in bright chrome electrolytes. According to some suppliers of process chemicals, their use in hard chromium electrolytes is also possible. According to the current state of knowledge, the use of such substances should be considered on a case-by-case basis.

Also **alternative technologies**, such as PTFE-coated balls on top of bath¹³ are mentioned, among other options. However, in this respect, the state of knowledge is that this alternative will not reduce chromium emission from the chroming bath but, in contrast, chromium emissions appear to increase, as compared to emissions released in cases where no mist suppression is applied at all. Another physical alternative, namely in the form of a mesh or a blanket¹⁴, could be considered for large-scale series plating of uniform products. However, this kind of alternative will still require considerable research.

No surfactants are required e.g. in processes where surfaces are coated in a closed coating reactor. This is a **technical solution** in the field of hard chrome plating where neither any rinse water nor gas emissions will lead to environmental pollution by PFOS¹⁵.

Poulsen et al. (2013) have demonstrated that it is possible to use PFOS-free mist suppressants for non-decorative hard chromium plating (chromium VI) in closed loop systems, and according to these authors, the existing derogation could even be deleted.

According to the draft BAT/BEP Guidance (UNEP/POPS/COP.7/INF/21 2015), information is lacking at present with regard to the processes suitable for use of the above alternatives, as well as to processes where they cannot be used and why. In order to fill this gap to a certain extent, the column „Possible uses“ has been added in Table 3.

An example of an alternative procedure to hard chrome plating is high velocity oxygen fuel (HVOF) spraying of chromium layers, e.g. on printing rollers. In company C, about 20% of applications where hard chromium layers were deposited so far by electroplating could be replaced with the HVOF procedure. This procedure is also suitable to deposit tungsten carbide layers, which are even harder than hard chromium layers. However, such layers are more porous and less resistant to corrosion¹⁶.

The following table 3 is based mainly on manufacturer's data and literature research and makes no claim on completeness or freedom from error.

¹³ in the form of PTFE (polytetraethylene)-coated balls

¹⁴ <http://www.subsport.eu/case-stories/179-de/?lang=de>

¹⁵ http://www.topocrom.com/content/pdf/Artikel_Verfahren_k_muell.pdf

¹⁶ High velocity oxygen fuel spraying/coating

Table 3: Overview of substitutes and their uses

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
Fumetrol 21	Atotech Skandinavien AB (Sweden)	27619-97-2	Hard chromium	x		1H,1H,2H,2H-perfluorooctane sulfonic acid; 6:2 FTS	Yes	Poulsen et al. 2013; Atotech	http://www.atotech.com/products/general-metal-finishing/functional-chrome-plating/fumetrolr-21-lf-2.html
Fumetrol® 21 LF 2	Atotech	k.A.	Hard chromium		x	“PFOS- and PFC-free formulation ¹⁸ ” according to manufacturer, but contains 1H,1H,2H,2H-Perfluorooctansulfonsäure 6:2 FTS (H4PFOS); low foam formation; chromic acid mists in the working environment visibly prevented; less drag-out; lower bath losses	Yes	Atotech; own research	http://www.atotech.com/products/general-metal-finishing/functional-chrome-plating/fumetrolr-21-lf-2.html

¹⁷ Safety data sheet (SDS)

¹⁸ <http://www.atotech.com/products/general-metal-finishing/functional-chrome-plating/fumetrolr-21-lf-2.html>, On the other hand, the SDS states it contains a „polyfluorinated sulfonic acid“ with the CAS-No.: 27619-97-2, 1H,1H,2H,2H-Perfluorooctanesulfonic acid (H4PFOS)

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
						due to spray mist formation; reduced contamination of the ventilation system; lower contamination of the coating units			
Wetting agent CR	Atotech	27619-97-2	Hard chromium chromium (VI)	x		1H,1H,2H,2H-perfluorooctane sulfonic acid; 6:2 FTS	Yes	Poulsen et al. 2013; Atotech	http://www.ahc-surface.com/pdf-downloads/Sales%20of%20Chemicals%20-%20Instructions/Chromium/Chromium%200514/RIAG%20Cr%20Wetting%20Agent_E.pdf
MiniMist Liquid	MacDermid	27619-97-2			x	maleic acid	Yes	Poulsen et al. 2013	
MACUPLE X XD7571	MacDermid	203-742-5	?		x	maleic acid	Yes	MacDermid, own research	
SurTec 850 S	SurTec Scandinavia	not given in SDS	?		x	No information on the alternative product; however, PFOS-free; (no longer listed on SurTec website as a product)	Yes	Poulsen et al. 2013	SurTec 850 no longer offered (written notice on 26 Nov 2015 SurTec)

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
SurTec 850 SK4 (quadruple concentration of the SurTec 850 S above)	SurTec Scandinavia	Not given in SDS	May be used in all Cr(VI)-based Processes; including hard chromium		x	No information on alternative product, except that it is claimed to be PFOS-free and fluorine-free. Including hard chromium; may be used in all Cr(VI)-based Processes.	Yes	Poulsen et al. 2013	
SLOTO-CHROM CR	Schloetter	27619-97-2	Decorative chrome plating	x		Tridecafluorooctane sulfonic acid (H4PFOS)	Yes	own research	https://www.schloetter.de/fileadmin/pdf/public_de/05/05_053_Netzmittel_SLOTOCHROM_CR_1270.pdf
CL-AK Chrom-protector BA	CL-Technology	Not available	Bright chromium and hard chromium	?	?	Mixture of surfactants, no further information available (about ingredients etc.)	Yes	own research	http://cl-technology.de/funktionelle_prozesse/technische_verchromung/technische_verchromung/chromnetzmittel_ba/index_ger.html
CHROM NETZMITTEL-LF	CL-Technology	Not available	Bright chromium and hard chromium	?	?	Mixture of surfactants, no further information available (about ingredients etc.)	Yes	own research	http://www.cl-technology.de/funktionelle_prozesse/te

