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Final report

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Best available techniques for PFOS substitution in the surface treatment of metals and plastics and analysis of alternative substances to PFOS when used in equipment for chromium plating and plastic etching

Final report

by

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Abstract:

Best available techniques for the substitution of PFOS in surface treatment of metals and plastics and analysis of alternative substances to PFOS for use in chromium plating and plastic etching

This research project gives an overview of the baths operated in Germany for chromium plating of metals and plastics and for plastic etching.

Processes in which perfluorooctane sulphonic acid (PFOS) was previously used are described. The type and quantity of the fluorine-free and fluorine-containing mist suppressants used were determined for the different types of baths: functional chromium plating (hard chromium plating), decorative chromium plating (bright chromium plating) and plastic etching. According to the data collected in this study, PFOS has been replaced by 6:2 fluorotelomer sulphonic acid (6:2 FTS) in functional chromium plating and in plastic etching. In decorative chromium plating, PFOS was completely replaced by fluorine-free mist suppressants, 6:2 FTS or by the use of chromium (III)-based processes that do not require fluorine-containing mist suppressants. The nationwide consumption of mist suppressants has been estimated on the basis of the industry data collected. The extrapolation of this data for 6:2 FTS consumption in the electroplating industry results in approx. 12 tons for the year 2017.

6:2 FTS as well as the fluorine-free mist suppressants used as an alternative have been characterised by short portfolio fiches. According to current knowledge, 6:2 FTS is toxic, bioaccumulative only in invertebrates and forms persistent degradation products. The report describes the degradation and behaviour of 6:2 FTS in the environment in detail.

Using the example of two facilities in which PFOS (old bath) and 6:2 FTS were or are used, the path of the mist suppressants applied was traced from the point of use to the point of discharge into the public sewerage system or watercourse. It was then investigated how the release of these fluorinated mist suppressants can be reduced in the process itself and in wastewater treatment.

The report further describes existing and developing chemical and physical alternatives to surface treatment that do not use chromium(VI) or fluorinated mist suppressants and presents possible obstacles to their use.

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6:2 FTS	6:2 fluorotelomer sulphonic acid; 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctane sulphonic acid (common name: H4PFOS)
ABS	Acrylonitrile-butadiene-styrene copolymer
ABS/PC	Acrylonitrile-butadiene-styrene copolymer/polycarbonate
ATE	Acute toxicity estimate
BAuA	Federal Institute for Occupational Safety and Health
BAT/BEP	best available techniques and best environmental practices
CTAC	Chromium Trioxide Authorization Consortium CTAC
CLP	Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures
CrO_3	Chromium trioxide
CVD	chemical vapour deposition
ECHA	European Chemicals Agency
EHLA	Extreme high speed laser metal deposition
ELV	End-of-Life Vehicles
FGK	Fachverband Galvanisierte Kunststoffe (Association of Galvanised Plastics)
FTS	Fluorotelomer sulphonic acids
HVOF	High velocity flame spraying
IAT	Ion exchange resins
IUW	IUW Integrierte Umweltberatung (Integrated Environmental Consulting)
IED	Industrial Emissions Directive; Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control);
KrWG	Closed Substance Cycle Waste Management Act
LDS	Electric arc wire spraying
LMD	Laser Metal Deposition
mN/m	= 10^{-3} Newton/metre; unit of measurement of surface tension
MSDS	Material safety data sheet - see SDS
NOEC:	NOEC: No Observed Effect Concentration
PBT	(P) persistance , (B) bioaccumulation potential, (T) toxicity
PFAS	Perfluorinated and polyfluorinated alkyl substances
PFAAs	Perfluoroalkyl acids
PFBS	Perfluorobutanesulphonic acid

PFHxS	Perfluorohexanesulphonic acid
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulphonic acid
PFPeA	Perfluorpentanacid
PFT	Perfluorinated surfactants
POP	Persistent Organic Pollutant
POP-VO	European Regulation (EC) No. 850/2004 of the European Parliament and of the Council of 29th April 2004 on persistent organic pollutants and amending Directive 79/117/EEC, last amended by Article 1 of the Regulation of 30th March 2016
PTFE	Polytetrafluorethylene
PVD	physical vapour deposition
PVDF	Polyvinylidene fluoride
REACH	(Registration, Evaluation, Authorisation and Restriction of Chemicals)
TS	Dry matter (for concentration data in wastewater sludge)
ttr	Thermal tolerance bandwidth
TZW	Technologiezentrum Wasser (Water Technology Centre)
SDS	Safety data sheet, see also MSDS
RoHS	Restriction of Hazardous Substances,
UBA	Federal Environment Agency
UNEP	(United Nations Environment Programme)
WEEE	Waste Electric and Electronic Equipment
ZVO	Zentralverband Oberflächentechnik e.V.

Summary

Background

Perfluorooctane sulphonic acid (PFOS) was used as a mist suppressant in the chromium plating of metal and plastic surfaces. The reason for this is the high chemical resistance of PFOS to chromic acid and chromosulphuric acid, which have a strong oxidising effect.

The advantage of the chemical resistance in industrial processes implies the disadvantage of the high persistence of PFOS. PFOS is also toxic and bioaccumulative.

This led to a ban on this substance in 2008 by the European POP Regulation (EC) No. 850/2004 (EU POP Regulation – amended by European Regulation No. 757/2010) on persistent organic pollutants (POPs) implementing the Stockholm Convention.

The following exemptions to the ban on the use of PFOS are included in this Regulation:

- until 26 August 2015: mist suppressants for monitored electroplating systems;
- Spray suppression agents for non-decorative hard chromium plating (chromium VI) in closed loop systems.

After the expiry of the first mentioned exemption in 2015, PFOS may only be used in electroplating as a mist suppressant for non-decorative hard chromium plating (chromium VI) in closed loop systems. In this study, hard chromium plating is referred to by the increasingly precise term "functional chromium plating".

The Regulation also provides that the use of PFOS will be phased out as soon as the use of safer alternatives is technically and economically feasible. The need for the exemptions will be reviewed at regular intervals and progress will be reported.

Objective of the project

The aim of this research project is to fill knowledge gaps for the reporting and information requirements under the POP Regulation and for the BAT/BEP Guidance on the use of PFOS under the Stockholm Convention. In addition, this project aims to determine the state of the art in chromium plating and plastic etching.

This research project was carried out by IUW Integrierte Umweltberatung in cooperation with Oeko-Institut and POPs Environmental Consulting on behalf of the Federal Environment Agency from April 2018 to February 2020.

It gives an overview of the plants operated in Germany for chromium plating of metals and plastics and for the etching of plastics.

Processes in which perfluorooctane sulphonic acid (PFOS) was formerly used were described. The type and quantity of the fluorine-free and fluorine-containing mist suppressants used were determined for the various types of equipment: functional chromium plating (hard chromium plating), decorative chromium plating (bright chromium plating) and plastic etching. According to the data collected, PFOS was nationwide replaced by 6:2 fluorotelomer sulphonic acid (6:2 FTS) in functional chromium plating and in plastic etching. In decorative chromium plating, PFOS was completely replaced by fluorine-free mist suppressants, 6:2 FTS or by the use of chromium(III)-based processes that do not require fluorine-containing mist suppressants. On the basis of the industry data collected, the nationwide consumption of mist suppressants in this area was estimated. The extrapolation for 6:2 FTS consumption in the electroplating industry resulted in approx. 12 tons for the year 2017, based on the pure active substance.

6:2 FTS as well as the fluorine-free mist suppressants used as alternatives were characterised by short portfolio fiches. According to current knowledge, 6:2 FTS is toxic, only bioaccumulative in invertebrates and forms persistent degradation products. The degradation and behaviour of 6:2 FTS in the environment was described.

Using the example of two facilities in which PFOS (old facility) and 6:2 FTS were or are used, the path of the mist suppressants used was traced from the point of use to the point of discharge into the public sewerage system or watercourse. It was investigated how the release of these fluorinated mist suppressants can be reduced in the process itself and in wastewater treatment.

Existing and developing chemical and physical alternatives to surface treatment that do not use chromium(VI) or fluorinated mist suppressants are described and possible obstacles to their use are presented.

Reasons for the use of PFOS or alternative mist suppressants in surface treatment

The use of PFOS in chromium(VI)-containing process solutions serves to lower the surface tension. In chromium plating electrolytes, this reduces emissions of toxic chromium(VI) aerosols into the ambient air. In plastic etching, mist suppressants improve the wetting of hydrophobic surfaces. The drainage of chromic acid from the workpieces is improved in all applications, thus reducing the carry-over of process solutions.

Characterization of the surface treatment industry

For the three relevant fields of application, functional chromium plating (hard chromium plating), decorative chromium plating (bright chromium plating) and plastic etching in the context of galvanic plastic metallization, the study describes

- the fields of application in industry
- the number of facilities in Germany
- the plant sizes, measured in treatment vat volumes
- the properties of the deposited layers
- physical-chemical and technical framework parameters
- Application concentrations for PFOS and chromium trioxide
- Special features of the requirements for wastewater treatment

Special processes such as black chromium plating as part of decorative chromium plating, closing the chromic acid cycle in decorative chromium plating, de-chromium plating of defective batches and product carriers and the specifics of plastic metallization are also discussed.

As a special feature, it is pointed out that when converting from chromium(VI) to the less toxic chromium(III) electrolytes, the real potential for hazardous incidents within the meaning of the 12th Federal Immission Control Ordinance may increase under certain circumstances due to the potential risk of chlorine gas formation.

Up to now, the number of chromium-plating plants and plastic etching facilities nationwide has never been completely statistically recorded. Also the German central association for surface technology (Zentralverband Oberflächentechnik e.V.; ZVO) does not have a complete record of the above-mentioned plants either. In order to obtain as comprehensive an overview as possible of the plants, the mist suppressants used therein and the technical reduction measures, relevant facilities in the surface treatment industry were identified in a multi-stage process. After the selection procedure, more than 100 facilities were sent a questionnaire in cooperation with the ZVO. The aim of the survey was to obtain information on the type and size of the plants operated, as well as the type of application and annual consumption of the mist suppressants used. The participants also provided information on the measures taken in production and wastewater treatment plants to reduce mist suppressant emissions.

A total of 30 facilities replied to the survey. These facilities together had an effective treatment vat volume of 2,800 cubic metres, of which 940 cubic metres were specified as process solutions containing chromium(VI). Of these facilities, 23.3% operated decorative chromium plating plants, 40% operated functional chromium plating plants and 3.3% were active in both business areas. 33.3% of the plants were plastic electroplating plants in which process solutions containing chromium(VI) are used both in etching and bright chromium baths.

In the 30 facilities surveyed, a total of 19.8 tons of mist-suppressant solutions containing approximately 1 ton of active ingredient were used in 2017 in all process solutions containing chromium(VI).

The reported data showed that, based on the active ingredients, the share of the fluorine-containing 6:2 FTS in the total mist suppressant consumption in the area of chromium(VI)-containing process solutions is approximately 47.5 %. For the fluorine-free mist suppressants, the use of a mixture of (Z)-octadec-9-enylamine, ethoxylated and oleylamine ethoxylate accounts for approx. 27.1% of the market, while a mist suppressant based only on oleylamine ethoxylate has a volume consumption of approx. 20.6%. It should be noted that fluorine-free mist suppressants have been reported exclusively for use in decorative chromium plating, and here both the operating concentration and consumption are significantly higher than in 6:2 FTS, as they are rapidly degraded under the strongly oxidative conditions in chromosulphuric acid.

According to the data collected, significant market dominance is shown for 6:2 FTS. It is used in 60% of the decorative chromium plating plants (15 out of 25 bright chromium plants). For both functional chromium plating (13 facilities with 18 plants) and plastic etching (10 facilities with 12 plants) the survey showed that solely 6:2 FTS-based mist suppressants were used in these process solutions.

On the basis of the data reported in the survey from 30 facilities, an attempt was made to draw conclusions about the overall market for mist suppressants in this sector in Germany for the year 2017. The calculation for 6:2 FTS showed that around 7,338 kg of active ingredient was used in decorative chromium plating, 3,763 kg in functional chromium plating and 687 kg in plastic etching. In total, the annual consumption for 6:2 FTS in 2017 was therefore approx. 12 tons.

This extrapolation was carried out analogously for all reported mist suppressants. The details are presented in the study. The extrapolation was compared with a current survey by the ZVO in 2019, which is based on a survey of chemical suppliers, which showed an annual consumption of around 10 tons for 6:2 FTS. Both results differ by about 15%, which seems acceptable in view of the time elapsed since 2017 and the uncertainty regarding the extrapolation of only 30 facilities.

Comparison of the mist suppressants used

In order to allow a better comparison of the properties of different fluorine-free mist suppressants available on the market that are used as alternatives to PFOS, information was collected from their Material Safety Data Sheets (MSDS) and summarised in short portfolio fiches. These portfolio fiches contain data on chemical composition, concentrations in mixtures, and classifications and hazard statements according to the CLP Regulation, including information on physical and chemical as well as toxic and ecotoxic properties, and, if applicable, classification as PBT or CMR substances. In total, data were collected and compiled for 15 mist suppressants or mist suppressant mixtures marketed by 13 different suppliers. Four mixtures were reported as fluorinated. They contain 6:2 FTS. Eleven mixtures were reported as non-fluorinated. For two of these mixtures no information on ingredients was provided.

Three mixtures contained both 6:2 FTS and other active ingredients: methyl dipropylene glycol, methanol and maleic acid in combination with methanol. For these mixtures, the concentrations for 6:2 FTS were similar to those containing only 6:2 FTS and ranged from 1 to 10%. Some of the additional ingredients have additional classifications such as toxic if swallowed, aquatic toxicity and toxic if inhaled.

11 mixtures did not contain fluorinated substances. Contained were: (Z) -Octadec-9-enylamine, ethoxylated; oleylamine ethoxylate, each in combination with 1,2-propylene glycol or 2-(2-methoxyethoxy) ethanol; amines, C12-C14 alkyl, ethoxylated; tallow alkylamine ethoxylate; sodium dodecyl sulfate; 3 [dodecyl(dimethyl)ammonio]propane-1-sulfonate, 3-hydroxypropane-1-sulphonic acid and dimethyl cocosalkylamine; ethoxylated isodecanol and sulfochlorinated paraffin oils. For some of these mixtures similar hazard warnings to 6:2 FTS existed (see below). Others had additional classifications of concern, such as suspected harm to the unborn child or aquatic toxicity. Of particular interest were the two mixtures for which no information on the substances contained in the safety data sheet was given. Accordingly, they do not contain any substances classified as hazardous and used in concentrations above 1% in the mixture.

Short portfolio fiche of the polyfluorinated mist suppressant 6:2 FTS

For the preparation of the 6:2 FTS short portfolio fiche, data from nine different suppliers who sell ten 6:2 FTS-containing mist suppressants on the German market were taken into account. One supplier launched two almost identical mist suppressants with different names and only minor differences in concentration onto the market. The 6:2 FTS concentrations in the mist suppressants are between 1% and 10% and usually between 1% and 3%.

6:2 FTS is registered under REACH and has been on the market for decades. For substances registered under REACH, the information in the suppliers' safety data sheets (SDS) must match the information in the registration dossier. This also applies to mixtures containing substances hazardous to health in concentrations of more than 1%. A "summary short portfolio fiche for 6:2 FTS" has been created from the information in all safety data sheets (SDS), which, among other things, addresses the differences between the individual SDS. As the information in the safety data sheets for 6:2 FTS may not completely correspond to the current information in the corresponding registration dossier (REACH registration dossier 2019) due to the earlier date of preparation, the missing information in the SDS as well as differing information in the registration dossier were listed additionally.

According to the current state of knowledge, 6:2 FTS-containing mist suppressants must be labelled with the hazard symbols GHS05, GHS07 and GHS08.

Properties of 6:2 fluorotelomer sulphonic acid:

Behaviour in the process:
Polyfluorinated compounds such as 6:2 FTS are less stable than perfluorinated compounds, such as PFOS, under the strongly oxidizing conditions in process solutions containing chromium(VI). In order to achieve or maintain the same reduction in surface tension, a significantly higher

amount of 6:2 FTS must be dosed compared to PFOS. The additional consumption is 2 - 5 times higher, depending on the application. Compared to PFOS, this generally leads to higher emissions of 6:2 FTS or their degradation products into the environment.

The current knowledge on 6:2 FTS was compiled in a literature study:

Degradation of 6:2 FTS in the environment: No degradation of 6:2 FTS occurred in anaerobic sewage sludge and anaerobic river sediments. In aerobic sediments, however, there was a rapid degradation of 6:2 FTS, with a half-life of less than 5 days. Also the single measurement of the 6:2 FTS elimination in a wastewater treatment plant, which was carried out in the context of this project, indicates a faster aerobic degradation.

6:2 FTS shows no bioaccumulation in the microbial systems, fish and mammals investigated so far. A certain bioaccumulation is observed in invertebrates. The primary final degradation products of 6:2 FTS in the environment are PFBA, PFPeA and PFHxA, and to a lesser extent PFHpA. No degradation of these short-chain perfluorinated substances is known in the environment (soil or water). At the same time, these substances are very mobile in the environment. It is currently being examined whether short-chain perfluorinated substances and their precursor compounds (such as 6:2 FTS) should be regulated as "Substances of Very High Concern" (SVHCs) under REACH.

Detection of 6:2 FTS in the environment: The 6:2 FTS released into the environment does not originate solely from technical products that specifically contain 6:2 FTS. The second major source is 6:2 FTS precursor compounds from which 6:2 FTS are formed by degradation. These 6:2 FTS precursor compounds are also used, for example, in fire-fighting foams. Environmental media (drinking water, groundwater, river water, sediment, soil) contaminated by fire-fighting exercises or the fluorochemical industry sometimes contained high 6:2 FTS concentrations.

From landfills, PFAS can escape with the leachate and enter water bodies. In 6 of 20 sampled landfills in Germany, 6:2 FTS were found in concentrations up to 75 ng/l in the landfill leachate.

Industrial and municipal wastewater treatment plants are important point sources of water-soluble or volatile PFAS. 6:2 FTS was found in samples from 5 of 6 wastewater treatment plants in Germany. Due to the degradation of fluorinated precursor compounds in the wastewater treatment plant, the concentration of persistent short-chain perfluorinated carboxylic and sulphonic acids, and in some cases the concentration of 6:2 FTS, may be higher in the wastewater treatment plant effluent than in the influent. In previous PFAS measurements in sludge from six European wastewater treatment plants, the concentration of 6:2 FTS was the second highest (up to 80 ng/g) after PFOS. With the current treatment of wastewater, FTS cannot be completely removed. By discharging "treated" wastewater into surface waters, FTS can enter the environment and degrade into persistent short-chain perfluoroalkyl acids (PFAAs). In the treatment of contaminated river water to drinking water, it was found that FTS and short-chain PFAAs could not be removed from the water by sand filtration systems and could hardly be removed by activated carbon.

Uptake of 6:2 FTS and degradation compounds in plants: Plants and animals take up 6:2 FTS via the environmental media. Short-chain PAS can accumulate strongly in leafy vegetables and fruits. Water, soil and plants were analysed for 26 PFCs on a site contaminated with fire extinguishing foams at Stockholm Airport. While PFOS had the highest proportion (about 50%) in soil and groundwater, plants mainly contained 6:2 FTS (about 50%), as well as short-chain PFAAs, especially PFPeA (about 24%). It was shown that different plant species and plant parts accumulate PFAS to different degrees. The relative proportion of 6:2 FTS was higher in the branches than in the foliage.

Ecotoxicity: According to studies by the chemical company DuPont de Nemours, PFOS is 10 times more effective than 6:2 FTS in terms of acute toxicity. Other authors, however, concluded that the acute toxicity of 6:2 FTE on aquatic organisms is of the same order of magnitude as that for PFOS and PFOA. With regard to chronic toxicity to aquatic organisms, it is noted that, although concentrations of fluoro-teleomer acids in aquatic systems are low, these substances are continuously introduced into aquatic ecosystems and may accumulate there. Aquatic organisms may be exposed to these substances throughout their lifetime. Chronic effects may occur at lower threshold levels.

Concentrations in human blood: When blood serum samples from the USA and Hong Kong were examined, the 6:2 FTS concentrations were two orders of magnitude lower than those of PFOS. In blood samples from Hong Kong, 6:2 FTS concentrations were lower than in the USA.

Deficits of previous toxicological studies and legal regulations: Experimental and epidemiological data show damage to the immune system at low levels of various PFAS. It is also known that damage to brain development in the womb is one of the most sensitive endpoints of many pollutants. The REACH registration dossier so far does not include testing of 6:2 FTS for immune, nervous or endocrine system disorders or for carcinogenic effects. 6:2 FTS is also a precursor compound of short-chain persistent PFAS and various intermediates. These should also be included in the risk assessment, as short-chain PFAS have properties of concern.

Reduction and treatment measures for PFAS in the surveyed electroplating plants

80% of the facilities surveyed stated that they were implementing measures to reduce PFAS emissions via wastewater. 6.7% of the facilities answered "no", 13.3% made no statements. The most frequently mentioned measures were production-integrated measures aimed at the economical dosing of mist suppressants or chromic acid and thus also mist suppressant recovery.

36.7% of the facilities surveyed used adsorption systems based on ion exchangers or activated carbon to reduce emissions of PFAS in the wastewater path. However, the majority of the facilities did not know the concentration of the mist suppressants used in their wastewater.

Fate of the fluorinated mist suppressants used

The remaining of the fluorinated mist suppressants used was analysed in two plants.

Fate of 6:2 FTS: At a company that had already replaced PFOS in the decorative chromium plating of metal parts with 6:2 FTS since 2010, the analytical tracking of the polyfluorinated mist suppressant used was carried out from production via the downstream municipal sewage treatment plant to the water. The wastewater and sludge samples (weekly mixed samples) were analysed by an accredited laboratory for the sum of the currently common 20 PFAS (incl. 6:2 FTS).

The 6:2 FTS containing wastewater substream was treated via three ion exchange columns for separation of 6:2 FTS. The measurement results show over an investigation period of 1.5 years that the PFAS ion exchangers function reliably. They permanently and safely remove both 6:2 FTS and the PFOS that is still "bleeding out" after 9 years from the treated electroplating wastewater substream to concentrations < 5 µg/l (determination limit). No other PFAS were found in the electroplating wastewater. The loaded ion exchange resins were fed to the high-temperature incinerator and the PFAS were finally destroyed.

In the course of the investigation, 6:2 FTS were found not only in the wastewater partial stream known to contain 6:2 FTS, but also in other partial streams of the electroplating plant, which were considered 6:2 FTS-free until the investigation. As hidden mist suppressant sources, an ultrasonic degreasing solution with 2300 µg /l 6:2 FTS and a demetallisation solution with 1900 µg /l 6:2 FTS could be found. Ad- and desorption processes on the plastic-coated plating racks are assumed to be the cause of this.

Only approx. 6.2 % of the inlet load of 6:2 FTS was removed from the treated electroplating wastewater by metal hydroxide precipitation in the company's own waste water treatment plant.

The PFAS load derived from the electroplating plant investigated was quantitatively recovered in the inflow of the downstream municipal wastewater treatment plant, for which no other 6:2 FTS sources were known. According to the single measurement, approx. 89.1% of the inflow load was withdrawn from the wastewater in the municipal sewage treatment plant in relation to 6:2 FTS. This may be due to the fact that this is a long-term adapted sewage treatment plant whose biology has adapted particularly well to the regularly inflowing 6:2 FTS load.

Note: Only about 75% of the 6:2 FTS freight used in the raw wastewater of the electroplating plant could be recovered. The report presents possible reasons for this deficit, which, however, could not be clarified within the scope of the study.

Conclusion: Due to the above-mentioned carry-over of the 6:2 FTS in the electroplating machine, it must be assumed that a pure substream treatment of the chromium(VI)-containing wastewater substream to 6:2 FTS is not sufficient. It is therefore recommended to treat the total wastewater flow of an electroplating plant at 6:2 FTS. For a possible determination of a limit value, the determination of a monitoring value for PFOS/PFAS in part D of annex 40 of the Waste Water Ordinance would therefore be preferable.

Fate of PFOS: As there are currently no more known electroplating plants in Germany that still use PFOS, the remaining of PFOS were determined on the basis of an investigation into the electroplating of plastics, which IUW Integrierte Umweltberatung had already carried out in 2008 on behalf of the Thuringian Ministry of Agriculture, Nature Conservation and the Environment. Since the company already had a process technology with chromic acid cycles that minimized material losses, the annual consumption of PFOS was only about 3.5 kg.

In the raw wastewater of the electroplating plant investigated, 496 µg/l PFOS were detected in the monthly mixed sample. In the same period of time, a monthly mixed sample of the wastewater treated exclusively by means of metal hydroxide precipitation yielded 50.1 µg/l PFOS after mixing with other waste water partial streams of the electroplating plant. No adsorption step for PFOS was used yet. The proportion of PFOS load removed from the wastewater by adsorption processes to the metal hydroxide sludge is unknown because sludge analyses were not considered at that time.

Since the agricultural use of the sludge from the downstream municipal sewage treatment plant was no longer possible due to its high PFOS content, the two-stage activated carbon adsorption plant recommended in the above-mentioned study was installed in the wastewater substream. For the operation of the adsorption plant, the PFOS-containing wastewater substreams were separated and, after chromium(VI) reduction, passed through a 2-column plant in the effluent via a specially selected activated carbon (suitable ion exchangers were not yet known at that time). Initially, PFOS residual concentrations of < 10 µg/l could be reliably maintained in the wastewater except for individual outliers. Finally, PFOS concentrations well below 10 µg/l up to the analytical determination limit (1 µg/l) could be determined over longer operating phases.

New processes for fluorine-free chromium plating and plastic etching

The alternative methods are differentiated into PFOS substitution:

1. by using other fluorine-containing or fluorine-free mist suppressants in the same processes
2. by using other wet-chemical processes (e.g. chromium(VI)-free process solutions)
3. by using technological alternatives (e.g. use of other physical processes)

The use of other fluorine-containing or fluorine-free mist suppressants has already been described.

