Danish Ministry
of the Environment
Environmental
Protection Agency

Substitution of PFOS for use in non-decorative hard chrome plating

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Environmental Project No. 1371 2011
Miljøprojekt

Content

Preface

This project was initiated by the Danish Environmental Protection Agency as part of the programme “Miljøeffektiv Teknologi – Substitution af problematiske kemikalier” (Environmentally effective technology – Substitution of problematic chemicals”.

The project was carried out in the period August 2009 to February 2011.

Sidsel Dyekjær and Mikkel Aaman Sørensen from the Danish EPA supervised the project.

The purpose of this project was to find an alternative to PFOS use as a mist suppressant in non-decorative hard chrome plating, a PFOS use which presently is exempted from the EU ban of use of PFOS, because of lack of alternatives.

Various chemical and physical alternatives were tested in laboratory scale. A non-PFOS alternative as mist suppressant chemical was tested in a larger scale at a hard chrome plating company in Denmark.

Summary and conclusions

Non-PFOS mist suppressant can be used for hard chrome plating

In this project “Substitution of PFOS for use in non-decorative hard chrome plating”, experiments on both laboratory scale and larger industrial scale have shown that it is possible to substitute PFOS as mist suppressant in the non-decorative hard chrome plating process.

Background and purpose

Hard chrome plating is a surface treatment process where a layer of chromium is electrochemically deposited on the surface of metals. The electrochemical process produces a significant amount of gases to be released from the process tank. These gases rise to the surface as bubbles. Most bobbles burst at the surface and when they burst, they form aerosols which are released to the atmosphere. The aerosols consist of process liquid containing chromic acid and thus may expose the environment if no mist suppressant agent is used.

Some years ago it was discovered that addition of polyfluorinated surfactants (PFOS and derivatives) to the chromic acid bath would lower the surface tension by forming a thin foamy layer on the surface of the chrome bath. That mist suppressant layer dramatically reduced the formation of chromium-VI-aerosols (Cr^{6+}), which are well-known as carcinogenic, allergenic and dangerous for the environment. Thus, introduction of PFOS as mist suppressant helped solving huge occupational safety problems as well as environmental problems in the hard chrome plating industry.

PFOS and similar compounds are, however, an environmental and health problem as these substances are being biomagnified through the food chain. PFOS has many adverse effects, among others; it is an endocrine disrupting substance that affects the human fertility.

The purpose of this project was to examine the possibilities of replacing the use of PFOS as mist suppressant for non-decorative hard chrome plating.

In addition, this project surveyed the use of PFOS and alternatives within the non-decorative hard chrome plating industry in Denmark as well as worldwide.

The investigation

The investigation was managed by FORCE Technology in cooperation with IPU, DTU Mechanical Engineering, and the surface treatment company a.h. nichro Haardchrom A/S that was assisted by the development company SurfCoat A/S.

The laboratory experiments were carried out by IPU and the large scale testing was carried out at a.h. nichro Haardchrom A/S. FORCE Technology was responsible for the chromium emission measurement during the large scale testing.

Main conclusions

The main conclusions of the project are:

- A non-PFOS mist suppressant chemical alternative was found (at large scale testing) to be useful as an alternative to PFOS. The effectiveness, the durability, and the price level were similar to that of PFOS. The non-PFOS alternative is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS.
- A non-fluorinated mist suppressant chemical alternative was found and might be a promising substitute for PFOS. However, as continuously addition of the mist suppressant is needed, the usefulness of the alternative seems to be limited for automated hard chrome processes and must be assessed in each case.
- A physical alternative – in the form of PTFE coated balls – does not seem to lower the chromium emissions from the chrome bath. Quite the contrary, the chromium emissions seem to increase compared to using no mist suppressant at all.
- A physical alternative – in the form of a mesh or blanket solution – could be suitable for large scale series plating of uniform products. However, this kind of alternative was not investigated further in this project.
- Finally, the laboratory results of this project showed that the Cr^{6+} emission can be reduced radically by avoiding air convection. This indicates that large scale tests of a physical method that prevents air convection could turn out to be an alternative to PFOS. Such method would be a suitable alternative to PFOS in mass production systems. However, in plating system for frequently varying productions, it will be more difficult to establish a closed system because of the flexibility required to such systems. However, this alternative solution was not investigated further in this project, but would be a very interesting solution to investigate further.

Project results

Survey of the Danish and global use of PFOS in the chrome plating industry

A survey of the Danish use of PFOS in the chrome plating industry showed that the annually use of PFOS in the Danish chrome plating industry is between 10 to 28 kg (calculated as pure PFOS). This number was found by contact to the Danish hard chrome platers and suppliers of PFOS as mist suppressants to the Danish market.

The global use of PFOS in the chrome plating industry was estimated to be around 32 to 40.7 tons of PFOS (calculated as pure PFOS). This number was derived by contact to various global suppliers of PFOS as well as an Internet search after various sources to this kind of information. Most literature does not distinguish between the amount of PFOS used for non-decorative hard chrome plating (chromium-(VI)) and for other purposes within metal plating. Therefore, in most cases, the estimated amounts cover the entire metal plating industry and not only non-decorative hard chrome plating. Furthermore, most literature data is more than five years old and therefore it does not account for the fact that PFOS in the EU was banned for other purposes than non-decorative hard chrome plating.

Survey for alternative solutions to PFOS

A survey for alternative chemical and physical mist suppressants was carried out. This survey showed that the following alternatives were most promising for use in plating system for frequently varying productions, as in the case of the participating plating company a.h. nichro Haardchrom A/S:

- Physical alternatives
    - Use of PTFE coated balls

- Chemical alternatives
    - The fluorinated alternative Fumetrol® 21 from Atotech, which is based on 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid.
    - The fluor-free alternative TIB Suract CR-H from TIB Chemicals (but no information about the chemical substance, as this is confidential).

Laboratory experiments

The above mentioned two chemical alternatives and the physical alternative (PTFE coated balls) were tested on laboratory scale before choosing the most promising alternative for larger scale testing at a.h. nichro Haardchrom A/S. The different alternatives as well as PFOS and a reference without mist suppressant were tested and the chromium-(VI) emissions were measured. The experiments were carried out both without exhaust (no airflow in the experimental container) and with simulated exhausting.

The results showed that:

- The commercial PFOS product results in very effective reduction of the Cr^{6+} emission.
- Addition of TIB Suract results in reduction of the Cr^{6+} emission. In the experiment with continuous addition of TIB Suract, the additions followed the suggestions of the datasheet of the product, despite that the applied additions were not sufficient to prevent mist formation. This alternative was therefore not working as well as Fumetrol® 21.
- Addition of Fumetrol® 21 results in reduction of the Cr^{6+} emission. In the case of simulated exhausting, Fumetrol® 21 reduces the Cr^{6+} emission more than the additions of TIB Suract and PTFE balls.
- Addition of PTFE balls results in increased Cr^{6+} emission, also when used in combination with addition of Fumetrol® 21.
- The results evidently show that the Cr^{6+} emission in a system with simulated exhausting is significantly higher than in a system with very low convection of air. This shows that the Cr^{6+} emission can be reduced radically by avoiding air convection.

Based on these results, it was decided to test Fumetrol® 21 in a larger scale at a.h. nichro Haardchrom A/S. Even though the results without exhaust were very promising, this alternative solution was not found suitable for the varying production at a.h. nichro Haardchrom A/S.

Large scale testing at a.h. nichro Haardchrom A/S

Large scale testing of the effect of Fumetrol® 21 (Atotech) as an alternative to PFOS was carried out at the hard chrome plating plant a.h. nichro Haardchrom A/S in Hvidovre, Denmark.

The primary purpose of the test was to see if the Fumetrol® 21 could be used as an alternative to PFOS as mist suppressing agent with similar abilities to suppress chromium-(VI) emissions from the chrome bath. 14 days of testing was therefore carried out both with the use of PFOS and with the use of Fumetrol® 21 as mist suppressant. The conditions in the chrome bath and the subjects to be chromated were the same in both cases. Five measurements were carried out in both experiments, on day 1, day 3, day 7, day 10, and day 14 of the make-up of the chrome bath (i.e. addition of mist suppressing agent).

The results showed that the alternative compound 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (Fumetrol® 21) in a large scale test:

- works as effective as PFOS as mist suppressing agent,
- seems to have the same durability as PFOS as mist suppressing agent,
- has the same price level as PFOS as mist suppressing agent,
- can be substituted right away, when PFOS is burnt out in the chrome bath, without the need of changing the entire chrome bath chemicals, and
- is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS.

This project has therefore shown that it is possible to use a non-PFOS mist suppressant for non-decorative hard chrome plating.

Sammenfatning og konklusion

PFOS-fri skumdæmper kan anvendes til hårdforkromning

I dette projekt “Substitution af PFOS til brug i ikke-dekorativ hårdforkromning” har forsøg både i laboratorium i lille skala og på en virksomhed i lidt større skala vist, at det er muligt at erstatte PFOS som skumdæmper i den ikke-dekorative hårdforkromningsproces.

Baggrund og formål

Hårdforkromning er en overfladebehandling, hvor et lag af chrom lægges elektrokemisk på overfladen af metaller. Den elektrokemiske proces udvikler en betydelig mængde af gasser, som bliver frigjort fra procesbadet. Disse gasser stiger til overfladen som bobler. De fleste bobler brister ved overfladen, og når de brister, danner de aerosoler, som frigøres til atmosfæren. Aerosolerne består af procesvæske, der indeholder chromsyre, og de kan således udsætte miljøet for fare, hvis der ikke bruges nogen skumdæmper.

For nogle år siden blev det opdaget, at tilsætning af polyfluorerede midler, der påvirker overfladespændingen (PFOS og derivater), til chromsyrebadet, sænker overfladespændingen ved at danne et tyndt skumlag på overfladen af chrombadet. Dette skumlag formindskede dramatisk dannelsen af chrom-VI-aerosoler (Cr^{6+}), som er kendte for at være kræft- og allergifremkaldende samt farlige for miljøet. Således var introduktionen af PFOS som skumdæmper med til at løse store arbejdsmiljømæssige og miljømæssige problemer i hårdforkromningsindustrien.

PFOS og lignende forbindelser er dog et miljø- og sundhedsmæssigt problem, da disse stoffer bliver opkoncentreret gennem fødekæden. PFOS har blandt andet mange uønskede bivirkninger. Det er et hormonforstyrrende stof, som påvirker den menneskelige frugtbarhed.

Formålet med dette projekt var at undersøge mulighederne for at erstatte brugen af PFOS som skumdæmper ved ikke-dekorativ hårdforkromning.

Endvidere har dette projekt kortlagt brugen af PFOS og alternativer inden for den ikke-dekorative hårdforkromningsindustri i Danmark så vel som i hele verden.

Undersøgelsen

Undersøgelsen blev ledet af FORCE Technology i samarbejde med IPU, DTU Mekanik og overfladebehandlingsfirmaet a.h. nichro Haardchrom A/S, som blev assisteret af udviklingsfirmaet SurfCoat A/S.

Laboratorieforsøgene blev udført af IPU, og forsøgene i større skala blev udført hos a.h. nichro Haardchrom A/S. FORCE Technology var ansvarlig for chromemissionsmålingen under testningen i større skala.

Hovedkonklusioner

Projektets hovedkonklusioner er:

- Et kemisk alternativ til en PFOS-fri skumdæmper viste sig (ved forsøg i større skala) at være et brugbart alternativ til PFOS. Effektiviteten, holdbarheden og prisniveauet var det samme som for PFOS. Det PFOS-frie alternativ er en miljømæssig forbedring, da det er mindre persistent, mindre bioakkumulerende og mindre giftig sammenlignet med PFOS.
- Et kemisk alternativ til en ikke-fluoreret skumdæmper blev identificeret og kunne være en lovende erstatning for PFOS. Da kontinuerlig tilsætning af skumdæmperen er nødvendig, ser nytten af alternativet dog ud til at være begrænset for automatiserede hårdforkromningsprocesser, og der er behov for en særskilt vurdering i hvert enkelt tilfælde.
- Et fysisk alternativ – i form af PTFE-belagte bolde – ser ikke ud til at dæmpe chromemissionerne fra chrombadet. Snarere tværtimod ser chromemissionerne ud til at øges, sammenlignet med hvis der slet ikke bruges skumdæmper.
- Et fysisk alternativ – i form af en net- eller tæppeløsning – kunne være egnet til serieforkromning af ensartede produkter i større målestok. Dette alternativ blev dog ikke undersøgt nærmere i dette projekt.
- Endelig viste laboratorieresultaterne i dette projekt, at Cr^{6+}-emissionen kan reduceres radikalt ved at undgå luftbevægelse (simuleret udsugning). Dette indikerer, at en fysisk metode, der forhindrer luftbevægelse, kunne vise sig at være et alternativ til PFOS. Sådan en metode ville være et egnet alternativ til PFOS i masseproduktionssystemer. Men i overfladebehandlingssystemer med ofte varierende produktioner vil det være sværere at etablere et lukket system på grund af fleksibiliteten, der kræves af sådanne systemer. Denne alternative løsning blev dog ikke undersøgt yderligere i dette projekt, men det ville være en meget interessant løsning at undersøge yderligere.

Projektresultater

Undersøgelse af det danske og globale forbrug af PFOS i hårdforkromningsindustrien

En undersøgelse af det danske forbrug af PFOS i hårdforkromningsindustrien viste, at det årlige forbrug af PFOS i den danske forkromningsindustri er mellem 10 til 28 kg (beregnet som ren PFOS). Dette tal blev fundet ved at kontakte de danske hårdforkromere og leverandører af PFOS som skumdæmpere til det danske marked.

Det globale forbrug af PFOS i hårdforkromningsindustrien blev beregnet til at være ca. 32 til 40,7 tons PFOS (beregnet som ren PFOS). Dette tal stammer fra kontakt til forskellige globale leverandører af PFOS samt en internetsøgning efter forskellige kilder til denne slags oplysninger. Det meste af litteraturen skelner ikke mellem mængden af PFOS, der bruges til ikke-dekorativ hårdforkromning (chrom-(VI)) og til andre formål inden for metaloverfladebehandling. Derfor dækker de estimerede mængder i de fleste tilfælde hele metaloverfladebehandlingsindustrien og ikke kun ikke-dekorativ hårdforkromning. Desuden er de fleste litteraturdata mere end fem år gamle, og dermed tages der ikke højde for, at PFOS blev forbudt i EU til andre formål end ikke-dekorativ hårdforkromning.

Undersøgelse af alternative løsninger til PFOS

En undersøgelse af alternative kemiske og fysiske skumdæmpere blev gennemført. Denne undersøgelse viste, at følgende alternativer var de mest lovende til brug i overfladebehandlingssystemer med ofte varierende produktioner, som i tilfældet med det deltagende overfladebehandlingsfirma a.h. nichro Haardchrom A/S:

- Fysiske alternativer
    - Brug af PTFE-belagte bolde

- Kemiske alternativer
    - Det fluorerede alternative Fumetrol® 21 fra Atotech, som er baseret på 1***H***,1***H***,2***H***,2***H***-perfluoroctan sulfonsyre.
    - Det fluor-fri alternativ TIB Suract CR-H fra TIB Chemicals (men der var ingen oplysninger om det kemiske indholdsstof, da det er fortroligt).

Laboratorieforsøg

De to ovennævnte kemiske alternativer og det fysiske alternativ (PTFE-belagte bolde) blev testet på et laboratorium før valget af det mest lovende alternativ til testning i større skala hos a.h. nichro Haardchrom A/S. De forskellige alternativer samt PFOS og en reference uden skumdæmper blev testet, og chrom-(VI)-emissionerne blev målt. Eksperimenterne blev udført både uden udsugning (intet luftflow i forsøgsbeholderen) og med simuleret udsugning.

Resultaterne viste, at:

- Det kommercielle PFOS-produkt resulterer i en meget effektiv reduktion af Cr^{6+}-emissionen.
- Tilsætning af TIB Suract resulterer i en reduktion af the Cr^{6+}-emissionen. I eksperimentet med kontinuerlig tilsætning af TIB Siract (hvor der blev tilsat ifølge forskrifterne på det tekniske datablad), var det dog ikke tilstrækkelige til at forhinde en Cr^{6+}-emission. Dette produkt virkede altså ikke så godt som Fumetrol® 21.
- Tilsætning af Fumetrol® 21 resulterer i en reduktion af Cr^{6+}-emissionen. I tilfældet med simuleret udsugning reducerer Fumetrol® 21 Cr^{6+}-emissionen mere end tilsætningerne af TIB Suract og PTBE-bolde.
- Tilsætning af PTFE-bolde resulterer i øget Cr^{6+}-emission, også når de bruges i en kombination med tilsætning af Fumetrol® 21.
- Resultaterne viser tydeligt, at Cr^{6+}-emissionen i et system med simuleret udsugning er markant højere end i et system med meget lille luftbevægelse. Dette viser, at Cr^{6+}-emissionen kan reduceres radikalt ved at undgå luftbevægelse (simuleret udsugning).

Baseret på disse resultater blev det besluttet at teste Fumetrol® 21 i større målestok på a.h. nichro Haardchrom A/S. Selvom resultaterne uden udsugning var meget lovende, blev denne alternative løsning ikke fundet egnet for den vekslende produktion, der foregår hos a.h. nichro Haardchrom A/S.

Forsøg i større skala hos a.h. nichro Haardchrom A/S

Forsøg i større skala af effekten af Fumetrol® 21 (Atotech) som et alternativ til PFOS blev udført hos hårdforkromningsvirksomheden a.h. nichro Haardchrom A/S i Hvidovre, Danmark.

Det primære formål med forsøget var at se, om Fumetrol® 21 kunne anvendes som et alternativ til PFOS som skumdæmpningsmiddel med samme egenskaber til at dæmpe chrom-(VI)-emissioner fra chrombadet. Et forsøg over 14 dage blev derfor udført både med brug af PFOS og med brug af Fumetrol® 21 som skumdæmper. Forholdene i chrombadet og de genstande, der skulle forkromes, var de samme i begge tilfælde. Fem målinger blev udført i begge eksperimenter, på dag 1, dag 3, dag 7, dag 10 og dag 14 efter at chrombadet blev blandet (dvs. tilsætning af skumdæmpningsmiddel).

Resultaterne viste, at den alternative forbindelse 1***H***,1***H***,2***H***,2***H***-perfluor octan sulfonsyre (Fumetrol® 21) i et forsøg i større skala:

- arbejder lige så effektivt som PFOS som skumdæmpningsmiddel,
- ser ud til at have samme holdbarhed som PFOS som skumdæmpningsmiddel,
- har samme prisniveau som PFOS som skumdæmpningsmiddel,
- kan erstattes straks, når PFOS er ”brændt af” i chrombadet, uden at det er nødvendigt at skifte alle kemikalierne i chrombadet, og
- er en miljømæssig forbedring, da det er mindre persistent, mindre bioakkumulerende og mindre giftig sammenlignet med PFOS.

Dette projekt har derfor vist, at det er muligt at bruge en PFOS-fri skumdæmper til ikke-dekorativ hårdforkromning.

1 Introduction

1.1 Purpose

The purpose of this project was to examine the possibilities of replacing the use of PFOS as mist suppressant for non-decorative hard chrome plating either by chemical substitution or technology shift or a combination.

In addition, this project surveyed the use of PFOS and alternatives within the non-decorative hard chrome plating industry in Denmark, as well as worldwide.

If a sufficient alternative for mist suppression in hard chrome plating was identified, this alternative could also be relevant for other metal plating processes.

1.2 Background

1.2.1 The hard chrome plating process

Hard chrome plating is a surface treatment process where a layer of chromium is electrochemically deposited on the surface of metals. Today it is mainly used where hard-wearing, abrasion-resistant, and corrosion-resistant surfaces are required, for example, for hydraulic systems, axles in bearing constructions, printing bowls, toothed wheels, equipment for the foodstuff industry, and surgical instruments.

Electrochemical deposition of hard chrome is characterised as having a very low current efficiency because at the cathode only approximately 20% of the applied current is used for the deposition of chromium, whereas the rest of the current is used for hydrogen development. At the anode, the main chemical reaction results in oxygen development.

Thus, the electrochemical process produces a significant amount of gases to be released from the process tank. These gases rise to the surface as bubbles. Most bobbles burst at the surface. When they burst they form aerosols which are released to the atmosphere. The aerosols consist of process liquid containing chromic acid and thus may expose the environment if no mist suppressant agent is used (Pilat and Pegnam, 2006; Koropchak and Rowchowhury, 1990).

Often a layer of polypropylene balls on the surface of the chromic acid bath is used to reduce the heat loss.

Figure 1-1-1: An industrial hard chrome plating system. The sample to be deposited with chromium is submerged in the electrolyte (in the middle of the photo). The surface of the electrolyte is covered with plastic balls, acting as a flexible isolation layer and preventing evaporation of water from the heated electrolyte.

1.2.2 PFOS for control of aerosol formation

Some years ago, it was discovered that addition of polyfluorinated surfactants (PFOS and derivatives) to the chromic acid bath would lower the surface tension by forming a thin foamy layer on the surface of the chrome bath. That mist suppressant layer dramatically reduced the formation of chromium-(VI)-aerosols (Cr^{6+}), which are well-known as carcinogenic, allergenic, and dangerous for the environment. Thus, introduction of PFOS as mist suppressant helped solving huge occupational safety problems as well as environmental problems in the hard chrome plating industry.