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
Non Mist-L	Uyemura	Not available	um	?	?	dients etc.) not PFOS-based, no further information available	not found	Poulsen et al. 2013	chnische_verchromung/e650/index_ger.html http://www.uyemura.com/electroless-gold-miralloy-tin-nickel-plating.htm#mist
Cancel ST-45	Plating Resources, Inc. (plating.com)	Not available	Bright chromium on chromium (VI) basis.	?	?	not PFOS-based, no further information available	not found	Poulsen et al. 2013	http://www.plating.com/cancelst45.htm
FS-600 High foam	Plating Resources, Inc. (plating.com)	Not available	Decorative chromium	x		not PFOS-based, however, fluorinated substitute; no more information available	not found	Poulsen et al. 2013	
FS-750 Low foam	Plating Resources, Inc. (plating.com)	Not available	Decorative chromium and hard chromium	x		not PFOS-based, however, fluorinated substitute; no more information available	not found	Poulsen et al. 2013	

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
Ankor Wetting Agent FF	Enthone Inc. (a Cookson Electronics Company)	26635-93-8	Bright chromium		x	(Z)-Octadec-9-enylamine,ethoxylated, Oleylaminethoxylate, Fluorine-free. Must be added continuously in order to maintain performance. However, only suitable for decorative chrome plating, not for hard chrome plating.	Yes	Poulsen et al. 2013	http://enthone.com/Product_Finder/ANKOR_Wetting_Agent_FF.aspx
ANKOR® Hydraulics MS	Enthone Inc. (a Cookson Electronics Company)	27619-97-2	Hard chromium	x		3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane sulfonic acid (H4PFOS), non-foaming wetting agent; successfully used in plants of most different types; suitable with subsequent vacuum evaporation	Yes	Ethone	http://enthone.com/Industries/Heavy_Equip_Energy/Technology_Selector/Products/ANKOR_Hydraulics.aspx
ANKOR® PF 1	Enthone Inc. (a Cookson Electronics Company)	27619-97-2	Hard chromium	x		3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane sulfonic acid (H4PFOS), non-foaming wetting agent in combination with ANKOR Hydraulics process and developed	Yes	Ethone	http://enthone.com/Product_Finder/ENTHONE_PF_OS-Free_Solutions.aspx

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
						especially for this use.			
ANKOR® Dyne 30 DC	Enthone Inc. (a Cookson Electronics Company)	27619-97-2	Bright chromium on chromium (VI) basis	x		3,3,4,4,5,5,6,6,7,7,8,8,8-T Tridecafluorooctane sulfonic acid (H4PFOS)	Yes	Ethone	http://enthone.com/Product_Finder/ENTHONE_PFOS-Free_Solutions.aspx
ANKOR® Dyne 30 MS	Enthone Inc. (a Cookson Electronics Company)	27619-97-2	Hard chromium Plastic etchant Bright chromium on chromium (VI) basis	x		3,3,4,4,5,5,6,6,7,7,8,8,8-T Tridecafluorooctane sulfonic acid (H4PFOS), Non-foaming wetting agent, successfully used in plants of most different types;	Yes	Ethone	http://enthone.com/Product_Finder/ANKOR_Dyne_30_MS.aspx
UDIQUÉ® Wetting Agent PF 2	Enthone Inc. (a Cookson Electronics Company)	27619-97-2	Plastic etchant	x		Low-foaming wetting agent	Yes	Ethone	http://enthone.com/Product_Finder/ENTHONE_PFOS-Free_Solutions.aspx

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
TIB Suract CR-H	ny) TIB Chemicals	Not available	Bright chrome plating		x	The alternative (Alkylsulfonate) has a soap structure and is fluorine-free.	Yes	Poulsen et al. 2013 Blepp et al. 2013	http://www.tib-chemicals.com/anorganische-spezialchemikalien/galvanochemikalien/produktliste-nach-chemie/
PROQUELOF	Kiesow Dr. Brinkmann	27619-97-2	Non-decorative hard chrome plating	x		1H,1H,2H,2H-perfluorooctane sulfonic acid; 6:2 FTS	Yes	Poulsen et al. 2013; Blepp et al. 2013	http://www.kiesow.org/aktuelles/aktuelles-detailseite/article/proquel-of-mit-grossem-erfolg/
F-53 Chromic Fog Inhibitor	Hangzhou Dayangchem Co. Ltd.	Not available		x		Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate	not found	Poulsen et al. 2013 Wang et al. 2013	
F-53B Chromic Fog Inhibitor	Hangzhou Dayangchem Co. Ltd.	Not available		x		Perfluorochloro ether sulfonate for hard chrome plating (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane	not found	Poulsen et al. 2013 Wang et al. 2013	

Product-name	Manufacturer	CAS No.	Possible uses	Fluorinated	fluorine-free	Remark	SDS ¹⁷ exists (Yes/No)	Reference	Website
Helio Chrome Wetting Agent FF	Walter Kasper	27619-97-2	Hard chromium	x		sulfonate) 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane sulfonic acid (H4PFOS) wetting agent for Hard chromium plating. PFOS free, non-foaming	Yes	Walter Kasper and own research	http://kwalter.de/assets/files/sdb_downloads/13/13_de_2015.pdf
Antifog CR	Chemisol GmbH & Co. KG	Not available	Bright chromium		x	According to producer: PFOS-und halogen-free surfactant.	Not found	Chemisol and own research	http://www.chemisol.de/docs/ga_antifog_cr.pdf
Antifog V4	Chemisol GmbH & Co. KG	Not available	Hard chromium		x	According to producer: PFOS-und halogen-free surfactant.	Not found	Chemisol and own research	http://www.chemisol.de/docs/ga_antifog_v4.pdf
Antispray S	Coventya	26635-93-8	Bright chromium		x	(Z)-Octadec-9-enylamine,ethoxylated (Oleylaminethoxylat)	Yes	Coventya	http://www.coventya.com/assets/Technical-Information/Decoration/german/Process-Flash-ANTISPRAY-S-10.2012-de.pdf

The synoptic view of substitutes shows a large selection meanwhile being offered on the market. H4PFOS (CAS-Nummer 27619-97-2, 1H,1H,2H,2H-Perfluorooctansulfonsäure) is the substitute used most often.. In a few exceptional cases such as F53, there is neither a CAS Number nor a safety data sheet ¹⁹. The risks with regard to degradability, persistence and ecotoxicity of these materials cannot yet be estimated as these aspects are still insufficiently tested. According to table 3, nine products are free of fluorine. These comprise essentially three substances: the alkyl sulfonate Suract CR-H produced by TIB, maleic acid (CAS-No. 203-742-5) and Oleylamine ethoxylate (CAS-Nr. 26635-93-8).