Wet chemical PFOS substitution in decorative chromium plating by Chromium III process

The advantages and disadvantages of the chromium(III) process compared to conventional decorative chromium plating on chromium(VI) basis are presented and commented on in detail. A short summary is given in the following table:

Process parameters	Chromium(III) electrolyte	Chromium(VI) electrolyte
Use of PFOS / PFAS	not required	predominantly required
Anodes	iridium-tantalum mixed oxide anodes, expensive, non-toxic, longer service life when used correctly	lead anodes, cheap, toxic. substitution requirement, service life 2-3 years
Anode sludge / disposal	there is no anode sludge formation	leaded anode sludge must be disposed of
Chromic acid content	0 g/l	180 – 300 g/l
Boric acid content	approx. 50 g/l	0 -2 g/l
Electrolyte additives	4-8	2-3
Analytical requirements	complex and personnel-intensive	little complex and little personnel-intensive
Corrosiveness and toxicity of the electrolytes	low	high
Electrolyte composition	complex, maintenance-intensive	simple, robust
Power interruption	no problems	problems due to formation of passivation layer
Requirements for mist suppressants and extraction	moderate and usual in electroplating plants	very high
Hydrogen generation / explosion protection requirements	moderate and usual in electroplating plants	very high
Requirements for occupational safety	moderate and usual in electroplating plants	very high
Power consumption for chromium deposition	moderate	high
Bath circulation/filtration	required	not required
Sensitivity to enrichment of foreign metals	very high, from approx. 10 mg/l	low, from approx. 3 g/l

Process parameters	Chromium(III) electrolyte	Chromium(VI) electrolyte
Foreign metal removal by ion exchange	continuously required	mostly only required for electrolyte return and evaporator (= closed circuit)
Waste water treatment	mostly complex splitting and heavy metal precipitation	chemical reduction and heavy metal precipitation
Authorization according to REACH	not required	required
Seveso III-relevant	no	yes
Market acceptance	increasing	decreasing

The original problems with colour deviations and "yellowish" chromium surfaces deposited from chromium(III) electrolytes have now been largely solved. In the waste water treatment of rinsing water, problems with complexing agents occur in individual cases when the heavy metal limits are observed.

Wet chemical PFOS substitution in functional chromium plating

Unlike in other European countries, functional chromium-plating on a chromium III basis has not yet become established in Germany for quality reasons.

In various applications, hard chromium coatings can be replaced by nickel-based coatings. The coating of complex geometries is possible. The following have become established:

- Electroless nickel with embedded hard material particles (dispersion layers) in the textile machine industry and in mechanical engineering.
- Electroless nickel layers with embedded phosphorus or nanoparticles in the automotive and electrical industries and in mechanical engineering. However, the hardness of hard chromium layers can only be achieved by heat treatment, which is not always possible.
- Nickel alloy deposition (NiL35) with combination layer of two alloys of the metals copper, tin and nickel. This is a salt resistant coating. It is therefore used in wind power off-shore plants and hydraulic cylinders of harbour cranes.
- Nickel-tungsten alloy deposition (possibly with finely dispersed diamond-carbon inclusions) Due to the high cost of tungsten, this has so far been a niche technology.

  Nickel-based processes can generally cause problems in wastewater treatment due to the complexing agents they contain. These processes are not suitable for the food and pharmaceutical industries due to possible nickel emissions from the surfaces.

Functional chromium plating from ionic liquids:

> The hard chromium layers are deposited from anhydrous ionic liquids based on chromium(III) salts. The process is still undergoing research and development.

Functional chromium plating in closed reactors under negative pressure:

> In this so-called "chemistry-to-part" technology, the chromium electrolyte and the rinse water (triple cascade) are pumped from the respective storage tanks into a closed reactor. The process therefore works with low exhaust air and waste water and has been industrially tested for years. Due to the closed reactor technology, the use of mist suppressants can be completely avoided.

Applications: Pressure rollers, pipes, injection nozzles, inlet and outlet valves, components for brake cylinders and shock absorbers

Limits of the process: Since hydrogen and oxygen are also released during chromium plating in closed reactors, special attention must be paid to explosion protection in this process technology. For small reactors, the process is designed for high volumes due to the high degree of automation. For large reactors, several storeys may be necessary.

Wet-chemical PFOS substitution in the plastic etching by the use of other oxidizing agents

There are processes primarily for the activation of acrylonitrile-butadiene-styrene (ABS) based on:

- potassium permanganate and phosphoric acid
- manganese(III) and sulphuric acid
- microporous foaming with strong acids

The processes are being researched on an industrial scale in pilot plants, but they have not yet been established on a large scale. The German association of electroplated plastics (FGK; Fachverband Galvanisierte Kunststoffe) has the goal of achieving chromium(VI)-free electroplating of plastics by 2024.

Since all the above-mentioned alternative processes continue to work with strong acids and oxidizing agents in an aqueous environment, it can be assumed that oxidation-resistant, probably fluorinated, mist suppressants will continue to have to be used.

Substitution of PFOS by using technological alternatives to wet chemical chromium plating

High velocity oxygen fuel (HVOF) process

A now widely used process to replace functional chromium plating is high-speed flame spraying. In this process, metal powder mixtures are applied in a burning gas jet at supersonic speed. For example, tungsten carbide and chromium carbide are used in a cobalt or nickel/chromium matrix to replace hard chromium. The HVOF process has already been used by 450 facilities in Germany in 2019, although the proportion replacing functional chromium plating is unknown. The areas of application are largely the same as for functional chromium plating.

The HVOF process can be used for coating rotationally symmetrical or flat components. Internal coatings are possible up to a diameter of 100 mm. It is not suitable for complex geometries, for workpieces with undercuts and for internal coatings. Disadvantages of the process are the required sound insulation and the sometimes complex preparation of the components. If the process parameters are not kept within the optimum range during the high-temperature flame spraying of chromium, the formation of chromium(VI) compounds is possible in combination with atmospheric oxygen. If the HVOF technique is used correctly, however, chromium(VI) formation can be avoided.

Physical Vapour Deposition (PVD)

In physical vapour deposition, the starting material is converted into the gas phase in a vacuum by means of physical processes by evaporation or from solids atomically, e.g. by laser bombardment. It then separates again, often accelerated by electrical fields, as a stream of particles at 160 - 500°C on the colder workpiece by condensation. In order to coat all surfaces as homogeneously as possible, the workpieces must be set in rotation during the coating process.

Today, hard material coatings based on titanium nitride (TiN), titanium carbonitride (TiCN), titanium aluminium nitrite (TiAlN) or diamond (DLC) are mainly used as coatings. For die-cast parts made of aluminium and magnesium, chromium-based coating systems such as chromium nitride (CrN), chromium vanadium nitride (CrVN) and chromium aluminium nitride (CrAlN) are mainly used.

The areas of application are largely identical to those of functional chromium plating. In the aerospace industry, experts estimate that functional chromium plating will very likely be displaced in the long term by the industry leader with the increasing use of PVD coatings.

Due to its application in vacuum chambers, the limits of the process are the size of the components and the required relatively high hardness of the base materials. In addition, narrow, deep internal bores cannot be coated economically. This limits the areas of application.

Plasma Nitriding

Plasma nitriding works with a nitrogen-hydrogen mixture which is ionised in a closed vacuum furnace at negative pressure by applying a voltage between the container wall and the charge. The ionized gas atmosphere diffuses into the peripheral zone of the metal components, increasing the surface hardness and improving the corrosion behaviour of castings and low- to high-alloy steels. The surface temperatures are 350 - 600 °C.

Applications include transmissions, crankshafts, camshafts, cam followers, valve components, extruder screws, forging dies, tools for cold forming, injection nozzles, plastic injection tools, long shafts, axles, clutches and engine parts. In the field of automotive tools, plasma nitriding has already completely replaced the hard chromium process for some manufacturers.

Extreme high speed laser metal deposition (LMD)

Extreme high-speed laser deposition welding is a further development of laser metal deposition (LMD). In laser deposition welding, metal powder is applied to the surface of a base material and melted by laser. In the EHLA process, the powdered filler material already hits the laser light above the melting bath, which heats it up to close to the melting point on its way to the component.

Depending on the requirements for the wear layer, tungsten carbide, titanium and chromium carbides, but also iron, nickel and cobalt-based powders are used. The deposition rate is up to 1000 cm^2/min, coating thicknesses are 10-250 µm and the feed rate is >100 m/min.

Possible applications: Brake discs, valves, piston rings, shafts in the automotive industry; metering rollers, printing cylinders, plate cylinders in the printing industry; hydraulic cylinders, rollers, pistons, rods in mechanical engineering. The process is more economical for brake discs than hard chromium plating.

Limits of the process: The process can only be used for rotationally symmetrical workpieces. Complex geometries and workpieces with undercuts, blind holes, etc. cannot be coated. To be an alternative to hard chromium, productivity, process stability and automation must be further optimized.

Sulfonation of plastics with sulphur trioxide in the gas phase

In the conditioning of plastics prior to electroplating, chromium(VI) can be replaced by gas phase activation with sulphur trioxide (sulfonation) at room temperature in the area of special plastics in niche applications. This process completely dispenses with the use of PFAS.

Work is currently underway to extend the application of the process to ABS plastics, which currently account for around 90% of the total quantity of metallized plastic.

Plasma etching as an alternative etching process for the pretreatment of ABS plastics

This purely physical process for etching and activating ABS in an oxygen plasma and then removing the etching products with caustic soda solution dispenses completely with the use of hazardous or toxic chemicals.

The limitations of the process are the slower throughput rates compared to the previous chromic acid-based etching process, the investment costs for the closed reactors and the additional space required.

The innovative process was first presented in 2018 and is currently still in the development stage.

Outlook:

PFOS has mainly been substituted by 6:2 FTS in the electroplating process. The remaining of this substance could not be determined quantitatively in the plant investigated, as only about 75% of the quantity used was found in the raw wastewater. Further research is needed here.

1 Introduction

Perfluorooctane sulfonate (PFOS) is an anthropogenic, synthetic substance and does not occur naturally in the environment. PFOS is classified under chemical law as a persistent organic pollutant (POP). It is also bioaccumulative and toxic to mammals. It has been produced since the 1950s and used in electroplating plants in Germany since the 1970s at the latest.

After PFOS was detected in humans and other living organisms worldwide, the U.S. company 3M, which was the world's largest PFOS producer at the time, decided in 2000 to voluntarily phase out the production and use of PFOS by the end of 2002. This business decision caused a significant decrease in the use of PFOS in the EU. In China, however, production volumes initially increased as a result (UBA documents 85/2014), at least until 2014.

There were approximately 2,500 electroplating plants in Germany in 2010. According to Lanxess, the only remaining PFOS producer in Germany at that time, approx. 3,000 kg of PFOS, measured as pure substance, were marketed to German electroplating plants in 2010 via distributors and formulators - especially in galvanic hard and bright chromium plating. In 2011, the ZVO estimated that about 50% of the PFOS amount was used in hard chromium plating, the rest in bright chromium plating, and in plastic etching solutions (UBA documents 85/2014).

The European POP Regulation (EC) no. 850/2004 (EU POP Regulation)[1] on persistent organic pollutants serves to implement the Stockholm Convention and resulted in a ban on the production, marketing and use of perfluorooctane sulphonic acid (PFOS).

The EU POPs Regulation originally recognises the following exemptions from the ban on PFOS for individual uses in surface coating:

- until 26th August 2015: mist suppressants for monitored electroplating systems;
- Spray suppression agents for non-decorative hard chromium plating (chromium VI) in closed loop systems.

Now that the former exemption has expired, only the exemption for the use of PFOS for non-decorative hard chromium plating (chromium VI) in closed loop systems applies.

The Regulation also provides that the use of PFOS will be phased out as soon as the use of safer alternatives is technically and economically feasible. The need for the exemptions will be reviewed at regular intervals.

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[1] Regulation (EC) No. 850/2004 of the European Parliament and of the Council of 29th April 2004 on persistent organic pollutants and amending Directive 79/117/EEC, last amended by Article 1 of the Regulation of 30th March 2016

2 Objective and background

Due to the restriction in use by the European POP regulation, an extensive substitution of PFOS in mist suppressants has taken place in Germany. Today, to the knowledge of the Federal Environment Agency, short-chain polyfluorinated compounds are often used, which are often not precisely known to users and authorities. The most common substitute for PFOS in electroplating in Germany is 1H,1H,2H,2H-perflouroctane sulfonate (6:2 fluorotelomer sulfonate, 6:2 FTS).

Until now, not much was known about the type and amount of polyfluorinated mist suppressants (PFOS alternatives) used. Similarly, there is little knowledge about the potential treatment and mitigation options for these compounds, so it can be assumed that organic fluorine compounds are entering the receiving waters via the wastewater.

This research report provides an overview of facilities operating in Germany for the chromium plating of metals and plastics and for the etching of plastics. The aim was to determine which plants use fluorinated mist suppressants, which fluorine compounds they contain, and how these compounds can be mitigated in the process itself and in wastewater treatment. Existing surface coating processes and those under development that do not use either chromium(VI) or fluorinated mist suppressants at all should also be taken into consideration and any obstacles to their use identified.

3 Methodological approach and determinations

The characterisation of the surface treatment industry, the industry overview and the description of methods, plants and processes are based on the results of the literature research described below and the interviews conducted, as well as on the experiences of IUW Integrierte Umweltberatung. To determine the annual use of mist suppressants in the chromium(VI) sector of the surface treatment industry, 130 mist suppressant users were interviewed by means of a questionnaire and the results were evaluated.

To investigate the fate of the mist suppressants used in production and wastewater treatment, samples of process solutions, waste water and sludge were taken on site after consultation with the operators. The analytical investigation was carried out by an accredited laboratory.

A literature research of scientific studies and journals was conducted for this study. Legal texts and current publications of associations and information from the electroplating industry were evaluated. In addition, relevant stakeholders were contacted and interviews were conducted. The contractor used the following keywords for the Internet research for the individual work steps. For this purpose, see the table below.

Table 1: Keywords for internet research

German keywords	English keywords
Verchromung • Hartverchromung • Funktionelles Verchromen • Glanzverchromung • Kunststoffgalvanisierung	**Chromium plating** • Hard chromium plating/hard chromium plating • Functional chromium plating • Bright chromium • Plating on plastics (POP), electroplating of plastics
Netzmittel • PFOS Galvanik • Netzmittel für Chrombäder • Netzmittelfrei • Chrom VI • Antischleiermittel, Mittel zur Sprühnebelunterdrückung	**Wetting agents** • PFOS metal plating • Wetting agent for chromium baths • Free of wetting agents • Chromium VI • Mist suppressant / fume suppressant
Substitute / Ersatzstoffe • PFOS-freies/ PFOS-frei / ohne PFOS • Substitute • Ersatzstoffe • Adsorption • Absorption • Verfahrenstechnik	**Substitutes / Alternatives** • PFOS free • Substitutes • Alternatives • Adsorption • Absorption • Process technology

The following databases, platforms, and journals were evaluated for the research:

- Google Scholar + advanced Google search
- REACH-CLP Helpdesk of the Federal Institute for Occupational Safety and Health (BauA)
- Elsevier
- Plasma + Oberfläche
- “Umwelttechnik” journal

- "Galvanotechnik" journal
- Leuze Publishing House
- Zentralverband Oberflächentechnik e.V. (ZVO)
- Springer professional
- Stockholm Convention / UNEP / EU POP VO / ECHA

The study was processed in the following work steps (3.1 - 3.3):

3.1 Industry overview through description of procedures, plants and processes

Per- and polyfluoroalkyl substances (PFAS) are organic compounds, in which the hydrogen atoms on the carbon skeleton of at least one carbon atom have been completely replaced by fluorine atoms (OECD 2018). This chapter describes in more detail the methods, facilities, and processes in which PFAS are used in the surface treatment industry. The processes involved are as follows:

- Hard chromium plating or functional chromium plating
- Bright chromium plating or decorative chromium plating
- Plastic etching and decorative chromium plating of plastics

At the end of the industry overview, the potential increase in the incident potential of surface treatment industry operations when converting from chromium(VI) to chromium(III) is discussed.

3.2 Determination of mist suppressant use and mist suppressant emissions

First, a screening of possible substitutes was carried out on the basis of existing literature, current technical lectures, as well as UBA documents 63/2016 "Use of PFOS in electroplating - characteristics of a closed loop, use of substitutes (Blepp, Willand, Weber 2016)". Suitable studies and information for this final report are listed in the bibliography and list of sources (see Chapter 7). The findings and information obtained were supplemented with the help of interviews with experts and checked for topicality in order to develop a meaningful set of questions.

The specific use of mist suppressants in the processes described in section 4.2 was determined by surveying the facilities in the surface treatment industry. For this purpose, a questionnaire was developed in consultation with the German Federal Environment Agency (UBA) and sent to a representative number of facilities.

On the basis of the information provided, a projection was made of mist suppressant consumption in Germany.

In addition, the fate of the mist suppressants used was examined in more detail using two facilities as examples, and the results were presented.

3.3 New processes for fluorine-free chromium plating and plastic etching

Chapter 6 describes the latest state of development of processes for fluorine-free chromium plating and plastic etching and the status of physical processes that do not require the use of fluorinated mist suppressants.

First, the substitution of PFOS by flour-containing and fluorine-free mist suppressants is discussed.

In a second step, the substitution of PFOS by using modified wet-chemical processes is highlighted.

Specifically, these are:

- Chromium III process in decorative chromium plating and functional chromium plating
- Wet-chemical alternatives to nickel-based functional chromium coatings:
  - Nickel-tungsten alloy deposition
  - Electroless nickel with dispersion layers
  - Electroless nickel coatings with embedded phosphorus or nanoparticles
  - Nickel alloy deposits
  - Hard chromium plating from ionic liquids
- Alternatives to plastic etching with chromium (VI)
  - Plastic etching with potassium permanganate
  - Plastic etching with manganese (III) base
  - ABS plastic activation by a combination of chemical and physical processes

Finally, the substitution of PFOS by using technological alternatives to the wet-chemical chromium plating of metals and plastics is discussed:

- Functional chromium plating in a closed reactor at negative pressure
- Thermal spraying (high velocity flame spraying; HVOF process)
- Physical vapor deposition, known as PVD
- Plasma Nitriding
- Laser deposition welding (LMD) and extreme high-speed laser deposition welding (EHLA)
- Sulfonation of plastics with sulphur trioxide in the gas phase
- Plasma etching as an alternative etching process for the pretreatment of ABS plastics

4 Characterisation of the surface treatment industry

4.1 Reasons for the use of PFOS and PFAS in surface treatment

The surface treatment industry in Germany is very diversified and uses a large number of different physico-chemical processes. This study only takes that part of the industry into consideration which has continued to use PFOS for the surface treatment of metals and plastics in recent years and now predominantly uses alternatives.

Following the general ban on the use of PFOS by the POP Regulation since 2010, PFOS has only been continued to be used in three areas of application in the surface treatment industry:

- Functional chromium plating (hard chromium plating)
- Decorative chromium plating (especially bright chromium plating)
- Plastic etching and chromium plating

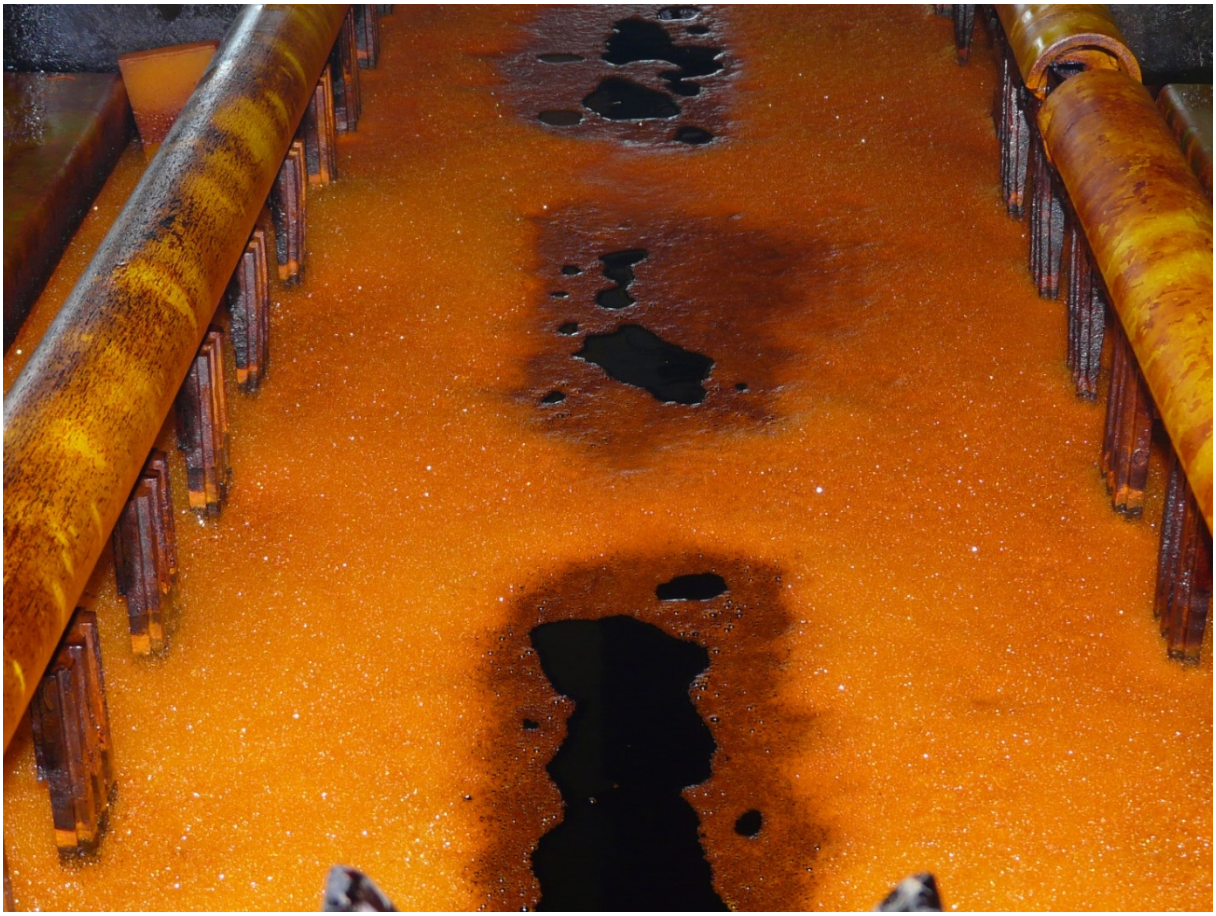
PFOS is used because of its high chemical stability (resistance) to the strong oxidising agent chromium(VI) and to sulphuric acid/chromosulphuric acid at elevated temperatures. It is used in electroplating systems for the purpose of reducing the surface tension of the process solutions in which the workpieces to be processed are immersed. This achieves the following objectives:

4.1.1 Reduction of chromium VI aerosol formation

The use of PFOS in chromium electrolytes reduces the formation of toxic chromium(VI) aerosols over the process solutions, which are formed by outgassing of hydrogen and oxygen on the electrodes. It thus makes an important contribution to occupational safety in electroplating plants as a “mist suppressant" or “fume suppressant". In English-language publications, it is therefore also referred to as a "chromium mist suppressant (CMS).

Due to physical reasons, the efficiency of classic chromium plating is only about 20%, although it is somewhat higher for modern electrolytes. This means that up to 80% of the current used is lost through oxyhydrogen formation or in the form of heat. The oxygen and hydrogen bubbles formed at the anode and cathode burst as they escape from the surface of the liquid and carry away chromic acid droplets. The resulting chromic acid aerosols are toxic and have a strong corrosive effect on the environment. When mist suppressants are used, a closed blanket of foam of oxyhydrogen can form, which can naturally lead to deflagration if an ignition source is present.

Figure1: PFAS-containing foam blanket made of oxyhydrogen during decorative chromium plating



Source: IUW Integrierte Umweltberatung

The higher the surface tension to be overcome at the surface of the electrolyte, the higher the kinetic energy of the droplets. For this reason, the surface tension of the chromium electrolyte is reduced as far as possible (to as low as 22 mN/m) in the chromium plating processes by the use of mist suppressants. Although this does not completely prevent the formation of chromic acid aerosols, it does greatly reduce them. As a more recent development, there are polyfluorinated mist suppressant mixtures that significantly reduce the formation of aerosols even without the formation of a closed foam blanket.

Due to the partial carry-over of PFOS into the subsequent sinks, PFOS must be regularly re-dosed. The exact PFOS quantity for subsequent dosing can be determined e.g. by measuring the surface tension or after determination by test series according to ampere hours.

Historically, chromic acid fumes were suppressed as early as 1936 by applying a 1-2 cm thick top layer of a water-immiscible oil such as fish oil, spermaceti oil, cottonseed oil or petroleum (name: Chromprotekt) (Atterer et al. 1962). It was not until the 1970s that PFOS was increasingly used to reduce chromic acid aerosols.

4.1.2 Improvement of the wetting properties

Particularly in chromium(VI)-containing plastic etching, good wettability of the plastic workpieces to be processed must be achieved in order to improve the chemical attack of the chromosulphuric acid on the hydrophobic plastic surface. For this purpose, the surface tension of the chromium(VI)-containing plastic etching is reduced by PFOS or other mist suppressants. It is possible that the need to use perfluorinated or polyfluorinated mist suppressants in the aqueous plastic etching will basically exist even if chromium(VI) is replaced by other strong oxidising agents, such as potassium permanganate.

4.1.3 Reduction of carry-over and quality improvement

The use of PFOS or other mist suppressants reduces the surface tension of the process solutions containing chromium VI. This improves the drainage behaviour of the process solution from the coated surface and results in faster dripping of the chromium(VI)-containing process solution. This reduces the carry-over to the following sinks. The complete removal of these process solutions from the surface is a prerequisite for producing marketable chromium(VI)-free products. In addition, the deposited surfaces are formed more uniformly, which contributes to an improvement in the quality.

4.1.4 Advantages of PFOS and PFAS over other mist suppressants

Under the chemically extremely aggressive or oxidising conditions of process solutions containing chromic acid, non-fluorinated, more biodegradable mist suppressants are rapidly decomposed. PFOS does not form degradation products in the process solutions (sludge or floating oily degradation products) that can lead to degradation of the quality of the workpiece surfaces.