The most common fluorinated surfactant used in the business today is tetraethyl ammonium perfluorooctane sulfonate (CAS no. 56773-42-3; Fluortensid-248), a derivative of PFOS.

The fluorinated mist suppressant is added only when necessary, i.e. when an increased formation of aerosols in the chromic acid bath is foreseen. Some methods (mentioned by suppliers) exist today for measuring, when additional mist suppressant is needed, but these methods are not used in most plants. It is merely the experience of the workers and their assessment that determines when additionally mist suppressant is needed. This means that larger amounts of PFOS than strongly needed may be used, even though the high price probably prevents excessive use of PFOS.

When the chrome bath is contaminated and cannot be used anymore, the liquid has to be disposed of as chemical waste. In Denmark, it is sent to a chemical waste plant where the chromium is precipitated. The filter cake is incinerated and the slag from the incineration is disposed on a landfill. The liquid is sent to a wastewater treatment plant after removal of chromium and other metals[1]. The residues of PFOS and degradation products will follow the waste water and end up in sewage sludge.

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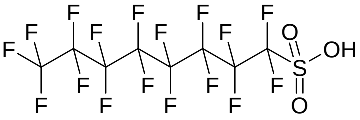
[1] Personal communication with customer service at Kommunekemi a/s February 2011.

A great part of PFOS used in this industry will probably end up in the nature. That is confirmed by the high levels of PFOS recently found in agricultural soils treated with sewage sludge in the US and in Germany (Renner, 2009). On the other hand, the German national metal plating association (ZVO) states that in the case of Germany only 20% of the applied is lost.[2] The US EPA has recently discovered that the metal plating industry is a major contributor to the pollution of perfluorinated chemicals into sewage water in the US, and this is especially alarming as the chemicals pass undegraded through sewage treatment plants into lakes and streams. There are reports of very high concentrations of PFCs being flushed into the sewers at concentrations as high as 54,000 parts per trillion. The usual concentration of PFC in the water going into the metal shops is 2.5 parts per trillion. The US EPA will test at more metal platers, and the findings could lead to new rules restricting PFCs in metal shops in the US (Chicago Tribune, 2010).

1.2.3 PFOS - chemistry and properties

Perfluorooctane sulfonic acid (PFOS) is the best known perfluorinated compound. PFOS has a linear perfluoroalkyl carbon chain of 8 and a sulfonic acid functional group.



PFOS

The production and sale of PFOS has dropped drastically since the year 2000 where the multinational company 3M, that was the main producer of the substance, voluntarily decided to stop the production and sale of PFOS and related compounds. Since then Chinese producers have taken over the production of PFOS, but not on the same scale. The annual production of PFOS in China at 15 enterprises is presently about 200 tons (Mei Shengfang, 2010).

PFCs – polyfluorinated[3] substances – are a large group of chemical substances with related properties. Most PFCs contain an alkyl chain typically between 4 and 12 carbon atoms where all or most of the hydrogen atoms have been replaced by fluorine. The strong fluorine-carbon bonds make the chain very stable and non-degradable in the environment. The substances also contain a more reactive functional group, which may be an alcohol, a carboxylic acid, a sulfonic acid, a phosphoric acid, or their derivatives.

According to OECD, about one thousand of polyfluorinated compounds (PFCs) are in use today. Any of these substances is surface active substances with an extreme low surface tension, and they often repel water, grease, and dirt. These properties are useful for various applications, such as dirt repellents in e.g. clothes and carpets, grease-proof paper in food packaging, in fire fighting foams, and many other industrial purposes such as in the

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[2] Personal information from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), D-40724 Hilden; March 6, 2009.

[3] ”Poly” means that many of the hydrogen atoms in the alkyl chain have been replaced with fluorine; ”per” means that ***all*** hydrogen in the alkyl chain have been replaced with fluorine.

semiconductor industry, in the photo industry, and as mist suppressants in the metal plating industry.

In recent years, PFOS and other polyfluorinated compounds (PFCs) have become a global environmental problem. These substances have been determined widespread in surface water, sediment, sludge, soil, outdoor/indoor air/dust, soils, animals, and humans, and have been found even in remote polar areas such as Greenland (Giesy and Kannan 2002; Bossi et al., 2005ab; Jensen et al., 2006).

The polyfluorinated substances are being biomagnified through the food chain. As opposed to the most common persistent organic pollutants (POPs), polyfluorinated compounds are not concentrated significantly in fatty tissue. On contrary, they are associated to proteins in blood and internal organs, such as spleen, lever, and kidney. Polar bears in top of the arctic food chain have especially high concentrations of PFOS in the blood and liver.

PFOS has many adverse effects, among others; it is an endocrine disrupting substance that affects the human fertility. Recent studies show a correlation between the amount of PFOS in human blood and the time it takes for women to get pregnant and a reduction in men’s semen quality (Fei et al., 2009; Joensen et al., 2009).

1.2.4 Regulations and other initiatives

Already in 2004, PFOS-related compounds were added to the “List of Undesirable Substances” by the Danish EPA.

The European Parliament and Council has regulated PFOS substances in Directive 2006/122/EC of December 12, 2006 on “restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates)”. According to this directive, PFOS compounds may no longer be marketed or used as a substance or as part of preparations in concentrations equal to or above 0.005 % (w/w), and may no longer be used in semi-manufactured products or articles in a concentration equal to or above 0.1 % (became effective from June 27, 2008). Some exceptions on the ban of PFOS in the EU exist, among others the use as mist suppressants for non-decorative hard chrome plating (chromium-(VI)). This directive was automatically incorporated in the REACH Regulation annex XVII by 1.6.2009.

In May 2009, PFOS was listed as a persistent organic pollutant in the Stockholm Convention. Hard metal plating and decorative plating became specific use exemptions. (SC UNEP/POPS/POPRC.5/INF/3, 2009).

In December 2009, the US EPA published their action plan on long-chained perfluorinated chemicals[4]. The US EPA intends to consider initiating rulemaking under TSCA section 6 to manage long-chain PFCs. If the US EPA can obtain certain findings with respect to these chemicals, TSCA

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[4] US EPA ”Long-chain Perfluorinated Chemicals (PFCs) Action Plan Summary. http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html. Long-chained PFCs are defined in the action plan and can in short be explained as PFAS (perfluoroalkyl sulfonates) with a chain length of 6 or higher and as PFAC (perfluoroalkyl carboxylates) with a chain length of 8 or higher.

section 6 provides authority for the US EPA to ban or restrict the manufacture (including import), processing, and use of these chemicals.

In September 2010, the US NASF organisation (National Association for Surface Finishing) has supported a 3-year phase out of PFOS-based mist suppressants for chromium plating[5].

1.2.5 Alternatives to PFOS

Previously, PFOS was used for both decorative chrome plating and hard chrome plating processes but new technology applying chromium-(III) instead of chromium-(VI) has made PFOS use in decorative chrome plating outdated and unnecessary. For hard chrome plating, however, the process with chromium-(III) does not function. Instead larger closed tanks, or increased ventilation combined with an extraction of chromium-(VI), are suggested as alternative solutions for the applications where a use of chromium-(III) is not possible yet (TNO, 2006).

Hence, it is still permitted to use PFOS and its derivates within the electroplating industry. The reason for the ongoing use of PFOS is that no satisfactory alternatives have been found so far.

The chromic acid bath that is used for hard chrome plating is extremely reactive and oxidizing, and PFOS is used because it is very resistant to that harsh environment and has an extremely low surface tension. It is very difficult to find another chemical with such useful properties. However, there are PFOS-free fluorinated alternatives on the market based on e.g. fluorotelomers.

Another way to make PFOS obsolete is to introduce alternative technology which is resistant to the extremely oxidizing chromium bath and which can keep the chromic acid aerosol formation to a minimum and prevent bursting.

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[5] http://www.nasf.org/Content/NavigationMenu/GRISSUES/Environment/default.htm

2 Survey of the global use of PFOS in the chrome-plating industry

Previously, PFOS was used for both decorative chrome plating and hard chrome plating processes but new technology applying chromium-(III) instead of chromium-(VI) has made PFOS use in decorative chrome plating outdated – even though it may still be used somewhere around the world. As of June 2008, the use of PFOS as mist suppressant in decorative chrome plating became illegal in the EU (Directive 2006/122/EC).

For hard chrome plating, the process with chromium-(III) does not function. Therefore, the use of PFOS as mist suppressing, wetting agent for hard chrome plating has been considered essential, and is still permitted in the EU today and is an accepted use in the Stockholm Convention.

This chapter describes the use of PFOS in the chrome plating industry. The information gathered usually covers total chrome plating including decorative plating, but it is essential to realise that non-decorative hard chrome plating is carried out under much more aggressive conditions, for which reason PFOS is still used extensively for this purpose.

The survey was carried out in the period October 2009 to summer 2010.

2.1 Use of PFOS in Denmark

The companies in Denmark carrying out non-decorative hard chrome plating were contacted in order to learn about the yearly consumption of PFOS as mist suppressant. Only four companies in Denmark are carrying out such work. These four companies are:

- “a.h. nichro Haardchrom A/S” situated in Hvidovre
- “Chembo A/S” situated in Kvistgård
- “Galvano APS” situated in Svendborg
- “NOF Nordic Overfladebehandling” situated in Gelsted.

Two of these companies are using PFOS based mist suppressants and two are not. The non-PFOS based alternative used by the two companies is, however, a fluorinated alternative. Precisely, which fluorinated substance that is used is confidential but it is probably the fluorotelomer derivative 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (CAS no. 27619-97-2)(see Table 3-1) that has been identified as an alternative in other mist suppressant chemicals.

Furthermore, different suppliers of PFOS for the chrome plating industry were contacted as well as the Danish chrome plating industry in order to learn about the annually consumption of PFOS for non-decorative hard chrome plating. The suppliers were asked about what they had sold to Danish companies, and the Danish chrome plating industry was asked to estimate their annual consumption of PFOS. Information from these suppliers showed that the total annual purchase of (pure) PFOS in the chrome plating industry in Denmark in 2008 and/or 2009 was about 28 kg. The chrome plating industry in Denmark estimates that about 10 kg of (pure) PFOS is used annually for non-decorative hard chrome plating. The difference between the two figures may be due to the fact that purchase and use are not coinciding, e.g. large amount of PFOS has been bought for more than one year. Furthermore, the calculation of the 10 and 28 kilos respectively, has been based on an estimated range of total use of PFOS mist suppressant chemical multiplied with the range of PFOS content as stated on the material safety data sheet. The calculations are therefore uncertain. Finally, the information from the suppliers is from different years. Some suppliers gave information for the year 2008 and some for the year 2009. In 2008, the ban of PFOS entered into force in Denmark. Some of the PFOS sold may therefore have been to other metal plating than non-decorative hard chrome plating.

The concentration of the PFOS in the mist suppressant chemical formulation is typically 1-15 % depending on the formulation (supplier), and the amount of the formulation to be used for a hard chrome plating bath is typically between 10 – 60 ml for a 100 liter chrome bath – of course depending on the concentration of PFOS in the mist suppressant chemical. Additional PFOS needs to be added to the chrome bath on a regular basis, as PFOS is being degraded in the chrome bath. The degree of PFOS consumption depends on the electrical charge (ampere hours) used for the chrome bath.

2.2 Global use of PFOS

In order to find out which PFOS based mist suppressants that are used for non-decorative hard chrome plating (chromium-(VI)), a number of suppliers of mist suppressant were contacted and asked to give information about the global use of PFOS mist suppressant.

The following suppliers of mist suppressants for the Danish and international markets were contacted:

- Atotech Skandinavien AB (Sweden)
- EngTech Scandinavia A/S (Denmark)
- Surtec Scandinavia ApS (Denmark)
- Galvano Kemi (Denmark)
- Enthone (Cookson Electronics) (Sweden)
- Kiesow Dr. Brinkmann GmbH (Germany)
- GalvaNord (Elplatek) (Denmark)
- Dr. Günter Dobberschütz (Germany)
- CL Technology GmbH (Germany)
- Schlötter Galvanotechnik (Germany)
- Chembright (China)
- MacDermid (US)
- Plating Resources, Inc. (USA)

The consumption of PFOS in Denmark and the Nordic countries was estimated by using information about the percentage concentration of PFOS in the commercial product and multiplying this with the total sale of PFOS based mist suppressant products.

Furthermore, an Internet/literature search was performed in order to estimate the consumption of PFOS for non-decorative hard chrome plating (chromium-(VI)) in other areas of the world. The results are shown in Table 2-1.

Most literature does not distinguish between the amount of PFOS used for non-decorative hard chrome plating (chromium-(VI)) and for other purposes within metal plating. Therefore, in most cases, the amounts in the table below cover the entire metal plating industry and not only non-decorative hard chrome plating. Furthermore, most literature data is more than five years old and therefore it does not account for the fact that PFOS in the EU was banned for other purposes than non-decorative hard chrome plating.

One of these sources is the OECD report published in 2005. OECD conducted a survey about the production and use of PFOS, PFAS, and PFOA, related substances and products/mixtures containing these substances. In this report, the total use of PFOS related substances for metal plating was estimated by information from 10 different OECD countries. The data provided represented the year 2003 (OECD, 2005).

However, there is one new source of information from the European Commission (2010). They have gathered information about the implementation of the restriction of PFOS in electroplating applications. In this paper, the European countries have reported the amounts used of PFOS as mist suppressant – sometimes explicitly stated as mist suppressant for hard chrome plating. Most figures are new – from 2008 or 2009. Figures from 2008 may be higher than figures from 2009, as the restriction on PFOS within the chrome plating industry entered into force in the middle of 2008. For most of the European countries, including Denmark, it is stated that PFOS is not used for non-decorative hard chrome plating. However, this may not be entirely true, as in the case of Denmark, the Danish EPA has reported that there is no use of PFOS in the non-decorative hard chrome plating industry in Denmark, as no use of PFOS can be found within the Danish Product Register. However, as the mist suppressants used in this industry is not classified as dangerous, no reporting to the Danish Product Register is required.

Because of this recent inventory of the use of PFOS for non-decorative hard chrome plating in the EU, the PFOS use data for the EU only represents the use for non-decorative hard chrome plating, as this is one of few exemptions from the restriction of use of PFOS. However, data from other parts of the world may include the entire metal plating sector and not only non-decorative hard chrome plating.

Another new report prepared for UNIDO (United Nations Industrial Development Organization) Regional Office in China from December 2009 has also collected all publicly available information on the uses of PFOS (Carloni, 2009). Data on use has been reported between the year 2000 and 2008. This data is presented in the text below if other sources have not been found.

Table 2-1 Total annual reported use of PFOS based mist suppressants for (non-decorative hard) chromium-(VI) plating. More detailed descriptions/explanations can be found below.

Country	PFOS (kg)* annually	Industry covered	References/comments
Denmark	10 – 28 kg	Non-decorative hard Cr-(VI) plating (and perhaps partly other metal plating activities for the year 2008).	Info from Danish industry (2009) and suppliers to Danish industry (2008). Calculated.
Norway	0 kg	Chrome plating.	SC UNEP/POPS/POPRC.5/INF/14, 2009.
Sweden	26 – 71 kg (250 kg)	Hard chrome plating and decorative chrome plating.	KEMI, 2004, states a use of 26 kg. Swedish Product Register (2008)

Country	PFOS (kg)* annually	Industry covered	References/comments
			states a use of 71 kg. European Commission, 2010 states a use of 250 kg.
Finland	5 – 20 kg	As mist suppressant in Cr-(VI) electroplating.	European Commission, 2010. No information on when the data is from.
Nordic countries (including DK)	90 kg	Non-decorative hard chrome plating (and perhaps partly other metal plating activities for the year 2007/2008).	Info from suppliers Nordic suppliers (data a mix from 2007, 2008, and 2009). Calculated.
Germany	1883 kg	All electroplating processes.	European Commission, 2010. No information on when the data is from.
Belgium	< 218 kg	Cr-(VI) electroplating. As mist suppressant and wetting agent.	European Commission, 2010. No information on when the data is from. 218 kg is reported as a total of use as mist suppressant and wetting agent.
Czech Republic	< 23 kg	Cr-(VI) electroplating. As mist suppressant and wetting agent.	European Commission, 2010. Expected use in 2009. Use as mist suppressant in 2008 as was reported to be 165 kg.
Italy	(< 2000 kg) 0 kg	As acid mist suppressant (for the year 2003). Now a use of zero.	OECD (2005). EC (2010).
Romania	0 kg		Secretariat of the Stockholm Convention (SSC, 2008).
Slovenia	65 kg	As wetting agent for Cr-(VI) plating.	European Commission (2010).
UK	120 – 135 kg	As mist suppressant for Cr-(VI) electroplating (for the year 2008 (last half)).	European Commission (2010). Use after the restriction of PFOS entered into force.
France	200 – 695 kg	Total metal chrome plating including decorative plating (200 kg in 2006). 695 kg was used for chrome plating in 2008.	SC UNEP POPRC Draft (2010). European Commission (2010).
The Netherlands	< 150 kg	Chrome plating.	SC UNEP POPRC Draft (2010).
EU	2700 – 3200 kg (8,600 – 10,000 kg)	Today – after the restriction of PFOS for other uses than hard chrome plating. For metal plating including decorative plating (for the year 2003).	European Commission (2010). Together with information on sale to Nordic countries. OECD (2005), RPA & BRE (2004).
Switzerland	200 – 500 kg	As mist suppressant and surfactant within metal plating (for the year 2007).	FOEN, 2009.
Canada	3,000 kg	As surfactant in the electroplating sector (for the year 2004). Primarily used for metal plating.	CEPA, 2006.
USA	< 7983 kg	Total use/production of PFOS related substances. The use for metal plating is of course much smaller.	Carloni, 2009.
China	25,000 kg	Entire metal plating industry including decorative plating (for the year 2006?).	MEP of China (2008).
Japan	0 kg	Total metal plating including decorative chrome plating as well as other metal plating processes (2007). According to new information (2010), Japan has stopped the use of PFOS for metal chrome plating today.	SC UNEP/POPS/POPRC.3/13 (2007). Carloni (2009). SC UNEP POPRC Draft (2010).
Australia	1,070 kg	As mist suppressant for metal plating.	Calculated amount by use of NICNAS Alert No. 8, 2008 & NICNAS Alert No. 5, 2007.
Latin America	?		No information
Africa	> 0 kg		PFOS is used in some African countries for metal plating. The amount is unknown (Carloni, 2009).
Worldwide	891 kg	Non-decorative hard chrome plating (and perhaps partly other metal plating activities for the year 2008/2009).	Info exclusively from contacted suppliers (data from 2008 or 2009). Info from three suppliers. Many contacted suppliers did not respond.
Global	**32 – 40.7 tons**		**Sum of the above (calculated)**

* Calculated as pure PFOS and not as diluted PFOS product

2.2.1 Denmark

As described above in section 2.1 ”Use of PFOS in Denmark”, the information from the Danish non-decorative hard chrome industry together with information from suppliers of mist suppressant chemicals to the Danish industry indicates that the total use of PFOS for one year is between 10 and 28 kg calculated as pure PFOS. The concentration of PFOS in the mist suppressant chemical formulation is typically 1-15% depending on the formulation (supplier).

The low value is the use estimated by the industry and the high value is amounts sold by suppliers to Danish companies. Both numbers are calculated by multiplying the estimated/sold amount with the content of PFOS indicated by percentage range on the material safety data sheet.

2.2.2 Nordic countries

When information was obtained from suppliers about the use of PFOS in Denmark, the Nordic suppliers were at the same time asked about information on sold amounts of PFOS to Nordic countries. The contacted suppliers reported a total amount of 90 kg calculated as pure PFOS for the years 2007/2008 or 2009 (depending on the supplier). In all, three of the contacted suppliers sold PFOS mist suppressant chemicals to the Nordic countries during this time period. The total amount (calculated as pure PFOS) was 90 kg. There could be other suppliers of PFOS for use as mist suppressants for non-decorative hard chrome plating in the Nordic countries.

Norway

Norway has reported in an action plan for PFAS (perfluoroalkyl substances) and PFOS-related substances that the major areas of use for PFOS-related substances in Norway are fire-fighting foams and the chrome-plating industry (SFT, 2005). No information about the specific use of PFOS is mentioned.

In Carloni (2009), it is reported that Norway has submitted information to the Stockholm Convention on Persistent Organic Pollutants – POPs Review Committee (POPRC) that the estimated use of PFOS in Norway for metal plating is 3-5 liters. It seems that is data is from 2005 or 2006.

According to a document by the Stockholm Convention on Persistent Organic Pollutants (SC UNEP/POPS/POPRC.5/INF/14, 2009), the Norwegian Galvano Industry Organisation (NGLF) has reported that their suppliers no longer provide wetting/anti-mist agent for chromium plating. Instead they provide PFOS-free tensides. NGLF considers the performance of these alternatives to be insufficient and is currently developing better alternatives to PFOS and alternative technology to solve the problem with airborne loss of hexavalent chromium from the baths. Where possible the chromium-(VI) process is being substituted by the chromium-(III) process. This information seems more recent than the information from Carloni (2009). It is therefore assumed that the use of PFOS in Norway is zero.

Sweden

In an action plan from 2004, Sweden has reported that the use of PFOS-related chemicals for metal plating in 2002 was 3% of the total use of PFOS-related chemicals i.e. 3% of 862 kg = 26 kg (KEMI, 2004). This estimate was based on information from suppliers as well as information from the Swedish Product Register.