In many cases, PFOS was substituted by polyfluorinated surfactants (PFS) such as H4PFOS or 6:2 FTS (Fumetrol 21; Enthone products etc.). As a rule, such fluorinated substitutes are substances chemically closely related to PFOS. This is why, on principle, a possibly comparable potential for negative environmental impacts should be assumed. Furthermore, their degradation will presumably release perfluorinated and thus, highly persistent degradation products. Another striking fact is that the PFC content is not specified for most of the products. Presently, there is no legal restriction for the use of H4PFOS as the most widespread alternative, or of other fluorinated substitutes.

In addition, the amounts consumed of these substitutes for PFOS to achieve similar characteristics are at any rate several times higher²⁰. Often, the fluorine-free substitutes and their ingredients are unknown. Therefore, these products are difficult to assess. The completely fluorine-free products require higher technological expenditure by the user (operator of an electroplating plant), as compared to the use of PFOS or fluorine-containing alternatives. The input must be diluted and, unlike for fluorinated surfactants, added in relatively small doses distributed over the day. In addition, a continuous circulation of the electrolyte is recommended, e.g. by stirring or pumping. It has been proven that the technical specifications required by the customer are complied with.

The issue of BAT in the use of PFOS in electroplating plants has been existing already for several years in the sub-working group of the Federal-Länder Working Group (Waste Water) for a reconceptioning of Annex 40 to the German wastewater ordinance (Abwasserverordnung, AbwV). Among other concerns, a checklist was to be compiled for measures to be considered in order to avoid and reduce releases of PFOS from electroplating systems into the environment.

When developing alternative substances, environmental hazards should also be taken into account. Also in this respect, a type of continuous compilation and examination of substitutes for special functional requirements could be included as an issue, in order to enable substitution in the medium to long term.

8.1.2 Exposure

According to Zangl et al. (2012), the annual release into the environment amounts to 5 - 7% of the PFOS quantities used. Another source (UK_EK 2004) has documented that for each company, about 79 mg of PFOS are released as airborne emissions over a period of one year.

The processes in electroplating are very similar as to the type and extent of environmental emissions. The most significant emissions originate from the rinsing steps between the electrolytes and from replacement of used solutions. The data most suitable would be those related both to the production throughput and to the surface area treated (in m²). However, such information is hardly available.

¹⁹ Could possibly be requested in China.

²⁰ For H4PFOS, the quantity required to achieve the same effects (desired retention of aerosols) is 2-10 times that of PFOS.

The table below shows the substance properties of PFOS and 6:2 FTS (DuPont 2012). It can be seen from the table that 6:2 FTS has a rapid bioelimination and therefore, is not bioaccumulative. In contrast, PFOS is highly biopersistent and bioaccumulative. Short-chain fluorosurfactants such as PFBS are clearly more readily water-soluble, which is why they do not accumulate in organisms. However, they affect groundwaters, are persistent and become distributed in the environment.

Thus, the lower stability of 6:2 FTS as compared to PFOS will presumably also result in decomposition in the chrome plating process and consequently, in the formation of other fluorinated products.

Table 4: Substance properties of 6:2 FTS and PFOS DuPont (2012)

	6:2 FTS F(CF ₂) ₆ CH ₂ CH ₂ SO ₃ -	PFOS F(CF ₂) ₈ SO ₃ -
Acidity pH Value	2-3	< -1
Acute toxicity to fish, LD50	>107 mg/L	78 mg/L
Acute toxicity to <i>Daphnia</i> EC50	>109 mg/L	58 mg/L
Acute toxicity to algae EC50	>96 mg/L	48.2 mg/L
90-Day Fish Early Life-Stage NOEC	2.62 mg/L	0.29 mg/L
Bioaccumulation	Non-bioaccumulative	bioaccumulative
Acute oral toxicity LD50 (rat, male)	2 000 mg/kg	233 mg/kg
28 days rat oral, NOAEL repeated exposure	15 mg/kg/day	1.77 mg/kg/day

As compared to PFOS, the alternatives are largely lacking ecotoxicological studies as well as information on degradation products, environmental relevance, bioaccumulation and toxicity. It can be argued that on principle, the switch to shorter-chained C₆-C₄ fluorine compounds does not constitute an ecofriendly alternative to PFOS²¹, because also these PFCs and their degradation products are persistent and thus, will accumulate in the environment.

Due to their degradation products and high mobility in the groundwater or drinking water and the higher quantities required in the process, the use of H₄PFOS (or other fluorosurfactants) has to be assessed as critical (Wienand et al. 2015). It is not finally clarified whether the above conclusion would actually apply for all alternatives listed in Table 3. Incentives for the recording of the routes of exposure of other (fluorine-free) alternatives would move on the discussion on the substitution of PFOS and establish a broader scientific and technical base for a PFOS-free electroplating sector.

²¹ Generally, bioaccumulation and toxicity will decrease with molecule length.

In addition, as result of the few studies available, PFBS was found to be present in the technical PFOS formulations (with the exception of the wetting agent NCR, Blasberg-Werra-Chemie). This is a problematic fact since PFBS has obviously to be classified as environmentally relevant and has also been found already in groundwater, surface and mineral waters. PFBS will sorb only on fresh activated carbon. A correspondingly frequent replacement of activated carbon has often proved as uneconomical.

Generally, process technology with minimized substance losses is considered to represent the best available technology. It is a result of system optimization between measures to avoid substance losses and eco-friendly disposal of unavoidable residual waste water and waste.

9 Outlook – Future development

9.1 Substitution of PFOS and chromium(VI)-free processes

In the field of functional chrome plating, the substitution of classical hard chrome electrolytes based on chromium(VI), where the use of chemically extremely stable surfactants such as PFOS or H4PFOS has been frequently required so far, by PFOS/PFC-free chromium(III) processes or by HVOF spraying has already started in individual cases. The potentials and limits of the substitution procedures constituted the main topic at the ZVO Oberflächentage conference held in October 2015.