"The downside of the extreme chemical resistance of PFOS is the fact that it is also virtually indestructible in the cycles of nature. It therefore accumulates in living organisms in the food chain and reaches the top of the food chain back to its originator: humans (Blepp, Willand, Weber 2016)."

Before the general ban on the use of PFOS by the EU POP Regulation, PFOS was used in the electroplating industry in Germany in hard and bright chromium electrolytes, in plastic etching containing chromic acid, in alkaline zinc and zinc alloy electrolytes, in precious metal deposition, e.g. in strongly acidic gold, palladium and rhodium baths, and in externally electroless nickel dispersion coating.

As early as 2006, the use of PFOS-free surfactants in anodising aluminium was described as a best available technique (BAT) in the Best Available Techniques (BAT) data sheet for surface treatment of metals and plastics (EIPPC BREF STM 2006)[2].

Even after the general ban on the use of PFOS by the POP Regulation in Germany, PFAS continue to be used as mist suppressants for wet chemical processes in surface treatment.

In some applications, PFOS has been almost completely substituted by 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid, also known as 1H,1H,2H,2H-perfluorooctane sulfonate or 6:2 fluorotelomer sulphonic acid (6:2 FTS). On the reasons for using PFOS or 6:2 FTS, Dr. Wolfgang Podesta writes:

"Due to their unique structure, the compounds have both hydrophobic and lipophobic properties and can lower the surface tension at least twice as much as analogous molecules with pure C-H bonds because of the high polarity of the C-F bond: for instance, $C_8H_{17}SO_3Na$ exhibits a surface tension of 65 mN/m in water, while $C_8F_{17}SO_3Na$ exhibits a value of 32 mN/m at the same concentration. In addition, perfluorinated compounds such as PFOS and PFOA are significantly

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[2] Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, Chapter 5.2.5.2

more stable than polyfluorinated or fluorine-free compounds, where the weaker C-H bond (413kJ/mol) acts as a “predetermined breaking point", due to the exceptional strength of the C-F bond (490 kJ/mol) (Podesta 2014)."

4.1.5 Restrictions on the use of fluorine-free mist suppressants in process solutions containing chromium(VI).

Replacing PFOS and PFAS in electroplating with fluorine-free, biodegradable mist suppressants would solve the problem of emissions of persistent perfluorinated and polyfluorinated compounds from this industry into the environment. So far, such trials have demonstrated positive results only in the decorative chromium plating field. In plastic etching and functional chromium plating, only individual testing facilities exist to date. According to current knowledge, the mist suppressant mixtures used are mainly based on mixtures of "conventional", non-fluorinated surfactants.

The possibilities for using fluorine-free surfactants in the above-mentioned processes are limited by their instability in the strongly oxidising chromic acid solutions and the faults in the product quality due to the degradation products formed.

4.2 Plant inventory in Germany

It is characteristic of today's surface treatment industry in Germany that a large number of different physico-chemical processes are used. In the following, only those processes for the electrolytic chromium plating of metals and plastics or for the etching of plastics are described in which PFOS is or was used. In all these applications, chromium(VI) is or was simultaneously used. As a special case, the de-chromium plating of racks and defective batches is briefly discussed.

The respective process principles are described and differentiated. Possible applications and limitations of use of the processes are discussed.

Up to now, the number of chromium plating plants nationwide has never been completely recorded statistically. In order to obtain as comprehensive an overview as possible of the plants for chromium plating of metals and plastics and for etching of plastics in Germany, a multi-stage approach was planned.

In a first step, data from the Federal Institute for Occupational Safety and Health were used to identify the facilities using galvanic chromium plating processes in Germany. As part of its reporting obligations under EU Directive 2006/122/EC, the BAuA prepared surveys in 2009 on the existing stocks of PFOS-containing mist suppressants and wetting agents in electroplating plants. The result was an "Inventory on the use of PFOS as mist suppressants for non-decorative hard chromium plating (chromium VI) and wetting agents for monitored electroplating systems". Unfortunately, this inventory was not updated in the follow-up period.

In a second step, the updating of the data situation and the identification of companies that have since been newly established or renamed operators was carried out in cooperation with the industry association, Zentralverband Oberflächentechnik e.V. (ZVO), with which IUW Integrierte Umweltberatung has maintained contact. Naturally, however, the ZVO could only report on its currently approx. 125 member companies in this field. In addition, the experience of IUW Integrierte Umweltberatung and companies identified through internet research were used.

In a third step, the data generated by the REACH authorisation and notification processes were used. In accordance with the REACH regulations, chromium trioxide may no longer be used or placed on the market without a valid authorisation since 21st September 2017, the so-called "Sunset date". Companies that do not have an authorisation must, in principle, be notified within 3 months in accordance with Article 66 REACH. Notified companies that only formulate electroplating chemicals or use chromium(VI) differently than in the context described here were not considered.

At the beginning of the project, the following initial situation was assumed on the basis of research by IUW: In Germany, there are probably more than 1000 plants relevant for the project. The largest proportion of these are accounted for by decorative chromium plating plants (mainly bright chromium plating plants), followed by functional chromium plating plants (hard chromium plating plants). Plants for etching and chromium plating of plastics account for the smallest share, with well under 100 plants. This rough preliminary estimate was confirmed and refined by the information provided by the ZVO in the course of the project.

A complete and precise record of all plants, e.g. by means of a comprehensive questionnaire campaign with allocation of detailed criteria, such as plant size, mist suppressants used, mist suppressant consumption, etc., was realistically not considered to be expedient, if only because of the large number of plants and the incomplete response rate to be expected within the framework of this project. The ZVO also does not have a complete record of the above-mentioned plants.

Therefore, representative plant data for relevant plant types were collected according to the principle "pars pro toto". The questionnaire was agreed in advance with the German Federal Environment Agency as the client during the preliminary meeting for the project.

4.2.1 Functional chromium plating (hard chromium plating)

In galvanic chromium plating, elementary chromium is deposited electrolytically at the cathode from the hexavalent chromium in the electrolyte. Chromium behaves "nobly" due to the rapid formation of an oxide layer on the surface. This property results in the high resistance of hard chromium layers to most chemicals and chloride-induced corrosion. Different chromium bath types and process variants contribute to the improvement of corrosion protection. An additional increase in corrosion protection can be achieved through prior nickel plating.

The special structure of the hard chromium layer is responsible for its strength. The hardest chromium layers reach approximately the hardness of the mineral corundum and are thus harder than iron, cobalt and nickel and many nitrided or case-hardened steels. Vickers hardness without heat treatment is 800-1,100 HV. Because of the low treatment temperatures, no temperature-related distortion of the workpieces occurs during hard chromium plating. The coefficient of friction is very low. A hard chromium-plated surface does not tarnish even at higher temperatures and thus proves to be "optically" resistant and durable (ZVO 2017a)".

In functional chromium plating, which has so far mainly been referred to as hard chromium plating, the metal parts to be treated are electrolytically chromium plated at temperatures between 50 and 75°C in an aqueous solution of chromic acid and other acids.

Sulphuric acid electrolytes contain 250-500 g/l chromium trioxide (CrO_3). In standard sulphuric, chromium(VI)-containing hard chromium electrolytes, the anodes are usually made of lead or lead alloys. The efficiency of these electrolytes is about 18%.

Today, however, mixed-acid high-performance electrolytes are used most frequently. In addition to chromic acid in lower concentrations (240-260 g/l CrO_3), they usually contain methanesulphonic acid or methanedisulphonic acid, hydrofluoric acid, fluorides or silicofluorides, and are usually operated at temperatures of 53-57°C. Platinised titanium electrodes or mixed oxide electrodes are used in these hard chromium electrolytes. The efficiency of mixed acid electrolytes reaches a maximum of 28% (Lausmann and Unruh 2006).

PFOS is or was generally used in chromium plating electrolytes in a concentration range of 30-80 mg/l in order to reduce the surface tension of the process solution.

Steels, cast iron, aluminium, non-ferrous metals and their alloys are used as base materials. Hard chromium plating is usually preceded by mechanical surface treatment, such as grinding, polishing or blasting, and wet chemical pretreatment, such as degreasing and etching.

The thicknesses of the applied functional hard chromium coatings are usually between 10 µm and 100 µm. They can also be only approx. 2 µm for precision hard chromium plating or as thin as 5000 µm, e.g. for reparation hard chromium plating.

Oxidation of the resulting chromium III to chromium VI is possible in the hard chromium bath by selective use of a larger anode surface. Therefore, no diaphragm electrolysis, also known in the industry as "oxamate", is required as in plastic etching. In addition, some chromium VI hard chromium electrolytes require low concentrations of chromium III (order of magnitude 1-2 g/l) to work well. Higher concentrations lead to quality problems in the deposition of the chromium layers.

The previously used term "hard chromium plating" is increasingly being replaced by the more accurate term "functional chromium plating." "We speak of functional galvanic coatings when the coatings or combinations of coatings are intended to impart properties to the surface that the base material does not possess, but which are indispensable for the function of the part, to improve its functional behaviour, to optimise it or extend its service life. Functional galvanic coatings are of particular importance when different surface properties are required simultaneously or a specific combination is needed (Jenlink 2015)."

"The terms "functional chromium plating" and "functional chromium plating with a decorative character" seem to be more suitable for a distinction than the previously used terms of "decorative hard chromium plating" and "non-decorative hard chromium plating" (Blepp, Willand, Weber 2016)"

4.2.1.1 Properties of functional chromium coatings

Technical hard chromium coatings have some technologically high-grade properties and, above all, properties that are difficult to replace in their entirety:

- extreme hardness and wear resistance
- high adhesive strength on the base materials
- good abrasion resistance
- good tribological properties (low coefficient of friction, good lubrication, good wear resistance)
- high temperature resistance (up to approx. 400°C)
- high resistance to chemicals
- low wettability
- good corrosion resistance if the metal surface has been nickel-plated beforehand
- low treatment temperatures – and thus no distortion of the components

- hard chromium coatings are anti-adhesive – and are therefore easy to clean
- wide coating thickness minimum and maximum
- easily decoatable, e.g. for repairs
- decorative
- toxicological harmlessness - therefore the use in pharmaceutical, medical technology and food industry is possible.

These technologically high-quality properties are difficult to replace, especially in their entirety.

4.2.1.2 Areas of application for functional chromium plating

Typical areas of application for functional chromium plating are primarily highly stressed components in:

- Aircraft construction and shipbuilding
- Automotive industry: e.g. cylinders, piston rods and rings, shock absorbers
- Mechanical engineering: cutting tools
- Paper, printing and packaging industry: pulleys, cylinders, rollers
- Cement industry: pumps and pipes
- Food industry: cooling and drying rollers
- Medical technology: pistons and piston rods in hydraulics and pneumatics
- Printing industry: Cylinders
- Mining, the oil, gas and steel industry: pipelines, ball plugs, valve balls
- Pharmaceutical industry: stirring, mixing, and metering equipment
- Chemical industry: reaction vessels, covers and guide tubes
- Textile industry: thread guiding parts
- Military technology: Armoured conduits and barrels
- Medical technology: Pistons and piston rods in hydraulics and pneumatics
- Tools in mould construction
- Cooling technology: e.g. carbon steel cooling systems in absorption refrigerators

This compilation is not exhaustive, but can provide a rough overview.

4.2.1.3 Plant sizes

For the characterisation of the plant size, the effective treatment vat volume in the sense of the Industrial Emissions Directive (Directive 2010/75/EU IED) or the Federal Immission Control Ordinance was chosen. According to the IED and its national implementation in the 4th Federal Immission Control Ordinance, "surface treatment plants with a volume of the effective treatment vats of 30 cubic metres or more for the treatment of metal or plastic surfaces by an electrolytic or chemical process" are subject to approval. Since the volume of the effective treatment vats, as a key figure for the plant size, is known among the operators of electroplating plants, this criterion was adopted for the plant size.

For functional chromium plating, plant sizes range from a few litres of effective treatment vat volume for restoration work to 100 cubic metres. However, most plants have a size of 1–10 m^3 effective treatment vat volume.

4.2.1.4 Requirements for wastewater treatment

Hard chromium baths are operated at temperatures of approx. 50 -70 °C. Compared to decorative chromium plating, significantly greater coating thicknesses are deposited. For this reason, the processing cycles or immersion times of the workpieces in the baths are comparatively long. This results in high evaporation losses during the process. These evaporation losses can be compensated for once more with rinsing water containing chromium(VI) and PFOS, so that hard chromium plating is a potentially wastewater-free process.

In fact, there are plants in Germany that do not discharge any wastewater from this process themselves, but dispose of all process solutions externally. In practice, however, carryover, splashing, ground washing water, exhaust air washing water, minor accidents and wastewater from pretreatment, maintenance and cleaning processes occur, so that many hard chromium plating plants nevertheless have a physico-chemical wastewater pretreatment plant downstream.

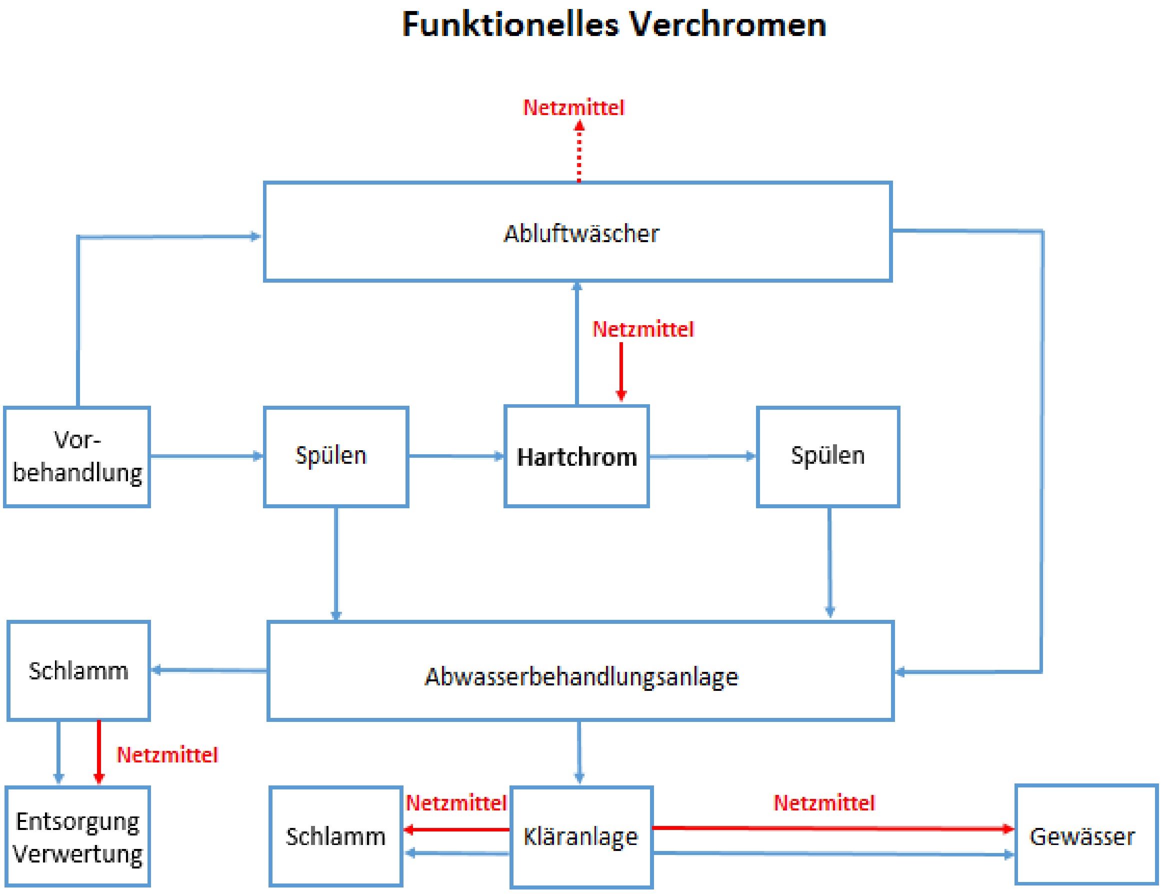
A simplified diagram of the process can be found in Figure 2. According to this, wastewater from pretreatment (e.g. degreasing and etching) is treated together with rinsing water after the chromium plating process and occasionally washing water from the exhaust air scrubber in a wastewater treatment plant. Usually, the toxic chromium(VI) is first reduced to chromium(III) in a strongly acidic environment using sodium bisulfite. Subsequently, the heavy metals are precipitated as poorly soluble hydroxides by means of caustic soda and/or calcium hydroxide in an alkaline environment. The resulting metal hydroxide sludge is disposed of or recycled as hazardous waste.

The mist suppressants, most of which are fluorinated, are added directly to the chromium baths or, in the case of large plants, to appropriate preparation stations.

If the mist suppressants are not already degraded by the process in the chromium bath itself, they enter the wastewater path and leave the plant, mostly dissolved in the treated wastewater and to a small extent also bound to the metal hydroxide sludge by adsorption.

With functioning exhaust air purification systems in accordance with the state of the art, the mist suppressant emissions via the exhaust air path are negligible, since they are substances of low volatility that remain dissolved in the process solution or the rinsing waters.

Figure 2: Simplified block diagram of functional chromium plating



Source: Own representation

4.2.1.5 Number of facilities in Germany

According to an estimate by the ZVO, there were around 2400 electroplating shops in Germany in 2017, and around 600 of these operated plants for functional chromium plating. These are both companies that operate functional chromium plating as an in-house process and so-called contract electroplating shops that offer this process as an external service (ZVO 2018a).

Due to the required approval under REACH and the increase in chromium(VI)-free substitute processes, the current number - as of the end of 2019 - of facilities with functional chromium plating is estimated by the ZVO to be only approximately 200.

4.2.1.6 Functional chromium plating in closed plants

There are plants in which functional chromium plating is carried out in closed reactors. This ensures that no chromium(VI) aerosols leave the system. A reduction of the surface tension and thus mist suppressants of any kind can therefore be dispensed with.

An example of this is described in Chapter 6.2.4 .

4.2.2 Decorative chromium plating (bright chromium)

In decorative chromium plating, the chromium is currently still mainly deposited from hexavalent chromium electrolytes. However, replacement with chromium(III) electrolytes is considerably easier and therefore already further advanced than in functional chromium plating.

"Decorative chromium plating represents the preferred surface finish for a majority of electroplated consumer and equipment goods. The economic benefit, at a comparably small cost, is the visually attractive surface with very high hardness, chemical resistance and toxicological safety. This ensures a long service life for the coated goods, which contributes to the sustainability of the products. An example of this is the chromium plating of furniture parts, e.g. swivel chair legs. In addition to decorative reasons, corrosion protection and wear resistance also play a role here.

The transitions between decorative chromium plating, previously usually referred to as bright chromium plating, and hard chromium plating are fluid in some applications for technical reasons. It therefore seems useful to focus on the intention and function of the deposited chromium layer.

An example of this is the use of chromium plating on fittings in the sanitary industry. Even with intensive commercial use and the use of abrasive or acidic cleaning agents, this chromium surface protects high-quality water taps and similar goods for decades. The decorative chromium surface thus helps to conserve resources.

However, chromium plating is also used for consumer goods for which visual properties alone are important. For example, the chromium plating of plastic articles for optical purposes, such as the chromium plating of sealing caps on perfume bottles, can be regarded as clearly "decorative". (Blepp, Willand, Weber 2016)“

4.2.2.1 Properties of bright chromium coatings

Bright chromium coatings are predominantly deposited in the decorative sector. Other applications, such as soft chromium electrolytes, are or were used only in exceptional cases, e.g. for vintage car restorations. However, these applications will not be considered in detail here due to their minor importance.

In bright chromium plating, thin chromium layers in the order of magnitude 0.2 to 1.0 µm are deposited. Due to the low coating thicknesses of such chromium layers, the brightness of the finished chromium-plated workpiece is determined not only by the chromium layer itself but also by the layer underneath. In most cases, a nickel layer is deposited before the chromium layer for optical and corrosion protection reasons. If the sub-layer is matt, the chromium layer will also have a matt shine; this is then referred to as matt chromium layers.

The essential properties of bright chromium coatings are:

- great hardness
- chemical resistance
- corrosion resistance
- bright surface and
- toxicological harmlessness

Bright chromium electrolytes are operated at 28 -50°C and contain 150-250 g/l CrO_3. The electrodes are usually made of lead, or lead alloys.

Chromium(III)-based bright chromium electrolytes have been gaining acceptance in the industry since 2019. Solutions to initial problems with the deviating colour of the "yellowish" chromium surfaces are getting better and better. In the meantime, there are chromium(III)-based electrolytes "which deliver identical colour values as surfaces from chromium(VI) processes (Käszmann 2019b)." The limits of the applicability of chromium(III)-based bright chromium baths are discussed in Chapter 6.2.1.4.

4.2.2.2 Areas of application for decorative chromium plating

Typical areas of application for decorative chromium plating include:

- Furniture industry: Swivel chair legs, furniture fittings, clothes racks
- Sanitary industry: bathroom fittings
- Construction industry: railings, bars
- Automotive industry: interior area, door handles, mouldings, etc.

Furthermore, the process is used for lighting fixtures, medical technology, aviation, mechanical engineering, two-wheeler industry, household, electrical and hi-fi and generally for consumer goods.

4.2.2.3 Plant sizes

The plant sizes for bright chromium plating range from an effective treatment vat volume of 1 to 30 cubic metres. However, most plants have a size of 4-20 m^3 of effective treatment vat volume.

4.2.2.4 Special case of black chromium plating

Black chromium plating is a special case of decorative chromium plating. Through increased current density in conjunction with special admixtures, chromium oxides of various oxidation states are deposited in amorphous layers. Sulphur-containing compounds, e.g. from thiocyanates, can also lead to black chromium layers. Cyanides can form in black chromium baths. A more or less high content of cyanide in the electrolytes and rinsing waters is therefore to be expected.

The amorphous layer structure absorbs light, so that the surface appears deep black. Compared with bright chromium coatings, black chromium coatings have lower surface hardness but better corrosion protection. In addition, black chromium coatings conduct electrical current and heat well.

Black chromium electrolytes are operated at room temperature up to max. 45°C and therefore often need to be cooled. They contain 290-450 CrO_3 g/l. Black chromium baths contained PFOS in a concentration range of 30-80 mg/l.

Black chromium plating is mainly used for solar collectors, the optics industry, medical and dental technology, measurement technology, the electronics industry, aircraft construction, weapons technology, and in bicycle and furniture manufacturing.

The limitations of the black chromium plating process are mainly the lower abrasion resistance and lower hardness of the coatings compared to bright chromium coatings.

Up to now, black chromium coatings have been deposited predominantly from hexavalent chromium electrolytes. In the meantime, the first black chromium electrolytes based on chromium(III) have appeared on the market.

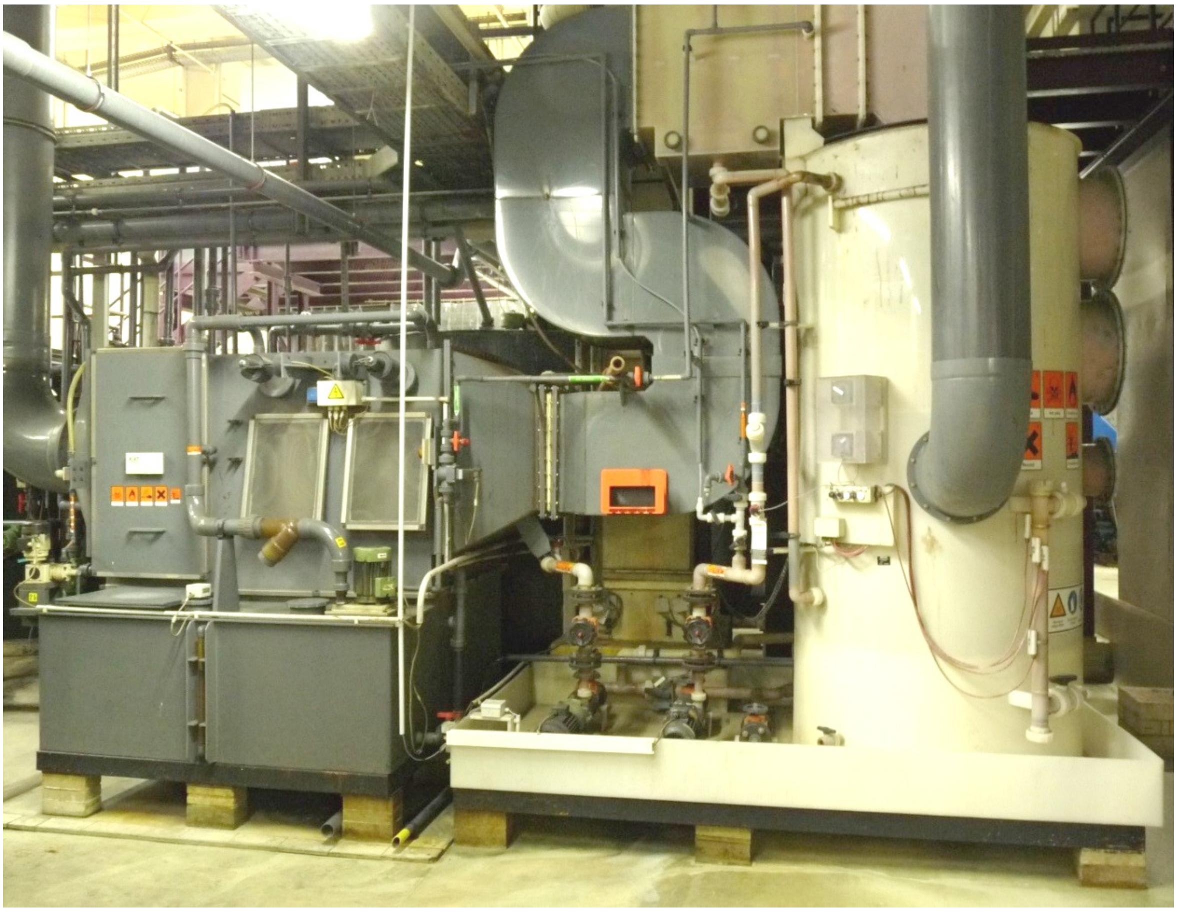
4.2.2.5 Plant sizes for black chromium plating

The plant sizes for black chromium plating range from an effective treatment vat volume of a few litres to a maximum of 10 cubic metres. However, most plants have a size of 0.5 -2 m^3 effective treatment vat volume.