More recent information from the Swedish Product Register shows that the use of PFOS and PFOS-related substances (substances that degrade to PFOS in the environment) is about 71 kg in 2008 for the industry “surface industry and coating of metals”[6].

However, these numbers (from 2002 and 2008) are for the entire metal plating industry and the 2002 data before the phase out of the use of PFOS for decorative chrome plating as well. The Swedish Product Register has a rule (similar to Denmark) that only quantities exceeding 100 kg annually should be reported to the Product Register. The amount registered here will therefore always be underestimated.

The information received in this project from the three suppliers – a total supply of PFOS mist suppressants of 90 kg – therefore seems reasonable for the annual use within all Nordic countries.

According to the European Commission (2010), the amount of PFOS used for chrome (VI) electroplating processes in Sweden is 250 kg annually. There is no information on which year the data is from. This is a much higher number (ten times higher) than the amount estimated in 2004 by the Swedish Chemicals Agency. There is no information on how they have reached this amount. As the consumption according to the suppliers of mist suppressants contacted in this study is much lower – even though it is a sum for all Nordic countries – it seems that the amount of 26 to 71 kg for use in Sweden alone is more believable than the amount of 250 kg.

Finland

According to the European Commission (2010), the amount of PFOS used as mist suppressants in chrome VI electroplating processes is 5 to 20 kg annually. There is no information on which year the data is from. The consumption of PFOS is similar to that calculated for Denmark for 2009.

2.2.3 Germany

In the OECD report (2005), it is stated that Germany had a production of PFOS (tetraethyl ammonium perfluorooctane sulfonate) of between 10 and 30 tons in the year 2003 (OECD, 2005). That produced amount covered use as mist suppressant in the electroplating industry as well as surfactant in the photographic processing industry. This amount covers, therefore, more than just non-decorative hard chrome plating and will be lower today after the restriction of PFOS has entered into force. Furthermore, as this amount represents a produced amount, the PFOS may be sold and used in other countries, and not only in Germany.

According to the European Commission (2010), the amount of PFOS used for all electroplating processes in Germany is 1883 kg annually. There is no information on which year data is from. If the information is from 2008 or earlier, the amount also covers other allowed uses within the electroplating industry. The European Commission states that the amount of PFOS covers all electroplating processes in Germany. The amount used for non-decorative hard chrome plating only will be somewhat smaller.

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[6] Information from IVL, September 2010.

2.2.4 Belgium

According to the European Commission (2010), the amount of PFOS used as mist suppressant and wetting agent is 218 kg annually. There is no information on which year data is from. The amount used for non-decorative hard chrome plating only will be somewhat smaller.

2.2.5 Czech Republic

According to the European Commission (2010), the amount of PFOS used as mist suppressant for hard chrome plating was 278 kg in 2007 and 165 kg in 2008 where the ban of PFOS entered into force. Only 23 kg is expected to be used as both mist suppressant in hard chrome plating and wetting agents in the electroplating process in 2009. The amount used for non-decorative hard chrome plating only will be somewhat smaller.

2.2.6 Italy

The OECD (2005) survey about the production and use of PFOS related substances stated that in the year 2003 Italy had a manufacture/import of less than 2000 kg PFOS as acid mist suppressant. This amount probably covers more than just non-decorative hard chrome plating and will be lower today after the restriction of PFOS has entered into force. Furthermore, this amount could represent a produced amount (the survey just states "manufacture/import"). The PFOS may therefore be sold and used in other countries and not only in Italy.

However, according to the European Commission (2010), the amount of PFOS used as mist suppressant for hard chrome plating in Italy is zero. In this document it is stated that PFOS is "not used in processes subject under the derogation in paragraph 3 (c) of Directive 2006/122/EC", i.e. mist suppressants for non-decorative hard chrome plating (chromium-(VI)) and wetting agents for use in controlled electroplating systems.

2.2.7 Romania

In April 2008, the Ministry of Environment and Sustainable Development in Romania has informed the Secretariat of the Stockholm Convention that Romania neither produces nor uses PFOS (SSC, 2008). This is also reported in the document from the European Commission (2010). In this document, it is stated that PFOS is "not used in processes subject under the derogation in paragraph 3 (c) of Directive 2006/122/EC", i.e. mist suppressants for non-decorative hard chrome plating (chromium-(VI)) and wetting agents for use in controlled electroplating systems.

2.2.8 Slovenia

According to European Commission (2010), Slovenia used 65 kg PFOS as a wetting agent for chrome (VI) plating in 2008. The amount used in 2007 was about the same (about 54 kg).

2.2.9 UK

The OECD (2005) survey about the production and use of PFOS, PFAS, PFOA, and related substances, stated that the UK manufactured/imported less than 500 kg PFOS (tetraethylammonium salt) for metal chrome plating in the year 2003. According to RPA & BRE (2004), the majority of the 500 kg is used in chrome plating. They estimated that about 470 kg is used within chrome plating, but stated that the amount could be as high as 2,500 kg (based on estimation that UK represents 20% of the total EU consumption). This amount of course covered more than just non-decorative hard chrome plating and will be lower today after the restriction of PFOS has entered into force.

According to the European Commission (2010), the amount of PFOS sold in the UK was 380 kg in 2008. After July 2008, where the restriction of PFOS entered into force, 150 kg were used and only as mist suppressant. It is stated that only 80-90% of this amount, i.e. 120 to 135 kg, is used during electroplating work. This amount is used as the amount for the UK, as it is more up-to-date.

2.2.10 France

According to a Draft Guidance document on Alternatives to PFOS and its derivatives prepared for the Stockholm Convention on Persistent Organic Pollutants, the use of PFOS in France for chrome plating is 200 kg. There is no information on when the data is from (SC UNEP POPRC Draft, 2010).

According to the European Commission (2010), the amount of PFOS purchased for use in chrome (VI) electroplating processes was 695 kg in 2008. It is stated that the amount of PFOS was stocked, but no use occurred in 2008.

2.2.11 The Netherlands

According to a Draft Guidance document on Alternatives to PFOS and its derivatives prepared for the Stockholm Convention on Persistent Organic Pollutants, the use of PFOS in the Netherlands for chrome plating is less than 150 kg. There is no information on which year data is from (SC UNEP POPRC Draft, 2010).

According to the European Commission (2010), the amount of PFOS - actually the compound TEA-PFOS (Tetraethyl ammonium perfluorooctyl sulfonate) used for metal plating surface treatment - is between 65 and 390 kg annually. There is no information on when the data is from. The amount used for non-decorative hard chrome plating only is of course smaller. Therefore, the above amount below 150 kg is assumed to be more correct.

2.2.12 EU

The OECD (2005) survey about the production and use of PFOS related substances stated that use as mist suppressant for chrome plating is one of the essential uses of PFOS. It is estimated that the total use of PFOS related chemicals within the metal plating industry was 10,000 kg in 2003. This amount covered the entire metal plating industry and not only non-decorative hard chrome plating. Furthermore, this amount was much higher than today, because of the restriction of the use of PFOS in 2008.

This estimated amount of 10,000 kg PFOS is probably based on the report by Defra (RPA & BRE, 2004) which stated that a company in Germany has estimated the use of PFOS-related substances in the metal plating industry in the EU was between 8,600 and 10,000 kg.

According to the European Commission (2010), the following countries have reported that PFOS is "not used in processes subject under the derogation in paragraph 3 (c) of Directive 2006/122/EC", i.e. mist suppressants for non-decorative hard chrome plating (chromium-(VI)) and wetting agents for use in controlled electroplating systems: Bulgaria, Denmark (however, this is not true according to the discoveries in this project), Estonia, Greece, Spain, Ireland, Italy, Cyprus, Latvia, Lithuania, Luxembourg, Hungary, Malta, Austria, Poland, Portugal, Romania, and Slovakia.

This means that the total use in the EU today is estimated to be around 2,684 to 3,194 kg and probably larger, if some of the countries above have not registered a use of PFOS, although PFOS still are used (as is the case of Denmark). The sum of 2,684 to 3,194 kg is found by adding the amounts (or ranges) reported by Germany, Belgium, Czech Republic, the UK, France, and the Netherlands together with the amounts of PFOS sold to Nordic countries (reported by suppliers in this project).

However, it is clear that the use of PFOS has declined drastically because of the restriction of the use of PFOS in 2008. The estimated use of 10,000 kg PFOS in 2003 is therefore drastically reduced. However, this amount of 10,000 kg also covered the entire metal plating industry and not only non-decorative hard chrome plating.

Europe

The amount listed above covers the EU countries. The amount of PFOS used in Europe is larger. Switzerland (below) is the only non-EU European country where information of the use of PFOS has been found.

2.2.13 Switzerland

According to the OECD (2005) survey, the use of PFOS for metal plating in the year 2000 was estimated to be 190 kg.

A substance flow analysis of PFOS and PFOA in Switzerland has been performed. According to that survey, the use of PFOS for metal plating (mist suppressant and surfactant) was estimated to be about 300 kg of PFOS annually (but within the range of 200-500 kg annually) for the year 2007 (FOEN, 2009).

2.2.14 Canada

Canada performed in 2005 a use pattern survey of PFOS (CEPA, 2006). Companies were required to report if they were involved in manufacture, export, or import of PFOS in amounts exceeding 100 kg in concentrations of greater than 10 grams per kilogram for the 2004 calendar year. The survey showed that the import of PFOS related compounds have essentially ceased since 2002 and showed that there are no manufactures or exporters of PFOS in Canada. Only one substance was imported into Canada representing a quantity of approximately 3 tons of PFOS. The imported substance was sold as a product that is used as a surfactant in the electroplating sector. The survey stated that the potential does exist for PFOS and PFOS containing products and articles to be imported into Canada in greater quantities in the future as some PFOS production has been identified in other countries.

In Carloni (2009), it is stated that this import of 3 tons PFOS mostly is used for metal plating. Furthermore, it is stated that there are approximately 219 users of this PFOS in the sector, resulting in an average annual use of PFOS per user of about 14 kg. This is in line with the annual use of Danish chrome platers.

2.2.15 USA

The US EPA's Toxic Substances Control Act established in 2000, 2002, and 2007, SNURs (Significant New Use Rules) for the use of PFOS and PFAS in the USA. In 2000 13 PFOS and PFAS related chemicals were covered by the SNUR and in 2002 additional 75 PFAS related chemicals. The SNURs require prior notice before any new manufacture or import of these PFAS chemicals. Some uses are exempted from the rule. In 2007 the last SNUR was published. Additional 183 PFAS substances were added and the exemption of allowing one specific PFOS related chemical compound for use in metal plating was added as well. The PFOS chemical allowed for metal plating in the USA is tetraethyl ammonium perfluorooctane sulfonate with the CAS no. 56773-42-3 (US EPA, 2010; Carloni, 2009).

According to Carloni (2009), this regulation of PFOS and PFOS related substances has resulted in a large decrease in the amounts of these substances being used in the USA – from approximately 2.9 million kg in the year 2000 to less than 7,983 kg in the year 2006. This amount is for all uses – the amount used for chrome plating is of course smaller.

In this project, a few US suppliers of mist suppressants for chrome plating were contacted. One supplier replied that they only sell PFOS free mist suppressants for chrome plating. There is no information on the amount sold.

2.2.16 China

China is the solely producer of PFOS after 3M stopped production in 2002. About 200 tons of PFOS is now produced annually in 15 factories in China. The production has a value of several million $.[7]

In April 2008, The Ministry of Environmental Protection of China (MEP) has sent information to the Secretariat of the Stockholm Convention about the use of PFOS for metal plating in China. According to this information, China has not compiled a complete list of sectors that use PFOS, but has made an initial estimation based on an investigation. MEP (2008) reports that annually about 25 tons of PFOS-containing mist suppressants are used in the chrome plating industry in China. The PFOS containing mist suppressants used in China are FC-80 (CAS no. 2795-39-3 – PFOS potassium salt) and FC-248 (CAS no. 56773-42-3 – PFOS tetraethylammonium salt).[8]

2.2.17 Japan

For the Draft Risk Management Evaluation performed by the Stockholm Convention on Persistent Organic Pollutants, it is stated that there are about

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[7] Mei Shengfang. China Association of Fluorine and silicone industry. Presentation at the International Workshop on new POPs, Beijing, 1-2 July, 2010.

[8] Jun HUANG, Tsinghua University. Presentation at the International Workshop on new POPs, Beijing, 1-2 July, 2010.

1000 metal plating companies in Japan that use PFOS. Information from Japan in 2007 stated that only about 50 of these companies have changed their process to Chromium-(III) instead of Chromium-(VI). This means that 950 companies in Japan used PFOS in their metal plating processes in 2007 (SC UNEP/POPS/POPRC.3/13, 2007). Since then more companies could have changed to the Chromium-(III) process, where PFOS is not necessary, instead of the Chromium-(VI) process.

According to Carloni (2009), Japan has in 2007 reported to the POPs Review Committee (POPRC) of the Stockholm Convention that the total amount of PFOS estimated for use in metal plating in Japan is 2-3 tons annually.

A 2009 survey showed that the Japanese use of PFOS for metal plating has ceased. Today, in Japan, only three essential applications are left for PFOS – and chrome plating is not one of them. PFOS is no longer allowed to be used for chrome plating in Japan.[9] Instead the compound Fumetrol® 21 is used as alternative.[10]

2.2.18 Australia

According to the Australian Government (NICNAS Alert No. 8, 2008), the use of PFOS imported into Australia was 760 kg and 1,350 kg in the years 2006 and 2007 respectively. No PFOS chemicals are produced in Australia. This data was achieved by a national survey performed in May, 2008. According to this survey, 99% of this PFOS amount was used as mist suppressants in metal plating. The current stocks of PFOS were 7.8 tons, where only 3% of this amount was PFOS stocks for metal plating – the PFOS stocks was mostly held by the fire fighting industry (97%).

A similar survey was carried out in 2006 (NICNAS Alert No. 5, 2007). Here the stocks of PFOS in the end of 2005 were reported to be 9.36 tons PFOS. There is no report of how much of that PFOS amount is for metal plating. In 2004 and 2005 no import of PFOS was reported. It is, however, stated that it is likely that importers and users may not know if products contain PFOS as the ingredient may not be listed on the Material Safety Data Sheet.

The difference in the stocks between 2007 and 2005 is assumed to have been used (9.36 -7.8 tons = 1.56 tons). As mentioned above only 3% of the stocks in 2007 was for metal plating purposes. If it is assumed that only 3% of the stocks of PFOS in Australia is PFOS for mist suppressants for metal plating for both the year 2005 and 2007, then there has been an extra use of PFOS in the years 2005 and 2007 of 47 kg (3% of 9.36 – 7.8 tons), which is an average of 23.5 kg per year. To this amount should be added the average of the total imported amounts in 2006 and 2007 of 2.1 tons (99% of 0.76 + 1.35 tons). Using this information results in an average of about 1070 kg PFOS per year in the period of 2006 to 2007 used as mist suppressants in metal plating in Australia.

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[9] Takashi Fukushima, the Japanese Ministry of Economy, Trade and Industry. Presentation at the International Workshop on new POPs, Beijing, 1-2 July, 2010.

[10] Personal information from Takashi Fukushima, Director for Chemical Management Policy from MEKI, the Japanese Ministry of Economy, Trade and Industry, July 2010.

2.2.19 Latin America

According to Carloni (2009), there is limited information about the use of PFOS for chrome plating in Latin America. Brazil has provided information about the use of PFOS to the POPs Review Committee (POPRC) of the Stockholm Convention. PFOS and PFOS related substances in Brazil are mostly used in pesticides.

2.2.20 Africa

Three African countries have submitted information about the use of PFOS to the POPs Review Committee (POPRC) of the Stockholm Convention (Carloni, 2009). No amounts were reported only that:

- Algeria has metal plating as one of five main use areas for the use of PFOS.
- Congo has not identified or registered any PFOS or PFOS related substances.
- Zambia has listed metal plating as one of six areas of use for PFOS and PFOS related substances.

3 Survey of possible alternatives to PFOS for chrome plating

In this chapter the possible alternatives to PFOS as mist suppressant for hard chrome plating are described. Both chemical alternatives and possible physical alternatives are described.

The chemical alternatives described are identified primarily by contact to suppliers of mist suppressants for the chrome plating industry but also information from professional and international organisations was included.

3.1 Chemical alternatives

The chemical alternatives to PFOS and derivatives as mist suppressant for hard chrome plating are either fluorinated or non-fluorinated.

3.1.1 Information from organisations and institutions

The opinion of the German Central Association of Surface Treatment Professionals e.V. (ZVO) is convinced that there still is a need for PFOS for hard chrome plating, but the industrial sector will continue to reduce the use of PFOS and replace it by alternatives where possible (ZVO, 2008). ZVO emphasise that the use of fluorine-free products requires higher technical efforts compared to the use of PFOS and that there is no long-term experience. ZVO has reported the availability of PFOS-free alternative products from 10 German supplier companies.[11] Information is lacking about the exact chemical compounds. Three of the products were fluorinated chemicals and seven were fluorine-free chemicals. The non-fluorinated alternatives were not stable enough in the hard chrome bath. It is stated that all 10 alternative products could be used for decorative chrome plating, for which alternative Chromium-(III) processes already exist. Alternative surfactants for this process are presently studied at the University of Wuppertal, Germany.[12]

The Norwegian Galvano Industry Organisation (NGLF) has reported that their suppliers no longer provide PFOS wetting/anti-mist agent for chrome plating. They provide PFOS-free tensides instead. However, NGLF considers the performance of those alternatives to be insufficient and is currently developing better alternatives to PFOS and alternative technology to solve the problem with airborne loss of chromium-(VI) from the baths. But NGLF reports that the industry has started to phase out the use of PFOS containing wetting/mist agent, by using the Chromium-(III) process instead of the Chromium-(VI) process, where possible, even though the substituting cost is estimated by industry to be approximately 100,000 NOK (~15-16,000 US $) per bath (Information from SFT, 2009).

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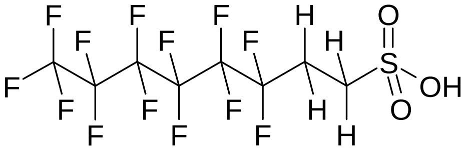
[11] Personal information from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), D-40724 Hilden; March 6, 2009.

[12] Personal information from Jutta Hildenbrand, Uni-Wuppertal, October 15, 2009.

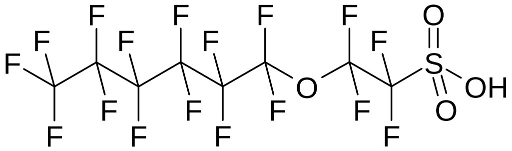
Larger closed tanks or increased ventilation combined with extraction of Chromium-(VI) from filters have been suggested as alternative solutions for the applications where a use of Chromium-(III) is not yet possible. However, increased ventilation will result in increased energy consumption and therefore CO_2-emission and loss of chromium from the bath. Therefore, increased ventilation is not considered to be working in practice.

The 2006 OECD survey has identified use of perfluorobutane sulfonate (C_4 PFAS) as an alternative mist suppressant (OECD, 2006). However, according to a Chinese producer of PFOS chemicals, C_4 fluorochemicals cannot be used as mist suppressants for non-decorative hard chrome plating.

In China the PFOS available alternatives used for chrome plating are F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate), F-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) and Fumetrol® 21(1***H***,1***H***, 2***H***,2***H***-perfluorooctane sulfonic acid).[13] In addition they use physical measures, e.g. ventilation, close tank, and physical covers (net, balls).



1***H***,1***H***, 2***H***,2***H***-perfluorooctane sulfonic acid (Fumetrol® 21)



F-53 basic skeleton
(in F-53B one of the fluorine atoms is replaced with chlorine)

In Japan, where PFOS is not considered essential for chrome plating any more, Fumetrol® 21 is also used as an alternative.[14]

3.1.2 Contact to producers and suppliers/Internet search

In order to find out which chemical alternatives that exist to PFOS as mist suppressant for non-decorative hard chrome plating, the four companies in Denmark carrying out non-decorative hard chrome plating and their suppliers of mist suppressant were contacted.

The suppliers were asked to present alternatives to PFOS as mist suppressant, if any. The following suppliers of mist suppressants for the Danish and international markets were contacted:

- Atotech Skandinavien AB (Sweden)
- EngTech Scandinavia A/S (Denmark)

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[13] Jun HUANG, Tsinghua University. Presentation at the International Workshop on new POPs, Beijing, 1-2 July, 2010.

[14] Personal information from Takashi Fukushima, Director for Chemical Management Policy from MEKI, the Japanese Ministry of Economy, Trade and Industry, July 2010.

- MacDermid (USA)
- Surtec Scandinavia ApS (Denmark)
- GalvanoKemi (Denmark)
- Enthone (Cookson Electronics) (Sweden)
- Kiesow Dr. Brinkmann GmbH (Germany)
- Dr. Günter Dobberschütz (Germany)
- CL Technology GmbH (Germany)
- TIB Chemicals (Germany) – a producer of chemicals (does not sell directly to chromium platers, but to some of the companies mentioned on this list)
- Schlötter (Germany)
- Plating Resources, Inc. (USA)
- Uyemura International (USA)
- Growel Grauer & Weil India Ltd. (India)
- Chembright (China)

Suppliers of mist suppressants on the international market were found by searching on the Internet with different search words and different combinations of search words (in both German and English) like:

- “mist suppressant” /”fume suppressant”
- “hard chrome plating”/”hard chromium plating”
- “PFOS free”
- “PFOS-freies” / ”PFOS-frei” / “ohne PFOS”
- “Netzmittel für Chrombäder” /”tenside chrombad”

The following non-PFOS chemical alternatives were found (see Table 3-1).