The thematic block of „Functional Metal“ was completed by a broader view provided by Mr. H. Horsthemke of Enthone GmbH in his multi-faceted and practical paper entitled „Systematic approach and status of the evaluation of hard chrome alternatives“ (Horsthemke, H. (2015). The author explained the multitude of requirements in terms of positive properties a hard chrome alternative would have to fulfill at the same time. As a result, it became clear that in the foreseeable future, the classical hard chrome layer cannot be substituted by a single process but only by a multitude of alternatives depending on the individual case. Mr. Horsthemke demonstrated the fields of application where Cr(III)-based, Cr-free electrolytic and non-electrolytic processes could substitute the hard chrome surface. However, he also pointed out that chromium(VI) may also be formed in cases of originally chromium(VI)-free alternatives, such as HVFO spraying of chromium alloys. Finally, he suggested to check the costs of alternatives as compared to the use of chromium(VI) in an almost emission-free plant, such as in a closed reactor at negative pressure²².

Hence, the future of a REACH-authorized handling of chromium(VI) could consist in closed plants operated, as required, at negative pressure. Because almost zero chromic acid aerosols are emitted into the ambient air by plants of this type, the latter can be operated without using per- or polyfluorinated surfactants such as PFOS. This has been confirmed by the experience of the companies Topocrom in Stockach, Gramm Technik GmbH in Heimerdingen (Altheimer, R. 2014) and Hartchrom AG in Steinach.

9.2 Substitution of PFOS by fluorine-free surfactants

In this respect, the different electroplating processes should be considered in a differentiated way. So far, the potential use of alkyl sulfonates in electroplating has not yet been systematically analyzed. An analysis of this type could be carried out in cooperation with a number of electroplating companies who in the medium or short term (in the context of an approval planning) would agree to completely give up the use of PFCs. Reasonably,

²² Galvanotechnik, Issue 11/2015

such an analysis would also include the specialized companies and the manufacturers of alkyl sulfonates and other PFC-free surfactant systems.

Based on the positive experience in bright chrome plating, it appears to make sense to systematically search for other fields of application for alkyl sulfonates in electroplating (particularly hard chrome plating) where PFC-containing systems are still used. Presently, shorter-chained per- and polyfluorinated compounds are increasingly used instead of PFOS. This approach is similar to that taken in the textile sector. In the field of outdoor clothing, per- and polyfluorinated compounds have been used to achieve a long-lasting weatherproof finishing („Durable Water Resistant“, DWR). Also in this field, C8 PFCs were initially substituted by C6 and C4 fluorine compounds.

By using alkyl sulfonates and comparable fluorine-free surfactants, it should be possible within a relatively short period of time to completely do without the use of per- and polyfluorinated compounds in the majority of processes in electroplating. This also includes the shorter-chained per- and polyfluorinated substances presently used as PFOS substitutes. It cannot be excluded that for very special functional requirements, substitution will only be possible on a medium to long-term basis. Nevertheless, it would be an important result of a process-specific potential analysis. In this respect, incentives are required so that more research is invested in the use and ecotoxicological assessment of fluorine-free substances.

With regard to the exception stipulated in the EU POP Regulation for hard chrome plating („mist suppressants for non-decorative hard chromium plating (chromium VI) in closed loop systems“), a list could be maintained compiling the technical options where already today, fluorine-free or technical alternatives are used.

Supported by environmental authorities and by means of stakeholder hearings, test series resulting in product innovations and meeting with interest among companies, more PFC-free alternatives could be discovered, promoted and made more transparent for all actors involved. It is also assumed that a forced public promotion of the subject would greatly accelerate the process of substitution of PFOS in the electroplating sector. There is a need for subsequent action taking up the above issues.

9.3 Data required to establish a PFOS limit value in waste water

Literature studies and interviews have shown that so far, there have been no publications or systematic evaluations of PFOS levels in effluents to be achieved in treated waste waters from electroplating. However, such evaluation would constitute the precondition to enable an establishment of a PFOS limit value in industrial waste water in Annex 40 to the German Wastewater Ordinance or the future BAT for surface treatment of metals and plastic materials. There is a great need for research for fixing a new limit value for PFOS²³.

9.4 Update of the POP Regulation

As substantiated in Chapter 6.2.1, it is suggested by the authors to consider whether in an update of the POP Regulation, the use of PFOS could be conditioned not only by a “closed loop system”, but also for functional chrome plating, by a “controlled electroplating system”.

²³ Decision at the 74th Environmental Conference

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11 Annex

11.1 Documentation of interviews (Final Protocols)

The questionnaire was harmonized with the Federal Environment Agency. The respective questions have been documented in the Final Protocol analogous to the Overview of interview partners in listed Table 2.

11.1.1 Company A

Table 5: Documentation Company A Business data

Business data	
Plant classification	
Plant type	Functional chrome plating subcontractor hard chrome plant
Treatment bath volume chromium m ³	54 m ³ hard chrome electrolyte
Year of construction of the plant	1978 / 2011
Basic materials to be treated	35 m ³ mixed acid chrome electrolyte (based on methane sulfonic acid) 300 g/L chromium trioxide with PFOS Sulfuric acid electrolytes: 20 m ³ with PFOS Dechroming: 9 m ³ with NaOH

Table 6: Documentation Company A Interview

Ser.No.	Question	Answer
1	Which electroplating processes in your company use PFOS/PFC?	Hard chrome electrolytes, application concentration PFOS: ca. 50 mg/l
2	Please describe the measures taken in your company for recycling and/or retention of PFOS/PFC.	Rinsing of components above the process bath; Closed loop for chromium VI and PFOS by process-integrated recycling of chromium electrolytes. The foreign metals accumulating in the closed loop system such as iron, nickel, zinc, copper and aluminium are removed from the system by batchwise purification of the electrolytes by means of cation exchange.
3	Were or are there any factors impeding or excluding a largely closed loop or better retention of PFOS/PFS?	Evaporation technology is not applied because extraction from the chromium baths is performed via the same exhaust air plant as that from the hydrochloric pickling and alkaline de-