4.2.2.6 Requirements for wastewater treatment

For wastewater treatment from the decorative chromium plating area, the same applies as for functional chromium plating, mentioned in section 4.2.1.4. However, some special features must be taken into account. For example, decorative chromium plating systems cannot simply be operated without wastewater. The deposited coating thicknesses are much smaller. As a result, the residence times of the workpieces in the chromium bath are considerably shorter than in functional chromium plating. This leads to higher carryover losses per unit of time. The temperature of the electrolyte is lower, resulting in significantly lower evaporation rates than with functional chromium plating. This results in excess rinsing water, which leads to significantly higher wastewater volumes. Some facilities use evaporation or vaporisation plants in the rinsing water circuit to recover the chromic acid dragged out and the mist suppressants it contains, or to withdraw water from the system.

Figure 3: Evaporation system of a plant for decorative chromium plating



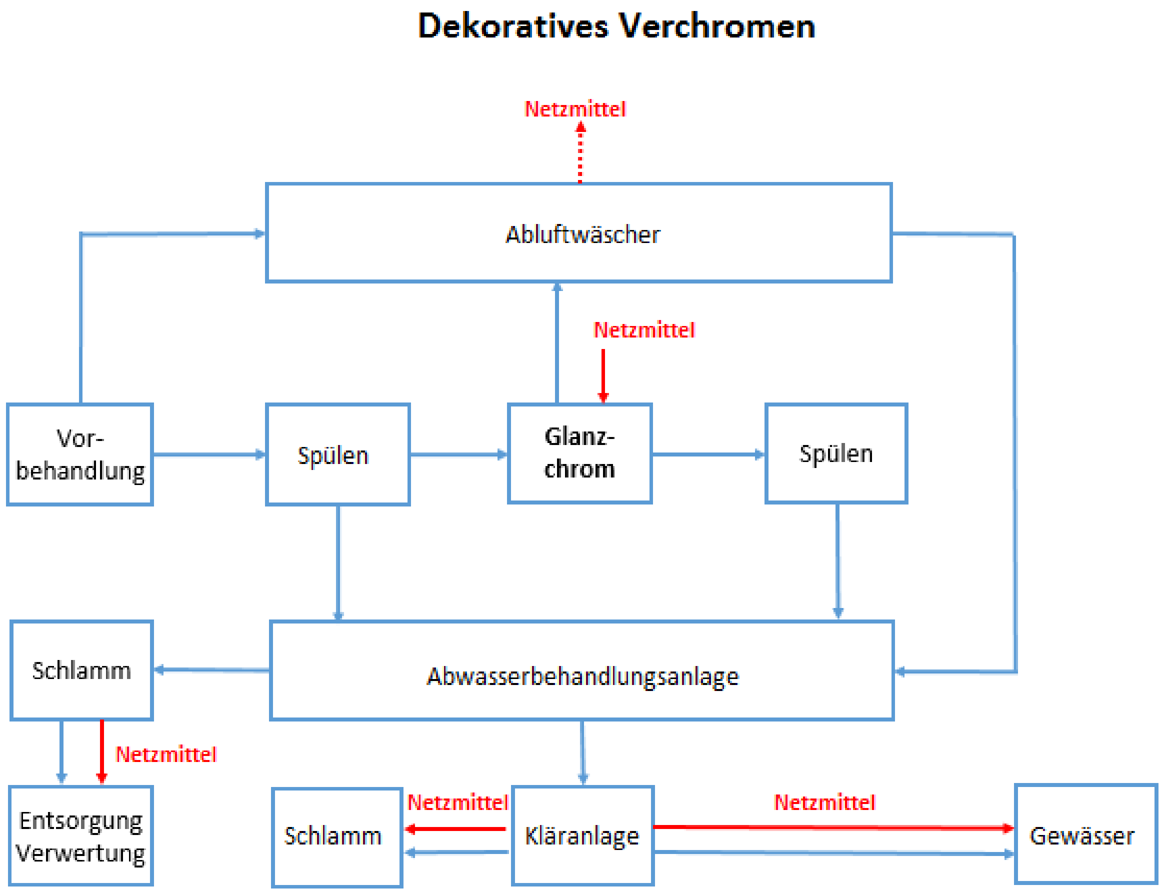
Source: IUW Integrierte Umweltberatung

In the almost closed circuit created in this way, impurities such as foreign metals accumulate, which can be removed from the rinsing water through ion exchangers. The regenerates of these ion exchangers not only contain foreign metals, they also contain mist suppressants and are treated for chromium(VI) in a wastewater pretreatment plant, just like the washing water from the exhaust air scrubbers. This resource-saving procedure can now be regarded as state of the art for decorative chromium plating from an effective treatment vat volume of the chromium(VI) electrolyte of 1m^3.

Note: the plastic electroplating process described in section 5.9.2 also uses a comparable technique.

The following Figure 4 shows the process in a greatly simplified manner, i.e., without an evaporation or vaporisation system. Nevertheless, the principle of the fate of the mist suppressants used becomes clear.

Figure 4: Simplified block diagram of decorative chromium plating



Source: Own representation

4.2.2.7 Number of facilities in Germany

According to an estimate by the ZVO in 2018, there are approximately 800 facilities in Germany that operate plants for decorative chromium plating. These are both companies that operate decorative chromium plating as an in-house process and so-called contract electroplating shops that offer this process as an external service (ZVO 2018a). The facilities that decoratively chromium plate plastics form a separate group and are not counted here.

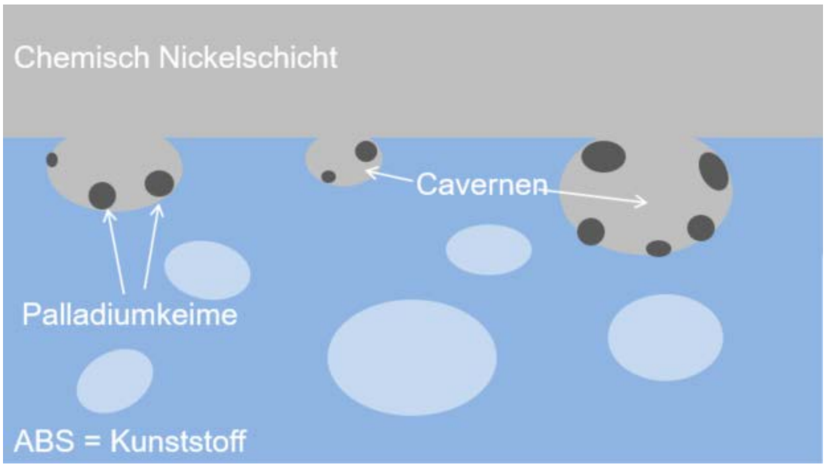
4.2.3 Galvanic plastic metallisation and plastic etching with chromium(VI)-containing etching solutions.

PFOS has been used in the past in chromium(VI)-containing plastic etching solutions. In contrast to the etching of metals, this process step is not carried out as an independent process step, but always in combination with further treatment of the etched plastic with the aim of metallic electroplating. The concentration of CrO_3 in plastic etching can be very high and can be up to 950 g/l. Today, however, most plastic pickles etchings contain concentrations of only 300-450 g/l. The PFOS concentrations in plastic etchings were 20-50 mg/l. Today, PFOS may no longer be used in plastic etching, as the exemption for this in the Stockholm Convention or the POP Regulation has expired.

“In order to be able to electroplate plastics, such as the most commonly used acrylonitrile-butadiene-styrene copolymerisates (ABS), they must first be made electrically conductive. For this purpose, approx. 1 µm large pores (caverns) are first etched into the plastic surface with very strongly oxidising etching solutions. Only the butadiene component is chemically attacked. The etching solution used is mainly a highly concentrated chromo-sulphuric acid solution at elevated temperatures. In order to achieve wettability of the hydrophobic plastic surfaces, a surfactant resistant to the chromo-sulphuric acid must be added. PFOS was previously used for this purpose (Blepp, Willand, Weber 2016).”Today, polyfluorinated mist suppressants are predominantly used here as alternatives to PFOS.

Palladium ions are introduced into the caverns (so-called "activation"), which are subsequently reduced to elementary palladium using an "accelerator." Alternatively, a colloidal seeding process is used, in which colloidal palladium is used in a tin hydroxide protective colloid and the palladium seeds are exposed by treatment with an acid mixture. The plastic parts are then placed in a nickel electrolyte operating without external current. The palladium seeds catalyse the reductive deposition of the nickel. The deposited nickel in turn acts as a catalyst for further nickel deposition, as does the palladium, so that a closed conductive nickel-metal layer is formed. The following diagram shows a section through the resulting surface:

Figure 5: Principle sketch - plastic metallisation



Source: Own representation

Building on the surface that has thus become electrically conductive, further metals (layer sequence mostly copper, nickel, chromium) can then be deposited. Chromium is still the preferred final surface for the vast majority of electroplated plastic parts. PFOS alternatives are also used for the final decorative chromium plating.

4.2.3.1 Areas of application for electroplated plastic metallisation

- Typical areas of application for electroplated plastic metallisation are:
- Automotive industry: interior and exterior, door handles, mouldings and emblems
- Sanitary industry: showers

Other applications include: Costume jewellery, watches, film and photo cameras, electronic appliances, household goods, furniture fittings, music industry, gift items, etc.

4.2.3.2 Plant sizes

The plant sizes for both plastic etching and downstream bright chromium baths are mostly in an effective treatment vat volume range of 3-20 cubic metres.

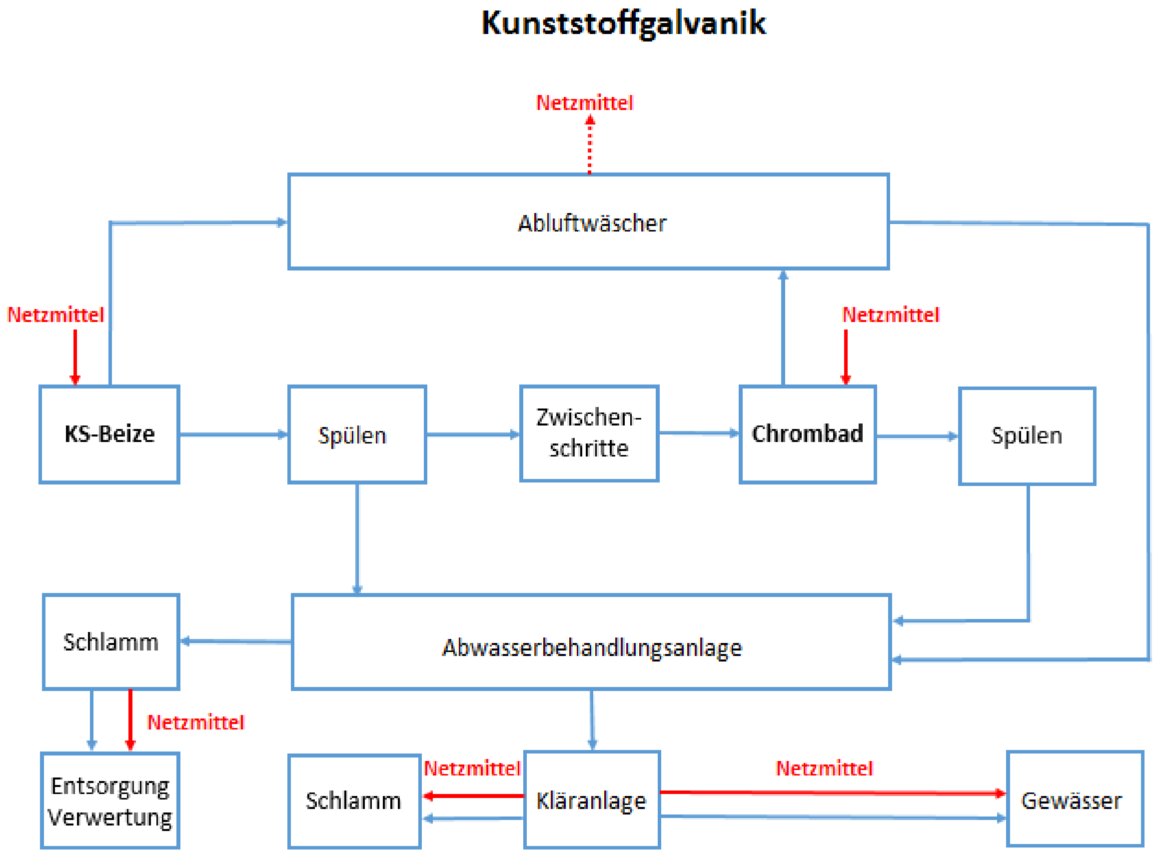
4.2.3.3 Requirements for wastewater treatment

For the wastewater treatment of chromium(VI)-containing wastewater streams from the galvanic metallisation of plastics, the same applies as described under 4.2.2.6 for the decorative chromium plating area. In contrast, however, wastewater containing mist suppressants and chromium (VI) is not only generated from bright chromium baths, but also from the area of plastic etching. During the etching of plastics, part of the chromium(VI) is reduced, as intended, to chromium(III) in the etching process. In order to reverse this process, the etching is electrochemically treated during periods of shutdown, whereby the chromium(III) formed is reoxidised to chromium(VI) at a titanium anode. In addition, organic ballast substances are degraded. This is a bath maintenance measure that considerably increases the service life of the etching.

It has been shown that even perfluorinated substances such as PFOS and PFBS are electrochemically degraded during this process (Fath 2008).

The diagram below shows the process in a highly simplified manner, i.e. without electrochemical bath maintenance measures or evaporation technology. Nevertheless, the principle of the fate of the mist suppressants used becomes clear.

Figure 6: Simplified block diagram - plastic metallisation



Source: Own representation

4.2.3.4 Special features of plastic metallisation

The process of plastic metallisation differs from the chromium plating of metals in that the plastic surface, which initially does not conduct the electric current, must first be made conductive. To date, etching solutions containing chromium(VI) have been predominantly used for this purpose. The mist suppressant emissions from this process are therefore fundamentally higher, since mist suppressants are used both in the plastic etching solution and in the subsequent decorative chromium plating bath. A wastewater-free process, as in functional chromium plating, is not possible here.

4.2.3.5 Number of facilities in Germany

According to an estimate by the ZVO in 2018, there are approximately 30 facilities in Germany that operate plants for galvanic plastic metallisation. These are both companies that operate galvanic plastic metallisation as an in-house process and so-called contract electroplating shops that offer this process as an external service (ZVO 2018a). Due to the general market development and the trend towards ever lighter components, especially in means of transport, it can be expected that the share of plastic electroplating plants in the total number of electroplating plants in Germany will increase in the future.

4.2.4 De-chromium plating of racks and defective batches as a source of PFAS

In the literature, the process step of de-chromium plating is not mentioned as a possible emission source for mist suppressants. On the one hand, defective batches are de-chromium plated, i.e. workpieces in which defects have occurred during the chromium plating process and whose chromium coating has to be removed again. On the other hand, the racks used to transport the workpieces through the electroplating machine and on whose metallic contact points chromium is unintentionally deposited are de-chromium plated. Depending on the base material, wet chemical de-chromium plating is performed either by a chemical immersion process using acids or electrolytically, in which case the racks or workpieces are connected as an anode in so-called chromium stripper solutions, e.g. based on sodium hydroxide.

As shown in Chapter 5, the process step of rack demetallisation can lead to PFAS emissions from unexpected places into the wastewater pathway. In the demetallisation solution studied there, 1900 µg/l of 6:2 FTS was detected. In these processes, the mist suppressants previously used in the chromium plating process can be desorbed from the plating racks and enter the wastewater pathway via treatment of the dechroming solution or the resulting rinsing waters.

4.2.5 Degreasing solutions as a source of PFAS

Another, hitherto unnoticed source of PFASs can be spent process solutions of degreasing baths. As shown in Chapter 3.6, PFAS can adsorb to plastic-coated racks and desorb again when they are reused. This can lead to increased PFAS concentrations in the degreasing solution. In the case of ultrasonic degreasing operated at 70°C, 2300 µg/l 6:2 FTS were detected in the degreasing solution prepared. Since degreasing solutions and their rinsing waters are usually not treated for PFAS, the PFAS contained therein enter the wastewater of electroplating shops untreated.

4.2.6 Potential increase of the incident potential during the conversion from chromium(VI) to chromium(III)

In this subchapter, a brief outline is given of the incident potential in the case of conversion from chromium(VI) to chromium(III) as defined in the 12th Federal Immission Control Ordinance. This is also required in the light of the 12 criteria for determining the state of the art in the Federal Water Act (WHG), the Federal Immission Control Ordinance (BImSchG) and the Closed Substance Cycle Waste Management Act (KrWG). In particular, criterion no. 11 "Need to prevent accidents and reduce their consequences for people and the environment" must be observed here.

Accidents involving the development of toxic gases cannot be ruled out when converting from chromium(VI) to chromium(III) processes. The potential for hazardous chemical reactions in electroplating shops is generally relatively high. In electroplating shops, a large number of chemicals are used, some of which are highly concentrated, and some of which can enter into exothermic chemical reactions with one another, often with the formation of toxic gases. In contrast to the chemical industry, there is often a lack of adequately trained personnel, especially in smaller operations. As a result, accidents involving toxic gas clouds due to unintentional mixing of chemicals occur time and again. "This also applies to the discharge of wastewater (especially concentrates) into incorrect collection basins (Willand 2014)"

In this transition, both chromium(VI)-containing and chromium(III)-containing process solutions are usually operated simultaneously for some time for reasons of process reliability and continuity of supply. In the past, there were usually no concerns about mixing rinsing waters or process solutions from different chromium baths, as these electrolytes were all chromium(VI)-based. However, chromium(III)-containing chloride-based chromium baths and their rinsing waters contain chloride ions in sufficiently high concentrations so that when these solutions are mixed with chromium(VI)-containing solutions in the collection tanks of the wastewater treatment plant, free chlorine gas can be generated by oxidation. At least one chlorine gas accident is known to have occurred in this manner.

Instead of the previous practice of carelessly mixing chromium electrolytes or their rinsing waters, a case-by-case consideration should therefore be made, especially when using chloride-based chromium(III) electrolytes. Here, it may be necessary to keep these process solutions and their rinsing waters separate during wastewater treatment and, above all, during waste collection and disposal.

5 Mist suppressant use and emissions by type and quantity

5.1 General information on the use of mist suppressants and their emissions

The ingredients and concentrations of the mist suppressant mixtures used were determined on the basis of manufacturer and operator data. A distinction is made here between perfluorinated, polyfluorinated and fluorine-free products. In principle, the chemical-analytical separation of the mist suppressant mixtures used in the surface treatment industry into individual substances and subsequent chemical analysis of the contained mist suppressants with concentration determination would be desirable.

An analytical determination of the individual substances in the mist suppressant mixtures used would go beyond the scope of the present project and is therefore not part of this study.

5.2 Survey of mist suppressant users

In order to determine the annual use of mist suppressants in the chromium(VI) sector of the surface treatment industry, a survey of mist suppressant users was carried out with the aid of a questionnaire.

A two-page questionnaire was drawn up in cooperation with the Federal Environment Agency. Operators of plants for decorative chromium plating, functional chromium plating (hard chromium plating) or plastic electroplating plants were contacted by email and asked for information. The questionnaire can be found in Appendix A.

It contains questions regarding the following points:

- General information - contact details, industry and production area;
- Plant classification - Classification of operating plants using process solutions containing chromium(VI) by plant type (hard chromium plating, decorative chromium plating, or plastic etching);
- Operation site and mist suppressant consumption - for each plant operated, data were requested regarding
  - the total effective treatment vat volume and the effective treatment vat volume with process solutions containing chromium(VI);
  - Plant details (year of construction, classification);
  - Mist suppressant consumption (names of mist suppressants; consumption in kg/a);
  - Reduction/treatment measures carried out in the process/wastewater, their applicability in other plants, and the mist suppressant concentration (active ingredient) in the wastewater;
- Alternative processes - use of alternative processes to surface treatment with solutions containing chromium(VI).

A multi-stage procedure was chosen to identify the relevant facilities:

First, those facilities were identified that had participated in the surveys of the Federal Institute for Occupational Safety and Health (BAuA) within the framework of the reporting obligations according to EU Directive 2006/122/EC on the use of PFOS in electroplating plants (BAuA inventory data from 2009). This database was updated by IUW and supplemented with companies that have since become known or changed their name. In a third step, the facilities that became known through the REACH approval process for chromium trioxide were also included. This data research was carried out by the Öko-Institut. In this way, 130 companies relevant to the project were identified, to which the questionnaire was sent.

In parallel, the Zentralverband Oberflächentechnik e.V. (ZVO) was also persuaded to write to its member companies asking them to participate in the questionnaire. With 125 member companies, the ZVO had a similar number of companies. For data protection reasons, the intersection was unknown.

UBA accepted that this approach would probably result in an unknown number of duplicate inquiries to companies. No complaints were received in this regard from the companies contacted.

The response from the two campaigns mentioned above was manageable. A total of 30 companies completed and returned the questionnaire. The smaller part of the refusals (12) was due to the inquiry of the ZVO. In 30% of the cases, follow-up inquiries or clarification discussions with the companies were necessary.

Some of these were companies that offer surface treatment for different areas as a service. These companies are called contract electroplating companies. In some cases, companies were specialised in a specific sector (e.g. sanitary sector or automotive suppliers) or they were companies that operate their electroplating plant as their own electroplating operation ("in-house"), e.g. for mechanical engineering or in gravure cylinder production.

All in all, the 30 companies operate plants with an effective treatment vat volume of approx. 2,800 m^3. Of these, approx. 940 m^3 are effective treatment vats with process solutions containing chromium(VI) (in some cases, no information was provided on the total effective treatment vat volume). For the plants with chromium(VI)-containing solutions, the total mist suppressant consumption adds up to approx. 19.82 t/year. Further details are specified in the following sections.

During the data collection, it was noticeable that there were no responses from facilities with small chromium(VI) effective treatment vat volumes of less than 1000 litres, although such plants were also contacted with the questionnaire. The fact that small facilities or facilities with small plants are underrepresented in this survey should be considered when interpreting the results. One possible explanation for this is that small facilities have fewer human resources and expertise to adequately respond to such a questionnaire survey.

The following results are evaluated on the basis of the questionnaire response.

5.3 Results of the survey of mist suppressant users

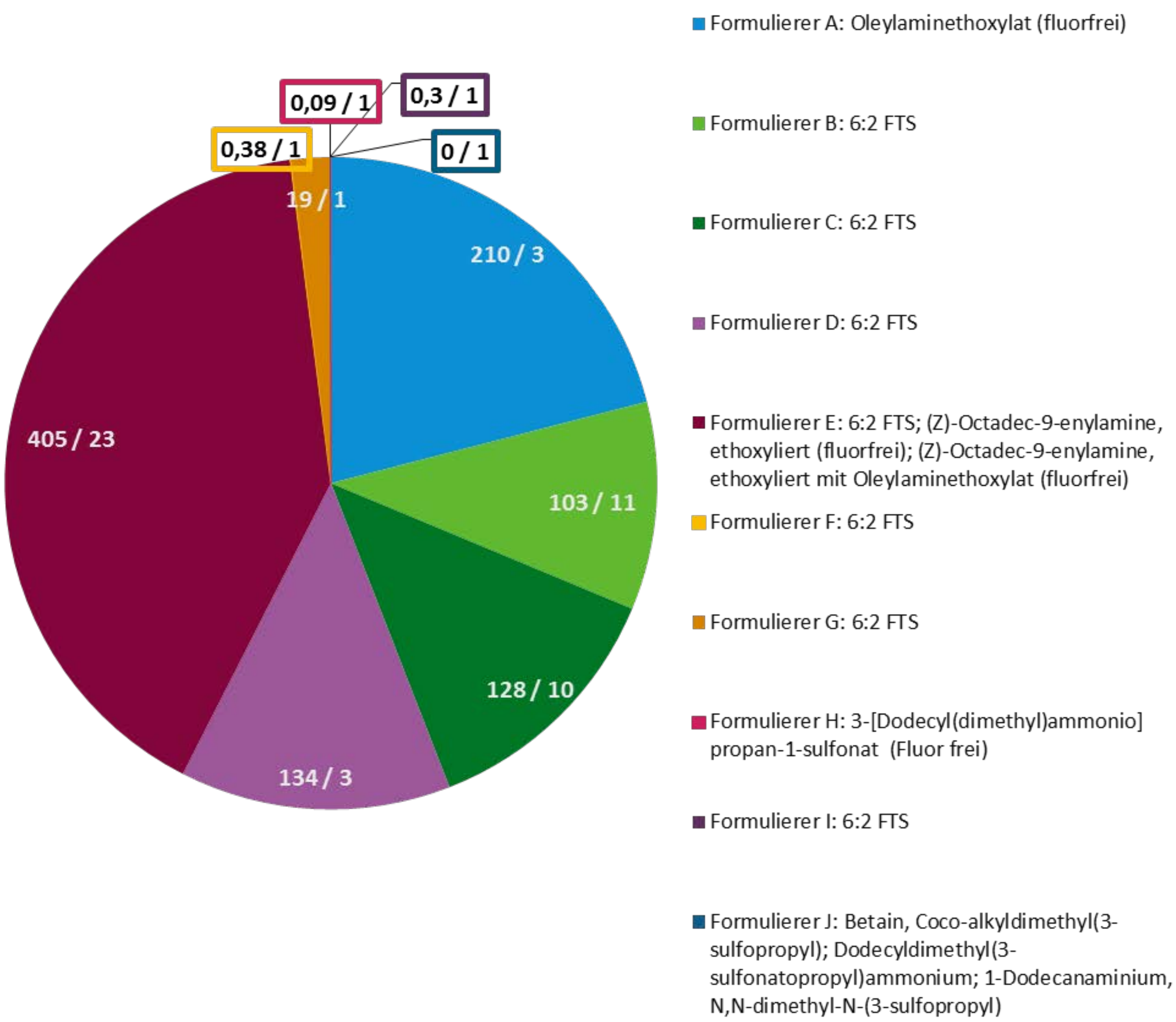
5.3.1 Market shares of chemical formulators

In the information on the use of mist suppressants, the questionnaires list products from nine different chemical formulators. Since this is information from only 30 companies, it cannot be assumed that the entire German market could thus be covered in a fully representative manner.