Table 3-1 Non-PFOS alternatives identified

Product name	Company	Substance	Fluori-nated	Fluor-free
Fumetrol 21	Atotech	Based on CAS 27619-97-2 1*H*,1*H*,2*H*,2*H*-perfluorooctanesulfonic acid	X	
Wetting agent CR	Atotech	Based on CAS 27619-97-2 1*H*,1*H*,2*H*,2*H*-perfluorooctanesulfonic acid	X	
MiniMist Liquid/ ChromKlad Wetter	MacDermid	Based on CAS 27619-97-2 1*H*,1*H*,2*H*,2*H*-perfluorooctanesulfonic acid	X	
SurTec 850 S	SurTec Scandinavia	No information about the alternative product other than it is PFOS free	?	
SurTec 850 SK4 (quadruple concentration of the SurTec 850 S above)	SurTec Scandinavia	No information about the alternative product other than it is PFOS free and **free of fluorine**. Can be used in all Cr-(VI) based processes – including hard chrome.		X
Netzmittel Dün 20	GalvanoKemi	No information about the alternative product other than it is non-PFOS, but contains fluor	X	
Wetting agent SLOTOCHROM SV 31	Schloetter.com	No information about the alternative product other than it is **free of fluorine**. It is stated that wetting agent must be added every day in order to work properly. Schlöetter informs that it cannot be used for hard chrome plating – only decorative chrome plating		X
CL-Chromprotector BA	CL-Technology.de	No information about the alternative product other than it is completely PFT (perfluorinated organic tenside) free. Contains 0.2 % ethanol. Other hazardous ingredients are not listed.	?	
Non Mist-L	Uyemura.com	Non PFOS based	?	
Cancel ST-45	Plating Resources, Inc. (plating.com)	Non PFOS based – no more information available	?	
FS-600 High foam	Plating Resources, Inc. (plating.com)	Non PFOS based, but is fluoropolymer based – no more information available	X	
FS-750 Low foam	Plating Resources, Inc. (plating.com)	Non PFOS based, but is fluoropolymer based – no more information available	X	

Product name	Company	Substance	Fluori-nated	Fluor-free
Ankor Wetting Agent FF	Enthone Inc. (a Cookson Electronics Company)	**Free of fluorine**. Contains (Z)-Octadec-9-enylamine, ethoxylated. It is stated that the product must be added continuously in order to maintain the proper levels and performance. However, it can only be used for bright chromium, not for hard chrome plating.		X
TIB Suract CRH	TIB Chemicals	The alternative has a soap-based structure and is **free of fluorine**. This product is sold to some of the companies listed in this table under different names – but which is confidential. Must be added continuously in drips (100 ml/hour) with circulation in order to work properly.		X
PROQUEL OF	Kiesow Dr. Brinkmann	Contains no PFOS. Contains an aqueous surfactant solution with an anionic surfactant. It is based on a fluorinated surfactant. No further specific information about the chemical content. Can be used for non-decorative hard chrome plating.	X	
F-53 Chromic Fog Inhibitor	Hangzhou Dayangchem Co. Ltd.	Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate	X	
F-53B Chromic Fog Inhibitor	Hangzhou Dayangchem Co. Ltd.	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 sulfonate)	X	

Most of the alternatives identified are non-PFOS based alternatives, but are still fluorinated. Some alternatives are based on CAS 27619-97-2 also called 1***H***,1***H***,2***H***,2***H***-perfluorooctanesulfonic acid (or 6-2 FTS (fluorotelomer sulfonate)). This compound has the following structure (see Figure 3-1) compared to PFOS that is fully fluorinated (see Figure 3-2).

Figure 3-1 Alternative to PFOS as mist suppressant - 1*H*,1*H*,2*H*,2*H*-perfluorooctanesulfonic acid (CAS 27619-97-2)

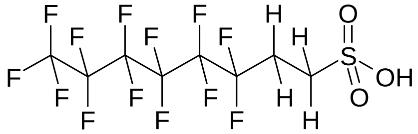
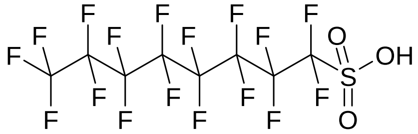


Figure 3-2 PFOS mist suppressant - Heptadecafluorooctanesulfonic acid (CAS 1763-23-1)



Talking to the different companies has shown that the non-PFOS based but fluorinated alternatives do work and some companies have used these alternatives for a long period. The alternatives identified are:

- Fumetrol® 21 from Atotech, which is based on 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (CAS No. 27619-97-2).
- Wetting Agent CR, Atotech, which is based on the same substance as above (CAS No. 27619-97-2).
- MiniMist Liquid, MacDermid, which is based on the same substances as above (CAS No. 27619-97-2).
- SurTec 850 S, SurTec Scandinavia. There is no information about the substance other than it is PFOS-free.
- Netzmittel Dün 20, GalvanoKemi. There is no information about the substance other than it is PFOS-free. It is likely that it is based on the same substance as mentioned above.

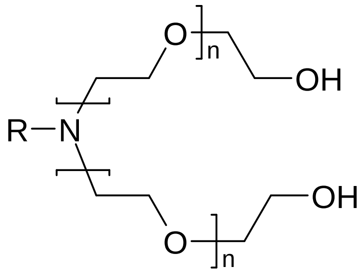
- PROQUEL OF, Kiesow Dr. Brinkmann. There is no information about the substance other than it is PFOS-free and based on a fluorinated surfactant. It is likely that it is based on the same substance as mentioned above.
- Non Mist-L, Uyemura.com. There is no information about the substance other than it is not based on PFOS.
- FS-600 High Foam, Plating Resources, Inc. There is no information about the substance other than it is PFOS free, but it is fluoropolymer based.
- FS-750 Low Foam, Plating Resources, Inc. There is no information about the substance other than it is PFOS free, but it is fluoropolymer based.
- F-53 and F-53B, Hangzhou Dayangchem Co, Ltd. These alternatives have been presented at an International workshop on new POPs in Beijing, 1-2 July, 2010. They are based on the structure CF_3-$(CF_2)_5$-O-$(CF_2)_2$-SO_3K as also presented in section 3.1.1.

However, for this project, it is also interesting to investigate alternatives that are non-PFOS and non-fluorinated. The following alternatives without fluorine have been identified:

- SurTec 850 SK4, SurTec Scandinavia. There is no information about the chemical substance, as this is confidential. It can be used for hard chrome plating. This substance should be a quadruple concentration of the SurTec 850 S. SurTec 850 S is, however, only stated to be PFOS free according to the technical datasheet.
- Wetting agent SLOTOCHROM SV 31, Schloetter (but no information about the chemical substance, as this is confidential). However, this alternative cannot be used for hard chrome plating.
- Ankor Wetting Agent FF, Enthone (based on CAS 26635-93-8) – however, it can only be used for bright chromium, not for hard chrome plating.
- TIB Suract CR-H, TIB Chemicals (but no information about the chemical substance as this is confidential). It can be used for hard chrome plating.

The Ankor Wetting Agent FF® from Enthone (CAS 26635-93-8) is ethoxylated oleyl amine ($R-N(CH_2CH_2O)H_m(CH_2CH_2O)H_n$); see the structure below). However, it can only be used for bright chromium, not for hard chrome plating.

Figure 3-3 Alternative to PFOS as mist suppressant – ethoxylated oleyl amine[15]



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[15] Structure found at http://chemicalland21.com/specialtychem/perchem/ETHOXYLATED%20OLEYL%20AMINE.htm

3.2 Physical alternatives (IPU)

Physical alternatives could be attractive solutions compared to chemical alternatives as most chemical alternatives are fluorine based or potentially harmful to the electrolyte or unstable in the electrolyte. A physical alternative could possibly prevent chromium emission by three mechanisms:

1. Avoid formation of aerosol
2. Promote condensation of aerosol close to the electrolyte surface
3. Avoid transportation of aerosol from the surface of the electrolyte

The three mechanisms are discussed in more details below.

Avoid formation of aerosol
As the aerosols are developed when the developed hydrogen bobbles break and as hydrogen development is an unavoidable part of the chromium process no practical usable physical method for avoiding formation of aerosol is identified, only chemical alternative as described in 3.1.

Promote condensation of aerosol close to the electrolyte surface
A strategy for promotion of condensation of aerosol close to the electrolyte surface could be the use of highly hydrophobic surfaces in order to promote droplets from the electrolyte to form and fall back to the solution. Among hydrophobic surfaces, PTFE (coated) balls or mesh, are considered as the most suitable solutions because of highly hydrophilic properties combined with the chemical resistance towards the chromium electrolyte.

In contrast to a dense cover, an “open” ball or mesh solution will enable developed hydrogen to penetrate through the cover. Such an “open” solution is expected to be found as a useful alternative if the open cover simultaneously will enable hydrogen penetration and promote condensation of aerosol close to the surface. Furthermore, it can be expected that the low surface tension of the PTFE will assist condensation of the aerosol.

A mesh solution could be suitable for large scale series plating of uniform products whereas the ball solution will be more suitable for small scale plating for products of varying sizes.

Avoid transportation of aerosol from the surface of the electrolyte
At the initial stage of the present project, no physical alternative for avoiding transportation of aerosol from the surface of the electrolyte was identified. However, as discussed in chapter 5 when presenting the test results, no ventilation can apparently lower the chromium emission significantly.

Development of process lines with a cover that prevents ventilation can be possible for large scale series plating of uniform products, whereas such process solutions are considered by plating shops to be more difficult to implement in small scale plating processes for products of varying sizes; such implementations would require a significant redesign of the production line.

The very significant reduction of Cr^{6+} emission in the laboratory experiments when no ventilation was applied (as presented in chapter 5) inspires for further evaluations on possible physical alternatives for avoiding transportation of aerosol from the surface, which could be used in plating systems for frequently varying productions.

4 Assessment of the feasibility of the alternatives

The alternatives identified for use as mist suppressants for non-decorative hard chrome plating are very limited – at least when it comes to information about the chemical substances used in the mist suppressant products.

In the following sections the economic, technical, and environmental aspects of the alternatives are described in order to choose the alternatives to be investigated further in the last part of the project.

4.1 Economic assessment

An economic assessment of the non-PFOS alternatives depends on:

- The price of the chemicals and or physical alternatives
- The amount needed during use
- The expenses during substitution
- Expenses to possible continuous addition of chemicals
- Expenses related to possible break down of a continuous addition system, due to problems related to non-sufficient or excess additions of chemicals.

The price of the chemicals

Different suppliers of PFOS and non-PFOS alternatives were contacted in order to learn more about the price of the chemicals. However, we only received information about the price for a few of the chemicals and mostly for the PFOS products.

The information received from the suppliers suggests that the price of the PFOS products used as mist suppressant for non-decorative hard chrome plating is around 100 to 200 DKK (13 EUR to 27 EUR) per kilo/liter. The price is dependant on the concentration of PFOS in the chemical. The cheaper products contain about 2-3 % PFOS whereas the more expensive products contains 3-7 % PFOS.

In comparison one of the alternatives was found to cost 120 DKK (16 EUR) per kilo/liter. The price is not fully comparable as no information was received on the amounts to be used compared to a PFOS product. However, the supplier informed that the product was cheaper than using PFOS. Other information about the price of the non-PFOS alternatives was sparse. One supplier informed that their non-PFOS alternative is more expensive than PFOS (but not how much more expensive).

In conclusion, the economic assessment of the non-PFOS alternatives based on the price alone is inconclusive. Some alternatives may be cheaper and some may be more expensive.

The amount needed during use

As mentioned above the total price of the alternative mist suppressant compared to using PFOS based mist suppressant of course depends on how much mist suppressant that has to be used during use. However, we have not received any information regarding this issue, other than some suppliers stated that their alternative was cheaper to use compared to PFOS and other stated that their alternative was more expensive to use compared to PFOS.

The expenses during substitution

In cases where a plater will shift from a PFOS-containing plating system to a plating system with an alternative to PFOS, it will normally not be necessary to exchange the electrolyte. Normally, it will be sufficient to stop addition of PFOS and start the use of the alternative when addition of mist suppressant is needed. In this case the only additional expense is the possible higher price/consumption of the PFOS alternative.

Expenses to possible continuous addition of chemicals

This will depend on the amount of chemical additions required to maintain a stable electrolyte. Often chromium depositions run continuously over night. If this will require additions of chemicals during nighttimes supervision of the system is required, due to the potential risk of breakdown of an addition system. If an addition system stops unexpected the consequences could be a large emission of chromium aerosol (see results in chapter 4) resulting in large economic and environmental problems. If an addition system unexpected overdoses an additive the consequences could be overfloating of the chromium electrolyte, resulting in large economic and environmental problems.

Estimated costs of the use of an automatic addition system together with supervision over night time are expected to be 1,000 DKK per day (134 EUR) for supervision including log registration. An automatic addition system could result in expenses of approximately 350,000 DKK per year (47,000 EUR) plus expenses of establishment of the supervision equipment (estimation from a.h. nichro Haardchrom/Surfcoat).

Expenses to possible break down of a continuous addition system

This depends on the time interval from the break down until the breakdown is identified and the process stopped, which further depends on whether human supervision is used during night time. If no supervision is used out of normal working hours, the expenses can be very severe for the plater, depending on how much of the building, installations, and equipment being contaminated.

4.2 Usability – technical

Chemical alternatives which require no continuous addition and can be expected to be stable in the electrolyte will be technically easy to implement in a production. Such solutions exist among the fluorinated alternatives (e.g. Fumetrol® 21).

Non-fluorinated chemical alternatives might contain amine (e.g. Ankor Wetting Agent from Enthone). Amine might decompose into nitrate which is harmful for the chromium electrolyte, resulting in low quality depositions.

Among the physical alternatives hollow PTFE (coated) balls or mesh are considered as the most usable solution from a technical point of view as discussed in section 3.2. From a practical point of view a mesh solution will be very difficult to work with in case of plating complex geometries and varying geometries. Hollow PTFE coated balls will be very flexible to work with as they will float at the surface of the electrolyte and will cover the electrolyte surface in a very flexible way. Massive PTFE balls will sink because of the high density compared to the chrome electrolyte. Several suppliers of massive PTFE balls exist. However, apparently hollow PTFE balls are not available on the market as a standard product. The effect of PTFE close to the electrolyte surface could be tested by using massive balls, kept close to the surface by a titanium mesh. A potentially successful result could possibly motivate future manufacturing of hollow PTFE (coated) balls.

4.3 Comparative environmental and health assessment

The information about chemical alternatives to PFOS as mist suppressant for hard chrome plating is very limited.

One substance (1***H***,1***H***,2***H***,2***H***-perfluorooctanesulfonic acid (CAS No. 27619-97-2; C_6-fluorotelomer chemistry)) has positively been identified in three different alternative products used in more countries. The same substance may be used in other alternative products that are non-PFOS, but fluorine-based. However, we have not been able to confirm this because of confidentiality.

Derivatives of perfluorobutane sulfonates (C_4-perfluoroalkyl-chemistry) have also been suggested and may be in use – even though a Chinese producer of PFOS chemicals have informed that C_4 fluorochemicals cannot be used as mist suppressants for non-decorative hard chrome plating.

In China some perhalogenated alkyl ether sulfonates (F-53 and F-53B) are used as alternatives.

Finally, an alternative from Enthone described as a ***N***-polyethoxylated oleylamine has been identified. It is, however, not likely that this alternative can be used for non-decorative hard chrome plating and it will not be included in the comparison. It is probably rather harmless and at least not persistent.

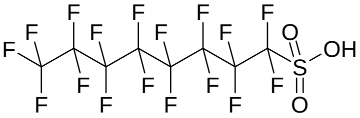
Because the 1***H***,1***H***,2***H***,2***H***-perfluorooctanesulfonic acid (Fumetrol® 21), PFBS, F-53 and F-53B are the only identified chemical alternatives that can be used for hard chrome plating, and where the chemical composition have been identified, their environmental and health aspects will be compared with PFOS.

4.3.1 PFOS

This description of the environmental and health problems of PFOS is mostly based on the comprehensive description carried out in the project Survey of Chemical Substances in Consumer Products No. 99 (Jensen et al., 2008).

4.3.1.1 Chemistry

Perfluorooctane sulfonic acid (PFOS) is the best known perfluorinated compound. PFOS has a linear perfluoroalkyl carbon chain of 8 and a sulfonic acid functional group.



PFOS

The C-F binding in PFOS and other PFCs is very strong. Thus the perfluoro chain is a stable identity which in practice is non-degradable in nature. The sulfonates are polar species which will not accumulate in fatty compartments but mainly in blood and liver, and these substances will often interact with polar sites in sediments. The low biodegradability of PFCs is, together with their tendency to bioaccumulate, characteristics which are typical of persistent organic pollutants (POPs).

4.3.1.2 Environmental fate and levels

PFOS has been detected in all environmental compartments globally. Most studies have, however, been performed on the North American continent, in Europe, and in Japan.

PFOS and its salts are very stable and are not biodegradable in nature but will persist in the environment. Only under extreme laboratory conditions with addition of potent chemicals, high-energy radiation, and high temperatures some degradation may occur with formation of degradation products.

A prevailing hypothesis on the origin of non-volatile perfluorinated compounds such as PFOS in remote places is that volatile precursors undergo long-range air transportation and hereby reach remote areas.

The contamination of surface water by PFOS may pose an important intake source for the consumer if the surface water is used for production of drinking water. Particularly contaminated surface waters (e.g. some rivers in central Europe) significantly contribute to discharge of PFOS in seas and oceans.

Several studies have been published dealing with concentrations and fate of PFCs in municipal waste water treatment plants (WWTPs), as these systems have been identified as important sources for PFOS to the aquatic and terrestrial environments. PFOS was not degradable in WWTPs, and PFOS has been found in waste water and sewage sludge from WWTPs.

High PFC concentrations in wildlife have been reported for a wide range of animals globally, including in the Arctic and the Antarctic. Especially PFOS has been more or less found in all samples with concentrations varying from sub-ng/g levels to several µg/g, with birds living close to a fluorochemical plant as the worst case. The bioaccumulation potential of PFOS has been confirmed by several bioaccumulation studies in different food webs.

Temporal trend studies have been performed on archived biologic materials, in general covering time spans from the 1970s-1980s to the present. The PFCs concentrations, especially those of PFOS, have been found to gradually increase up to the present years. In a study from the Canadian Arctic, a decrease in PFOS concentration has been observed after 2000 which was explained as a rapid response after the stop of PFOS production in the USA. However, such a decline has not been found in Greenland.

4.3.1.3 Ecotoxicity

The toxicity of PFOS has been studied in different aquatic organisms (algae, invertebrates, and fishes). Generally, PFOS is not toxic at the typical concentrations determined in the aquatic environment. However, adverse effects have been observed for specific cellular functions, such as mechanisms involving the uptake of xenobiotics. Other biological endpoints affected by PFOS are survival, growth, and emergence.

A recent study of life-time exposure to PFOS showed adverse affects on the life-cycle (egg development, hatching, larval development, survival, metmorphosis, and body mass) of the damsefly ***Enallagma cyathigerum*** (Bots et al., 2010)**.**

Generally, the toxicity of PFOS is species dependent and sometimes gender-dependent for the same species. It is therefore difficult to perform risk assessment for these compounds on the basis of the few published studies.

4.3.1.4 Human exposure and levels

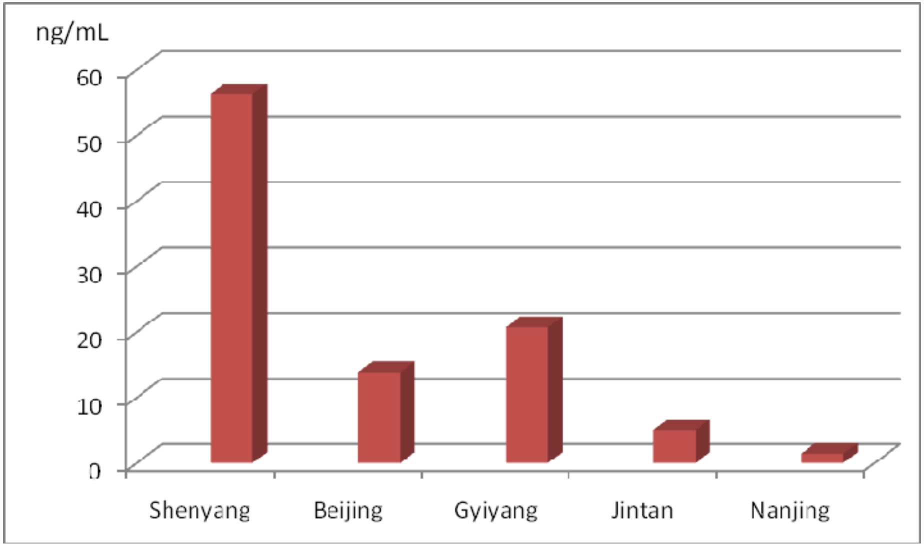
The main exposures to perfluorinated substances seem to be by direct consumer product exposure, through contaminated food intake, or by inhalation/ingestion of indoor dusts.