Ser.No.	Question	Answer
		greasing (old stock). This is why reuse of the washing water would be impossible. Evaporation losses of ca. 1 m ³ from the regeneration plant are replenished daily. In contrast, there is an excess rinse water volume of ca. 30 m ³ /day (6600 m ³ /year). The rinse water is not treated for PFOS.
4	Would the measures taken for recycling and/or retention of PFOS/PFC be practicable, on principle, also in other, comparable companies?	Yes. According to the operator, a regeneration plant is economically reasonable for treatment bath volumes of ca. 10 m ³ and above.
5	What is the annual PFOS/PFC consumption as related to the respective pure substance?	In recent years, the average consumption of Bayowet 248 (Lanxess), was ca. 12 litres per year. At a concentration of 560g PFOS/L, this corresponds to an annual consumption of ca. 6.7 kg PFOS.
6	Which are the metrological criteria and intervals of replenishment of PFOS/PFC?	The PFOS-containing surfactant is replenished depending on the demand. Formerly, the surface tension was measured by means of a ring tensiometer. Today, replenishment is carried out on the basis of many years of experience.
7	Are there any factors opposing a metrologically controlled replenishment of PFOS/PFC?	No
8	Do you know the electrochemical degradation rate for PFOS/PFC in the process?	No
9	How long would PFOS/PFC remain in the cycle?	55 m ³ chromium electrolyte with 50 mg PFOS/L contain 2.75 kg PFOS. Since annually, 6.7 kg PFOS are replenished, the substance remains in the cycle for $2.75 : 6,7 = 0.41$ years, in a first approximation.
10	Which other measures for extension of the PFOS/PFC cycle have been examined and which of these are applicable? Which measures have proved inapplicable and why?	Failed attempt to enhance recycling by vacuum evaporator. A Halar-coated steel vacuum evaporator was used on a trial basis. Due to material problems and lacking resistance to concentrated chromic acid, the evaporator became defective very soon. Note: The material is possibly attacked by hydrofluoric acid formed from the SiF ₆ of the mixed acid electrolyte.
11	On which emission pathways and how often are PFOS/PFC discharged from the cycle?	The following leaks can be identified in the PFOS cycle: Disposal of the chromium hydroxide sludge

Ser.No.	Question	Answer
		<p>from waste water treatment;</p> <p>Disposal of the barium sulfate sludge from “blunting” (?). (Note: a process to remove excess barium from some electrolytes).</p> <p>Disposal of lead chromate sludge and used porous lead anodes;</p> <p>Regenerates of the cation exchanger in the chromium(VI) cycle;</p> <p>Discharge of the treated waste water (ca. 30m³/d or 6600 m³/a)</p> <p>Disposal of racks (ca. 1x/a), tanks and waste air channels (at about 20-year intervals).</p>
12	What happens with PFOS/PFC-containing drip losses, ground effluent and effluent from the exhaust air scrubbers/droplet separators?	All such waste waters are treated via the chromium-VI batch.
13	Are analyses available regarding PFOS/PFC-containing wastes (e.g. ion exchange resins, adsorbents, electroplating sludges, used chromium electrolyte, barium sulfate sludge)?	No.
14	What are the quantities of PFOS/PFC discharged annually by means of disposal of the wastes mentioned above?	<p>Chromium hydroxide sludge: 6-8 t/a</p> <p>Lead chromate sludge: 400 kg/a</p> <p>Barium sulfate sludge: quantity and PFOS content unknown</p>
15	Which are the physico-chemical treatment techniques used to dispose of PFOS/PFC-containing wastes?	Chromium hydroxide sludges go to smelting for chromium recovery.
16	Which PFOS substitutes do you know and/or were offered to you by your chemical suppliers?	Proquel OF, Fa. Kiesow
17	What is your experience regarding PFOS substitutes?	None

11.1.2

11.1.3 Company B

Table 7: Documentation Company B Business data

Business data	
Plant classification	
Plant type	Plant for functional chrome plating
Treatment bath volume chromium m ³ :	7.2 m ³ hard chrome electrolyte, mixed acid Dechroming: 3.3 m ³ with NaOH
Year of construction of the plant	1996 (for this site, baths are older)
Basic materials to be treated	Different stainless steels (e.g. 1.4462)

Table 8: Documentation Company B Interview

Ser.No.	Question	Answer
1	Which electroplating processes in your company use PFOS/PFC?	We do no longer use PFOS since 2008 (change to wetting agent Proquel OF in 2008). There are only residual concentrations of PFOS in the baths / bath liners. Complete replacement of the chromic acid electrolyte is envisaged for 11/2015 so that PFOS it will no longer be contained.
2	Please describe the measures taken in your company for recycling and/or retention of PFOS/PFC.	Rinsing of components above the process bath, subsequently three-stage cascade rinsing.
3	Were or are there any factors impeding or excluding a largely closed loop or better retention of PFOS/PFS?	We operate on a PFOS-free basis and with an ion exchanger resin at the end of the waste water treatment chain (Lewatit MonoPlus M 500). Therefore, we cannot see any further option for retention.
4	Would the measures taken for recycling and/or retention of PFOS/PFC be practicable, on principle, also in other, comparable companies?	In principle, yes
5	What is the annual PFOS/PFC consumption as related to the respective pure substance?	In recent years, the average consumption of Proquel OF (Kiesow), was ca. 25-35 Litres per year. Proquel OF does no longer contain any PFOS. <i>Note by IUW: Proquel OF contains about 2% H4PFOS as the main active substance</i>

Ser.No.	Question	Answer
		<i>(1H,1H,2H,2H-per-fluorooctane sulfonic acid)</i>
6	Which are the metrological criteria and intervals of replenishment of PFOS/PFC?	The polyfluorinated surfactant is only replenished if required. By splashes, the plate test (white palm-sized plate) shows the amount of aerosols formed.
7	Are there any factors opposing a metrologically controlled replenishment of PFOS/PFC?	Due to the low quantities required, there is no need for a metering unit. Amounts in the mL range can be added manually in a better and safer way.
8	Do you know the electrochemical degradation rate for PFOS/PFC in the process?	No.
9	How long would PFOS/PFC remain in the cycle?	Currently no PFOS is added. Replacement of chromic acid envisaged in 11/2015.
10	Which other measures for extension of the PFOS/PFC cycle have been examined and which of these are applicable? Which measures have proved inapplicable and why?	Prior to considering the ion exchanger, application of a vacuum evaporator had been considered for waste water disposal. So far, a test period has been prevented by the high investment and operating costs of a vacuum evaporator.
11	On which emission pathways and how often are PFOS/PFC discharged from the cycle?	The following leaks can be identified in the PFOS cycle: Disposal of the chromium hydroxide sludge from waste water treatment; Disposal of lead chromate sludge and used porous lead anodes; Discharge of treated waste water; Disposal of racks (ca. 1x/a), tanks and waste air channels (at about 25-year intervals).
12	What happens with PFOS/PFC-containing drip losses, ground effluent and effluent from the exhaust air scrubbers/droplet separators?	All such waste waters are treated via the chromium-VI batch and the PFOS ion exchanger.
13	Are analyses available regarding PFOS/PFC-containing wastes (e.g. ion exchange resins, adsorbents, electroplating sludges, used chromium electrolyte, barium sulfate sludge)?	Yes, we have our waste water from the waste water treatment plant tested at three-months intervals.
14	What are the quantities of PFOS/PFC discharged annually by means of disposal of the wastes mentioned above?	Since we operate the waste water system in the electroplating plant, chromium-containing waste waters from hard chrome plating are treated every now and then (depending on the workload) in separate batches. The quantity of sludge from hard chrome plating cannot be