Figure 7 shows how the number of chemical formulators is distributed across the quantities of active ingredient consumed annually, as well as how the number of chemical formulators is distributed across the total number of plants. From the differences, it can be seen that the products of some formulators are only consumed in very small quantities (e.g. formulators F, H and I), whereas the products of other formulators are only used in comparatively few plants, but are consumed there in disproportionately high quantities (e.g. formulator A). Formulator A supplies only fluorine-free mist suppressants to the facilities in the user survey. As expected, this shows that the consumption of fluorine-free mist suppressants is significantly higher than that of mist suppressants containing fluorine. Formulator E is the market leader and supplies both fluorine-containing and fluorine-free mist suppressants to the companies surveyed.

Figure 7 shows the amount of active ingredient in the marketed mist suppressants for each chemical formulator. On this basis, an initial distinction can be made between polyfluorinated (e.g. 6:2 FTS) and fluorine-free mist suppressants (e.g. oleylamine ethoxylate(Z)-octadec-9-enylamine). The information provided in the user questionnaire shows that fluorine-free and fluorine-containing mist suppressants were only purchased by Formulator E.

Figure 7: Distribution of mist suppressant manufacturers (formulators) based on the annual active ingredient volume consumption (in kg; for 2017) of the users surveyed / indication of the number of plants

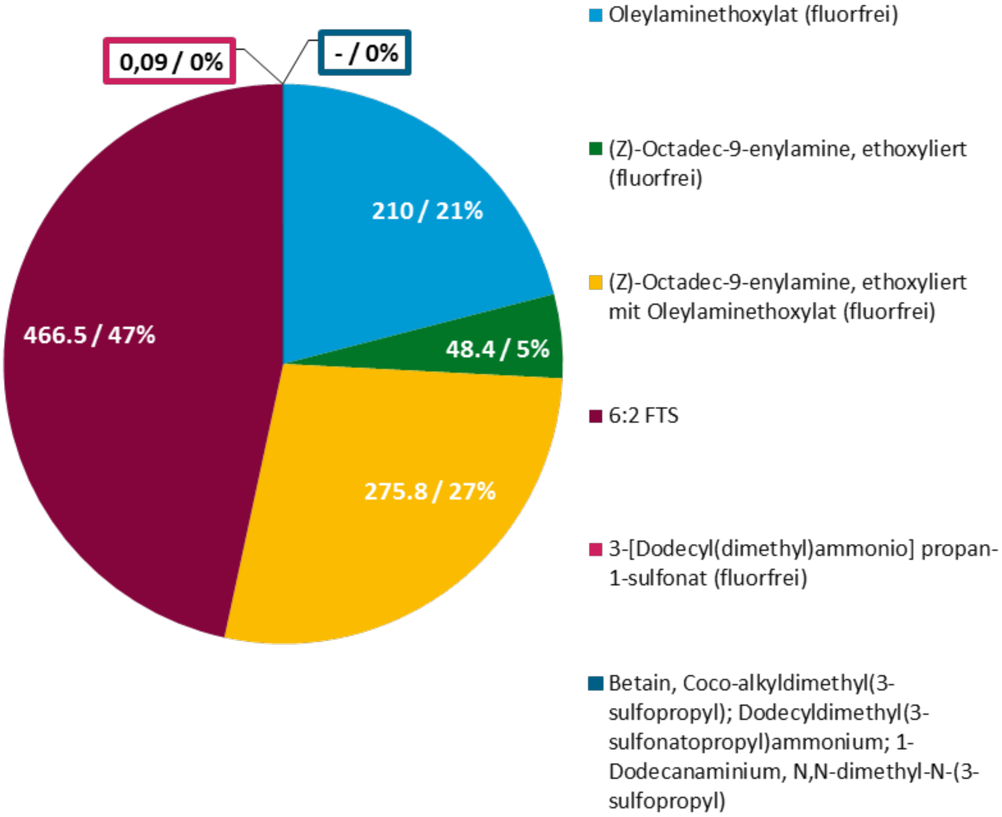


Source: Own representation

Figure 8 shows the calculated market shares of the individual active ingredients based on the annual active ingredient consumption specified in the user questionnaire. On the basis of this illustration, it becomes clear that the proportion of 6: 2 FTS (containing fluorine) in the total mist suppressant consumption in the sector of process solutions containing chromium (VI) is approx. 47.5%. The following two fluorine-free mist suppressants are used in larger amounts. The consumption of the mixture of (Z)-octadec-9-enylamine, ethoxylated and oleylamine ethoxylate is approx. 27.1%. An oleylamine ethoxylate-based mist suppressant has a volume consumption of approx. 20.6%.

6:2 FTS is by far the most frequently used substitute for PFOS. Fluorine-free mist suppressants are used less frequently. However, their consumption is much higher for the same application, since they are rapidly broken down under the strongly oxidative conditions in chromic acid.

Figure 8: Market shares of the fluorine-free and fluorine-containing mist suppressants based on the annual consumption of active ingredient (in kg; for 2017) of the users surveyed



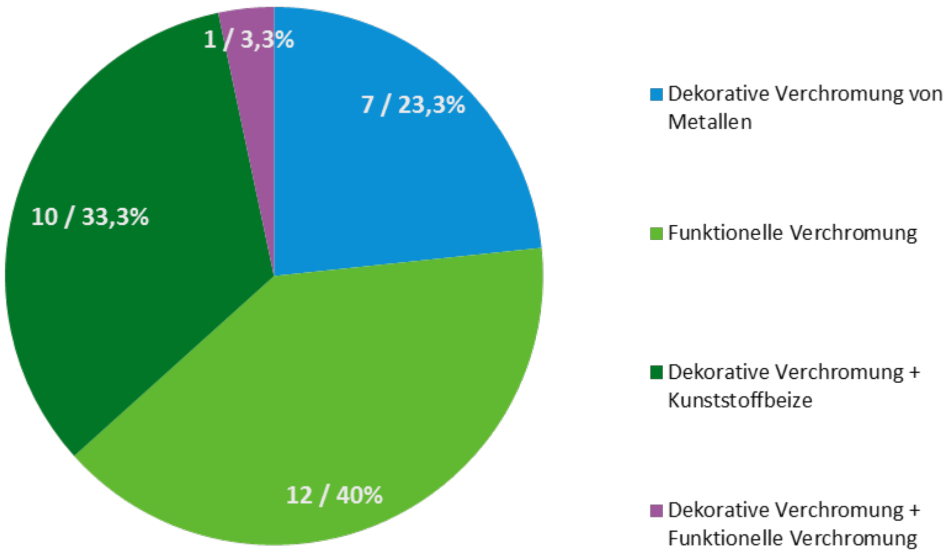
Source: Own representation

5.3.2 Distribution of facilities by area of application

Of the 30 companies that participated in the questionnaire survey, most are active in only a single area. 12 facilities operate plants for functional chromium plating only. One facility carries out both decorative and functional chromium plating operations. 7 facilities are only active in decorative chromium plating of metal and 10 facilities operate decorative chromium plating of plastics. For process-related reasons, these 10 facilities also engage in plastic etching.

Figure 9 shows the number and percentage distribution of processes in the facilities.

Figure 9: Distribution of companies by area of application in number and percent based on the user survey



Source: Own representation

5.3.3 Determination of active ingredient quantities when concentration ranges are specified

The active ingredient quantities (M) were determined on the basis of the concentration of the active ingredient in the mist suppressant used (c in %) and the annual consumption of the mist suppressant (V_j in m^3/year).

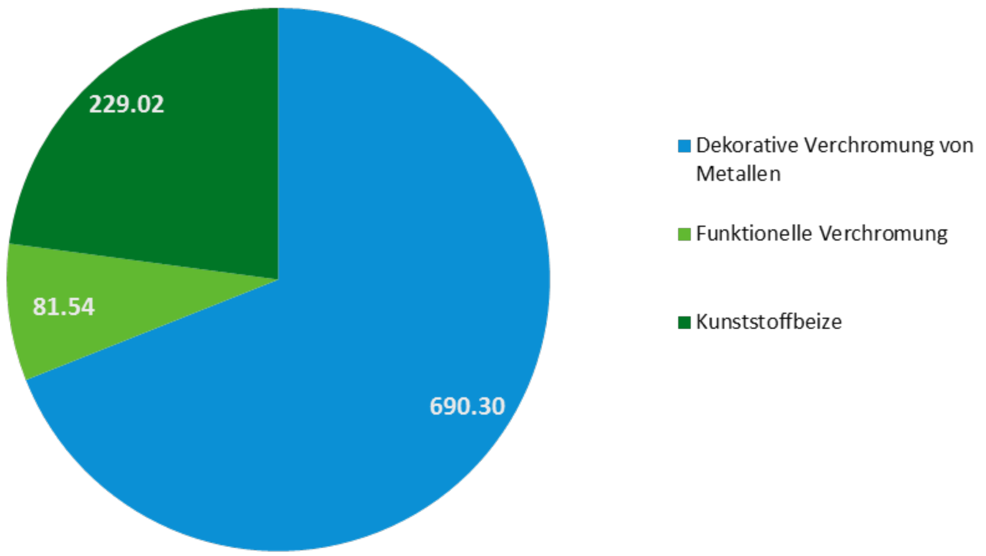
$$M = *$$

The concentrations were partly specified by the users in the questionnaire, while they were taken in part from the safety data sheets of the respective mist suppressant (see section 5.6 for further details).

For all active ingredients, the mean value of the specified concentration range in the safety data sheet (SDS) was used unless more precise information was available. For mist suppressant mixtures with several active ingredients, the calculation is based on the active ingredient component with the highest concentration. For example, the SDS for 6:2 FTS specify different active ingredient concentrations, ranging from 1% up to 10%.

Result: The amount of active ingredient consumed for the 30 facilities in 2017 was about 1000 kg, with about 690.3 kg consumed in decorative chromium plating, about 81.5 kg in functional chromium plating, and about 229 kg in plastic etching (Figure 10). These figures refer to the active ingredients, not to the diluted solutions used.

Figure 10: Representation of the distribution of annual active ingredient volume consumption (in kg; for 2017) by area of application in the user survey



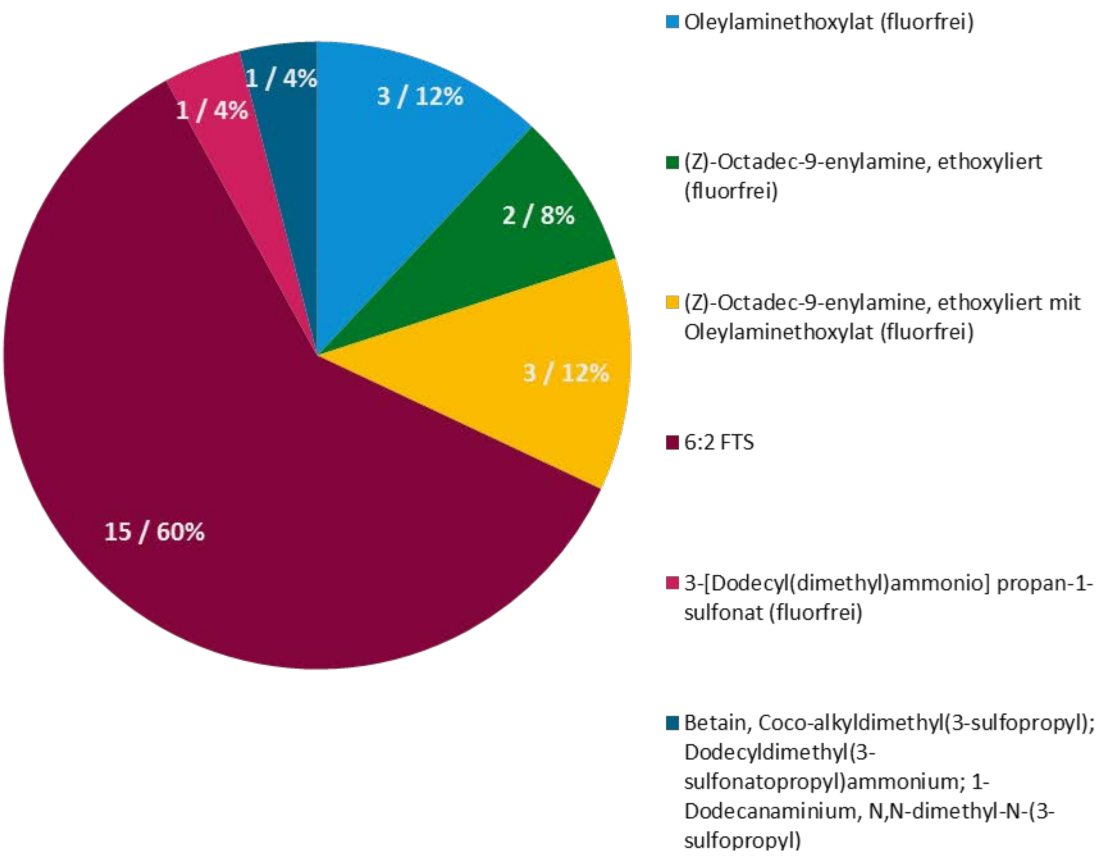
Source: Own representation

The following sections show the use and consumption of polyfluorinated and fluorine-free mist suppressants in the three application areas of decorative chromium plating, functional chromium plating and plastic etching.

5.3.4 Mist suppressants in decorative chromium plating

Of the 30 mist suppressant users who participated in the questionnaire survey, 18 work in the field of decorative chromium plating of metals or plastics. These 18 companies operated a total of 25 plants for decorative chromium plating. Five different mist suppressants were used in the decorative chromium plating field, and two of these mist suppressants contained similar chemical components (see Figure 11). 6:2 FTS was the most common mist suppressant used and was applied in approximately 60% of the facilities.

Figure 11: Use of different mist suppressants in decorative chromium plating – number /proportion of plants in the user survey

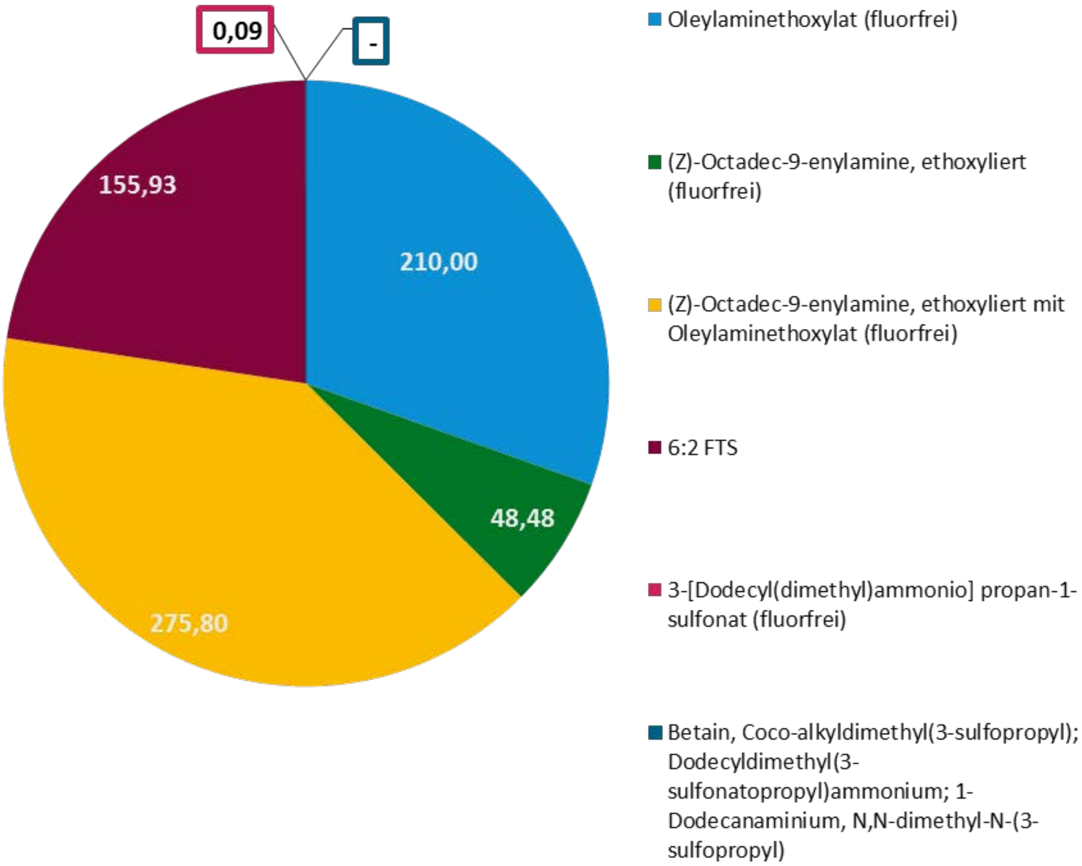


Source: Own representation

6:2 FTS-containing mist suppressants contain relatively low concentrations of the active ingredient. The volume consumption of the fluorine-containing active ingredient in the area of application is significantly lower than the consumption of the fluorine-free active ingredients: Oleylamine ethoxylate, (Z)-octadec-9-enylamine, ethoxylated; (Z)-octadec-9-enylamine, ethoxylated, and oleylamine ethoxylate; 3-[dodecyl(dimethyl)ammonio]propane-1-sulfonate 3-[dodecyl(dimethyl)ammonio]propane-1-sulfonate and betaine.

This is also evident in Figure 12 from the representation of the quantities consumed.

Figure 12: Active ingredients consumed in decorative chromium plating in 2017 (quantities in kg) in the user survey



Source: Own representation

In 2017, 155.93 kg of 6:2 FTS were consumed in the 13 companies studied. Of the fluorine-free active ingredients, 210 kg oleylamine ethoxylate; 175.8 kg (Z)-octadec-9-enylamine, ethoxylated with oleylamine ethoxylate and 48.5 kg (Z)-octadec-9-enylamine, ethoxylated, were consumed in the investigated companies, as well as insignificant amounts of two other mist suppressants.

5.3.5 Mist suppressants in functional chromium plating

13 of the 30 companies were active in functional chromium plating. They operated a total of 18 plants. In all facilities, only the polyfluorinated mist suppressant 6:2 FTS was used. A single facility initially reported a fluorine-free mist suppressant. This facility, however, could not provide any further information on the active ingredient and its annual consumption. Through further research, however, 6:2 FTS was retrospectively identified as the active ingredient in this application as well.

In 2017, 81.54 kg of 6:2 FTS was consumed in the 13 investigated companies with functional chromium plating.

5.3.6 Mist suppressants in plastic etching

Ten of the 30 companies operate plastic electroplating plants. They operate a total of 12 plastic etching plants. Only 6:2 FTS was used in plastic etching at the companies surveyed. In 2017, 229 kg of 6:2 FTS was consumed in the 10 companies.

5.4 Attempt to determine mist suppressant consumption among chemical distributors

Parallel to the questionnaire campaign among mist suppressant users, an attempt was made to inquire about mist suppressant consumption directly among chemical formulation companies in the surface treatment industry. However, the survey yielded few concrete results. In a personal communication, only one company stated that it sold only 50 kg of 6:2 FTS (pure substance) per year in the chromium(VI) sector. After it became foreseeable that significantly less than 50% of the actual annual mist suppressant consumption could be clarified in this way, the survey was discontinued.

In September 2019, the Zentralverband Oberflächentechnik e.V. (ZVO) determined the annual sales of 6:2 FTS in the surface treatment industry by the vast majority of chemical formulators by the order of magnitude. For more information, see section 5.5, under "Comparison of extrapolated 6:2 FTS consumption with data from other sources".

5.5 Extrapolation to the nationwide consumption of active ingredients

The extrapolation to the nationwide active ingredient consumption was made on the basis of the data obtained in the questionnaire campaign and the information provided by the ZVO on the respective number of facilities. The total active ingredient consumption was determined in each sector on the basis of the reported mist suppressant consumption and mist suppressant concentrations. This was extrapolated proportionally to the total number of facilities in that sector as reported by the ZVO.

Decorative chromium plating

In 2017, approximately 800 facilities were active in the decorative chromium plating sector in Germany (ZVO 2018a). Only 17 of these establishments participated in the questionnaire survey. Due to this relatively small number of cooperating facilities, the extrapolation is subject to large uncertainties.

Using the example of the most frequently used PFOS alternative, 6:2 FTS, it can be seen that a realistic order of magnitude for the mist suppressant consumption was nevertheless determined. In total, the annual consumption of 6:2 FTS determined by the ZVO independently of the present survey by interviewing chemical formulators and the nationwide consumption extrapolated on the basis of the questionnaire campaign are only about 15% apart.

Table 2 shows the data obtained from the questionnaire survey and the extrapolated quantity for nationwide active ingredient consumption:

Table 2: Extrapolation of active ingredient consumption in decorative chromium plating

Mist suppressants used	Quantity in kg. according to survey (for 2017)*	Extrapolated quantity in kg (for 2017)
Oleylamine ethoxylate (fluorine-free)	210.0	9,882
(Z)-Octadec-9-enylamine, ethoxylated (fluorine-free)	48.5	2,281
(Z)-Octadec-9-enylamine, ethoxylated with oleylamine ethoxylate (fluorine-free)	275.8	12,979

Mist suppressants used	Quantity in kg. according to survey (for 2017)*	Extrapolated quantity in kg (for 2017)
3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate 3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate (fluorine-free)	0.1	4
6:2 FTS	155.9	7,338
Betaine, Cocoalkyldimethyl(3-sulfopropyl); Dodecyldimethyl(3-sulfonatopropyl)ammonium; 1-Dodecanaminium, N,N-Dimethyl-N-(3-sulfopropyl)	-**	-

* From information provided by 17 out of a total of 800 facilities

** Insignificant quantities - in one case, no information was provided on the mist suppressant used and consumption.

Functional chromium plating

According to the ZVO, around 600 facilities were active in the functional chromium plating sector in Germany in 2017 (ZVO 2018a). Recent findings by the ZVO indicate that this number will have fallen to only around 200 facilities by the end of 2019. The present extrapolation is based on data for the year 2017. 13 facilities participated in the questionnaire campaign. The extrapolation exhibits a large degree of uncertainty.

Table 3 shows the data obtained from the questionnaire campaign and the extrapolated estimate for the annual nationwide consumption of active ingredients in functional chromium plating.

Table 3: Extrapolation of active ingredient consumption in functional chromium plating

Mist suppressants used	Quantity in kg. according to survey (for 2017)*	Extrapolated quantity in kg (for 2017)
6:2 FTS	81.54	3,763

* From information provided by 13 out of a total of 600 facilities

Plastic etching

In Germany, about 30 companies operated plastic etching plants in 2017 (ZVO 2018a). Ten of these facilities completed the questionnaire. In this case, the extrapolation has a relatively high statistical representativeness.

Table 4 shows the data obtained from the questionnaire survey and the extrapolated values for nationwide active ingredient consumption.

Table 4: Extrapolation of active ingredient consumption in plastic etching

Mist suppressants used	Quantity in kg. according to survey (for 2017)*	Extrapolated quantity in kg (for 2017)
6:2 FTS	229.02	687

* From information provided by 10 out of a total of 30 facilities

Overall, the extrapolation for all applications in electroplating shops results in a nationwide 6:2 FTS use of approx. 11.8 tons in 2017, with regard to the pure active ingredient. Of this, decorative chromium plating accounted for approximately 7.3 tons. In functional chromium plating, 3.7 tons were used and in plastic etching, approximately 0.7 tons. The above-mentioned uncertainty of the extrapolated figures must be taken into account here.

Comparison of the extrapolated 6:2 FTS consumption with data from other sources.

For the year 2010, the Federal Environment Agency states the annual PFOS use in the electroplating industry in Germany at 3400 kg. With a few exceptions in the decorative chromium plating sector, it can be assumed that PFOS has been almost completely replaced by 6:2 FTS until now. Since the quantity of 6:2 FTS used in production is 2 to 5 times that of PFOS, depending on the application, the electroplating industry must be using between 6.8 and 17 metric tons of 6:2 FTS today. The extrapolated annual consumption of 11.8 metric tons of 6:2 FTS lies in the central zone of this range and thus appears to be in a plausible order of magnitude.

A rough survey conducted by the ZVO in September 2019 among the majority of German chemical formulators supplying the electroplating industry revealed a current annual use of a maximum of 10 tons of 6:2 FTS in the electroplating industry. The value of 11.8 tons determined by extrapolation for 2017 is in the same order of magnitude and deviates by only about 15%.

Furthermore, the determined annual 6:2 FTS consumption was compared with the notified quantities in the REACH registration database.

Regulation (EC) No. 1907/2006 (REACH) requires companies to collect information on the properties and uses of substances they manufacture or import in quantities greater than one ton per year. This information is submitted to European Chemicals Agency (ECHA) in a registration dossier, which includes, among other things, information on the quantities of substance consumption. Currently, a maximum of 10-100 tons of 6:2 FTS for all applications (incl. fire extinguishing foams) have been submitted for registration in the REACH registration database for the entire EU[3]. The annual consumption determined does not contradict this.

5.6 Characterisation of the individual mist suppressants by means of portfolio fiches

In order to improve the comparability of the chemicals used with regard to their (eco)toxicological characterisation, short portfolio fiches were prepared for the individual mist suppressants.

The following parameters were specified as criteria for the characterisation of mist suppressants within the framework of a “short portfolio fiche":

- Data on physico-chemical properties, degradability and toxicity, if available
- Degradation products, as far as available
- Use quantity: Substances with large annual consumption quantities are examined in more detail
- Use concentrations
- Particularly critical properties: PBT substances or substances with CMR or endocrine disrupting properties which, according to scientific evidence, are likely to have serious effects on human health or the environment.

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[3] See information on 6:2 FTS in the REACH registration database at the following link REACH registration dossier (2019): https://echa.europa.eu/de/registration-dossier/-/registered-dossier/24637, last visited on 9.10.2019.

All data presented in this chapter are taken from the safety data sheets of the mist suppressant products.

5.6.1 Differentiation between fluorine-free and polyfluorinated mist suppressants

A total of 15 different active substances were identified in the mist suppressant determined by the questionnaire survey. Portfolio fiches were prepared for these substances, distinguishing between fluorine-free and polyfluorinated substances. Table 5 contains data on product names, suppliers, annual consumption volume data from the mist suppressant user survey, differentiation by PFAS content, application area and concentration (see 5.2), where available. The portfolio fiches for the individual mist suppressants can be found in Appendix B.