In contrary to most other persistent organic pollutants (POPs), PFOS has a low affinity to lipids in adipose tissues but binds to proteins in cell membranes and accumulates in various body organs of exposed organisms, including in liver, kidneys, testes, and brain.

In the blood perfluorinated chemicals are mainly bound to serum proteins, especially albumin. The mean half-lives in human blood were 5.4 years for PFOS in retired fluorochemical workers but the whole body half-life may be even longer since the elimination of these chemicals from the human body seems to be insignificant.

Blood levels of perfluorinated chemicals have been monitored in many countries. In most studies PFOS has been determined in far higher concentrations than other PFCs. Typical average serum levels of PFOS in industrialized countries are 20-30 ng/mL with maximum levels less than 100 ng/mL. Some of the highest PFOS blood levels (2-3 times the typical levels) in the general population were determined in industrial areas of the USA and China (see Figure 4-1), (Yeung et al., 2008). Such levels may be 10 times higher than in rural and remote areas.

Figure 4-1 PFOS in whole blood from China (Yeung et al. 2008).



The average PFOS level in blood serum from Denmark was 35 ng PFOS/mL with a maximum concentration of 107 ng/mL (Joensen et al. 2009).

4.3.1.5 Toxicology

The liver is the primary target organ for PFCs. PFOS causes peroxisome proliferation in the rodent liver as well as induction of various enzymes involved in lipid and steroid metabolism. Levels of serum cholesterol, thyroid hormones, and testosterone are reduced, and levels of estradiol are increased.

PFOS can rapidly and reversibly inhibit gap junction intercellular communication in a dose-dependent manner. Gap junction intercellular communication (GJIC) is the major pathway of intracellular signal transduction, and it is thus important for normal cell growth and function. Defects in this communication may lead to teratogenesis, neuropathy, infertility, diabetes, autoimmune disorders, cancer, and other diseases.

Some recent studies have compared the level of PFCs in human blood with the occurrence of various adverse effects or diseases.

- One study is based on data collected in the period 1999-2006 from about 4,000 Americans. The results show a correlation between the amount of PFOS and PFOA in the blood and the occurrence of thyroid related diseases (Melzer et al., 2010).
- Another study showed a positive association between serum concentrations of PFOS (and PFOA) and cholesterol level (Nelson et al., 2010).
- A further study has shown a direct correlation between serum concentrations of PFCs and the diagnosis ADHD (attention deficit hyperactivity disorder) at children (Hoffmann et al., 2010).
- Another study showed a correlation between the amount of PFOS in human blood and the time it takes for women to get pregnant (Fei et al., 2009).
- A study showed a correlation between the amount of PFOS in human blood and a reduction in men’s semen quality (Joensen et al., 2009).

The last two population studies are based on Danish cohorts and maybe the females difficulties to get pregnant are caused by the lower fertility of the males identified in the last study.

4.3.1.6 Risk assessment

The U.K. Committee on Toxicity (2006) has recommended a provisionally Tolerable Daily Intake (TDI) for PFOS of 0.3 µg/kg bw/d, using an uncertainty factor of 100. They conclude that for some small children the TDI may already be exceeded.

This assessment was based on results from animal experiments, which may be very arbitrary and unreliable, because of the large differences in blood half-lives between rodent (days) and humans (years). The renal clearances of PFOS are almost insignificant in humans, contrary to a large active excretion in experimental animals.

This means that PFOS in humans leave the blood mainly by redistribution to internal organs and not by elimination from the body as in rodents. This may increase the internal exposure time in critical human organs considerable.

4.3.1.7 Conclusion

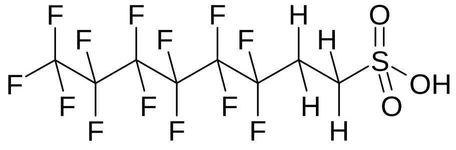
PFOS is found widespread in nature and in animals and humans because it is a very persistent chemical and non-degradable in nature. Furthermore, PFOS and its precursors do have a tendency to bioaccumulate and biomagnify in food chains.

PFOS causes various adverse effects in humans, and for children a very conservative Tolerable Daily Intake of PFOS may already be exceeded.

4.3.2 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (CAS No. 27619-97-2)

The basic structure of 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid is very similar to PFOS. Both contain a fluorinated C_8 alkyl chain, however, the alternative is not perfluorinated but has two non-fluorinated carbon atoms making it a polyfluorinated compound (fluorotelomer). Fluorotelomers are DuPont's alternatives to PFOS.

Figure 4-2 Alternative to PFOS as mist suppressant - 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (CAS 27619-97-2)



As for PFOS the perfluorinated part of 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid is not degradable. However, the non-fluorinated part of the alkyl chain can be degraded. 1***H***,1***H***,2***H***,2***H***-perfluorooctanesulfonic acid is, therefore, expected to be degraded in nature to the further non-degradable perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA) or their salts. The toxicity of PFHxA with a C_6 chain is 100 to 1000 times lower than for PFOA with a C_8-chain (Richard Holt, DuPont, 2010).

Chinese QSAR model results exist for persistence (half-lives) of Fumetrol® 21 in water, sediment, soil, and air, bioconcentration factors and toxicity to fish (BCFs) (see Table 4-1). This data shows that Fumetrol® 21 seems to be less persistent, less bioaccumulative, and less toxic compared to PFOS.

For PFHxA there is an MSDS indicating it as a corrosive and toxic substance with R- phrases R34-37 and S-phrases S26-36/37/39-45.

4.3.3 PFBS

Derivatives of perfluorobutane sulfonic acid are 3M's alternatives to PFOS.

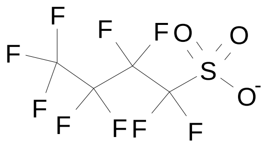


Figure 4-3 Perfluorobutane sulfonate

There is only information about PFBS and its potassium salt from unpublished laboratory test reports. These have been reviewed and evaluated in an Australian assessment (NICNAS).

PFBS is a strongly acidic and highly water soluble substance which has a low vapour pressure and is poorly adsorbed to soils and sediments and is therefore expected to remain in the water compartment on release into the environment.

PFBS is as persistent in the environment as other perfluorinated compounds, and it is detected in increasing concentrations in some water bodies, including the North Sea. However, bioaccumulation in wildlife and humans seems to be much less than for PFOS. PFBS will stay mostly in the water column due to much higher water solubility compared with higher homologues. In a laboratory fish test the bioaccumulation potential for PFBS was low.

The Australian report concludes that as use increases, for example, in its substitution for PFOS, levels of PFBS may build up and be distributed widely in the environment, given that its precursors are likely to be more volatile, yet structurally much similar to PFOS.
A range of not published tests show that PFBS is not very toxic to birds, algae, aquatic invertebrates, fishes, and sewage micro-organisms. In a quail reproduction study the dietary NOAEC was 900 mg PFBS/kg ww feed (Newsted et al., 2008). However, PFBS was for example not tested in the chironomid ***Chironomus tentans*** which is shown to be 2-3 orders of magnitude more sensitive to the effect of PFOS than other aquatic organisms. Whether this would also be the case with PFBS was unclear.

The body half-life of PFBSK in i.v. exposed monkeys is 4 days. No degradation was detected and urinary excretion of the chemical in these monkeys was a major route of elimination. In the blood high levels of binding of perfluorobutane sulfonate to human albumin occurred. The acute toxicity is low with rat oral and skin LD50 >2000 mg/kg bw. The test material was irritating to the eye and fulfilled the criteria for classification as irritating to eyes (R36). However, the chemical did not cause skin irritation and sensitization. In oral rat studies NOAEL values of 100-300 mg/kg bw/day were determined. The test material was not mutagenic in the applied bacteria tests.

In general the toxicity of PFBS is >100 times lower than that of PFOS and it is not bioaccumulative.

4.3.4 F-53

This chemical is a perfluorinated dialkyl ether sulfonate.

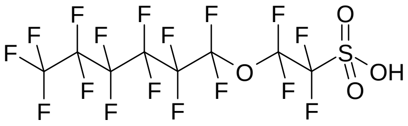


Figure 4-4 F-53 – a perfluorinated dialkyl ether sulfonate

The CAS no. has not been traced. The ether group makes the chemical chain degradable at that point resulting in shorter chain perfluorinated derivatives.

No data exists other than Chinese QSAR model results for persistence (half-lives) in water, sediment, soil, and air, bioconcentration factors (BCFs) and toxicity to fish exist (see Table 4-1).

4.3.5 F-53B

This chemical is a chlorofluorinated dialkyl ether sulfonate.

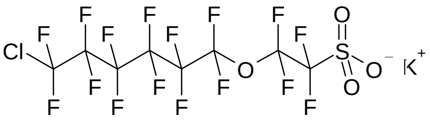


Figure 4-5 F-53B – a chlorofluorinated dialkyl ether sulfonate

The CAS no. has not been traced. The ether group and the chlorine substitution make the chemical chain more degradable resulting in shorter chain derivatives.

Chinese QSAR model results for persistence (half-lives) in water, sediment, soil, and air, bioconcentration factors (BCFs) and toxicity to fish exist (see Table 4-1).

4.3.6 Non-fluoro alternative

No information about the chemical substances in TIB Suract CR-H from TIB Chemicals was available, as this is confidential.

4.3.7 Comparison

The adverse effects of PFOS have been extensively studied and much more data exists on this chemical than on the available alternatives.

In general, the toxicity, persistence, and bioaccumulation of the perfluorinated chemicals increase with the length of the alkyl chain. PFCs with a fluorinated alkyl chain length of six (C_6) and below are not considered to be very accumulative. This means that the fluorinated PFOS alternatives with a shorter chain than PFOS will be less persistent, bioaccumulative, and toxic than PFOS, and thus an improvement. The available data is insufficient for prioritisation among the fluorinated alternatives. In Table 4-1 a few data is shown.

Table 4-1 Data on PFOS and alternatives

Chemical	CAS no.	Log K_{ow}	Persistence/half-lives (days)				Bioaccumulation		Toxicity		Ref
			Water	Sediment	Air	Soil	BCF	BMF	Rat NOAEL mg/kg bw/d	ECO 96 hr LC50 mg/l (fish)	
POP criteria		>5	>60	>180		>180	>5000				
PFOS	1763-23-1										PFOS risk profile 2006
PFOS K salt	2795-39-3	1	>15000		>2		2800 (fish)	22-160	0.1	4.7 *Lepomis macrochirus* (fathead minnow)	
PFOS NH4 salt	29081-56-9									85 *Lepomis macrochirus* (fathead minnow)	3M, 1999
PFOS DEA salt	70225-14-8									31 *Lepomis macrochirus* (fathead minnow)	
PFOS TEA salt	56773-42-3										
PFBS	29420-49-3										
PFBS K salt	29420-43-3						<1		1000	1900 (fathead minnow)	Richard Holt, Dupont, 2010
FC-53*			180	1600	180	360	56			1 (fish)	Jun Huang, 2010
FC-53B*			180	1600	180	360	56			0.56 (fish)	
Fumetrol 21*	27619-97-2		180	1600	12	360	3.2			10 (fish)	
PFHxA	307-24-4								>300		Richard Holt, Dupont, 2010

* Data based on Chinese QSAR models

4.3.8 Conclusion

Based on the information above and the economic limitations of the project, it was decided to further investigate the following alternatives that can be used for non-decorative hard chrome plating:

- The fluorinated alternative Fumetrol® 21 from Atotech, which is based on 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (CAS No. 27619-97-2).
- The fluor-free alternative TIB Suract CR-H from TIB Chemicals (but no information about the chemical substance, as this is confidential).
- Physical alternative – use of teflon balls.

These alternatives were chosen for the following reasons:

- The Fumetrol® 21 alternative contains a known compound (1***H***,1***H***,2***H***,2***H***-perfluorooctanesulfonic acid (CAS No. 27619-97-2)), and the project group together with the Danish EPA found it essential to test and illustrate that a known fluorinated non-PFOS alternative can be used as an alternative to non-decorative hard chrome plating. Furthermore, PFCs with a fluorinated alkyl chain length of six (C_6) (which Fumetrol® 21 has) and below is not considered to be very accumulative. This means that Fumetrol® 21

- The non-fluorinated alternative TIB Suract CR-H was chosen as one of two non-fluorinated alternatives that claim to be working as mist suppressant for non-decorative hard chrome plating as well.

- Finally, the use of a physical solution instead of or in combination with a chemical alternative was chosen as well in order to investigate other alternative possibilities with no or low content of fluorine.

5 Testing of alternatives to PFOS (laboratory scale) (IPU)

5.1 Testing in the laboratory (IPU)

Two chemical and one mechanical alternative have been tested on laboratory scale. The chemical alternatives are Fumetrol® 21 (a fluorochemical non-PFOS product by Atotech) and a non-fluoro-product by TIB called Suract CRH. The mechanical alternative is coverage of the electrolyte surface with PTFE balls.

5.1.1 Experimental procedure

A reference chromium electrolyte was prepared containing 300 g/L CrO_3 and 3 g/l H_2SO_4. A sketch of the laboratory reference setup is illustrated in Figure 5-1. The cell is made of doubled walled glass; the outer space is flushed with water heated by a thermostat to 55°C. The internal diameter is 120 mm, filled with 1.2 liter chromium electrolyte. An anode of lead metal is used (dimensions 50 x 4x 200 mm^3), and the cathode is made of steel with an initial diameter of 5 mm. A glass filter is placed 230 mm above the bath surface, enabling collection of chromium mist.

Various PFOS and PFOS alternatives were added to this reference electrolyte as described below. All depositions were running for 19 hours at a current density of 52 A/dm^2, corresponding to a current density per electrolyte surface area of 700 A/m^2.

The reference setup includes an air inlet. If no air is flushed through the inlet the air convection is very low in the cell as the dense glass filter prevents this. If air is flushed in close to the electrolyte surface this will promote air exhausting, simulating real plating conditions. Most of the experiments were carried out with and without airflow through the air inlet.

Analyses for Cr^{6+} were subsequently performed by measurements of absorbed chromium on the fibre glass filter by spectrophotometrical analysis. For the spectrophotometrical analysis, a Shimadzu UVmini-1240 equipment is used, with 1,5-diphenylcarbazide as an indicator and the absorbance was measured with a wavelength of 542 nm.

Depositions in the following systems were carried out:

- Reference electrolyte (as used at a.h. nichro Haardchrom) without mist suppressant
- Reference electrolyte with 100 massive PTFE balls
- Reference electrolyte with Fumetrol® 21
- Reference electrolyte with Fumetrol® 21 + 100 massive PTFE balls
- Reference electrolyte with TIB Suract CRH
- Reference electrolyte with PFOS

These are described in more details below.

Reference electrolyte with 100 massive PTFE balls:
100 massive PTFE balls with diameters of 5/8 inches (15.9 mm) were placed on a titanium grid and submerged into the reference electrolyte, resulting in two layers of balls – one layer below the electrolyte surface and one above.

Reference electrolyte with Fumetrol® 21:
5 ml/l Fumetrol® 21 were added to the reference electrolyte.

Reference electrolyte with Fumetrol® 21 + 100 PTFE balls:
100 massive PTFE balls with diameters of 5/8 inches (15.9 mm) were placed on a titanium grid and submerged into the reference electrolyte with addition of 5 ml/l Fumetrol® 21, resulting in two layers of balls - one layer below the electrolyte surface and one above.

A titanium grid was used because only massive PTFE balls were commercially available. These are, however, too dense and would sink to the bottom. Therefore, a titanium grid was applied in order to simulate PTFE coated balls floating on the surface.

Reference electrolyte with TIB Suract CRH:
TIB Suract CRH was added to the reference electrolyte. This experiment was performed both with and without continuous addition of the additive. 1 ml/l TIB Suract CRH was added in the experiment without continuous addition; in the experiment with continuous deposition 1 ml/l was added initially; subsequently 0.1 ml/l per hour, according to the suggestions from the datasheet of the product. Analysis for Cr^{6+} was subsequently performed by measurements of absorbed chromium on the fibre glass filter by spectrophotometrical analysis as described above.

Reference electrolyte with PFOS:
A PFOS containing commercial chromium electrolyte was tested in a comparable way as the above mentioned experiments. This electrolyte contained 260 g/l CrO_3 and 1.9 g/l H_2SO_4, a commercial PFOS (Fumetrol® 140[16]) product from Atotech, and a HEEF 25 product containing an alternative catalyst to H_2SO_4 (possibly a methane disulfonate derivate). Analysis for Cr^{6+} was subsequently performed by measurements of absorbed chromium on the fibre glass filter by spectrophotometrical analysis as described above.

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[16] From this point forward the PFOS containing chemical Fumetrol® 140 is for simplicity reasons just named “PFOS”.

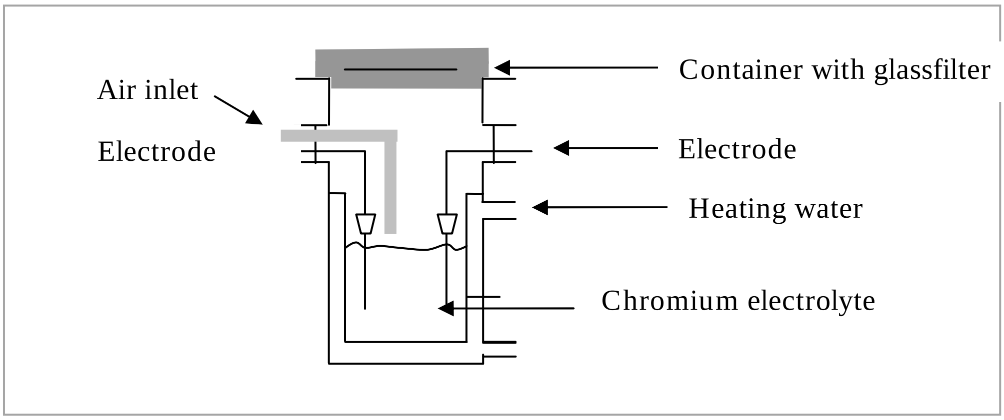

Figure 5-1: Schematic illustration of the electrochemical cell.

5.1.2 Results

The results of the analysis for Cr^{6+} (chromium-VI) are given in Table 5-1 and Table 5-2.

The commercial PFOS product results in very effective reduction of the Cr^{6+} emission.

The results evidently show that the Cr^{6+} emission in a system with simulated exhausting is significantly higher than in a system with very low convection of air. This shows that the Cr^{6+} emission can be reduced radically by avoiding air convection.

Addition of Fumetrol and TIB Suract results in some reduction of the Cr^{6+} emission. In the experiment with continuous addition of TIB Suract, the additions followed the suggestions of the datasheet of the product, despite that the applied additions were not sufficient to prevent mist formation.

Addition of Fumetrol® 21 results in reduction of the Cr^{6+} emission. In the case of simulated exhausting, Fumetrol® 21 reduces the Cr^{6+} emission more than the additions of TIB Suract and PTFE balls.

Additions of PTFE balls results in increased Cr^{6+} emission, also when used in combination with addition of Fumetrol.

Table 5-1: Cr^{6+} emission from experiments performed without airflow.

Electrolyte	Cr^{6+} emission [ug/(glass filter x 19h)]
Reference electrolyte	110
Reference electrolyte and PTFE balls	136
Reference electrolyte with Fumetrol® 21	72
Reference electrolyte with TIB Suract CRH	63**
Commercial electrolyte with PFOS	1.5

Table 5-2: Cr^{6+} emission from experiments performed with airflow (simulated exhaustion):

Electrolyte	Cr^{6+} emission [ug/(glass filter x 19h)]
Reference electrolyte	71,100
Reference electrolyte with Fumetrol® 21 and PTFE balls	732
Reference electrolyte with Fumetrol® 21	502
Reference electrolyte with TIB Suract CRH	850* / 22,500**
Commercial electrolyte with PFOS	*Not measured*

* Continuous additions of TIB Suract CRH were applied

** No continuous additions of TIB Suract CRH were applied

5.1.3 Discussion

TIB Suract requires very regular additions in order to maintain the reduction in Cr^{6+} emission. However, when regular additions are added, it seems to be a mist suppressant that can reduce Cr^{6+} emissions considerably – although not as effective as Fumetrol® 21 (the fluorinated alternative). The experiments show that it is difficult to predict the correct dosing of the additive. In case of breakdown of an addition system the consequences can be severe and supervision of the system would be required. Estimated costs of the use of an automatic addition system together with supervision overnight time are expected to be 1,000 DKK per day (134 EUR) for supervision including log registration. An automatic addition system could therefore result in expenses of approximately 350,000 DKK per year (47,000 EUR) plus expenses of establishment of the supervision equipment (estimation from a.h. nichro Haardchrom/Surfcoat). Use of TIB Suract might be possible in a highly automated mass production of chrome-plated products but for the purpose of the production at a.h. nichro Haardchrom (i.e. specialized products in few numbers, frequently varying production), such a system will be too uncertain to use, at least on the basis of the results on lab-scale.

Two layers of PTFE balls as an alternative to PFOS resulted in increased Cr^{6+} emission. The reason for this could be that the decreased free surface area of the electrolyte results in increased velocity of the chrome mist. This corresponds to practical experience of plates, related to plating inside for example a tube which will result in increased mist development locally at the end of the tube. Polypropylene balls, presently used during plating for the purpose of lowering heat loss and evaporation (of water), do not result in such locally increased mist formation if less than one layer of balls is used, i.e. the balls do not cover the entire surface (see Figure 1.1).