Ser.No.	Question	Answer			
		determined separately. We dispose of about 20 t per year.			
15	Which are the physico-chemical treatment techniques used to dispose of PFOS/PFC-containing wastes?	<table border="1"> <tr> <td>Electroplating sludge is disposed of onto an over-ground disposal site. 110109*</td> <td>Sludges and filter cakes containing dangerous substances</td> <td>Electroplating sludge containing nickel</td> </tr> </table>	Electroplating sludge is disposed of onto an over-ground disposal site. 110109*	Sludges and filter cakes containing dangerous substances	Electroplating sludge containing nickel
Electroplating sludge is disposed of onto an over-ground disposal site. 110109*	Sludges and filter cakes containing dangerous substances	Electroplating sludge containing nickel			
16	Which PFOS substitutes do you know and/or were offered to you by your chemical suppliers?	To replace Proquel AF, we were offered Proquel OF in 2008; the change was carried out immediately.			
17	What is your experience regarding PFOS substitutes?	No noteworthy differences were found.			

11.1.4 Company C

Table 9: Documentation Company C Business data

Business data	
Plant classification	
Plant type	Hard chromium plant
Treatment bath volume chromium m ³ :	Total hard chrome electrolyte: ca. 300 m ³ Sulfuric acid electrolytes: ca. 180 m ³ Mixed-acid chromium electrolytes: ca. 120 m ³ (based on methane sulfonic acid) Dechroming: 6 m ³ with NaOH + 6 m ³ with HCl 16 %
Year of construction of the plant	Successively since 1950, recycling facility since 2013
Basic materials to be treated	Primary substances: Steel, aluminium, brass, zinc die casting, titanium, gray cast Products: Rollers and cylinders for the printing and paper industry, piston rings, turbine shafts, toolmaking

Table 10: Documentation Company C Interview

Ser.No.	Question	Answer
1	Why doesn't your company use any surfactants PFOS/PF in hard chrome electroplating?	<p>Company C produces 80% high-tech surfaces complying with the highest requirements. Based on the 28-years professional experience of the head of department, better quality can be produced without using PFOS. This is why for quality reasons, neither PFOS/PFC not any other surfactants are used in hard chrome electrolytes throughout operations. The failure rate is < 2%.</p> <p>With regard do chromic acid, ambient air measurements and biomonitoring of the staff are performed on a regular basis. The latter have not resulted in any objections. Note: Chromic acid is replenished exclusively in liquid form from a preparation station.</p>
2	Please describe the measures taken in your company for recycling and/or retention of chromic acid.	<ol style="list-style-type: none"> 1. Rinsing of components above the process bath; 2. Closed loop for chromium VI by process-integrated recycling of chromium electrolytes; The foreign metals accumulating in the chromium electrolytes such as iron, chromium(III), nickel, zinc, copper, titanium and aluminium are removed from the system by batchwise purification of the electrolytes by means of cation exchange. To this end, electrolytes have to be diluted to about 100 g/L chromic acid. Prior to the start-up of this recycling plant, ca. 50% of electrolytes were disposed of externally. Amortization of the plant within 1 year. Since then, considerable annual savings. 3. Strong dimensioned and corrosion-resistant edge extraction systems made from titanium are used 360° around the bath surface. Extraction is performed in a sorted way, i.e. separately from sulfuric acid and mixed acid hard chrome baths and degreasing/dechroming. As a result, 100 % of the sorted solutions from the exhaust air scrubbers can be recycled into the respective chromium baths. The heat from the exhaust

Ser.No.	Question	Answer
		air is recovered. Limit values for exhaust air are complied with.
3	Were or are there any factors impeding or excluding a largely closed loop or better retention of chromic acid?	<p>The use of evaporation technology proved too expensive.</p> <p>The electrolytes are operated at 54°C – 70°C . Evaporation losses of ca. 15 m³ are replenished daily.</p> <p>The processes do not work completely effluent-free. Every day, ca. 16 m³ of less contaminated waste water is generated, above all from disassembly of cylinders. Concentrates and semi-concentrates are not treated.</p>
4	Would the measures taken for recycling and/or retention of PFOS/PFC be practicable, on principle, also in other, comparable companies?	<p>Yes, depending on the size of the business.</p> <p><i>Note by IUW: Contradicting the statements of Companies A and D, this answer should be scrutinized. Obviously, it applies only to large hard chrome plants. Company A estimates foreign metal removal via cation exchange to pay off for treatment bath volumes of 10 m³ and above</i></p>
5	Which other measures for extension of the chromic acid cycle have been examined and which of these are applicable?	None
6	On which emission pathways and how often is chromium(VI) discharged from the cycle?	<p>The following leaks have been identified in the chromium(VI) cycle:</p> <p>Regenerates of the cation exchanger in the chromium(VI) loop;</p> <p>Rinse water during disassembly of cylinders;</p> <p>Drip losses, ground effluent;</p> <p>Discharge of the treated rinse water (ca. 16 m³/d)</p>
7	How much waste is generated annually?	<p>Chromium hydroxide sludge: ca. 80 t/a</p> <p>Lead chromate sludge: ca. 6 t/a</p> <p>Alkaline degreasing techniques¹): ca. 15 m³/a</p> <p>1) these impair the wastewater pre-treatment plant by poor sludge formation.</p> <p>Consumption of chromium trioxide amounts to about 50 t per year.</p> <p>Note: Barium sulfate sludge from “blunting”(?)</p>