Table 5: Compilation of the data of investigated PFOS alternatives

Declared substances	CAS number	Product name/ mist suppressant	Supplier/s	Polyfluorinated / fluorine-free	Application area**	Mist suppressant concentration
(Z)-Octadec-9-enylamine, ethoxylated	26635-93-8	E1	E	fluorine-free	Decorative chromium plating; plastic etching	>10-25%
Oleylamine ethoxylate + 1,2-propylene glycol	26635-93-8; 57-55-6	Aa1	Aa	fluorine-free	Hard and decorative chromium plating	10-<25%
Oleylamine ethoxylate + 2-(2-Methoxyethoxy)ethanol	26635-93-8; 111-77-3	D1	D	fluorine-free	Decorative chromium plating	≥ 25 - < 50 %
Amines, C12-C14 alkyl, ethoxylated	61791-14-8	J1	J	fluorine-free	Hard and decorative chromium plating	10-25%
Tallow alkylamine ethoxylate + oleylamine ethoxylate+ potassium dichromate	61791-26-2; 26635-93-8; 7778-50-9	K1	K	fluorine-free	Decorative chromium plating	1-<3%
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid (6:2 FTS)	27619-97-2	B1; D2; La1; La2; E2; E3; E4; Ca1; Cb2; Cb3; G1	B; D; La; E; Ca; Cb; G	Polyfluorinated	Hard and decorative chromium plating; plastic etching	1-10%

Declared substances	CAS number	Product name/ mist suppressant	Supplier/s	Polyfluorinated / fluorine-free	Application area**	Mist suppressant concentration
6:2 FTS + (2-Methoxymethylethoxy)propanol + Phosphoric acid, mixed ester with partially fluorinated alcohol, ammonium salt	27619-97-2; 34590-94-8; No CAS - EC number 700-403-8	E5	E	Polyfluorinated	Hard and decorative chromium plating; plastic etching	≥5%- <8%
6:2 FTS + Methanol	27619-97-2, 67-56-1	F1	F	Polyfluorinated	Decorative chromium plating	10%
6:2 FTS + maleic acid + Methanol	27619-97-2, 110-16-7, 67-56-1	Lb3; Lb4	Lb	Polyfluorinated	Decorative chromium plating: Plastic etching	1 - <3%
Sodium dodecyl sulfate	151-21-3	B2	B	fluorine-free		2.5-5%
3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate + 3-Hydroxypropane-1-sulphonic acid + dimethyl coco alkylamine	68201-55-8, 15909-83-8; 61788-90-7	H1	H	fluorine-free	Decorative chromium plating	25-50%
Isodecanol ethoxylated	61827-42-7	Cb4	Cb	fluorine-free		>=25%-<40%
Paraffin oils, sulfochlorinated, saponified	68188-18-1	M1	M	fluorine-free		<2.5%
N1***	does not exist	N1	N	fluorine-free		25-50%
Ab2***	does not exist	Ab2	Ab	n.a.		n.a.

* Data taken from the mist suppressant user survey. (See information presented in section Survey of mist suppressant users 5.2)

** Data taken from the mist suppressant user survey or from the safety data sheets of the products

*** Specification of the mist suppressant - information on identity was requested - no response

n.a.: no information

Table 6 gives an overview of the available data on the acute toxicity of mist suppressants or the substances used in the mixtures. If substances without surface-active properties have been added to the mixtures, such as methanol or potassium dichromate, the toxicological data of these substances are not included.

Table 6: Overview of acute toxicity limits for PFOS alternatives in surface treatment

Substance name	**CAS number**	**Exposure levels (LD50, IC50, EC50, ErC50)**	
		Acute toxicity (animal experiment) *	**Environmental toxicity**
(Z)-Octadec-9-enylamine, ethoxylated	26635-93-8	LD50 Oral; <2000 mg/kg (rate) Acute toxicity estimate (ATE) value 2010 mg/kg (ATE)	n.a.
Oleylamine ethoxylate + 1,2-propylene glycol	26635-93-8; 57-55-6	n.a.	n.a.
Oleylamine ethoxylate + 2-(2-Methoxyethoxy) ethanol	26635-93-8; 111-77-3	Parameters: ATEmix calculated Exposure route: Oral Effective dose: 1111.1 mg/kg	n.a.
Amines, C12-C14 alkyl, ethoxylated	61791-14-8	Classification-relevant LD/LC50* values: Oral LD50 >500-<2000 mg/kg (rat)	Aquatic toxicity: EC50 >10-<100 mg/kg (Daphnia)
Tallow alkylamine ethoxylate + oleylamine ethoxylate+ potassium dichromate	61791-26-2; 26635-93-8; 7778-50-9	Tallow alkylamine ethoxylate: Oral LD50 200-2000 mg/kg (rat) Oleylamine ethoxylate: Oral LD50 300 - 2000 mg/kg (rat)	Tallow alkylamine ethoxylate: EC50 180 mg/kg (bacterium) 4 hours EC50/48H 1.7 mg/l (Daphnia) LC50/96H/freshwater 1.3 mg/l (thermal tolerance bandwidth - ttr) Oleylamine ethoxylate: EC50/48H 0.88 mg/l (Daphnia) Daphnia magna IC50/72H 1.1 - 10 mg/l (algae) LC50/96H/freshwater 1.3 mg/l (ttr)
6:2 FTS	27619-97-2	1. Parameters:	n.a.

Substance name	CAS number	Exposure levels (LD50, IC50, EC50, ErC50)	
		Acute toxicity (animal experiment) *	Environmental toxicity
		LD50; Oral (rat): 1800 mg/kg; 2. ATEmix, oral, > 2000 mg/kg; 3 ATE - Oral 28001.8 mg/kg; 4. ATE - Oral 30665.4 mg/kg; 5. Oral 12467.3 mg/kg, Dermal 245298.4 mg/kg, Inhalation (vapours) 2453 mg/l;	
6:2 FTS (ECHA registration dossier)	27619-97-2	Oral: LD50 (rat): > 300 - < 2000 mg/kg Inhalation: no studies are necessary because inhalation uptake in humans seems unlikely due to the vapour pressure of the substance. Dermal: LD50 (rat) > 2000 mg/kg (→	Data not sufficient for classification

Substance name	CAS number	Exposure levels (LD50, IC50, EC50, ErC50)	
		Acute toxicity (animal experiment) *	Environmental toxicity
		Classification according to CLP Regulation: no acute dermal toxicity)	
6:2 FTS + (2-Methoxymethylethoxy)propanol + Phosphoric acid, mixed ester with partially fluorinated alcohol, ammonium salt	27619-97-2; 34590-94-8; No CAS - EC number 700-403-8	Oral, ATE value 12897 mg/kg Inhalation (vapours); 2.56 mg/l	n.a.
6:2 FTS + Methanol	27619-97-2; 67-56-1	LD/LC50: Oral LD50 500 mg/kg (ATE)	LC50/96h >107 mg/l (Oncorhynchus mykiss - rainbow trout) EC50/48h >109 mg/l (Daphnia magna - water flea) ErC50/72h >96 mg/l (Pseudokirchneriella subcapitata)
6:2 FTS + maleic acid + Methanol	27619-97-2; 110-16-7; 67-56-1		
Sodium dodecyl sulfate	151-21-3	n.a.	n.a.
3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate + 3-Hydroxypropane-1-sulphonic acid + dimethyl coco alkylamine	68201-55-8; 15909-83-8; 61788-90-7	Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data) Oral LD50 > 2000 mg/kg (rat) (Limit test)	3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate: - Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data); - EC50/96h > 100 mg/L (algae) (calculation method ECOSAR 1.00) - LC50/14d ≥ 100 mg/L (fish) (calculation method ECOSAR 0.99h) - LC50/48h > 100 mg/L (Aquatic invertebrates- Daphnia magna) (calculation method ECOSAR 1.00)

Substance name	CAS number	Exposure levels (LD50, IC50, EC50, ErC50)	
		Acute toxicity (animal experiment) *	Environmental toxicity
			- LC50/96h > 100 mg/L (fish) (calculation method ECOSAR 1.00) - EC10/16h 180 mg/L (bacteria - Pseudomonas putida) (LTWS No. 1, ISO 10712) 3-Hydroxypropane-1-sulphonic acid: - Oral LD50 > 2000 mg/kg (rat) (Limit test); - EC50/96h > 100 mg/L (algae) (calculation method ECOSAR 0.99h) - LC50/96h 420 mg/L (fish - Leuciscus idus) (OECD 203)
Isodecanol ethoxylated	61827-42-7	Product: Acute oral toxicity: Estimate: 1.667 mg/kg (calculation method) Isodecanol ethoxylated: Acute oral toxicity: Estimate: 500 mg/kg (calculation method)	n.a.

Substance name	**CAS number**	**Exposure levels (LD50, IC50, EC50, ErC50)**	
		Acute toxicity (animal experiment) *	**Environmental toxicity**
Paraffin oils, sulfochlorinated, saponified,	68188-18-1	Oral LD50 1271 mg/kg (rat) (Acute oral toxicity) Dermal LD50 >2000 mg/kg (rat)"	EC50/24h 9.48 mg/l (Daphnia magna (water flea)) (Daphnia sp. Acute Immobilisation Test) EC50/48h 4.72 mg/l (Daphnia magna (water flea)) (Daphnia sp. Acute Immobilisation Test) LC50/96h 4.16 mg/l (Brachydanio rerio (zebrafish)) (fish, Acute Toxicity Test) NOEC - 96 mg/l (Brachydanio rerio (zebrafish)) (fish, Acute Toxicity Test) - 48 mg/l (Daphnia magna (water flea)) (Daphnia sp. Acute Immobilisation Test) EC50 (static) 94 mg/l (Scenedesmus subsicatus (Algae)) (algae growth inhibition test)

* Note: If only the single dose is considered, at which half of the animals are dead after a few days (=LD50), the hazardousness of chemicals is underestimated. Damage that is not fatal but severely impairs quality of life often occurs at far low doses or with chronic exposure to low doses. The most sensitive endpoint for exposure to pollutants is usually in the case of harm to children in the womb. Doses resulting in harm to the foetus can be many orders of magnitude lower than LD50 levels.

5.6.2 Short portfolio fiche of the polyfluorinated mist suppressant 6:2 FTS

For the mist suppressant 6:2 FTS, information from nine different suppliers[4] selling 6:2 FTS on the German market was taken into account. Based on the information provided in the safety data sheets (SDS), a summary "portfolio fiche - safety data sheet" was prepared, which, among other things, addresses the differences between the individual SDS. The SDS were compared to each other to document the similarities and divergence of the mist suppressants distributed. This section summarises that comparison to demonstrate the contents of the portfolio fiches.

For substances registered under REACH, the information in the safety data sheet for the substance must be consistent with the information in its registration dossier (ECHA 2015). This also applies to mixtures containing substances hazardous to health in concentrations greater than 1% (Brand 2017). Since the information in the safety data sheets for 6:2 FTS may not fully correspond to the latest specifications in the corresponding registration dossier (REACH registration dossier 2019) due to the earlier date of preparation, the information missing in the SDS, as well as deviating information in the registration dossier, is listed additionally.

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[4] A supplier brings almost identical mist suppressants with different names and minor differences in product properties (e.g. concentration) to the market;

The portfolio fiches prepared for other fluorine-free mist suppressants mentioned in Table 5 can be found in Appendix B.

In Table 7 to 16, information is compiled in the form of portfolio fiches on the following topics:

- Substance data;
- Safety data sheet (SDS);
- Classification of the substance;
- Physico-chemical properties;
- Human toxicity /hazard to humans/;
- Ecotoxicity /hazardousness to the environment /;
- Mobility;
- Safety instructions and workplace labels;
- substance lists; and
- Other (e.g. degradation products, by-products, monitoring, etc.).

In Table 7 to Table 16, different information from the SDS is compiled and different aspects are highlighted. In some cases, the portfolio fiches also include parameters for which no information is available for 6:2 FTS. The complete documentation and portfolio fiches of other mist suppressants can be found in Appendix B.

Table 7: Summary portfolio fiche for 6:2 FTS - substance data

Substance data		**Comments**
Product name:	Mist suppressant B1; mist suppressant D2; mist suppressant La1; mist suppressant La2; mist suppressant E2; mist suppressant E3; mist suppressant E4; mist suppressant Ca1; mist suppressant Cb2; mist suppressant Cb3; mist suppressant G1	Ten 6:2 FTS-containing products were found and documented on the market. Two of them (mist suppressant C1 and mist suppressant C2) are from the same manufacturer and differ only slightly (e.g. concentration).
Manufacturer	Formulator B; Formulator D; Formulator La; Formulator E; Formulator Ca; Formulator Cb; Formulator G	In total, at least 6 manufacturers supply 6:2 FTS-containing products to the market.
CAS:	27619-97-2	
Synonyms:	Tridecafluorooctane sulphonic acid	
	Polyfluorosulphonic acid	
	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonicacid	
	1H,1H,2H,2H-Perfluoroctanesulphonic acid	
	6:2 FTS	

Substance data		Comments
	H4PFOS	
Molecular formula:	$C_8H_5F_{13}O_3S$	
Main application area	Hard and bright chromium and plastic etching	In most cases, only the use in electroplating is indicated on the safety data sheet. In some cases, information comes from additional information sheets or from exchanges with the manufacturer/user.

Table 8: Summary portfolio fiche for 6:2 FTS - Safety data sheet and concentration data

Safety data sheet		Comments
Supplier	Formulator B; Formulator D; Formulator La; Formulator E; Formulator Ca; Formulator Cb; Formulator G	A total of 5 suppliers have versions for 6:2 FTS (formulator La and formulator E have joined forces).
Output period	15.04.2013-05.06.2018	It was not always possible to research more current safety data sheets.
Concentration data of the 6:2 FTS products on the German market	1 - 2.5% (3 indications); >1 - <3 % (2 indications); ≥ 1 - < 5 %; <3% (3 specifications); >3 - <5 %; 5 - 10%;	The 6:2 FTS concentration is between 1%-10% and mostly between 1%-3%.

Table 9: Summary portfolio fiche for 6:2 FTS - classification of the substance

Classification and labelling of 6:2 FTS			Number of specifications in the SDS	Comments
	Hazard class and category	GHS coding Hazard warnings		
Physical hazards				There is no data on the physical hazard of 6:2 FTS.
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed	11	According to suppliers, ingestion and eye contact are the main hazards of 6:2 FTS. Skin
	Skin Corr. 1B	H314 Causes severe skin burns and eye damage	3	

Classification and labelling of 6:2 FTS			**Number of specifications in the SDS**	**Comments**
	Skin Irrit. 2	H315 causes skin irritation	2	irritation is not indicated in all MSDS.
	Eye Dam. 1	H318 causes severe eye damage	9	No classification in REACH registration dossier as Skin Irrit. 2 and Eye Irrit. 2
	Eye Irrit. 2	H319 causes severe eye irritation	5	
	STOT Rep. Exp. 2 Specific target organ toxicity - repeated exposure	H373: May cause damage to the kidney through prolonged or repeated oral exposure	0	Classification of the REACH registration dossier
Dangerous to the environment	-	-		6:2 FTS was not classified as environmentally hazardous by any supplier
Other hazards	Other hazards that do not lead to a classification: None known.			
GHS pictograms	 GHS05 Corrosivity  GHS07 Exclamation mark  GHS08 Health hazard			The classification GHS08 is so far only indicated in the REACH registration dossier for the pure substance. A harmonised classification under the CLP Regulation has not yet been made (as of 11-2019).

Table 10: Summary portfolio fiche for 6:2 FTS - physical and chemical properties

Physical and chemical properties		**Comments**
Name	Value	
Molecular weight	428.17 g·mol^{-1}	
Physical state	solid (comes in aqueous solution in the market)	1-10% 6:2 FTS in solution
Appearance	colourless; colourless to pale yellow; colourless, yellow; colourless, brown; yellowish (4 indications); red; light brown (2 indications); light yellow, light brown;	
Smell	Odourless; No information available (2 indications); Onion (2 indications) Peculiar;	
Thickness	1.0075 g/cm^3; 1,005 g/cm^3 (3 indications); 1,008 g/cm^3 1,015 g/cm^3; 0,995 - 1,021; 0,995 - 1,025; 0.98 - 1.02 g/cm^3; 1,010 - 1,040	Despite the slight deviations, all densities given are around the approx. 1 g/cm^3 The REACH registration dossier gives a density of 1.953 g/cm^3 for the pure substance.
Melting point	not determined (3 indications); not available (5 indications); 0°C (3 indications);	What is meant here is presumably the aqueous solution. The REACH registration dossier gives a melting point of 87°C for the pure substance.
Boiling point	100°C (6 indications); > 100 (2 indications); No information available (3 indications);	What is probably meant here is the aqueous solution
Combustion point	not applicable (2 indications); not available (4 indications); not applicable (3 indications); not determined; none;	
Vapour pressure	23 hPa (4 indications); not determined (2 indications); not available (2 indications);	The REACH registration dossier specifies a vapour pressure of 1.96 Pa for the pure substance (at 20°C).

Physical and chemical properties		**Comments**
pH value	Approx. 2-3 (concentrate) 2 to 3; <2.5 (5 indications); 0.0- 2.5 (2 indications); 0.0- 3.0; acidic;	All pH values show that 6:2 FTS solutions are acidic
Water solubility	completely miscible in/with water (2 indications; lightly soluble in cold water (3 indications); completely miscible with cold water; completely soluble; miscible (4 indications);	The REACH registration dossier gives a water solubility of 658 g/l (at 20°C) for the pure substance.
Other chemical characterisation	VOC content (%): < 0.1; VOC content (%): 0.5;	

Table 11: Summary portfolio fiche for 6:2 FTS - Human toxicity /hazard to humans

Toxicity /hazard to humans		**Comments**
Name	Value	
Acute toxicity	ATE mix, oral, > 2000 mg/kg; Classification-relevant LD/LC50 values: Oral LD50 > 2000 mg/kg (rat); ATE - Oral 28001.8 mg/kg; ATE - Oral value 30665.4mg/kg (3 indications); Oral 12467.3 mg/kg, Dermal 245298.4 mg/kg, Inhalation (vapours) 2453 mg/l; Causes severe eye irritation; May be harmful if swallowed; Causes severe eye damage; May be harmful if swallowed;	Acute toxicity limits range from >2000 mg/kg to 30665.4 mg/kg (usually based on oral, rat).
Chronic toxicity	not available (3 indications); Prolonged skin contact may cause skin irritation (2 indications);	Apart from a few individual indications on chronic toxicity by skin contact, suppliers usually point out missing data for this parameter.
Carcinogenicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.	The evaluation of CMR properties is not possible due to insufficient data.
Mutagenicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.	

Toxicity /hazard to humans		**Comments**
Reproduction toxicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.	
Metabolism and depletion	not available.	
Additional toxicological information:	According to our experience and the information available to us, the product does not cause any harmful effects when handled and used as intended; (Percentage value of components in the mixture with unknown hazard for the aquatic environment: 1.6%)	

Table 12: Summary portfolio fiche for 6:2 FTS - Ecotoxicity /hazardousness to the environment

Hazardousness to the environment / ecotoxicity		**Comments**
Name	Value	
Persistence	No information is available; easily biodegradable;	For the most part, suppliers do not describe PBT properties for 6:2 FTS. In an individual case, the supplier describes the mist suppressant as easily biodegradable, but for the most part, suppliers indicate the lack of data availability regarding these properties. Classification of the REACH registration dossier: not PBT, not vPvB (very Persistent and very Bio-accumulative)
Bio-accumulation	No further relevant information available; indefinite;	
Toxicity	No further relevant information available; In case of intended use, no adverse effects on the environment are known or expected;	
PNEC: Predicted No-Effect Concentration (REACH)	not available.	
Ecotoxicological effects	no particular effects or hazards known. 1.6% - Percentage value of components in the mixture with unknown hazards for the aquatic environment 3.4% - Percentage value of components in the mixture with unknown hazards for the aquatic environment Water hazard class 1 (self-classification): slightly hazardous for water. Do not allow undiluted product or large quantities of it to reach groundwater, watercourse or sewage system;	

Hazardousness to the environment / ecotoxicity		**Comments**
	Behaviour in environmental compartments: not determined; Behaviour in wastewater treatment plants: not determined;	

Table 13: Summary portfolio fiche for 6:2 FTS - Mobility

Mobility		**Comments**
log Koc*	No values specified	No Koc values are given for 6:2 FTS.

* Koc or log Koc - The distribution coefficient between the organic carbon in soil and water indicates the sorption affinity of substances.

Table 14: Summary portfolio fiche for 6:2 FTS - Safety instructions and workplace labels

Safety instructions and workplace labels		**Number of specifications in the SDS**	**Comments**
P264	After use ... wash thoroughly.	3	Suppliers are required to label the chemicals in the safety data sheets in accordance with the GHS Regulation. The safety instructions are given by the suppliers as P-statements (Precautionary Statements) both with their coding ("P"+ 3-digit number) and as standardised text. Basically, the statements are similar, although there are variations from manufacturer to manufacturer: In case of exposure, almost all give indications regarding eye protection, which also fits the substance classification mentioned above (see Table 8).
P280	Wear protective gloves/protective clothing/eye protection/face protection.	8	
P305+P351+P338	In case of contact with eyes: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	8	
P337+P313	If eye irritation persists: Seek medical advice/consult medical assistance.	4	
P310	Immediately call POISON INFORMATION CENTRE/physician.	2	
P301+P312	Upon ingestion: If you feel unwell, call a POISON INFORMATION CENTRE/physician .	1	
P330	Rinse out mouth.	1	

Safety instructions and workplace labels		**Number of specifications in the SDS**	**Comments**
P270 (REACH registration dossier)	Do not eat, drink or smoke during use	0	Some suppliers give additional instructions on measures to be taken after oral exposure (ingestion). The REACH registration dossier does not list the following P-statements: P264, P337 und P313 and P501. P330 is only listed in the REACH registration dossier in connection with ingestion
P301+P330+P331 (REACH registration dossier)	Upon ingestion: Rinse mouth, do not induce vomiting	0	
P303+P361+P353 (REACH registration dossier)	In case of contact with skin (or hair): remove all contaminated clothing immediately, wash skin with water or take a shower	0	
P314 (REACH registration dossier)	If you feel unwell, seek medical advice / seek medical assistance.	0	
P501	Dispose of contents / container in accordance with local / regional / national / international regulations.	1	
Prevention	Wear eye protection or face shield. Wash hands thoroughly after use.	3	
Reaction	In case of contact with eyes: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	3	
Storage	Not applicable.	3	
Disposal	Not applicable.	3	
Hazardous ingredients	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid	3	
Additional labelling elements	Not applicable.	3	
Signal word	Warning	3	
Hazard warnings	Causes severe eye irritation	3	

Table 15: 6:2 FTS portfolio fiche - Substance lists

Information on substance lists in the SDS		**Comments**
REACH Appendix XIV, List of substances subject to authorisation	none of the components is listed	

Information on substance lists in the SDS		**Comments**
REACH Appendix XVII, Substances of Very High Concern	none of the components is listed; not applicable;	
Stockholm Agreement, Appendix B, Restriction, Manufacture	none of the components is listed	
Stockholm Agreement, Appendix B, Restriction, Use	none of the components is listed	
European inventory	All components are listed or excluded	

**Presumably the European Customs Inventory of Chemical Substances (ECICS) is meant

Table 16: Summary portfolio fiche for 6:2 FTS - Other (e.g. degradation products, by-products, monitoring, etc.)

Other (e.g. degradation products, by-products, monitoring, etc.)	**Comments**
Decomposition products may include the following compounds:	For 6:2 FTS, only individual suppliers have specified relevant data for this section.
halogenated compounds	
Carbon monoxide	
Carbon dioxide	
Sulphur oxide	

5.6.3 Portfolio fiche of mist suppressants, which contain other chemicals in addition to 6:2 FTS

In some products, other chemicals are used in addition to 6:2 FTS. These admixtures, their concentration in the mixture, and hazard warnings are summarised in the following table. For the individual substances, the harmonised classifications listed in Appendix VI of the CLP Regulation[5] were also checked. In these cases, the classifications and the relevant substance are identified in Table 17.

Obviously, the 6:2 FTS concentration in these mixtures is at a similar level as the concentration of 6:2 FTS in mist suppressants containing no other admixtures. In addition to the classification of 6:2 FTS, the SDS also list the classification of the other chemicals in the particular mixture, including respiratory sensitisation and acute toxicity to specific target organs. Only one product has an environmental hazard listed (aquatoxicity), which does not apply to 6:2 FTS based on the information provided in the SDS to date. Due to the classification of this product as "Harmful to aquatic organisms, with long lasting effects", wastewater should be treated carefully.

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[5] The CLP Regulation (EC) No. 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures requires manufacturers, importers and downstream users of substances or mixtures to properly classify, label and package their hazardous chemicals before placing them on the market. The classification and labelling of certain hazardous chemicals is harmonised to ensure adequate risk management throughout the European Union. Harmonised classifications are listed in Appendix VI of the CLP Regulation and must be applied by all manufacturers, importers and downstream users of such substances or mixtures containing such substances.