Additions of Fumetrol® 21 result in reduction of the Cr^{6+} emission. In the case of simulated exhausting, Fumetrol® 21 reduces the Cr^{6+} emission more than the additions of TIB Suract and PTFE balls.

The results show that the Cr^{6+} emission can be reduced radically by avoiding air convection. This method could be a suitable alternative to PFOS in mass production systems. However, in plating system for frequently varying productions, it will be more difficult to establish a closed (mechanical) system because of the flexibility required of such systems. Such implementations would require a significant redesign of the production line. Based on the laboratory experiments performed in the present project, it is therefore considered to be very difficult to design large scale experiments that prevent air convection and this alternative – even though being very promising - was therefore not considered a practical solution for the non-automated hard chromium process used at the participating company a.h. nichro Haardchrom A/S. However, the very significant reduction of Cr^{6+} emission, when no ventilation is applied, inspires for further evaluations on possible physical alternatives for avoiding transportation of aerosol from the surface which could be used in plating systems for frequently varying productions. The project group therefore recommends that this aspect should be investigated further as it could be a very interesting alternative to the use of chemical mist suppressants.

For the above reasons, Fumetrol® 21 appears to be the most promising alternative to PFOS in plating systems for frequently varying productions. It was therefore decided to perform the large scale testing with Fumetrol® 21 as an alternative to PFOS. Fumetrol® 21 was the only alternative tested in large scale due to the economic frame of the project.

6 Testing in large scale

Large scale testing of the effect of Fumetrol® 21 as an alternative to PFOS was carried out at the hard chrome plating plant a.h. nichro Haardchrom A/S in Hvidovre, Denmark.

The primary purpose of the test was to see if the Fumetrol® 21 could be used as an alternative to PFOS as mist suppressing agent with similar abilities to suppress chromium-(VI) emissions from the chrome bath.

6.1 Planning of large scale testing

In order to be able to compare the effectiveness of Fumetrol® 21 to the effectiveness of PFOS, experiments of comparable conditions were carried out combined with measurement of chromium emission in both cases.

Fumetrol® 21 (Atotech) containing the non-PFOS alternative – a polyfluorinated compound 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (CAS no. 27619-97-2) - was therefore tested against an existing PFOS product (Fumetrol® 140 (Atotech) containing a PFOS ammonium salt)[17].

The following aspects were discussed when planning the large scale testing in order to be able to fulfil the purpose of comparing Fumetrol® 21 to PFOS as a mist suppressing agent:

- Use of a reference measurement without mist suppressant
- Size of chrome bath
- Electrical charge of the chrome bath
- Identical measurements of PFOS and Fumetrol® 21
- Dosage of PFOS and Fumetrol® 21 to the chrome bath
- Duration and number of measurements
- Measurement of total chromium emissions
- Technical issues regarding the measurements

These aspects are discussed in more details below.

6.1.1 Use of a reference measurement without mist suppressant

Even though the purpose of the measurements primarily was to see if Fumetrol® 21 could work as well as PFOS as a mist suppressant for non-decorative hard chrome plating, it is also relevant to perform a measurement without mist suppressant as a reference to see how large the emission of chromium would be without the use of any mist suppressant. In this way we could get an idea of how well both PFOS and Fumetrol® 21 work as a mist suppressant compared to the reference: no mist suppressant.

It was decided to perform this reference measurement as the first thing during the test period when only the chromium bath was prepared. After the

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[17] The PFOS containing chemical Fumetrol® 140 is for simplicity reasons just named “PFOS” in this report.

measurement one of the mist suppressants could be added and the measurement could continue for this mist suppressant.

6.1.2 Size of chrome bath

In order to be able to compare PFOS and Fumetrol® 21 as mist suppressants it would be necessary to use two new chrome baths in order to avoid any left over or contamination of PFOS in the Fumetrol® 21 bath or the other way around.

Normally, a.h. nichro Haardchrom A/S only changes the chromium chemicals in the chrome bath once every 6 to 10 years as the change of the chrome bath is a very high-priced activity. Not only, the chromium salt chemicals for the chrome bath are costly but the used chrome bath chemicals that are replaced must be disposed of as chemical waste which is also costly.

It was therefore decided, in order to reduce the costs of the large scale testing, to use a small bath of 110 liters. This chrome bath functions just like the larger chrome baths and we would be able to control the electrical charge (ampere hours), the exhaust etc. just like the ordinary larger chrome baths used at a.h. nichro Haardchrom.

The test installation was therefore built at a.h. nichro Haardchrom around this 110 liters chrome bath, i.e. a miniature chrome plating bath with a hood and a vertical ventilation duct in which the sampling point was placed.

Details of the test installations, as well as drawings of the test installation, can be found in Appendix A.

6.1.3 Electrical charge of the chrome bath

It was decided to use a high electrical charge in the chrome bath in order to “stress test” the mist suppressant agent under the worst possible conditions. Under such conditions it was expected that the mist suppressant agent would loose its effect after a few days.

Details about the used electrical charge can be found in Appendix A.

6.1.4 Identical measurements of PFOS and Fumetrol® 21

The primary purpose of the test was to see if the Fumetrol® 21 could be used as an alternative to PFOS as mist suppressing agent with similar abilities to suppress chromium emissions from the chrome bath.

It was therefore decided that the measurements performed on PFOS and on the alternative Fumetrol® 21 should be identical. I.e. the exact same measurements should be performed on the same days after start up of the testing (= make-up of the chrome bath with mist suppressant). This would make it possible to compare the effect of Fumetrol® 21 compared to PFOS.

6.1.5 Dosage of PFOS and Fumetrol® 21 to the chrome bath

In order to test if Fumetrol® 21 works as well as PFOS it is of course also important to use the same concentration of PFOS and Fumetrol® 21 in the chrome bath. However, the two mist suppressant products PFOS and Fumetrol® 21 contain different amounts of the active ingredient. On the

Material Safety Data Sheet of PFOS (Fumetrol® 140) it is stated that the content of PFOS is 5-10% (w/w), and similarly it is stated on the Material Safety Data Sheet of Fumetrol® 21 that the content of the polyfluorosulfonic acid is 1-2.5% (w/w). This means that similar amounts of PFOS and Fumetrol® 21 added to the chrome bath would result in different concentrations of the active mist suppressant ingredients in the two cases.

It was decided to use the make-up concentrations as suggested in the technical data sheet for PFOS and Fumetrol® 21 in order to test the recommended make-up concentration for the two mist suppressants.

This would result in an addition of Fumetrol® 21 in the double amount compared to PFOS for make-up of the chrome bath. However, this also makes sense as PFOS according to the Material Safety Data Sheets seems to be twice as concentrated as Fumetrol® 21.

For further make-up details of the mist suppressants in the chrome baths, see Appendix A.

6.1.6 Duration and number of measurements

The duration of the different measurements was set at 24 hours in order to ensure a good average value with plenty of material (chromium) for analysis.

The duration of the reference measurement was set at 12 hours because it was expected that the chromium emission would be very high with no mist suppressant available to lower the chromium emissions. 12 hours should therefore be enough time to ensure a good average value but on the other hand hopefully not too long a time frame to risk clogging of the filter used for measuring. Clogging of the filter could happen if the chromium emissions were too high.

The number of measurements was primarily determined by the economic conditions of this project. However, it was decided to include measurements over a period of at least 10 days in order to get an idea of when the mist suppressant agent would loose its effect. In all, it was decided to carry out 11 measurements; one reference measurements and 5 measurements for each of the mist suppressants.

It was furthermore decided that the 5 measurements should be carried out on the exact same time after make-up of the chrome bath with mist suppressant. I.e. the measurements were decided to be carried out on day 1, day 3, day 7, day 10, and day 14 of the make-up of the chrome bath (i.e. addition of mist suppressing agent). The duration of the measurement period and the number of days between the measurements were decided based on the experiences of a.h. nichro Haardchrom and their expectations of how long the mist suppressant would work under the set conditions.

6.1.7 Measurement of total chromium emissions

Even though it is the emission of chromium-(VI) that is most relevant, it was decided to measure the total chromium emissions (i.e. both chromium-(VI) and chromium-(III)) because it is easier to measure compared to measurement of chromium-(VI).

Normally, the chrome bath will contain more than 90% chromium-(VI) so the relationship between the amount of chromium-(VI) and chromium-(III) will be proportional.

6.1.8 Technical issues regarding the measurements

It was decided to use the same technical conditions for all three tests carried out, i.e. reference measurement without mist suppressant, measurements with PFOS as mist suppressant, and measurements with Fumetrol® 21 as mist suppressant. This should of course ensure that the measurements could be compared with each other.

This means that the following technical conditions were controlled and kept at the same level during the entire testing period:

- Electrical charge
- Exhaust velocity (flow rate)
- The subjects to be chrome-plated
- The reference electrolyte bath (only difference was the added mist suppressant). The reference electrolyte bath used was identical to the electrolyte bath usually used at a.h. nichro Haardchrom.

The subjects to be chrome-plated were identical for both testing of PFOS and Fumetrol® 21. The subjects were kept in the chrome bath during the entire testing period (of 14 days) for each mist suppressant, i.e. no change of subjects to be chrome plated during the entire testing period for both mist suppressants. This ensures identical conditions for the two test periods.

It was decided to use a chrome bath topped with a hood and a vertical ventilation duct in which the sampling point should be placed. The sampling point was planned to be placed in a straight length of the duct in order to fulfil the conditions in Chapter 6 “Measurement section and measurement site” in EN 15259:2007 “Air quality. Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement, objective, plan and report.”

Details can be found in Appendix A.

6.2 Experimental procedure

The experimental procedure is described in details and illustrated in Appendix A and is therefore only briefly described in this section.

A hard chrome electrolyte was prepared in a 110 liter chamber. The test installation was a purpose built miniature chrome plating bath with a hood and a vertical ventilation duct in which the sampling point was placed.

Experiments were carried out in a reference electrolyte without mist suppressant and in the reference electrolyte with PFOS and Fumetrol® 21, respectively.

The following test programme was carried out (see Table 6-1).

Table 6-1 Test program for large scale testing at a.h. nichro Haardchrom

Day	Addition of mist suppressant	Reference	PFOS (Fumetrol® 140)	Comments
0	-	12 hours	-	Start up of chrome bath. Subjects to be chrome-plated were installed in the chrome bath. Reference measurement was carried out on the reference electrolyte chrome bath with no mist suppressant. Chrome-plating of products was carried out, i.e. high emissions of chromium were expected.
1	yes	-	24 hours	PFOS was added to the reference electrolyte chrome bath and measurement was carried out.
3	-	-	24 hours	Measurement was carried out.
7	yes	-	24 hours	Extra PFOS was added to the chrome bath as the mist suppressing agent no longer was active (visible findings). This was entirely based on the experiences of a.h. nichro Haardchrom as chromium emissions were visible and the mist suppressant did not produce the foamy layer as when working effectively. The PFOS was added in the morning on day 7, just before the measurement on day 7 was set up. The addition of PFOS was carried out to ensure that the last three measurements would not be carried out on a bath with a non-working mist suppressant agent.
10	-	-	24 hours	Measurement was carried out.
14	-	-	24 hours	Measurement was carried out.
				Two weeks of pause between measurements to prepare a new reference electrolyte chrome bath for Fumetrol® 21 measurements. The subjects to be chrome-plated were replaced with new identical subjects.
Day*	Addition of mist suppressant	Reference	Fumetrol® 21	Comments
1 (29)	yes	-	24 hours	Start up of new chrome bath with new mist suppressant and new identical subjects to be chrome plated. The same procedure as for PFOS testing was carried out, i.e. Fumetrol® 21 was added to the reference electrolyte chrome bath and measurement of chromium emissions was carried out.
3 (31)	-	-	24 hours	Measurement was carried out.
7 (35)	yes	-	24 hours	As for the PFOS testing period, extra Fumetrol® 21 was added on day 7 of the testing period as well. This was done deliberately in order to add new mist suppressant agent on the same time of the testing period. However, the visual inspection showed that the mist suppressant layer of Fumetrol® 21 also had stopped working at about the same day of the test period as PFOS did. It would therefore have been necessary to add Fumetrol® 21 anyhow. Fumetrol® 21 was added in the morning on day 7, just before the measurement on day 7 was set up
10 (38)	-	-	24 hours	Measurement was carried out.
14 (42)	-	-	24 hours	Measurement was carried out.

* Day 1 (29) indicates that it is the first day of Fumetrol® 21 testing, but day 29 since start up of the large scale testing.

The following technical conditions were controlled and kept at the same level during the entire testing period (testing of reference and the two mist suppressants):

- Electrical charge
- Exhaust velocity (flow rate)
- The subjects to be chrome-plated
- The reference electrolyte bath (only difference was the added mist suppressant). The reference electrolyte bath used was identical to the electrolyte bath usually used at a.h. nichro Haardchrom.

PFOS and Fumetrol® 21 were added to the reference electrolyte according to the make-up prescriptions in their respective technical data sheets. However, based on the experience of a.h. nichro Haardchrom, the make-up amount of both PFOS and Fumetrol® 21 was raised by 50% in both cases compared to the make-up concentration according to the data sheets. The reason for this raise in concentration was that a.h. nichro Haardchrom has experienced that this raise in make-up concentration is necessary in order to get the best working mist suppressant layer in a new chrome bath. However, both the concentration of PFOS and Fumetrol® 21 was raised, hence still being comparable amounts.

6.3 Results

The results of the chromium emission measurements are presented in Table 6-2 below.

Table 6-2 Test results – OBS i tabellen er der ikke ® ved Fuemetrol ® 21

Fumetrol 140 (PFOS)

Parameter	Unit	Reference	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	08/11/2010	09/11/2010	11/11/2010	15/11/2010	18/11/2010	22/11/2010
Measuring period	hh:mm	15:03 - 09:50	10:23 - 09:40	09:15 - 09:30	09:31 - 09:26	10:15 - 09:56	09:47 - 09:20
Addition of PFOS before measurement start *	Liter/m^2	-	1.8	-	1.8	-	-
Addition of PFOS before measurement start *	Liter/m^3	-	3.6	-	3.6	-	-
Days after addition	days	-	1	3	1	4	8

Flow and temperature

Temperature	°C	20	20	20	20	20	20
Flowrate	m^3(s,d)/h	180	180	180	180	180	180
Flowrate, operating conditions	m^3/h	200	200	200	200	200	200

Concentrations

Particles / mist	mg/m^3(s,d)	18	0.024	0.021	0.088	0.020	0.018
Particles / mist	% of reference	-	0.13	0.12	0.49	0.11	0.10
Cr	mg/m^3(s,d)	12	0.027	0.30	0.20	0.011	0.046
Cr	% of reference	-	0.23	2.50	1.67	0.09	0.38

Emissions

Particles / mist	mg/h	3,300	4.3	3.9	16	3.6	3.2
Cr	mg/h	2,200	5.0	56	36	2.0	8.3

Fumetrol 21 (non-PFOS)

Parameter	Unit	-	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	-	30/11/2010	02/12/2010	06/12/2010	09/12/2010	13/12/2010
Measuring period	hh:mm		10:30 - 10:07	09:50 - 08:45	09:30 - 09:40	10:02 - 09:17	09:40 - 10:03
Addition of Fuemetrol 21 before measurement start	Liter/m^2	-	3.7	-	1.8	-	-
Addition of Fuemetrol 21 before measurement start	Liter/m^3		7.2		3.6		
Days after addition	days	-	1	3	1	4	8

Flow and temperature

Temperature	°C		20	20	20	20	20
Flowrate	m^3(s,d)/h		180	180	180	180	180
Flowrate, operating conditions	m^3/h		200	200	200	200	200

Concentrations

Particles / mist	mg/m^3(s,d)		0.037	0.034	0.030	0.025	0.030
Particles / mist	% of PFOS		154	162	34	125	167
Particles / mist	% of reference		0.21	0.19	0.17	0.14	0.17
Cr	mg/m^3(s,d)	-	0.013	0.016	0.089	0.047	0.016
Cr	% of PFOS	-	48	5	45	427	35
Cr	% of reference	-	0.11	0.13	0.74	0.39	0.13

Emissions

Particles / mist	mg/h		6.8	6.3	5.5	4.5	5.5
Cr	mg/h		2.4	2.9	16	8.6	2.9

(s,d) indicates dry gas at standard conditions (0°C, 101,3 kPa)
* means "not included in accreditation no. 51"

The results show that the emissions of chromium (total chromium, i.e. both Cr^{6+} and Cr^{3+}) are at somewhat the same level on all five days of measurement. The chromium emissions when using Fumetrol® 21 as mist suppressant are between 5 and 427% of the corresponding chromium emissions when using PFOS. In 4 out of 5 measurements the chromium emissions when using Fumetrol® 21 are below the chromium emissions when using PFOS (between 5 and 48%). The uncertainty of the chromium measurements is about 10%. Therefore, the uncertainty cannot explain the much higher chromium emissions in sample no. 4 for Fumetrol® 21 compared to PFOS. However, when looking closer at the emissions in Table 6-2, it can be seen that the chromium emissions are rather stable when using Fumetrol® 21. The large difference of 427% between the chromium emissions when using Fumetrol® 21 compared to the use of PFOS is due to the fact that the chromium emissions of the similar sample no. 4 for some reason are much lower than the chromium emissions in the other PFOS samples. In other words, it is not possible to detect a significant difference between PFOS and Fumetrol® 21.

The durability of the mist suppressants is very good. The test does not show any significant decline in the effect for up to 8 days for both mist suppressants.

Both mist suppressants show a good effect on preventing chromium emissions from the chrome bath. On average less than 1 % of the mist formation without mist suppressants has been measured. There seems to be a tendency for Fumetrol® 21 to be slightly better than PFOS but it is not conclusive. However, when taken the amount of "active ingredient" added during the testing into account, the picture is a bit different (see Figure 6-1). The calculations below show that the Fumetrol® 21 chemical is not as concentrated as the PFOS chemical. PFOS has been added during the testing in a concentration that is about 3 times higher than the active ingredient of Fumetrol® 21. Hence, it seems that Fumetrol® 21 is performing slightly better than PFOS as a chromium mist suppressant.

Figure 6-1 Amount of "active ingredient" used in the tests

PFOS

PFOS (Fumetrol® 140) contains according to the MSDS 5-10% PFOS ("active ingredient").
PFOS has according to the MSDS a density of 1.000 to 1.025 g/cm^3. A value of 1.000 g/cm^3 is assumed in the calculations.
PFOS was added in a total amount of 7.2 liter/m^3, i.e. between 0.36 and 0.72 liter/m^3 of "active ingredient".

Fumetrol® 21

Fumetrol® 21 contains according to the MSDS 1-2.5% "active ingredient".
Fumetrol® 21 has according to the MSDS a density of 0.995 to 1.021 g/cm^3. A value of 1.000 g/cm^3 is assumed in the calculations.
Fumetrol® 21 was added in a total amount of 10.8 liter/m^3, i.e. between 0.108 and 0.27 liter/m^3 of "active ingredient".

This means that there has been added about 2.7 - 3.3, i.e. about 3 times less "active ingredient" of Fumetrol® 21 compared to PFOS.

The experience from a.h. nichro Haardchrom during the testing period was that there did not seem to be any large differences in the effect of PFOS and Fumetrol® 21 as mist suppressants. Both mist suppressants were very similar in their effectiveness and their appearance:

- The foamy layer on the top of the chrome bath was visually identical over the entire testing period.
- The time from make-up of the bath to the mist suppressant effect wearing off was the same for both PFOS and Fumetrol® 21. In both cases, additional mist suppressant was added on day 7 of the testing

period and in both cases the foam layer was disappearing and it was possible to see chromium emissions from the bath.

The Danish “end of pipe” emission limit value for hexavalent chromium is 0.25 mg/m³. This limit value is exceeded only in sample 2 of the PFOS measurements (0.30 mg/m³). The rest of the measurements (excluding the reference measurement) are below this emission limit value. All measurements have been performed upstream from the cyclone, i.e. representing emission values without exhaust devices. It is therefore highly probable that concentrations measured in the “end of pipe” downstream from the cyclone will be much lower than the Danish emission limit value.

As an overall conclusion, Fumetrol® 21 can replace PFOS without any risk of increasing the mist formation. With addition of the applied amounts of mist suppressants the durability of both suppressants is at least one week under the used “stressing” conditions.

The overall conclusion from a.h. nichro Haardchrom was also that Fumetrol® 21 can replace PFOS as a mist suppressant. a.h. nichro Haardchrom had on the basis of the large scale testing experiences no problems with a change in mist suppressants and therefore plans to use Fumetrol® 21 as mist suppressant in the future.

6.4 Economic considerations

There are three aspects of interest regarding the economic considerations:

- The direct difference in price for the two mist suppressants.
- The direct difference in price regarding disposal of chemical waste.
- Any indirect economic expenses needed for changing from PFOS to the alternative mist suppressant.

Currently, the costs of the tested Fumetrol products are 297 DKK per liter for Fumetrol® 21 and 601 DKK per liter for Fumetrol® 140 (PFOS). As mentioned in Figure 6-1 Fumetrol® 21 contains 1-2.5% “active ingredient” according to the MSDS, and PFOS (Fumetrol® 140) contains 5-10% PFOS (“active ingredient”) according to the MSDS. This means that the price of “active ingredient” for the two products can be estimated to be 12-30 DKK per ml “active ingredient” in Fumetrol® 21 and 6-12 DKK per ml “active ingredient” in Fumetrol® 140 (PFOS).