Ser.No.	Question	Answer
		of chromium electrolytes does not occur since deionized water is exclusively used for the preparation of all electrolytes, for exhaust air scrubbers and for rinse water and thus, no sulfates are introduced into the system.
8	Which alternatives to hard chrome plating are used at your company?	<p>An example of an alternative procedure is high velocity oxygen fuel (HVOF 2)) spraying of chromium layers, e.g. for printing rollers. In ca. 20% of applications, this process can replace hard chromium layers deposited by electroplating.</p> <p>This procedure is also suitable to deposit tungsten carbide layers, which are even harder than hard chromium layers. However, such layers are more porous and less resistant to corrosion.</p>
9	Which are the future developments you are expecting on the hard chromium market?	<p>Increasing use of chrome-ceramic coatings where alumina / diamond powders are incorporated into the hard chrome layer. This will lead to enhanced wear resistance of the coatings. Potential uses include ship engine pistons, for example, resulting in an extension of working lives and thus, maintenance intervals by 6 times and thus, reduced downtimes of ships.</p> <p>Note: Regarding HVOF: High velocity oxygen fuel coating is based on combustion of a fuel oxygen mixture (kerosene, acetylene) under high pressure in the combustion chamber. Subsequently, the gas mixture is accelerated to supersonic speed by means of an expansion nozzle. The powdery materials are injected into this gas jet and strongly accelerated. By means of this high-kinetic technique, it is possible to produce thick layers (porosity <2%) with excellent adhesion properties</p>

11.1.5 Company D

Table 11: Company D Business data

Business data	
Plant classification	
Plant type	Plant for functional chrome plating

Treatment bath volume chromium m ³ :	3.5 m ³ hard chrome electrolyte with PFOS Sulfuric acid electrolytes: m ³ with PFOS Dechroming: 0.530 m ³ with NaOH
Year of construction of the plant	2009
Basic materials to be treated	Steel

Table 12: Documentation Company D Interview

Ser.No.	Question	Answer
1	Which electroplating processes in your company use PFOS/PFC?	Hard chrome electrolyte, application concentration PFOS: ca. 50 mg/L
2	Please describe the measures taken in your company for recycling and/or retention of PFOS/PFC.	Rinsing of components above the process bath. Rinsing of the components in a static rinse to balance drag-out and evaporation losses. This is followed by a 7-fold cascade. Altogether, there are thus 8 rinse steps. In addition, a buffer tank connected to rinse tank 8 to receive excess rinse water is used at weekends to balance evaporation losses in the electrolytes. The working life of the electrolyte is 4-5 years.
3	Were or are there any factors impeding or excluding a largely closed loop or better retention of PFOS/PFC?	A proportional low drag-out of PFOS via the exhaust air scrubber cannot be further reduced. In addition, it is impossible to recirculate more water into the baths via the evaporation losses.
4	Would the measures taken for recycling and/or retention of PFOS/PFC be practicable, on principle, also in other, comparable companies?	On principle, this is at least conceivable. However, considerable technological changes would be required which, in realistic terms, is hardly practicable in many companies with existing plants. For new installations, it is worthwhile to consider this approach.
5	What is the annual PFOS/PFC consumption as related to the respective pure substance?	In recent years, the average consumption of FUMETROL 21 LF MAINTENANCE (Atotech) was ca. 4.7 litres per year. At a concentration of 53 g PFOS/L, this corresponds to an annual consumption of only ca. 250 g PFOS.
6	Which are the metrological criteria and intervals of replenishment of PFOS/PFC?	The PFOS-containing surfactant is replenished depending on the demand only. Company D uses the Hull cell check to determine the demand. See work instruction enclosed. The latter is, however, specific of the business and cannot be generalized. However, it can be adapted to the respective user without any problems.

Ser.No.	Question	Answer
7	Are there any factors opposing a metrologically controlled replenishment of PFOS/PFC?	This issue has not yet been considered because of the low quantities used in our plant.
8	Do you know the electrochemical degradation rate for PFOS/PFC in the process?	No, there is no information by the manufacturer.
9	How long would PFOS/PFC remain in the cycle?	3.5 m ³ chromium electrolyte with 50 mg PFOS/L contain 0.175 kg PFOS. Since annually, 0.235 kg PFOS are replenished, the substance remains in the closed loop for $175 : 235 = 0.7$ years, in a first approximation.
10	Which other measures for extension of the PFOS/PFC cycle have been examined and which of these are applicable? Which measures have proved inapplicable and why?	Due to the high number of rinses and the low consumption, no other tests were carried out. Chromium(III) and foreign metals are present at minor concentrations. Given the present mode of operation, their removal by means of cation exchange is not required. As related to the consumption, cation exchange technology is absolutely too expensive.
11	On which emission pathways and how often are PFOS/PFC discharged from the cycle?	Disposal of the chromium hydroxide sludge from waste water treatment; Disposal of lead chromate sludge and used porous lead anodes; Discharge of the treated waste water, rinse water from cleaning and maintenance operations. Disposal of racks (ca. 1x/a), tanks and waste air channels (at about 20-year intervals).
12	What happens with PFOS/PFC-containing drip losses, ground effluent and effluent from the exhaust air scrubbers/droplet separators?	All such waste waters are treated via the chromium-VI batch.
13	Are analyses available regarding PFOS/PFC-containing wastes (e.g. ion exchange resins, adsorbents, electroplating sludges, used chromium electrolyte, barium sulfate sludge)?	No
14	What are the quantities of PFOS/PFC discharged annually by means of disposal of the wastes mentioned above?	Lead chromate sludge: 250 kg/a
15	Which are the physico-chemical treatment techniques used to dispose of PFOS/PFC-containing wastes?	Chromium hydroxic sludges go to smelting for chromium recovery. The same applies to the amounts disposed of by us.

Ser.No.	Question	Answer
16	Which PFOS substitutes do you know and/or were offered to you by your chemical suppliers?	So far, no substitutes have been tested.
17	What is your experience regarding PFOS substitutes?	So far, none of the substitutes has been tested because of the low quantities used in our plant. However, we have been watching/supporting these processes carried out (at other plants?) by colleagues.