Table 17: Information regarding other 6:2 FTS-based mist suppressants

Substance name	CAS number	Coding, hazard warnings (GHS)*	Concentration
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid (6:2 FTS)	27619-97-2	H302 Harmful to health if swallowed; *H314 Causes severe skin burns and severe eye damage;* *H315 causes skin irritation*;* H318 causes severe eye damage; H319 causes severe eye irritation*; REACH registration dossier: H373 May cause damage to the kidney through prolonged or repeated exposure	1-10%
6:2 FTS + (2-Methoxymethylethoxy)propanol + Phosphoric acid, mixed ester with partially fluorinated alcohol, ammonium salt	27619-97-2; 34590-94-8; No CAS - EC number 700-403-8	H302 Harmful to health if swallowed; H318 causes severe eye damage; H319 causes severe eye irritation; H330 Danger to life if inhaled; H331 Toxic if inhaled; H412 Harmful to aquatic organisms, with long lasting effects.	≥5%- <8%
6:2 FTS + Methanol (CLP harmonised classification)	27619-97-2, 67-56-1	H302 Harmful to health if swallowed; H314 Causes severe skin burns and severe eye damage; H318 causes severe eye damage H371 can damage the organs. Methanol (corresponds to CLP harmonised classification): H225 Highly flammable liquid and vapour; H301 Toxic if swallowed; H311 Toxic upon skin contact; H331 Toxic if inhaled; H370 Causes damage to organs (through inhalation/skin contact/ingestion);	10%
6:2 FTS + maleic acid (CLP harmonised classification) + methanol(CLP harmonised classification)	27619-97-2, 110-16-7, 67-56-1	H302 Harmful to health if swallowed; H312 Harmful in case of contact with skin (stated by one manufacturer only) H314 Causes severe skin burns and severe eye damage stated by one manufacturer only) H318 causes severe eye damage; Maleic acid (corresponds to CLP harmonised classification):	1 - <3%

Substance name	CAS number	Coding, hazard warnings (GHS)*	Concentration
		H302 Harmful to health if swallowed; H315 causes skin irritation; H317 may cause allergic skin reactions; H319 causes severe eye irritation; H335 May cause irritation of the respiratory system; Methanol (corresponds to CLP harmonised classification): H225 Highly flammable liquid and vapour; H301 Toxic if swallowed; H311 Toxic upon skin contact; H331 Toxic if inhaled; H370 Causes damage to organs (through inhalation/skin contact/ingestion);	

* H315 and H319 are not listed in the REACH registration dossier: see https://echa.europa.eu/de/registration-dossier/-/registered-dossier/24637/2/1

5.6.4 Portfolio fiche of fluorine-free mist suppressants

Although there is a greater variety of products in non-fluorinated mist suppressants, the survey of mist suppressant users (see section 5.2) indicates that fluorine-free mist suppressants are used relatively rarely in German chromium plating plants. In addition, according to current knowledge, the fluorine-free mist suppressants have so far been used exclusively in decorative chromium plating.

Table 18 shows an overview of fluorine-free mist suppressants, as well as information on the concentration of the active substance and GHS hazard classification. For the individual substances, harmonised classifications listed in Appendix VI of the CLP Regulation were also checked. In such cases, the classifications and the relevant substance are identified in Table 18. Compared to polyfluorinated mist suppressants, higher concentrations are specified, which is, on the one hand, due to the fact that these alternative substances reduce the surface tension only at higher concentrations to the same extent as perfluorinated and polyfluorinated mist suppressants. On the other hand, a more or less rapid oxidation of these substances takes place in the process solutions containing chromium(VI), resulting in a significantly higher consumption.

As far as the hazardousness of fluorine-free mist suppressants is concerned, there is a wide range:

- Some mist suppressants are classified similarly to 6:2 FTS (hazard by ingestion; irritation and damage to eyes and skin). Although these classifications indicate a health hazard, these suppressants are used in chromium plating to protect employees from chromium(VI) and minimise the risk;

- Some fluorine-free mist suppressants have classifications listed that may cause concern. These are warnings about the risk of harm to the unborn child and/or the risk to aquatic organisms.
- Particularly noteworthy may be the mist suppressants that - at least according to the manufacturer's information - do not have to be classified according to the CLP Regulation and do not pose any potential hazards.

Table 18: Information on fluorine-free mist suppressants

Substance name	CAS number	Hazard warnings (GHS)*	Concentration
(Z)-Octadec-9-enylamine, ethoxylated	26635-93-8	H302 Harmful to health if swallowed; H315 causes skin irritation; H318 causes severe eye damage; H400 Very toxic to aquatic organisms.	>10-25%
Oleylamine ethoxylate + 1,2-propylene glycol	26635-93-8; 57-55-6	Mixture + oleylamine ethoxylate: H318 causes severe eye damage; 1,2-propylene-glycol: H302 Harmful to health if swallowed.	10-<25%
Oleylamine ethoxylate + 2-(2-Methoxyethoxy)ethanol (CLP harmonised classification)	26635-93-8; 111-77-3	H302 Harmful to health if swallowed; H318 causes severe eye damage; H400 Very toxic to aquatic organisms. 2-(2-Methoxyethoxy)ethanol (corresponds to CLP harmonised classification): H361d is likely to cause harm to the unborn child;	≥ 25 - < 50 %
Amines, C12-C14 alkyl, ethoxylated	61791-14-8	H302 Harmful to health if swallowed; H318 causes severe eye damage;	10-25%
Tallow alkylamine ethoxylate + oleylamine ethoxylate	61791-26-2; 26635-93-8; 7778-50-9	Mixture: H318 causes severe eye damage; H412 Harmful to aquatic organisms, with long lasting effects; Tallow alkylamine ethoxylate; H301 Toxic if swallowed; H318 causes severe eye damage; H411 Toxic to aquatic organisms, with long lasting effects. Oleylamine ethoxylate; H301 Toxic if swallowed; H318 causes severe eye damage;	1-<-3%

Substance name	CAS number	Hazard warnings (GHS)*	Concentration
		H400 Very toxic to aquatic organisms; H410 Very toxic to aquatic organisms with long lasting effects;	
Sodium dodecyl sulfate	151-21-3	H302 Harmful to health if swallowed; H318 causes severe eye damage; H315 causes skin irritation; H412 Harmful to aquatic organisms, with long lasting effects.	2.5-5%
3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate	68201-55-8, 15909-83-8; 61788-90-7	Mixture: H315 causes skin irritation; H319 causes severe eye irritation; H412 Harmful to aquatic organisms, with long lasting effects. 3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate: H315 causes skin irritation; H319 causes severe eye irritation; 3-Hydroxypropane-1-sulphonic acid; H290 may be corrosive to metals; H314 Causes severe skin burns and severe eye damage; H318 causes severe eye damage; Dimethyl coco alkylamine: H302 Harmful to health if swallowed; H314 Causes severe skin burns and severe eye damage; H400 Very toxic to aquatic organisms; H410 Very toxic to aquatic organisms with long lasting effects;	25-50%
Isodecanol ethoxylated	61827-42-7	H302 Harmful to health if swallowed; H318 causes severe eye damage.	>=25%-<40%
Paraffin oils, sulfochlorinated, saponified	68188-18-1	H302 Harmful to health if swallowed H315 causes skin irritation H316 causes mild skin irritation H319 causes severe eye irritation H313 may be harmful in case of contact with skin H412 Harmful to aquatic organisms, with long lasting effects	<2.5%
N1*	No CAS	The product is not classified according to CLP regulation.	25-50%

Substance name	CAS number	Hazard warnings (GHS)*	Concentration
Ab2*	No CAS	The product is not classified according to CLP regulation. Labelling according to Regulation (EC) No. 1272/2008 not applicable.	n.a.

* anonymised F-free products - more precise information was not available

5.6.4.1 (Z)-Octadec-9-enylamine, ethoxylated

Mist suppressant E1 is put on the market by formulator E and contains (Z)-Octadec-9-enylamine, ethoxylated in a concentration between 10% and 25%. Mist suppressant E1 is classified as "Harmful if swallowed" (H302), "Causes skin irritation" (H315) and Causes severe eye damage (H318) with respect to health hazards and as Very toxic to aquatic organisms (H400) with respect to environmental hazards. Mist suppressant H1 can be used in decorative chromium plating as well as in plastic etching.

5.6.4.2 Oleylamine ethoxylate + 1,2-propylene glycol

The mist suppressant Aa1 contains oleylamine ethoxylate and 1,2-propylene glycol and is distributed by the formulator Aa. The mist suppressant is classified as harmful if swallowed (H302) and causes severe eye damage (H318). According to the distributor, mist suppressant Aa1 can be used in both decorative chromium plating and hard chromium plating.

5.6.4.3 Oleylamine ethoxylate + 2-(2-Methoxyethoxy)ethanol

Mist suppressant D1 contains oleylamine ethoxylate in a concentration between 25% and 50% and 2-(2-methoxyethoxy)ethanol in a concentration between 3% and 10%. The mist suppressant D1 is marketed by formulator D as a mist suppressant for the electroplating of metal surfaces. The following hazard statements are given: "Harmful if swallowed" (H302), "Causes severe eye damage" (H318), “May cause harm to the unborn child" (H361d) and "Very toxic to aquatic organisms" (H400). The last two classifications indicate reproductive toxicity and acute toxicity to aquatic organisms.

5.6.4.4 Amines, C12-C14 alkyl, ethoxylated

Mist suppressant J1 contains amines, C12-C14 alkyl, ethoxylated and is marketed by formulator J as a mist suppressant for decorative chromium plating and hard chromium plating. Amines, C12-C14 alkyl, ethoxylated has an active ingredient concentration of 10-25% and is classified as harmful if swallowed (H302) and causes severe eye damage (H318).

5.6.4.5 Tallow alkylamine ethoxylate + oleylamine ethoxylate

Tallow alkyl amine ethoxylate and oleylamine ethoxylate are components of mist suppressant K1, which is distributed by formulator K. Tallow alkyl amine ethoxylate is distributed in a concentration of 5% to 10%. Mist suppressant K1 is used in decorative chromium plating. The hazard warnings are: Toxic if swallowed (H301), Causes severe eye damage (H318), Very toxic to aquatic organisms (H400), Very toxic to aquatic organisms with long lasting effects (H410) and Toxic to aquatic organisms with long lasting effects (H411). Mist suppressant K1 is classified as hazardous to water with water hazard class 2 (self-classification). A drinking water hazard is therefore possible even if small quantities leak into the subsurface.

5.6.4.6 Sodium dodecyl sulfate

Sodium dodecyl sulfate is a component of mist suppressant B2 for metal surface treatment sold by formulator B. Sodium dodecyl sulfate is present in the mist suppressant at a concentration of 2.5% to 5%. The following health hazard warnings are given: Causes severe eye damage (H318), harmful if swallowed (H302) and causes skin irritation (H315). The environmental hazard stated is: Harmful to aquatic organisms, with long lasting effects (H412). However, the product is stated to be water hazard class 1 (slightly hazardous to water, self-classification). It should not be discharged undiluted or in large quantities into groundwater, in the watercourse or in the sewage system.

5.6.4.7 3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate

The mist suppressant H1 is distributed by formulator H and is used as a fluorine-free electroplating auxiliary in decorative chromium plating. It is a mixture of, among others, 3-[dodecyl(dimethyl)ammonio]propane-1-sulfonate, 3-hydroxypropane-1-sulphonic acid and dimethyl cocoalkylamine. The mixture of substances is present at a concentration of 25% to 50% in the mist suppressant.

This mist suppressant is characterised as follows:

- Health hazards (Harmful if swallowed - H302, Causes severe skin burns and severe eye damage - H314, Causes skin irritation - H315, Causes severe eye damage - H318, and Causes severe eye irritation - H319)
- Environmental hazards (Very toxic to aquatic organisms - H400, Very toxic to aquatic organisms with long lasting effects - H410 and Harmful to aquatic organisms, with long lasting effects - H412)
- Physical hazards (May be corrosive to metals - H290);

The indication of the acute and chronic harmfulness of the mixture to aquatic organisms appears relevant here. Regarding persistence, mist suppressant H1 is indicated as "Not readily biodegradable" (calculated BIOWIN 4.10). The bioaccumulation potential is estimated to be low (bioconcentration factor (BCF): 71, log BCF 1.85, calculated, BCFWIN 2.15).

5.6.4.8 Isodecanol ethoxylated

Ethoxylated isodecanol is marketed as mist suppressant Cb4 by formulator Cb for plastic etching and is present in the mist suppressant in a concentration between 25% and 40%. Mist suppressant Cb4 is labelled by the manufacturer as "Harmful if swallowed" (H302) and "Causes severe eye damage" (H318). No information is available on hazards to the environment.

5.6.4.9 Paraffin oils, sulfochlorinated, saponified

Mist suppressant M1 is offered as an additive for PFOS-free chromic acid applications and is used in decorative chromium plating, hard chromium plating as well as black chromium plating. Mist suppressant M1 contains fluorine-free surfactants and is declared by the manufacturer to be fully degradable. It is compatible with all catalyst systems for chromium baths based on silicone fluoride or methane disulfonate.

Paraffin oils, sulfochlorinated, saponified are labelled with the following hazard warnings:

- Health hazards (Harmful if swallowed - H302, causes skin irritation - H315, causes mild skin irritation - H316, causes severe eye irritation - H319 and may be harmful in case of contact with skin - H313).

- Environmental hazards (Harmful to aquatic life with long lasting effects - H412).

5.6.4.10 Other substitutes

For two mist suppressant mixtures from the user survey, no hazard warnings were listed in the assigned safety data sheets: Mist suppressant N1 for decorative chromium plating and mist suppressant Ab2.

5.6.5 Evaluation of alternatives to PFOS in mist suppressants used

As shown in 5.6.4, even fluorine-free mist suppressant mixtures can, in individual cases, exhibit properties that indicate environmental pollution. However, since the halogen-free organic substances contained are quickly chemically oxidised in the solutions containing chromic acid and since they are predominantly biodegradable substances, it can be assumed that they pollute the aquatic environment to a much lesser extent and, above all, with a less lasting effect than PFAS.

In any case, the use of fluorine-free mist suppressants will lead to a reduction in environmental pollution with PFCs. Poly- or perfluorinated mist suppressants or their degradation products will always be persistent themselves and thus pollute the environment directly and/or via their degradation products. The carbon-fluorine bonds are the strongest bonds known to organic chemistry. They produce the particularly high biological, chemical and thermal stability of fluoroorganic compounds. They therefore resist strong acids, bases, oxidising agents and reducing agents. However, they are equally stable in the environment as well, since the carbon-fluorine bond is inert to photolytic and microbial degradation and is hardly metabolised (Parson et al. 2008).

Fluorine-free mist suppressants usually have better biodegradablility. Naturally, however, they are also less stable under the strongly oxidising conditions in process solutions containing chromium(VI) and may be decomposed there to form partly detrimental degradation products. This process starts more quickly at higher concentrations, and is minimised by rapid distribution and dilution of the dispensed mist suppressants in the process solution.

However, the completely fluorine-free products (mist suppressants) often require a higher technical effort by the user, i.e. the operator of an electroplating plant, compared to the previous use of PFOS. The mist suppressant dosage must often be diluted and - in contrast to the fluorosurfactants - in smaller dosages distributed throughout the day. In addition, continuous circulation of the electrolyte, e.g. by stirring or pumping, is recommended (ZVO 2007).

"Perfluorosurfactants lower surface tension more than corresponding non-fluorosurfactants. For example, to achieve 22 mN/m in ultrapure water requires the addition of 0.7 g/L (≙ 1.1 mmol/L) PFOS tetraethylammonium salt. With a comparable quantity of C8H17SO3Na 1.0 g/L (≙ 4.6 mmol/L), the surface tension of water can be lowered to only 65 mN/m. As a minimum, a surface tension of 36 mN/m can be achieved with 29 g/L (≙ 119 mmol/L) C10H21SO3Na (Wienand 2013)."

From the above, it can be concluded that the consumption when using non-fluorinated mist suppressants is in any case considerably higher than when using fluorinated mist suppressants, which was confirmed by the user survey.

5.7 Properties of 6:2 fluorotelomer sulphonic acid

5.7.1 Behaviour in the process and in wastewater treatment

Under the strongly oxidising conditions in process solutions containing chromium(VI), perfluorinated compounds are much more stable than polyfluorinated compounds with C-H bonds, such as 6:2 FTS, due to the extraordinarily stable C-F bond. One consequence of this is that, compared to PFOS, significantly higher amounts of 6:2 FTS must be added to achieve or maintain the same reduction in surface tension. Depending on the application, the additional requirement is 2 - 5 times that of PFOS. This leads to correspondingly higher emissions of 6:2 FTS or its degradation products into the environment. This effect is reinforced by the fact that 6:2 FTS binds up to 100 times worse to sludge than PFOS in biological wastewater treatment in municipal wastewater treatment plants (Podesta 2014).

In practice, PFOS exhibits the desired long-term stability, e.g. in hard chromium electrolytes. Unfortunately, PFOS is also very persistent in the environment, while the fluorine-free compounds are degraded more or less rapidly under the strongly oxidising conditions in the chromium electrolyte. Further properties of PFOS and 6:2 FTS are summarised in Table 19.

Table 19: Technical properties of PFOS and 6:2 FTS in comparison

Product	PFOS	6:2 FTS
PFAS type	perfluorinated, *anionic mist suppressant*	perfluorinated, *anionic mist suppressant*
Area of application	Hard and decorative chromium, Plastic etching	*Hard and decorative chromium, plastic etching*
Application quantity	< 100 ml/10 000 Ah	300–500 ml/10 000 Ah (additional dosage)
Stability in the process solution	very good	good to satisfactory
Solubility	good (ammonium salt)	good (free acid)
Surface tension	low (< 30 mN/m)	low (25–35 mN/m)
Foam formation (oxyhydrogen)	optimal	suitable
Surface	error-free	sensitive to errors
Water hazard class (WHC)	2 (see MSDS Lanxess)	3 (see MSDS DuPont)
Biodegradability	poor (bio-accumulative)	not bioaccumulative (Hoke et al 2015*); some bioaccumulation in marine invertebrates (Langeberg et al 2019);*
Ecotoxicity	ecotoxic and persistent	The risk to the aquatic environment is currently classified as low. However, 6:2 FTS degrades in the environment to persistent short-chain perfluorinated compounds. These have the property of being highly mobile. Currently, short-chain perfluorinated substances and their precursor compounds (such as 6:2 FTS) are under consideration

Product	PFOS	6:2 FTS
		to be regulated as “Substances of Very High Concern" (SVHCs) under REACH. (Brendel et al. 2018)

Source: Podesta (2014) with corrections and additions - additions based on findings from this study are indicated in italics or with direct source citation.

5.7.2 Commercial 6:2 FTS and other 6:2 FTS sources

In addition to the main target chemical, technical products contain varying concentrations of by-products or impurities that are unintentionally generated during production or degradation products that may be formed during production or storage. In addition, other input materials, which may also be fluorinated, can be added to the mixtures in a targeted manner. In the past, for example, approx. 10% PFBS was added to the PFOS used in electroplating for production reasons (better solubility). For 6:2 FTS, such additions of fluorinated auxiliary chemicals are currently not known. Production volumes and the exact composition of products are considered confidential business information (Field and Seow, 2017; Mumtaz et al. 2019).

6:2 FTS is synthesised via telomerisation. Investigation and screening of 6:2 FTS-based fire extinguishing agents found minor amounts of 10:2 FTS (46 ppb), 8:2 FTS, and 4:2 FTS as by-products, as well as a number of perfluoroalkyl acids (PFAAs), including low concentrations of PFOA, as constituents that may have been specifically added. 6:2, 8:2 and 10:2 FTS are registered under REACH and have been on the market for decades.

The extent to which the 6:2 FTS used in electroplating shops also contains by-products is unknown. No data are available on this to date.

The 6:2 FTS released into the environment does not originate solely from technical products that specifically contain 6:2 FTS. The second major source of 6:2 FTS in the environment is also anthropogenic fluorotelomer-based substances from which 6:2 FTS is formed by degradation. Several of these 6:2 FTS precursor compounds are used in fire extinguishing foams. When these substances are degraded in the environment, 6:2 FTS is one of the main degradation products (Zhang et al. 2016).

5.7.3 Degradation of 6:2 FTS

Environmental degradation of 6:2 FTS produces 5:2 and 6:2 fluorotelomer alcohols, saturated and unsaturated fluorotelomer acids, and perfluorinated acids (PFAAs), predominantly tetra- to hexafluorinated perfluoroalkyl acids, with minor quantities of perfluoroheptanoic acid (PFHpA) (Wang et al. 2011; Zhang et al. 2016; Houtz & Sedlak 2012). However, degradation of 6:2 fluorotelomer sulphonic acid does not produce perfluorinated sulphonic acids such as PFOS and PFHxS (Hoke et al. 2015). Houtz & Sedlak (2012) simulated accelerated degradation in the environment by oxidising 6:2 FTS (as well as other FTS) with persulfate. Short-chain perfluoroalkyl acids were formed as final degradation products of 6:2 FTS (Table 20). These substances are not known to degrade in the environment (soil or water), so they remain in the environment for long periods of time - probably centuries or millennia (Blum et al. 2015).

Table 20: Molar yield of perfluoroalkyl acids formed from precursor chemicals during oxidation with persulfate (according to Houtz and Sedlak, 2012).

Precursor chemical	Δ[PFBA]/ $[\text{Precursor}]_0$	Δ[PFPeA]/ $[\text{Precursor}]_0$	Δ[PFHxA]/ $[\text{Precursor}]_0$	Δ[PFHpA]/ $[\text{Precursor}]_0$	Δ[PFOA]/ $[\text{Precursor}]_0$	Δ[PFNA]/ $[\text{Precursor}]_0$
6:2 FTS (n = 8)	22% ± 5%	27% ± 2%	22% ± 2%	2% ± 1%		
8:2 FTS (n = 9)	11% ± 4%	12% ± 4%	19% ± 3%	27% ± 3%	21% ± 2%	3% ± 0.1%

The degradation of 6:2 FTS in environmental matrices is via intermediates and is slow. Wang et al. (2011) investigated the biodegradability of 6:2 FTS in wastewater treatment plants. For this purpose, they filled 30 ml of the 10-fold diluted activated sludge from three wastewater treatment plants into 129-ml-glass bottles and added the potassium salt of 6:2 FTS. The bottles were sealed and placed in a shaker incubator where they remained at room temperature and in the dark. After 90 days, 63.7% of the 6:2 FTS was still present. The degradation of 6.3% of the added 6:2 FTS was shown through the detection of individual stable degradation products. The fate of the remaining 6:2 FTS remained unclear. Wang et al. (2011) concluded that 6:2 FTS is poorly biodegradable and possibly persistent in the environment. Ochoa-Herrera et al. (2016) also found no degradation of 6:2 FTS in various anaerobic sewage sludge, and Zhang et al. (2016) found no degradation in anaerobic river sediments. In contrast, rapid degradation of 6:2 FTS occurred in aerobic sediments, with a half-life period of less than 5 days (Zhang et al. 2016). The single measurement of 6:2 FTS balance in a wastewater treatment plant measured in the course of project indicated a faster aerobic degradation for this long-term adapted wastewater treatment plant (chapter 5.9.1.4). This would have to be investigated and verified in more detail by further measurements.

Field and Seow (2017) summarise in their review article that there are few studies on the degradation of fluorotelomer sulphonic acids (FTS) compared to PFOS. In addition, they state that reports on biodegradation under aerobic conditions are contradictory and that there is no evidence of anaerobic biodegradation. The conditions necessary for biodegradation of FTS are not yet clearly understood. However, there is ample evidence that fluorotelomer sulphonic acids have the potential to biotransform into stable, persistent perfluoroalkyl acids (PFAAs) (Field and Seow 2017).

With the current treatment of wastewater, FTS cannot be completely removed. By discharging "treated" wastewater into surface waters, FTS can enter the environment and degrade into persistent short-chain perfluoroalkyl acids (PFAAs). Short-chain PFAAs are difficult and inadequate to remove from water using conventional activated carbon systems (Field and Seow, 2017). Treatment of contaminated river water to produce drinking water showed that FTS and other PFAS could not be removed from the water by sand filtration systems. Treatment with activated carbon also failed to reduce FTS concentrations; in some cases, they even increased, which was attributed to the degradation of FTS precursor compounds (Boiteux et al., 2017).

5.7.4 Discharge routes of 6:2 FTS / PFAS into the environment

The data situation on 6:2 FTS and their degradation products in the environment is incomplete, as FTS have not been analysed in many PFAS studies (Field and Seow, 2017). This section compiles information on this and generally describes the discharge of PFASs into the environment.

During production and use, per- and polyfluorinated chemicals (PFAS) can enter the environment. Industrial and municipal wastewater treatment plants are important point sources of water-soluble or volatile PFAS. 6:2 FTS was detected in samples from 5 out of 6 wastewater treatment plants in Germany (Frömel et al., 2016). Due to the degradation of fluorinated precursor compounds in the wastewater treatment plant, the concentration of persistent short-chain perfluorinated carboxylic and sulphonic acids, and in some cases the concentration of 6:2 FTS, may be higher in the wastewater treatment plant effluent than in the influent. (Ahrens et al., 2011; Frömel et al., 2016; Field and Seow, 2017). In previous PFAS measurements in sludge from six European wastewater treatment plants, the concentration of 6:2 FTS was the second highest (up to 80 ng/g) after PFOS (PERFORCE 2006).

PFAS can escape from landfills with the leachate and contaminate the watercourse (Ahrens et al. 2011). In 6 of 20 sampled landfills in Germany, 6:2 FTS was found in concentrations up to 75 ng/l in the landfill leachate (Busch et al., 2010; according to Field and Seow, 2017).

In the investigations of environmental contamination by 6:2 FTS, the reports in which the contamination was caused by the use of fire extinguishing foams containing fluorosurfactants (AFFF) prevail. Cases of groundwater contamination with 6:2 FTS caused by electroplating are known from North Rhine-Westphalia and Baden-Württemberg, but have not been published so far. In the USA, Lee and Mabury (2011) found high concentrations of 6:2 FTS in groundwater around sites where fire extinguishing foams were used.

Environmental media contaminated by fire extinguishing exercises or the fluorochemical industry sometimes contained high 6:2 FTS concentrations (Field and Seow, 2017):

- Drinking water (7 samples) from 2 private wells in Cologne: Well A:130-1420 ng/l, well B: < limit of quantitation (LOQ) (Weiss et al., 2012)
- Groundwater Ellsworth Air Force Base (USA), (26 samples, 96% > LOQ): not detected (ND)-270 ng/l; soil (16 samples, 69% > LOQ): ND-370 µg/kg; sediment (10 samples, 90% > LOQ): ND-370 µg/kg (Houtz et al. 2013)
- River water, downstream of a chemical plant (France), (44 samples): ND-195 ng/l; drinking water (12 samples): < LOQ-70 ng/l; river sediment (44 samples): < LOQ–44 ng/g TM (Boiteux et al., 2017)
- Groundwater Wurtsmith Air Force Base (USA) (18 samples, 83% < LOQ): ND–173 µg/l (Schultz et al., 2004)
- Groundwater Tyndall Air Force Base (USA) (4 samples, 100% > LOQ): 1080-14600 µg/l (Schultz et al., 2004).