During the test period of two weeks Fumetrol 21® was added in a total amount of 10.8 liter/m^3, i.e. between 0.108 and 0.27 liter/m^3 of “active ingredient” and PFOS was added in a total amount of 7.2 liter/m^3, i.e. between 0.36 and 0.72 liter/m^3 of “active ingredient”. Therefore, the expenses of the added products over the test period were 3,208 DKK per m^3 for Fumetrol® 21 and 4,327 DKK per m^3 for Fumetrol® 140 (PFOS). As it is concluded in section 6.3 that Fumetrol® 21 can replace PFOS as a mist suppressant, by using the above mentioned amounts of additions, the use of Fumetrol® 21 turns out to be cheaper than the use of Fumetrol® 140 (PFOS).

The project group has assessed that the difference in price regarding disposal of the chemical waste when using PFOS and the alternative mist suppressant Fumetrol® 21 would be close to zero. The large scale testing showed that more Fumetrol® 21 was added (due to the alternative being less concentrated): 10.8

liter/m^3 compared to 7.2 liter/m^3 PFOS. About 33% more Fumetrol ® 21 was therefore added compared to PFOS. This could influence the cost regarding disposal of chemical waste once the chrome bath is emptied. On the other hand, the mist suppressant “disappears”, i.e. is degraded and/or evaporated during use, therefore the difference may not be known when it comes to disposal of the chrome bath.

The indirect economic expenses needed for changing from PFOS to the alternative mist suppressant Fumetrol® 21 are assessed to be zero. The reason for this is that the alternative mist suppressant can be directly added to the chrome bath instead of PFOS when it is visible that the effect of PFOS is at a minimum, i.e. the existing PFOS in the chrome bath has been degraded. The polyfluorinated chemical of the alternative mist suppressant is chemically close to the same structure as PFOS and therefore it should not cause any problems to add the new alternative mist suppressant when a small amount of PFOS is still present in the chrome bath.

This aspect is important economically as a.h. nichro Haardchrom assesses that it will cost about 500,000 DKK (66,600 EUR) to replace the chromium chemicals in one of their large chrome baths (costs of the chromium chemicals and cost of disposal of the chemical waste), and for the entire company about 1.5 million DKK (200,000 EUR). Emptying and replacing the chemicals of the chrome bath is therefore only done when absolutely necessary, i.e. once every 6-10 years depending on the content of metal contamination (primarily cupper and iron from the mountings).

7 Assessment of an alternative to PFOS for hard chrome plating

7.1 Effectiveness

The large scale testing of PFOS and the alternative 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (Fumetrol® 21) demonstrated that both mist suppressants show a good effect on preventing chromium emissions from the chrome bath. On average less than 1% (between 0.11% and 0.74%) of the chromium emissions without mist suppressants (reference measurement) was measured when the alternative mist suppressing agent was tested.

The durability of the alternative mist suppressants was very good. The test did not show any significant decline in the effect for up to 8 days for both mist suppressants (additional mist suppressant was, however, added for both mist suppressants during the testing period of 14 days).

The experiences of a.h. nichro Haardchrom were that the alternative mist suppressing agent 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (Fumetrol® 21) showed similar mist suppressing effect and durability when comparing with PFOS under the same conditions.

When comparing the results from the large scale tests with the results from the laboratory tests similar trends are observed. Laboratory experiments without airflow and with PFOS showed a reduction of chromium emission to 1.4%, laboratory experiments with airflow and with Fumetrol® 21 showed a reduction of chromium emission to 0,7%. However, the laboratory experiments without airflow and Fumetrol® 21 show a surprisingly low reduction of chromium emission to only 65% (see Table 5-1). In order to evaluate this inconsistence repeated measurements should be carried out to establish whether this can be due to a measurements error. Despite this inconsistency the performed laboratory tests and results appear to be very indicative for the results of large scale tests.

7.2 Economy

As described in section 6.4, the expenses of the added products during the test period were 3,208 DKK per m^3 for Fumetrol® 21 and 4,327 DKK per m^3 for Fumetrol® 140 (PFOS). During the 14 days' testing period, the price per day is therefore 229 DKK per m^3 for Fumetrol® 21 and 309 DKK per m^3 for PFOS.

The difference in the costs of PFOS compared with the alternative 1***H***,1***H***,2***H***,2***H***-perfluorooctane sulfonic acid (Fumetrol® 21) during the two weeks' test period was approximately 80 DKK per day per m^3. This means that addition of Fumetrol® 21 is cheaper than the addition of PFOS. Due to the evaluation of the effectiveness and durability of the added amounts of the two products as described in Section 7.1, the direct cost of the use of

Fumetrol® 21 is lower as compared to PFOS. However, the difference in costs, when using Fumetrol® 21 compared to PFOS, is small and the costs of using the two mist suppressants are expected to be about the same when transferring the small scale testing results from 14 days to yearly large scale production.

The indirect economic expenses needed for changing from PFOS to the alternative mist suppressant Fumetrol® 21 are assessed to be zero since Fumetrol® 21 can be directly added to the chrome bath instead of PFOS when it is visible that the effect of PFOS is at a minimum.

It is assessed that the difference in price regarding disposal of the chemical waste when using PFOS and the alternative mist suppressant Fumetrol® 21 should be close to zero. However, Fumetrol® 21 is added in larger volumes as compared to the tested PFOS product which could influence the cost regarding disposal of chemical after long-term use. On the other hand, the mist suppressant "disappears", i.e. is degraded and/or evaporated during use, therefore the difference may not be known when it comes to disposal of the chrome bath. The expenses of disposal of large scale chromium electrolyte are very high (se example in Section 6.4). Emptying and replacing the chemicals of the chrome bath is therefore only done when absolutely necessary, i.e. once every 6-10 years depending on the content of metal contamination (primarily cupper and iron from the mountings).

7.3 Environment and health

The adverse effects of PFOS have been extensively studied and much more data exists on this chemical than on the available alternatives. Therefore, the toxicity data available for the alternative compound 1***H*,**1***H*,**2***H*,**2***H*-perfluorooctane sulfonic acid (Fumetrol® 21) is very limited.

PFOS is found widespread in nature and in animals and humans because it is a very persistent chemical and non-degradable in nature. Furthermore, PFOS and its precursors do have a tendency to bioaccumulate and biomagnify in food chains. PFOS causes various adverse effects in humans, and for children a very conservative Tolerable Daily Intake of PFOS may already be exceeded.

The alternative compound 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctane sulfonic acid (Fumetrol® 21) has a basic structure that is very similar to PFOS. Both contain a fluorinated C_8 alkyl chain. However, the alternative is not perfluorinated but has two non-fluorinated carbon atoms making it a polyfluorinated compound (fluorotelomer). Therefore, it is obvious that substituting PFOS with Fumetrol® 21 (or other chemical products containing 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctane sulfonic acid) will not be such a large environmental improvement as e.g. substituting PFOS with a non-fluorinated alternative. However, in this project, we have not been able to identify the chemical ingredients of non-fluorinated alternatives and the non-fluorinated alternative tested in pilot scale only seemed to be working with continuously addition of mist suppressing agent.

As for PFOS the perfluorinated part of the alternative 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctane sulfonic acid is not degradable. However, the non-fluorinated part of the alkyl chain can be degraded. Therefore, the 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctanesulfonic acid is expected to be degraded in nature to non-degradable perfluorinated compounds with a C_6- or C_7-chain. In general, the toxicity, persistence, and bioaccumulation of the perfluorinated chemicals increase with the length of the alkyl chain. The toxicity of a perfluorinated C_6-chain is 100 to 1000 times lower compared to a C_8-chain (as e.g. PFOS). Furthermore, computer models (QSAR) predict that the alternative The 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctanesulfonic acid seems to be less persistent, less bioaccumulative, and less toxic compared to PFOS.

Even though a substitution of PFOS (fully fluorinated/perfluorinated) with a (not fully fluorinated/polyflourinated) alternative is not a very large environmental improvement. Substituting PFOS with the alternative 1***H*,**1***H*,**2***H*,**2***H* -perfluorooctanesulfonic acid will on the other hand mean that the alternative is less persistent, less bioaccumulative, and less toxic than PFOS, and thus an environmental improvement.

This project has therefore shown that it is possible to use a non-PFOS mist suppressant for non-decorative hard chrome plating. The exception "PFOS used as mist suppressant for non-decorative hard chromium-(VI) plating" in the restriction of use of PFOS in appendix XVII of REACH (Reg. 1907/2006) can therefore be deleted according to the observations of this project. This is also in line with other observations from this project, i.e. the fact that Japan does not use PFOS at all for non-decorative hard chrome plating (is not allowed anymore). Instead a polyfluorinated compound is used as alternative.

7.4 Assessment of the usability of the alternative solution within other areas

As the PFOS alternative identified in the present project, Fumetrol® 21, is a flour containing product, it is not recommended to be used in processes where the use of PFOS is already forbidden as more environmentally friendly solutions exist for these processes.

According to the present legislation, PFOS is not forbidden in photoresists, photographic coatings, and hydraulic fluids for aviation. It is likely that the 1***H***,1***H***, 2***H***,2***H*-**perfluorooctane sulfonic acid (e.g. Fumetrol® 21) can be found as a useful alternative for photoresists and photographic coatings in an intermediate period until more environmentally alternatives may be found. Due to the very high safety concerns in aviation, PFOS may be found to be the safest solution for hydraulic fluids for aviation. Unless it can be guaranteed as safe as PFOS it is unlikely that the 1***H***,1***H***,2***H***,2***H*-**perfluorooctane sulfonic acid (e.g. Fumetrol® 21) can be accepted as an alternative for this purpose.

7.5 Conclusion

All in all it can be concluded that the alternative compound 1***H***,1***H***,2***H***,2***H*-**perfluorooctane sulfonic acid (Fumetrol® 21) in a large scale test:

- works as effective as PFOS as mist suppressing agent,
- seems to have the same durability as PFOS as mist suppressing agent,
- has the same price level as PFOS as mist suppressing agent,
- can be substituted right away when PFOS is burnt out in the chrome bath without the need of changing the entire chrome bath chemicals, and

- is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS.

This project has therefore shown that it is possible to use a non-PFOS mist suppressant for non-decorative hard chrome plating. The exception “PFOS used as mist suppressant for non-decorative hard chromium (VI) plating” in the restriction of use of PFOS in appendix XVII of REACH (Reg. 1907/2006) can therefore be deleted according to the observations of this project. This is also in line with other observations from this project, i.e. the fact that Japan does not use PFOS at all for non-decorative hard chrome plating (is not allowed anymore). Instead a polyfluorinated compound is used as alternative, like e.g. Fumetrol® 21.

The laboratory results also illustrated that a non-fluorinated mist suppressant alternative perhaps could be promising as a substitute for PFOS. However, as continuously addition of the mist suppressant is needed, the usefulness of the alternative seems to be limited for automated hard chrome processes and must be assessed in each case.

The laboratory results of the project showed that the Cr^{6+} emission can be reduced radically by avoiding air convection. This indicates that large scale tests of a physical method that prevents air convection could turn out to be an alternative to PFOS. Such method would be a suitable alternative to PFOS in mass production systems. However, in plating system for frequently varying productions, it will be more difficult to establish a closed system because of the flexibility required to such systems. Such implementations would require a significant redesign of the production line. However, the very significant reduction of Cr^{6+} emissions when no ventilation was applied inspires for further evaluations on possible physical alternatives for avoiding transportation of aerosol from the surface which could be used in plating systems for frequently varying productions. Therefore, the project group recommends that this aspect should be investigated further as it could be a very interesting alternative to the use of chemical mist suppressants – either as an alternative used in combination with e.g. smaller amounts of mist suppressants or as a substitute for using mist suppressants.

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Bilag A

Large scale testing of PFOS and Fumetrol® 21 at a.h. nichro Haardchrom A/S.

Test report of large scale testing of PFOS and Fumetrol® 21 at a.h. nichro Haardchrom A/S.

DANAK
Test Reg. nr. 51
Report No. 4622-01

FORCE TECHNOLOGY

a.h.nichro HARDCHROM A/S

Substitution of PFOS for use in non-decorative hard chrome plating

Test of effect and durability of mist suppressants Fumetrol 140 and Fumetrol 21

November / December 2010

Report issued by FORCE Technology

Accredited report No.: 4622-01
Project No.: 110-31010
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Summary

The Danish Environmental Protection Agency (Miljøstyrelsen) has engaged FORCE Technology and a.h.nichro HARDCHROM A/S to test the effect and durability of suppressants containing PFOS and an alternative suppressant that does not contain PFOS. For the purpose a.h.nichro provided a small test installation with ventilation and a measurement point. a.h.nichro also administered the operation of the chromium plating bath and the addition of suppressants during the test.

Table 1. Main results.

Fumetrol 140 (PFOS)

Parameter	Unit	Reference	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	08/11/2010	09/11/2010	11/11/2010	15/11/2010	18/11/2010	22/11/2010
Addition of PFOS before measurement start *	Liter/m^2	-	1.8	-	1.8	-	-
Addition of PFOS before measurement start *	Liter/m^3	-	3.6	-	3.6	-	-
Days after addition	days	-	1	3	1	4	8

Concentrations

Cr	mg/m^3(s,d)	12	0.027	0.30	0.20	0.011	0.046
Cr	% of reference	-	0.23	2.50	1.67	0.09	0.38

Fumetrol 21 (non-PFOS)

Parameter	Unit	-	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	-	30/11/2010	02/12/2010	06/12/2010	09/12/2010	13/12/2010
Addition of Fuemetrol 21 before measurement start	Liter/m^2	-	3.7	-	1.8	-	-
Addition of Fuemetrol 21 before measurement start	Liter/m^3		7.2		3.6		
Days after addition	days	-	1	3	1	4	8

Concentrations

Cr	mg/m^3(s,d)	-	0.013	0.016	0.089	0.047	0.016
Cr	% of PFOS	-	48	5	45	427	35
Cr	% of reference	-	0.11	0.13	0.74	0.39	0.13

(s,d) indicates dry gas at standard conditions (0°C, 101,3 kPa)
* means "not included in accreditation no. 51"

As an overall conclusion Fumetrol 21 can replace Fumetrol 140 (PFOS) without any risk of increasing the fume and spray formation. With addition of the applied amounts of suppressants the durability of both suppressants is at least one week.

FORCE Technology
4 February 2011

Lars K. Gram
Authorised Signatory

Tommy Hansen
Technician

1. Introduction

The Danish Environmental Protection Agency (Miljøstyrelsen) has engaged FORCE Technology and a.h.nichro HARDCHROM A/S to test the effect and durability suppressants containing PFOS and an alternative suppressant that does not contain PFOS. For the purpose a.h.nichro provided a small test installation with ventilation and a measurement point. a.h.nichro also administered the operation of the chromium plating bath and the addition of suppressants during the test.

The measurements where performed in November and December 2010.

Address (test installation): a.h. nichro HARDCHROM A/S
Søvangsvej 11-15
2650 Hvidovre

The results of the measurements are only valid for the actual plant, in the actual measuring periods and for the actual production.

2. Scope

The scope for the measurements is to test the durability and possible differences between two mist suppressants for chromium plating baths:

- Fumetrol 140 containing the perfluorinated compound perfluorooctane sulfonic acid (PFOS)
- Fumetrol 21 without PFOS or PFOS-derivates. Fumetrol contains in stead a poly-fluorinated compound 1H,1H,2H,2H-perfluorooctanesulfonic acid.

Datasheets for the two mist suppressants are shown in Appendix 1 and 2.

3. Test programme

Table 2. Overview of test programme.

Day	Addition of suppressant	Reference	Fumetrol 140 (PFOS)	Fumetrol 21 [1]
0	-	12 hours	-	-
1	yes	-	24 hours	24 hours
3	-	-	24 hours	24 hours
7	yes	-	24 hours	24 hours
10	-	-	24 hours	24 hours
14	-	-	24 hours	24 hours

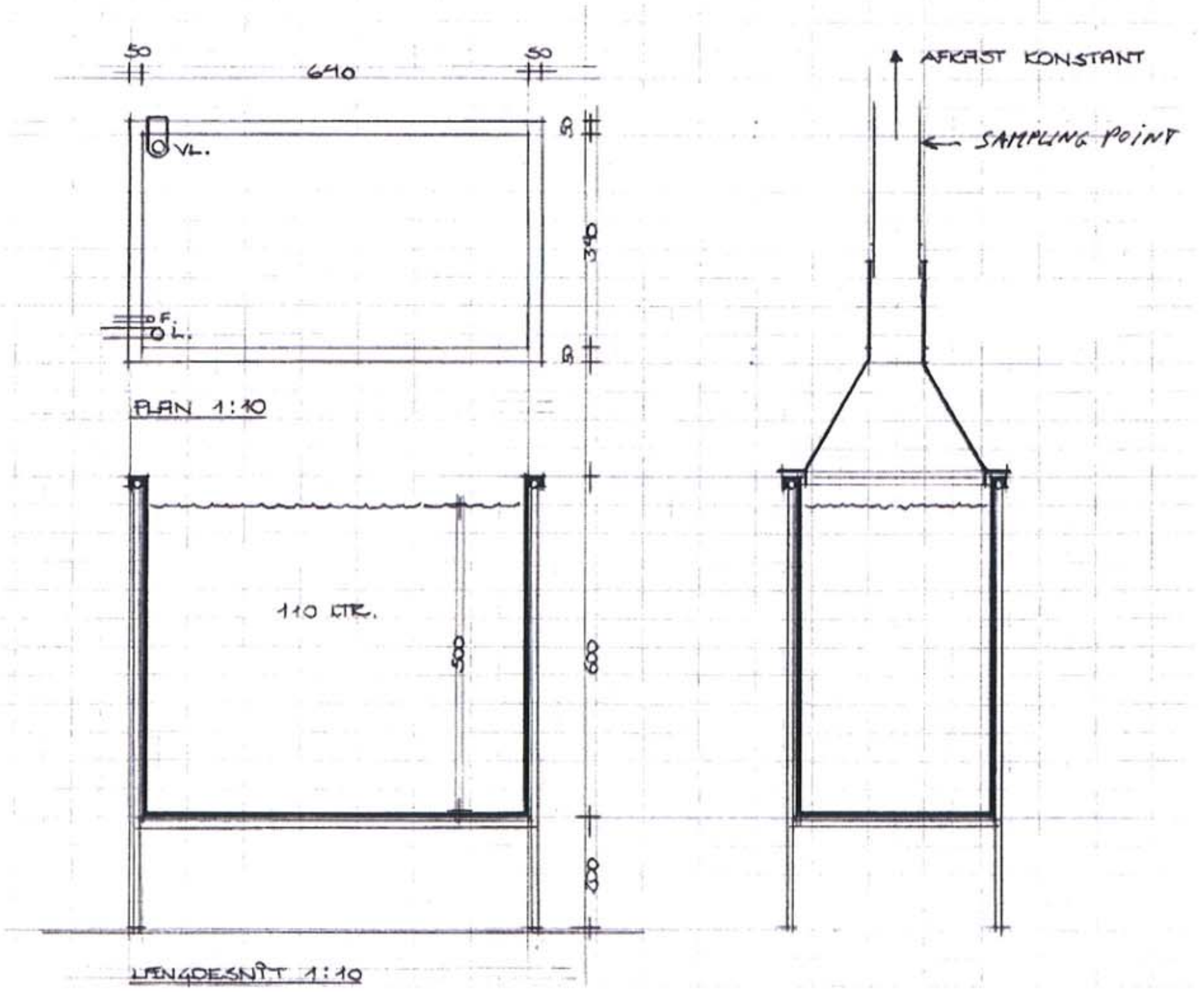
[1] Fumetrol 21 measurements where performed two weeks after end of Fumetrol 140 measurements, and not in parallel as indicated in Table 1.

4. Test installation, chromium plating

4.1. Description of test installation

The test installation is a purpose build miniature chromium plating bath with a hood and a vertical ventilation duct in which the sampling pint is placed:

Figure 1. Sketch of test installation.



4.2. Conditions of chromium plating during the test

The production was steady and normal, and kept at the same conditions throughout the test.

Plating tank volume 110 Litres
Plating tank temperature 50 °C
Plating tank surface top area 0.22 m^2
2 items plated = surface 4 dm^2.
Process parameter = 50 Amp./dm^2.

Regarding Fumetrol 140 (PFOS)
Initial make up 0.4 Litres = 1.8 L/m^2 surface area = 3.6 L/m^3 chromium solution.
Normal make up according to data sheet 0.275 Litres was raised with approx. 50% based on a.h. nichro experience.

Second make up 0.4 Litres = 1.8 L/m^2 surface area = 3.6 L/m^3 chromium solution. Based on visual estimation.

Regarding Fumetrol 21
Initial make up 0.8 Litres = 3.6 L/m² surface area = 7.2 L/m³ chromium solution.
Normal make up according to data sheet 0.550 Liters was raised with approx. 50% based on a.h. nichro experience.

Second make up 0.4 Litres = 1.8 L/m² surface area = 3.6 L/m³ chromium solution. Based on visual estimation.

4.3. Sampling location

The vertical duct was made in plastic and had an inner diameter of ø110 mm. The sampling point was placed in a straight length of duct and did fulfil the conditions in Chapter 6 "Measurement section and measurement site" in EN 15259.