11.1.6 Company E

Table 13: Documentation Company E Business data

Business data	
Plant classification	
Plant type	Rack electroplating – chrome plating plant
Treatment bath volume chromium m ³ :	Activation: 2 m ³ 10 g/L CrO ₃ Chrome plating: 4 m ³ 400 g/L CrO ₃ mixed acid chromium electrolyte with silicofluoride as activator + H4PFOS Dechroming: 4.75m ³ with NaOH
Year of construction of the plant	1994
Basic materials to be treated	Predominantly brass

Table 14: Documentation Company E Interview

Ser.No.	Question	Answer
1	Which electroplating processes in your company use PFOS/PFC?	Exclusively the chromium electrolyte.
2	Please describe the measures taken in your company for recycling and/or retention of PFOS/PFC.	Largely closed loop for chromium VI and PFOS by evaporation of excess rinse water. Use of 5 rinses after the chrome plating bath (3-fold cascade, hot chemical rinse with hydroxylammonium sulfate and final rinse with demineralized water). The foreign metals accumulating in the system such as copper, zinc and iron, and chromium are removed from the system by a cation exchanger which has to be regenerated with sulfuric acid at about weekly intervals. The exhaust air is scrubbed in a multi-stage procedure. The chromic acid aerosols contained are recycled into the chromium bath. The waste water from all rinse steps and all chromium-VI-containing and PFC-containing

Ser.No.	Question	Answer
		<p>waste water flow types – incl. ground effluent – are collected together. After reduction to Cr-III, neutralization and separation of the hydroxide sludge, all PFC-containing waste water is passed through a gravel filter and 3 300-L-ion exchanger columns. An ion exchanger resin by the company aqua plus is used. This is followed by a selective ion exchanger for removal of residual metal ions, a final neutralization and a final inspection shaft.</p> <p>The measures for a closed loop system largely comply with the current draft “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”, as described in 4.4.4 in the flow chart in Figure 4-2.</p> <p>The only noteworthy differences are:</p> <ul style="list-style-type: none"> - - only a cation exchanger is used to remove foreign metals; - - even more rinse steps are used; - the waste water is additionally treated for PFC by means of an ion exchanger.
3	Were or are there any factors impeding or excluding a largely closed loop or better retention of PFOS/PFS?	Drag-out of H4PFOS by scooping components and adsorption to the racks. The problem was solved by collection of all waste waters from all rinse steps and altogether all chromium-VI-containing waste waters, reduction to chromium(III) and purification through a gravel filter and ion exchanger for H4PFOS. The discharge values of the ion exchanger for H4PFOS are in the single-digit µg/L range.
4	Would the measures taken for recycling and/or retention of PFOS/PFC be practicable, on principle, also in other, comparable companies?	Yes. Installation of an evaporator may cause spatial problems.
5	What is the annual PFOS/PFC consumption as related to the respective pure substance?	In the 2010-2014 period, the average consumption was 190 litres Proquel OF, containing ca. 2% H4PFOS. Resulting annual consumption: ca. 3.9 kg.
6	Which are the metrological criteria and intervals of replenishment of PFOS/PFC?	The PFOS-containing surfactant is replenished depending on the demand after measurement of the surface tension by means of a bubble

Ser.No.	Question	Answer
		tensiometer by Sita. Replenishment of 1-3 litres of Proquel OF is carried out at 1-3-day intervals.
7	Are there any factors opposing a metrologically controlled replenishment of PFOS/PFC?	No.
8	Do you know the electrochemical degradation rate for PFOS/PFC in the process?	No.
9	How long would PFOS/PFC remain in the cycle?	This is unknown and can only be roughly estimated. In the production there are 4 m ³ of chromic acid electrolyte with a concentration of ca. 200 g/m ³ H ₄ PFOS, i.e. 0.8 kg H ₄ PFOS. The annual consumption is 3.8 kg. As a result, H ₄ PFOS will remain in the cycle for ca. 0.21 years (0.8 kg: 3,8 kg/a).
10	Which other measures for extension of the PFOS/PFC cycle have been examined and which of these are applicable? Which measures have proved inapplicable and why?	Attempts of electrochemical degradation of PFOS and later, H ₄ PFOS were made. Such attempts failed with the waste water of this electroplating plant. The reason was unavoidable nickel drag-out (e.g. via sump pits), which massively interfered with the degradation process.
11	On which emission pathways and how often are PFOS/PFC discharged from the cycle?	The following leaks can be identified in the H ₄ PFOS cycle: Disposal of ion exchanger resins loaded with H ₄ PFOS (targeted process); Disposal of the chromium hydroxide sludge from waste water treatment of the partial PFC flow; Disposal of the barium sulfate sludge from "blunting" (?) of the chromium bath. (Note: This is a process removing excess sulfate of the electrolyte). Regenerates of the cation exchanger in the chromium(VI) loop; Discharge of the waste water treated for H ₄ PFOS (ca. 4 m ³ /d).
12	What happens with PFOS/PFC-containing drip losses, ground effluent and effluent from the exhaust air scrubbers/droplet separators?	All such waste waters are treated via the chromium-VI batch and thus, the H ₄ PFOS ion exchanger.
13	Are analyses available regarding PFOS/PFC-containing wastes (e.g. ion	Not yet. Company F agreed to have their wastes ana-

Ser.No.	Question	Answer
	exchange resins, adsorbents, electroplating sludges, used chromium electrolyte, barium sulfate sludge)?	<p>lyzed for per- and polyfluorinated compounds.</p> <p>Chromium hydroxide sludge: H4PFOS: 62 mg/kg, PFOS: 4 mg/kg, PFHxA: 110 µg/kg, PFBS: 8 µg/kg</p> <p>Barium sulfate sludge: PFOS: 110 mg /kg, H4PFOS: 1600 mg /kg</p> <p>Lead chromate sludge: Could not yet be subjected to analysis because it is generated only rarely.</p>
14	What are the quantities of PFOS/PFC discharged annually by means of disposal of the wastes mentioned above?	Still unknown.
15	Which are the physico-chemical treatment techniques used to dispose of PFOS/PFC-containing wastes?	<p>The saturated and used ion exchanger resins of the H4PFOS treatment plant are subjected to high-temperature incineration.</p> <p>Chromium hydroxide sludges are immobilized by means of cement and used in landfill construction.</p>
16	Which PFOS substitutes do you know and/or were offered to you by your chemical suppliers?	Proquel OF by Kiesow
17	What is your experience regarding PFOS substitutes?	Tests with other substitutes were performed on a pilot-plant scale; however, they failed.