5. Applied measurement methods

5.1. Duration of measurements

Measurements with a duration of approximately 24 hours where decided in order to ensure a good average value with plenty of material for analysis. The reference measurement where performed with a duration of approximately 12 hours.

5.2. Measurement methods and uncertainty

Gas temperature: The gas temperature is measured with a pt100-thermocouple or a NiCr/NiAl-thermocouple connected to a digital thermometer or data logger.
Range: -40 - 600 °C
Uncertainty: 4 °C (absolute)
FORCE Technology method: EM-03-01
Reference/standard: VDI 3511 bl. 1-5, IEC 584-2, IEC 584-2 amd. 1

Flow: The gas velocity is measured by means of a pitot tube connected to an inclined tube manometer or a micro manometer, reading the dynamic pressure. The velocity is measured in a number of points in the cross section of the duct. From the velocity and the cross section area, the flow is calculated.
Range: 0 - 40 m/s
Limit of detection: 2.3 m/s
Uncertainty: 10 % of measured value (95% confidence interval).
FORCE Technology method: EM-02-01
Reference/standard: ISO 10780

Particles: A partial gas stream is aspirated isokinetically through a planar filter and a drying column. The gas flow is aspirated by means of a pump unit consisting of a gas tight pump, a calibrated gas meter and a flow meter.
Range: 0 - 50 mg/m³(n,t)
Limit of detection: 0.05 mg/m³(n,t)
Uncertainty: 10 % of measured value (95% confidence interval).
FORCE Technology method: EM-01-05
Reference/standard: EN 13284-1

Chromium and particles: A partial gas stream is aspirated isokinetically through a planar filter and a drying column. The gas flow is aspirated by means of a pump unit consisting of a gas tight pump, a calibrated gas meter and a flow meter.
Downstream from the filter the gasstream is aspirated through a series of three impingers, each containing approx. 100 ml 4.5% HNO_3 /1,7% H_2O_2-solution. All parts of the sampling system is build

in glass. After sampling the equipment is rinsed thoroughly with a HNO_3-solution, which is also analysed. At the laboratory the filter weighed, digested and mixed with the rinsing solution. Filter and impingers are analysed separately applying ICP-MS.
Range: 0 - 900 µg/m^3(n,t)
Limit of detection: 0.9 µg/m^3(n,t) (chromium)
Uncertainty: 10 % of measured value (95% confidence interval).
Reference/standard: EN 14385 (chromium) and EN 13284-1 (particles)

6. Results

The detailed results from the test are shown in Table 3.

Table 3. Test results.

Fumetrol 140 (PFOS)

Parameter	Unit	Reference	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	08/11/2010	09/11/2010	11/11/2010	15/11/2010	18/11/2010	22/11/2010
Measuring period	hh:mm	15:03 - 09:50	10:23 - 09:40	09:15 - 09:30	09:31 - 09:26	10:15 - 09:56	09:47 - 09:20
Addition of PFOS before measurement start *	Liter/m^2	-	1.8	-	1.8	-	-
Addition of PFOS before measurement start *	Liter/m^3	-	3.6	-	3.6	-	-
Days after addition	days	-	1	3	1	4	8

Flow and temperature

Temperature	°C	20	20	20	20	20	20
Flowrate	m^3(s,d)/h	180	180	180	180	180	180
Flowrate, operating conditions	m^3/h	200	200	200	200	200	200

Concentrations

Particles / mist	mg/m^3(s,d)	18	0.024	0.021	0.088	0.020	0.018
Particles / mist	% of reference	-	0.13	0.12	0.49	0.11	0.10
Cr	mg/m^3(s,d)	12	0.027	0.30	0.20	0.011	0.046
Cr	% of reference	-	0.23	2.50	1.67	0.09	0.38

Emissions

Particles / mist	mg/h	3,300	4.3	3.9	16	3.6	3.2
Cr	mg/h	2,200	5.0	56	36	2.0	8.3

Fumetrol 21 (non-PFOS)

Parameter	Unit	-	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Date	dd-mm-yy	-	30/11/2010	02/12/2010	06/12/2010	09/12/2010	13/12/2010
Measuring period	hh:mm		10:30 - 10:07	09:50 - 08:45	09:30 - 09:40	10:02 - 09:17	09:40 - 10:03
Addition of Fuemetrol 21 before measurement start	Liter/m^2	-	3.7	-	1.8	-	-
Addition of Fuemetrol 21 before measurement start	Liter/m^3		7.2		3.6		
Days after addition	days	-	1	3	1	4	8

Flow and temperature

Temperature	°C		20	20	20	20	20
Flowrate	m^3(s,d)/h		180	180	180	180	180
Flowrate, operating conditions	m^3/h		200	200	200	200	200

Concentrations

Particles / mist	mg/m^3(s,d)		0.037	0.034	0.030	0.025	0.030
Particles / mist	% of PFOS		154	162	34	125	167
Particles / mist	% of reference		0.21	0.19	0.17	0.14	0.17
Cr	mg/m^3(s,d)	-	0.013	0.016	0.089	0.047	0.016
Cr	% of PFOS	-	48	5	45	427	35
Cr	% of reference	-	0.11	0.13	0.74	0.39	0.13

Emissions

Particles / mist	mg/h		6.8	6.3	5.5	4.5	5.5
Cr	mg/h		2.4	2.9	16	8.6	2.9

(s,d) indicates dry gas at standard conditions (0°C, 101,3 kPa)
* means "not included in accreditation no. 51"

7. Conclusion

The results do not demonstrate a clear-cut trend over time, and it is not possible to detect a significant difference between Fumetrol 140 and Fumetrol 21.

Both mist suppressants, however, show a good effect on preventing fume and spray formation. On average less than 1 % of the mist formation without mist suppressants has been measured. There seems to be a tendency for Fumetrol 21 to be slightly better than Fumetrol 140, but it is not conclusive.

The durability of the mist suppressants is also very good. The test does not show any significant decline in the effect for up to 8 days for both mist suppressants.

The added make-up amount of mist suppressant, are according to the instructions for use, however, make-up was raised with approx. 50% based on a.h. nichro experience in both cases. The supplementary additions where equal for the two mist suppressants, and based on a visual inspection.

The Danish "end of pipe" emission limit value for hexavalent chromium is 0.25 mg/m^3(s,d). This limit value is exceeded only in the Fumetrol 140, sample 2 (0.30 mg/m^3(s,d)). The rest of the measurements (excluding the reference measurement) are below this emission limit value. All measurements have been performed upstream from the cyclone. It is highly probable that concentrations measured in the "end of pipe" downstream from the cyclone will be much lower than the Danish emission limit value.

As an overall conclusion Fumetrol 21 can replace Fumetrol 140 (PFOS) without any risk of increasing the mist formation. With addition of the applied amounts of mist suppressants the durability of both suppressants is at least one week.

8. Appendix

Appendix 1	Data sheet for Fumetrol 140
Appendix 2	Data sheet for Fumetrol 21

Appendix 1

Data sheet for Fumetrol 140

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31.01.2002

ATOTECH FUMETROL 140

SAFETY DATA SHEET

according to EC Directive 1907/2006/EC

Print Date: 09/04/2008 *Revision Number: 1*

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Product code: 1451251
Product name: **FUMETROL 140**

Use of the Substance/Preparation
Chemical plating of metals

Supplier

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2. HAZARDS IDENTIFICATION

Classification

Indication of danger: The product is non-dangerous in accordance with Directive 2001/58/EC

Most important hazards:

3. COMPOSITION/INFORMATION ON INGREDIENTS

Description Aqueous solution of chemicals

Components	CAS-No	EC-No.	Weight %	Classification
tetraethylammoniumheptadecafluorooctanesulphonate	56773-42-3	260-375-3	5-10	Xn;R22 R52/53

For the full text of the R phrases mentioned in this Section, see Section 16

4. FIRST AID MEASURES

General advice:	If symptoms persist, call a physician.
Skin contact:	Wash off immediately with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before re-use.
Inhalation:	Move to fresh air If symptoms persist, call a physician
Eye contact:	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.
Ingestion:	Call a physician or Poison Control Center immediately. Do not induce vomiting without medical advice. Never give anything by mouth to an unconscious person.
Protection of first-aiders:	Use personal protective equipment.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Extinguishing media which must not be used for safety reasons:	No information available
Special protective equipment for firefighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.
Specific hazards:	Heating or fire can release toxic gas, In case of fire hazardous decomposition products may be produced such as, Carbon oxides.
Specific methods:	Water mist may be used to cool closed containers. Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations.
Autoignition temperature:	Not applicable.
Flammability Limits in Air:	
Lower:	Not applicable.
Upper:	Not applicable.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions:	Prevent unauthorized access. For personal protection see section 8.
Environmental precautions:	Should not be released into the environment.
Methods for cleaning up:	Clean contaminated surface thoroughly. Keep in suitable, closed containers for disposal. Dispose of in accordance with local regulations. Soak up with inert absorbent material. Avoid formation of aerosol.
Methods for containment:	Prevent further leakage or spillage if safe to do so

7. HANDLING AND STORAGE

Handling

Technical measures/Precautions:	Use only in area provided with appropriate exhaust ventilation.

Safe handling advice:	Do not breathe vapours/dust. Remove and wash contaminated clothing before re-use. Handle in accordance with good industrial hygiene and safety practice. Do not ingest. For personal protection see section 8.

Storage

Technical measures/Storage conditions:	Keep containers tightly closed in a dry, cool and well-ventilated place.
Incompatible products:	No special storage conditions required

Storage Temperature

Above:	-5 °C
Below:	40 °C

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering measures to reduce exposure:
Ensure adequate ventilation, especially in confined areas

Personal protective equipment

Respiratory protection:	In case of insufficient ventilation wear suitable respiratory equipment.
Hand protection:	Wear protective gloves. The suitability for a specific workplace should be discussed with the producers of the protective gloves. Please observe the instructions regarding permeability and breakthrough time which are provided by the supplier of the gloves. Also take into consideration the specific local conditions under which the product is used, such as the danger of cuts, abrasion, and the contact time.
Gloves:	nitrile rubber
Skin and body protection:	long sleeved clothing. boots.
Eye protection:	tightly fitting safety goggles. Ensure that eyewash stations and safety showers are close to the workstation location.
Hygiene measures:	Avoid contact with skin, eyes and clothing. Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and immediately after handling the product. When using, do not eat, drink or smoke.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical state:	liquid	**Colour:**	colourless to yellow
Odour:	No information available	**Specific gravity:**	1.000 - 1.025
pH:	2.00 - 4.00	**Boiling point:**	> 100°C
Melting point:		**Vapour pressure:**	ca. 23 hPa
VOC Content(%):	Not applicable.	**Solubility in water:**	miscible
Flash point:	Not applicable	**Autoignition temperature:**	Not applicable.
Decomposition temperature:		**Risk of explosion:**	Not explosive

Explosion limits:
Upper: Not applicable.
Lower: Not applicable.

10. STABILITY AND REACTIVITY

Stability:	Stable under recommended storage conditions.
Materials to avoid:	none
Conditions to avoid:	To avoid thermal decomposition, do not overheat.
Hazardous decomposition products:	None reasonably foreseeable
Hazardous reactions:	None under normal processing.

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Component Information

Components	LD50/oral/rat	LC50/Inhalation/8h/rat	LD50/dermal/rabbit
tetraethylammoniumheptadecafluorooctanesulphonate - 56773-42-3	No information available	No information available	No information available

Product Information

LC50/inhalation/4h/rat = No information available
LD50/dermal/rabbit = No information available
LD50/oral/rat = No information available

Local effects

Skin contact:	Prolonged skin contact may cause skin irritation
Eye contact :	Contact with eyes may cause irritation
Inhalation :	May cause irritation of respiratory tract
Ingestion :	May be harmful if swallowed

Chronic toxicity:

Sensitization:
No information available

Carcinogenic substances

12. ECOLOGICAL INFORMATION

Environmental hazard

Ecotoxicity effects:	No data is available on the product itself
Aquatic toxicity:	No data is available on the product itself
Mobility:	No information available
Bioaccumulative potential:	not determined
Germany, Water Endangering Classes (VwVwS):	2

Product name: FUMETROL 140

13. DISPOSAL CONSIDERATIONS

Waste from residues / unused products:	Dispose of in accordance with local regulations.
Contaminated packaging:	Empty containers should be taken for local recycling, recovery or waste disposal
EWC waste disposal No:	According to the European Waste Catalogue, Waste Codes are not product specific, but application specific

14. TRANSPORT INFORMATION

Not classified as dangerous in the meaning of transport regulations.

IMDG

ADR/RID

ICAO/IATA

15. REGULATORY INFORMATION

Symbol(s)

The product is non-dangerous in accordance with Directive 2001/58/EC

Labelling

Safety datasheet available on request for professional users

Substances currently restricted by WEEE/RoHS (European Directive 2002/95/EC) or ELV (European Directive 2000/53/EC):

PBDE	PBB	CrVI	Hg	Pb	Cd
-	-	-	-	-	-

Please note: Current legislation restricting the use of certain substances applies to „homogeneous material" in finished articles being supplied to the market. Substances deposited during surface finishing may have a composition (weight percent) higher than the weight percent of the substance in the operating solution from which the deposit is made. Atotech encourages its customers to implement systems to ensure their finished products comply with the regulations in force.

International Inventories

All of the components in this product are on or exempt from the following inventories:
US TSCA, CANADA DSL / NDSL, Europe (EINECS/ELINCS/NLP), Australia, Korea, China, Philippines.

International Inventory Legend
TSCA: US - Toxic Substance Control Act
DSL: Canada - Domestic Substance List
NDSL: Canada - Non-Domestic Substance List
IECSC: China - Inventory of Existing Chemical Substances China
EINECS: EU Inventory of Existing Commercial Chemical Substances
ELINCS: EU List of Notified Chemical Substances
ECL: Korea - Existing Chemicals List
AICS: Australia - Inventory of Chemical Substances
ENCS: Japan - Existing and New Chemical Substances
PICCS: Phillipines - Inventory of Chemicals and Chemical Substances

16. OTHER INFORMATION

Text of R phrases mentioned in Section 3

- R22 - Harmful if swallowed.
- R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Revision Date: 09/04/2008

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text

Appendix 2

Data sheet for Fumetrol 21

SAFETY DATA SHEET

according to EC Directive 2001/58/EC

Print Date: 04/08/2008 *Revision Number: 2*

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Product code: 1680801
Product name: **FUMETROL 21**

Use of the Substance/Preparation
Chemical plating of metals

Supplier

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Emergency telephone number
Out of hours transport emergency (U.K. only): 01865 407333 CEAS NCEC CULHAM

Prepared By:
Product Safety Department (PSD), email: HES-Berlin@atotech.com

2. HAZARDS IDENTIFICATION

Classification

Indication of danger: The product is non-dangerous in accordance with Directive 2001/58/EC

Most important hazards:

3. COMPOSITION/INFORMATION ON INGREDIENTS

Description Aqueous solution of chemicals

Components	CAS-No	EC-No.	Weight %	Classification
Polyfluorosulfonic acid	27619-97-2	248-580-6	1-2.5	Xn;R22-41

For the full text of the R phrases mentioned in this Section, see Section 16

4. FIRST AID MEASURES

General advice:	If symptoms persist, call a physician.
Skin contact:	Wash off immediately with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before re-use.
Inhalation:	Move to fresh air If symptoms persist, call a physician
Eye contact:	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.
Ingestion:	Call a physician or Poison Control Center immediately. Do not induce vomiting without medical advice. Never give anything by mouth to an unconscious person.
Protection of first-aiders:	Use personal protective equipment.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Extinguishing media which must not be used for safety reasons:	No information available
Special protective equipment for firefighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.
Specific hazards:	In case of fire hazardous decomposition products may be produced such as, Carbon oxides.
Specific methods:	In the event of fire, cool tanks with water spray
Autoignition temperature:	Not applicable.
Flammability Limits in Air:	
Lower:	Not applicable.
Upper:	Not applicable.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions:	Prevent unauthorized access. For personal protection see section 8.
Environmental precautions:	Should not be released into the environment.
Methods for cleaning up:	Clean contaminated surface thoroughly. Keep in suitable, closed containers for disposal. Dispose of in accordance with local regulations.
Methods for containment:	Prevent further leakage or spillage if safe to do so

7. HANDLING AND STORAGE

Handling

Technical measures/Precautions:	Use only in area provided with appropriate exhaust ventilation.
Safe handling advice:	Do not breathe vapours/dust. Remove and wash contaminated clothing before re-use. Handle in accordance with good industrial hygiene and safety practice. Do not ingest. For personal protection see section 8.

Storage

Technical measures/Storage conditions:	Keep containers tightly closed in a dry, cool and well-ventilated place.
Incompatible products:	No special storage conditions required

Storage Temperature

Above:	-5 °C
Below:	40 °C

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering measures to reduce exposure:
Ensure adequate ventilation, especially in confined areas

Personal protective equipment

Respiratory protection:	In case of insufficient ventilation wear suitable respiratory equipment.
Hand protection:	Wear protective gloves. The suitability for a specific workplace should be discussed with the producers of the protective gloves. Please observe the instructions regarding permeability and breakthrough time which are provided by the supplier of the gloves. Also take into consideration the specific local conditions under which the product is used, such as the danger of cuts, abrasion, and the contact time.
Gloves:	nitrile rubber
Skin and body protection:	long sleeved clothing. boots.
Eye protection:	tightly fitting safety goggles. Ensure that eyewash stations and safety showers are close to the workstation location.
Hygiene measures:	Avoid contact with skin, eyes and clothing. Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and immediately after handling the product. When using, do not eat, drink or smoke.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical state:	liquid	**Colour:**	colourless
Odour:	characteristic	**Specific gravity:**	0.995 - 1.021
pH:	0.0 - 2.5	**Boiling point:**	> 100°C
Melting point:		**Vapour pressure:**	ca. 23 hPa
VOC Content(%):	Not applicable.	**Solubility in water:**	miscible
Flash point:	Not applicable	**Autoignition temperature:**	Not applicable.
Decomposition temperature:		**Risk of explosion:**	Not explosive

Explosion limits:
Upper: Not applicable.
Lower: Not applicable.

10. STABILITY AND REACTIVITY

Stability:	Stable under recommended storage conditions.
Materials to avoid:	none
Conditions to avoid:	Stable at normal conditions

Hazardous decomposition products: None reasonably foreseeable

Hazardous reactions: None under normal processing.

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Component Information

Components	LD50/oral/rat	LC50/Inhalation/8h/rat	LD50/dermal/rabbit
Polyfluorosulfonic acid - 27619-97-2	No information available	No information available	No information available

Product Information

LC50/inhalation/4h/rat = No information available
LD50/dermal/rabbit = No information available
LD50/oral/rat = No information available

Local effects

Skin contact:	Prolonged skin contact may cause skin irritation
Eye contact :	Contact with eyes may cause irritation
Inhalation :	May cause irritation of respiratory tract
Ingestion :	May be harmful if swallowed

Chronic toxicity:

Sensitization:
No information available

Carcinogenic substances

12. ECOLOGICAL INFORMATION

Environmental hazard

Ecotoxicity effects:	No data is available on the product itself
Aquatic toxicity:	No data is available on the product itself
Mobility:	No information available
Bioaccumulative potential:	not determined
Germany, Water Endangering Classes (VwVwS):	1

13. DISPOSAL CONSIDERATIONS

Waste from residues / unused products:	Dispose of in accordance with local regulations.
Contaminated packaging:	Empty containers should be taken for local recycling, recovery or waste disposal
EWC waste disposal No:	According to the European Waste Catalogue, Waste Codes are not product specific, but application specific

14. TRANSPORT INFORMATION

Not classified as dangerous in the meaning of transport regulations.

IMDG

ADR/RID

ICAO/IATA

15. REGULATORY INFORMATION

Symbol(s)

The product is non-dangerous in accordance with Directive 2001/58/EC

Labelling

Safety datasheet available on request for professional users

Substances currently restricted by WEEE/RoHS (European Directive 2002/95/EC) or ELV (European Directive 2000/53/EC):

PBDE	PBB	CrVI	Hg	Pb	Cd
-	-	-	-	-	-

Please note: Current legislation restricting the use of certain substances applies to „homogeneous material" in finished articles being supplied to the market. Substances deposited during surface finishing may have a composition (weight percent) higher than the weight percent of the substance in the operating solution from which the deposit is made. Atotech encourages its customers to implement systems to ensure their finished products comply with the regulations in force.

International Inventories

All of the components in this product are on or exempt from the following inventories:
US TSCA, CANADA DSL / NDSL, Europe (EINECS/ELINCS/NLP), Australia, China, Japan.

International Inventory Legend
TSCA: US - Toxic Substance Control Act
DSL: Canada - Domestic Substance List
NDSL: Canada - Non-Domestic Substance List
IECSC: China - Inventory of Existing Chemical Substances China
EINECS: EU Inventory of Existing Commercial Chemical Substances
ELINCS: EU List of Notified Chemical Substances
ECL: Korea - Existing Chemicals List
AICS: Australia - Inventory of Chemical Substances
ENCS: Japan - Existing and New Chemical Substances
PICCS: Phillipines - Inventory of Chemicals and Chemical Substances

16. OTHER INFORMATION

16. OTHER INFORMATION

Text of R phrases mentioned in Section 2

- R41 - Risk of serious damage to eyes.
- R22 - Harmful if swallowed.

Revision Date: 04/08/2008

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