The 6:2 FTS concentration in groundwater at Tyndall Air Force Base (1080-14600 µg/l) is the highest concentration of a PFAS compound measured in groundwater to date (Field and Seow, 2017)

Of 26 drinking water samples from Germany taken in a non-specific manner, 6:2 FTS was detected in only one sample (1.5 ng/l) (Gellrich et al. 2013). The limit of quantification was 1 ng/l.

6:2 FTS was also detected in the domestic environment: in carpets (up to 1.35 µg/m^2), in compostable waste (up to 1.5 µg/kg), in impregnating agents and polishes (0.1 mg/l), and in house dust (up to 2342 ng/g). Concentrations of 6:2 FTS in house dust were partly at the same level as PFOS and PFOA and partly an order of magnitude lower (Field and Seow, 2017).

5.7.5 Uptake of 6:2 FTS and degradation compounds in plants

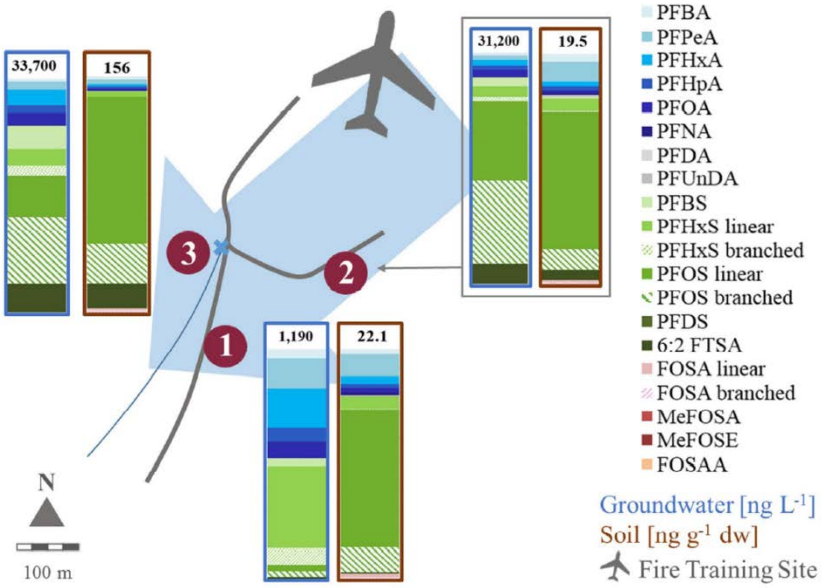
PFASs are absorbed by plants from the soil and also accumulate in the edible part of plants (Gobelius et al. (2017). Ghisi et al. (2019) showed that short-chain PFASs can accumulate to a great extent in leafy vegetables and fruits.

Gobelius et al. (2017) investigated the uptake and distribution of PFAS in plants growing on a Stockholm Airport site contaminated with fire extinguishing foam. The samples were analysed for 26 PFASs. Of these, 13 were detected in groundwater, 17 in soil, and 10 in plants (birch, spruce, bird cherry, goutweed, mountain ash).

The bar graphs in Figure 13 show the patterns and concentrations of PFAS in soils (brown) and groundwater (blue). The large pale blue arrow indicates the direction of groundwater flow. While PFOS was the highest in soil and groundwater (about 50%), plants contained predominantly 6:2 FTS (about 50%), as well as short-chain PFAAs, particularly perfluoropentanoic acid (PFPeA) (about 24%), some of which form during the degradation of 6:2 FTS (and other PFAS precursors) (Figure 14) (Gobelius et al. 2017)

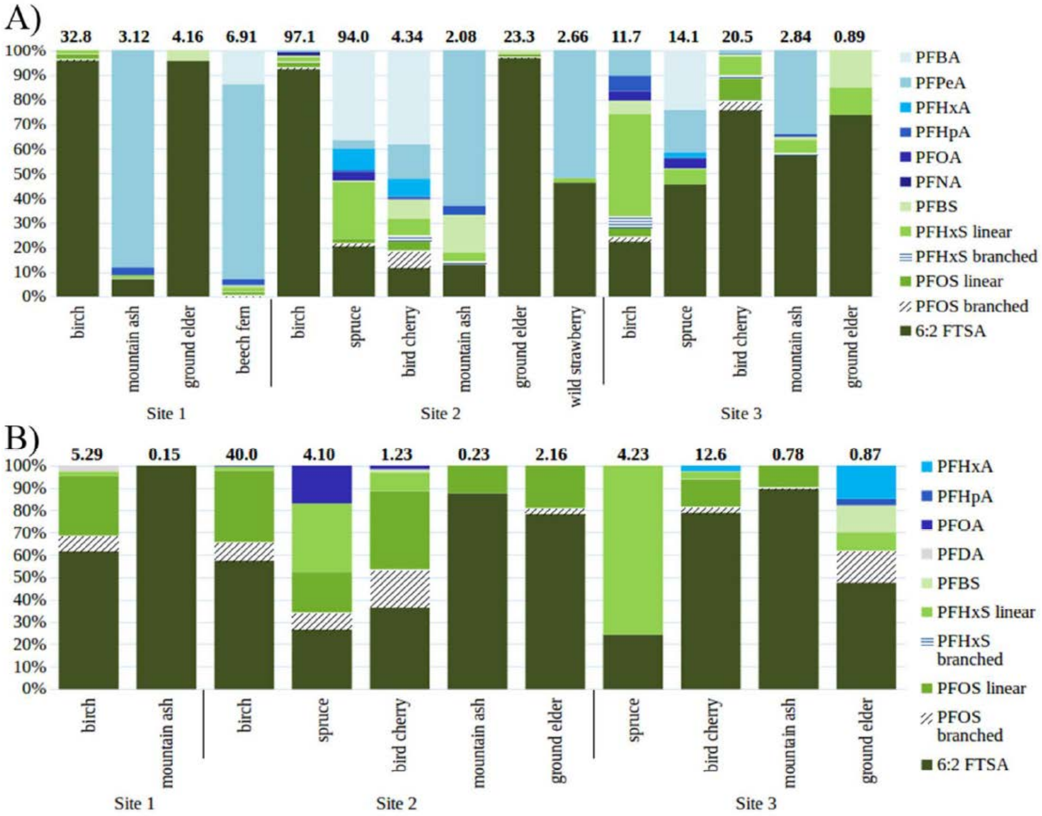
It was shown that different plant species and plant parts accumulate PFAS to different degrees. The relative proportion of 6:2 FTS was higher in branches than in foliage, whereas short-chain PFAAs had a higher proportion in foliage (Figure 14). The PFAS concentrations in foliage were highest in birch, followed by spruce, bird cherry, and goutweed. Compared to foliage, tree branches had lower PFAS concentrations, and even here, birch branches had the highest concentrations, followed by spruce branches.

Figure 13: Map of the three sampling locations at the airport site in Stockholm contaminated by fire extinguishing foams



Source: Gobelius et al. (2017)

Figure 14: Distribution of PFAS in A) foliage and B) branches



Source: Gobelius et al. (2017)

5.7.6 Ecotoxicity

According to investigations by the chemical company DuPont de Nemours, there is a clear difference between the toxicity of PFOS and 6:2 FTS from the results of the acute toxicity studies of 6:2 FTS for aquatic organisms. PFOS was generally at least 10 times more potent than 6:2 FTS (Hoke et al. 2015, Table 21).

Table 21 shows the results of tests for the assessment of environmental toxicity. The dose for acute toxicity in case of fish, water flea (Daphnia), and green algae is generally higher than 96 mg/l for 6:2 FTS, with values for PFOS varying from 48 to 78 mg/l (Table 21). Substances for which the acute toxicity for rainbow trout, water flea or green algae is less than 100 mg/l (for the median lethal dose (LD50) or median effective dose (EC50, ErC50)) are classified as environmentally hazardous under GHS. As can be seen from the table below, this threshold is just exceeded or undercut by 6:2 FTS.

Table 21: Comparison of 6:2 FTS und PFOS: Acute toxicity und Bio-accumulation

Parameters	K-6:2 FTS (6:2 FTSA)	PFOS
Anion	$C_6F_{13}CH_2CH_2SO_3^-$	$C_8F_{17}SO_3^-$
Length of the fluorinated carbon chain	6(8)	8(8)
O. mykiss (rainbow trout) 96-h LC50	> 107 mg/l[d] (>108 mg/l)	78 mg/l[a]
D. magna (Daphnia magna), 48-h EC50	> 109 mg/l[d] (>112 mg/l)	58 mg/l[a]
P. subcapitata (green algae), 72-h ErC50	> 96 mg/l[d] (>125 mg/l)	48.2 mg/l[a]
P. subcapitata (green algae), 72-h NOEC	47.6 mg/l[d] (>125 mg/l)	42 mg/l[a]
90-d O. mykiss (rainbow trout) ELS NOEC	2.62 mg/l[d] (no data)	0.29 mg/l[a] (P. promelas (fathead minnow))
14-d E. fetida (earthworms) LC50	500 mg/Kg[g] (no data)	500 mg/Kg[g]
56-d E. fetida (earthworms) EC10, Repro.	247 mg/Kg[g] (no data)	25 mg/Kg[g]
Aquatic bioaccumulation	not bioaccumulative in fish[d]; some bioaccumulation in invertebrates[e]	bio-accumulative[b]

Source: Hoke et al. 2015 (data summarised from Table 2, page 263) supplemented with Langberg et al. 2019;
b - Martin et al. 2003a.
c - Martin et al. 2003b.
d - Data are from Hoke et al. 2015.
e -Langberg et al. 2019.
g - Norwegian Pollution Control Authority (SFT) (2006).
NOEC: No Observed Effect Level or concentration is a toxicological endpoint in toxicity determination.
The NOEC corresponds to the highest exposure concentration of a substance in subchronic or chronic studies at which no statistically significant treatment-related effect can be observed

Field and Seow (2017) evaluated aquatic toxicity studies by Beach et al. (2006) and Colombo et al. (2008) (cited in Field and Seow, 2017) and reached a different conclusion. The aquatic toxicity of 6:2 FTS ranged from >107 to 47.6 mg/l for the three test species rainbow trout (Oncorhynchus mykiss), water flea (Daphnia magna), and green alga (Pseudokirchneriella subcapitata). Thus, the acute toxicity of 6:2 FTS to aquatic organisms was of the same order of magnitude as that for PFOS (>78-42 mg/l) (Beach et al., 2006) and PFOA (>100 mg/l) (Colombo et al. 2008).

Phillips et al. (2007) studied the aquatic toxicity of fluororteleomeric acids. They emphasise that although concentrations of fluororteleomeric acids in aquatic systems are low, it should not be misunderstood that these substances are continuously introduced into and potentially accumulate in aquatic ecosystems. Aquatic organisms may be exposed to these substances throughout their lifetime. It should not be forgotten that chronic, non-acute lethal effects may occur at lower effective thresholds. Lower effective thresholds for chronic toxicity would be indicated by their own laboratory experiments (Phillips et al., 2007).

Plants and animals absorb 6:2 FTS via environmental media. However, 6:2 FTS and precursor compounds are degraded or excreted in microbial systems and also in fish and mammals (sources are cited in Loi et al. 2013). Therefore, unlike long-chain perfluorinated compounds, no accumulation occurs through the food chain. After being assumed to show no bioaccumulation until early 2019 (NASF 2019), 6:2 FTS was recently found to have bioaccumulation in marine invertebrates (Langberg et al. 2019). To assess the ecotoxicity of 6:2 FTS, it is necessary to also further investigate the toxicity and behaviour of the short-chain perfluorinated degradation products (Ahrens et al., 2015; Loi et al., 2013).

The primary degradation products (PFBA, PFPeA, PFHxA) exhibit no bioaccumulation. PFHpA, which is formed to a small extent (about 2%) during the degradation of 6:2 FTS (Table 20Table 20; Houtz and Sedlak, 2012), shows lower bioaccumulation than PFOA (NICNAS 2015).

5.7.7 Concentration in human blood and state of knowledge on toxicity

Lee and Mabury (2011) examined 50 blood serum samples from the USA for fluorinated substances, including 6:2 FTS and 8:2 FTS (Figure 15). 20 samples each were from male and female donors. The other 10 samples were pooled samples, each from at least 10 individual donors. The age of the donors ranged from 18 to 70 years. Figure 15 shows the means and standard deviations in µg/l on a logarithmic scale. Lee and Mabury (2011) point out that the measured FTS concentrations in blood are not solely a consequence of exposure to these substances, but may also result from the degradation of precursor compounds (e.g. diPAPs).

The levels of 6:2 FTS in blood were 2 orders of magnitude smaller than those of PFOS and often (70%) below the detection limit.[6]

Concentrations of 6:2 FTS in blood samples from Hong Kong (Loi et al., 2013;Table 22) ranged from 0.39 to 7.79 pg/g (1 pg/g here corresponds to about 0.001 µg/l) and were even lower than in the samples from the USA. In the samples from the USA and in the samples from Hong Kong, the levels of 8:2 FTS were higher (mostly approx. a factor of 10; Table 22) than those of 6:2 FTS.

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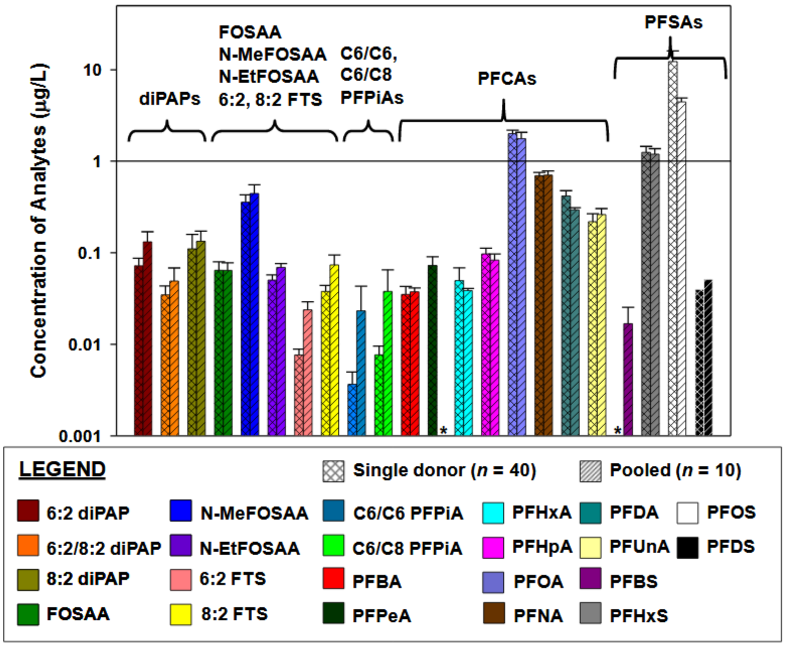
[6] However, it cannot be concluded from this that human exposure to 6:2 FTS is 2 orders of magnitude less than to PFOS, because 6:2 FTS - unlike PFOS - does not bioaccumulate in humans

Figure 15: Fluorinated compounds in blood serum from donors in the USA



Concentrations of compounds that could only be detected in less than 20% of the samples are not shown, but have been marked with an *

Source: Lee and Mabury (2011)

Table 22: Fluorotelomer sulphonic acids in blood samples from Hong Kong (pg/g)

Sample	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2
4:2 FTS	<1.61	<1.58	<1.58	<1.61	<1.61	<1.59	<1.56	<1.58	<1.58	<1.58
6:2 FTS	2.46	0.67	7.89	1.92	1.12	0.50	0.40	2.03	4.55	0.71
8:2 FTS	22.7	22.0	36.1	79.1	8.78	3.98	4.61	21.8	5.14	9.12
Sample	**C3**	**C4**	**D1**	**D2**	**D3**	**D4**	**E1**	**E2**	**E3**	**E4**
4:2 FTS	<1.60	<1.59	<1.58	<1.60	<1.58	<1.55	<1.59	<1.52	<1.58	<1.57
6:2 FTS	1.21	1.21	5.69	1.12	0.39	4.46	0.34	0.45	5.95	0.77
8:2 FTS	23.6	7.30	10.3	15.8	7.12	47.2	3.25	20.1	24.9	5.37

Source: Loi et al. 2013, Supporting information, excerpt from Table S8, page S23

5.7.8 Shortcomings of previous toxicological studies and legal regulations

In the REACH registration dossier, there is no testing to date for 6:2 FTS to assess cancer or disruption of the endocrine, immune, or nervous system, although, for example, experimental and epidemiological data show damage to the immune system at low PFAS levels as the most sensitive endpoint (Grandjean 2018, NASF 2019). Damage to brain development has not been examined, which is also one of the most sensitive endpoints (Grandjean, Landrigan 2014).

In the study by the European Commission (2017) "Study for the strategy for a non-toxic environment of the 7th Environment Action Programme", it has been pointed out that risk assessments, usually conducted by the proponents of marketing a chemical (e.g. the manufacturer), often underestimate the risk of harm. Additional scientific research on the potential hazards of chemicals would almost always lead to increased (and rarely decreased) concern about risks to human health and the environment.

Furthermore, it is not sufficient to assess the hazard of the substance 6:2 FTS. 6:2 FTS is at the same time a precursor compound of short-chain persistent PFAS (Table 20) and various intermediates. These should also be included in the risk assessment. This is because short-chain PFAS exhibit properties of concern:

- Transport over long distances
- Reaching remote regions
- (almost) no retention in soil and sediment
- Detected in surface water, groundwater, drinking water, and tap water
- Accumulation in plants
- Exposure of humans via the environmental pathway
- Occurrence in the environment irreversible, since very persistent
- Accumulation in the environment

Regarding the regulation of these PFAS and their precursor compounds, the Ministry of the Environment (BMU 2017) wrote: "*The Federal Environment Agency also assesses the short-chain PFC [PFAS], which are increasingly used as alternatives, as possibly being of very high concern due to their persistence and very high mobility, and is currently examining an appropriate risk management measure under REACH for perfluorohexanoic acid and its precursor compounds. In addition, the Federal Environment Agency is currently evaluating the environmental risks of two registered, economically significant precursor compounds of this perfluorinated carboxylic acid (6:2 fluorotelomer acrylate, 6:2 fluorotelomer methacrylate) in a REACH substance evaluation.*"

Chemicals with a high degree of persistence remain in the environment for long periods of time, resulting in exposure of humans, including vulnerable populations, and animals, plants, and environmental media. This can lead to previously overlooked or unanticipated adverse effects even for chemicals for which laboratory studies have not shown significant toxicity, e.g. when effects are chronic or occur at low concentrations. Very persistent chemicals released into the environment can render resources such as soil and water unusable far into the future and destroy our livelihoods.

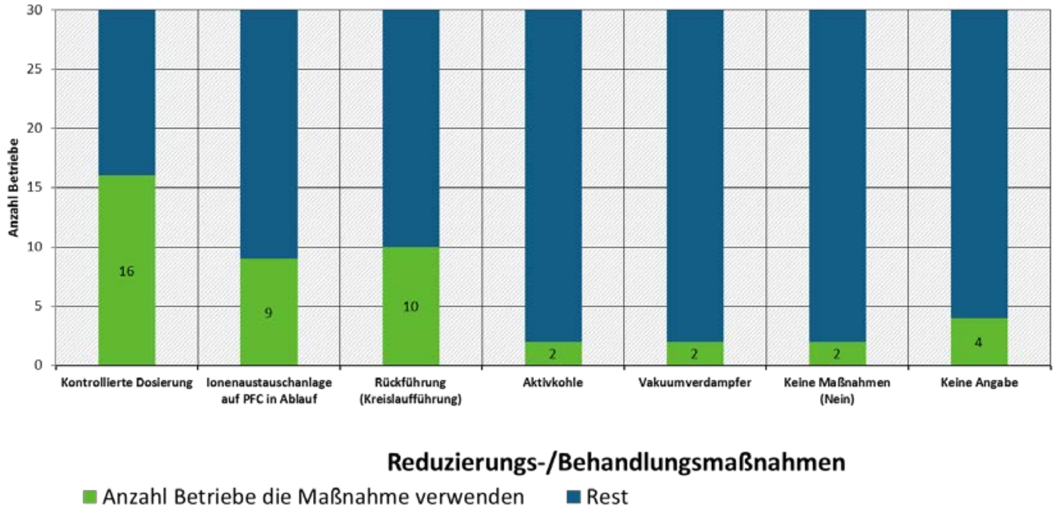
5.8 Reduction and treatment measures for PFAS

The questionnaire surveyed whether measures had been taken at the facilities to reduce PFAS emissions via wastewater. 80% of the facilities confirmed this. Only 6.7% of the facilities answered with a No. 13.3% of the facilities did not provide any information.

The type of measures can be differentiated into production-integrated measures, which are aimed at the economical dosing of mist suppressants or chromic acid recovery, and measures for adsorptive reduction of PFAS emissions in the wastewater path. Among the 30 facilities that gave feedback on this, there were also combinations or multiple responses of the above-mentioned measures. This concerned 11 facilities (approx. 37%). Figure 16 shows which measures were highlighted and how often they occurred.

Figure 16: Reduction/treatment measures used: Number of measures specified

The figure shows how many of the 30 facilities surveyed use a particular reduction/treatment measure. Of 30 facilities, 16 use measures to control dosing; 9 facilities have ion exchange systems in operation; 10 facilities work with recirculation; 2 with activated carbon adsorption; and 2 use vacuum evaporators. 2 facilities indicate that they do not use any measures and 4 other facilities did not provide any information at all.



Source: Own representation

Production-integrated reduction measures

For the monitoring of the dosing of the mist suppressants used, the statements in the order of increasing effort ranged from: "no measures", through “utilisation-dependent automatic dosing" and “mist suppressant is dosed by means of ampere-hour measurement via a dosing pump" and “metered addition of mist suppressant dependent on measured surface tension" to "addition according to analysis".

The range of production-integrated recirculation measures mentioned ranged from simple rinse water recirculation of the rinsing baths to the "use of vacuum evaporators in the recirculation system" and evaporators with an almost closed chromic acid circuit (> 90% decorative chromium plating only) to - according to the information provided - completely wastewater-free systems (functional chromium plating only).

Measures for adsorptive reduction of PFAS emissions

In order to reduce emissions of PFAS in the wastewater path, in addition to the above-mentioned measures for recycling or recirculating the process solutions containing chromic acid, the use of adsorption systems based on activated carbon (6.7% of the facilities) or ion exchangers (30% of the plants) was also mentioned.

The majority of the facilities did not know the concentration of the mist suppressants used in their wastewater, which was not to be expected due to the lack of uniform federal regulations in this regard.

5.9 Investigation into the fate of the mist suppressants used in production and wastewater treatment

5.9.1 Fate of 6:2 FTS using the example of a plant for decorative chromium plating of metals

In Germany, PFOS has now been almost completely replaced in the surface treatment industry. PFOS has predominantly been replaced by 6:2 FTS. Therefore, a company using 6:2 FTS in decorative chromium plating was selected for analytical tracking of the polyfluorinated mist suppressant used, from the production to the water. The aim was to trace the path of the 6:2 FTS from the operation site in a so-called bright chromium bath via the company's in-house wastewater pretreatment plant (with interface to the waste path) and the subsequent municipal, biological wastewater treatment plant (further interface to the waste path) to the point of discharge into the watercourse.

5.9.1.1 Selection of the plant for decorative chromium plating of metals

For the investigation, a plant for decorative chromium plating of metals with a relatively consistent utilisation was selected for the study.

A facility was selected that is connected to a municipal wastewater treatment plant into which no other electroplating shops discharge and for which no other relevant 6:2 FTS sources in the inflowing untreated wastewater are known.

5.9.1.2 Investigation period, sample type and parameters of the measurement campaign

The investigation period was chosen shortly after the 2018 summer break. This had the advantage that all plants were running in routine operation and no relevant operating personnel of the investigated plants were on vacation. During this time of year, there is a low probability of heavy rainfall that could affect the results of the municipal wastewater treatment plant due to a surge of rinse water in the sewage system during the onset of heavy rain or a rainwater discharge. Therefore, 10.09. -14.09.2018 was selected as the investigation period.

During the investigation period, light rainfall occurred for only a few hours on one day, so that the entire PFAS load discharged from the electroplating shop under investigation arrived at the downstream municipal biological wastewater treatment plant without rainwater discharge. If heavy rainfall had occurred during the investigation period, it could have been expected that during the rainfall a portion of the discharged electroplating wastewater would have been discharged directly into the watercourse via a rainwater discharge basin. This would have resulted in lower findings in the inflow of the wastewater treatment plant, which would have been difficult to quantify.

The weekly composite sample was selected as the sampling method for all wastewater and sludge samples. Since the facility produces in two shifts only 5 days a week, the weekly composite samples were obtained both at the treatment plant and at the facility by combining 5 daily composite samples each.

Since the flow time of the wastewater from the sampled electroplating shop to the downstream municipal wastewater treatment plant was less than 2 hours, the flow time could be neglected when preparing the daily composite samples.

The wastewater samples were analysed according to DIN 38407-F42 and the sludge samples according to the PV M 3400/F method by the Water Technology Centre (TZW) in Karlsruhe (accredited laboratory) for the 20 PFAS currently in use, including 6:2 FTS . The measurement uncertainty is between 35% and 45%, depending on the parameter. In detail, these include the following per- and polyfluorinated compounds:

Table 23: List of perfluorinated or polyfluorinated compounds

Perfluorobutanoate (PFBA)
Perfluoropentanoate (PFPeA)
Perfluorohexanoate (PFHxA)
Perfluoroheptanoate (PFHpA)
Perfluorooctanoate (PFOA)
Perfluorodecanoate (PFUnA)
Perfluorododecanoate (PFDoA)
Perfluorobutane sulfonate (PFBS)
Perfluoropentanesulfonate (PFPS)
Perfluorohexane sulfonate (PFHxS)
Perfluoroheptane sulfonate (PFHpS)
Perfluorooctane sulfonate (PFOS)
Perfluorodecane sulfonate (PFDS)
Perfluorooctane sulfonamide (PFOSA)
7H-dodecane fluoroheptanoate (HPFHpA)
2H2H-perfluorodecanoate (H2PFDA)
2H,2H,3H,3H-perfluorundecanoate (H4PFUnA)
1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FTS; H4PFOS)

In order to clarify desorption effects and previously unknown PFAS sources, two process solutions (samples 7 and 8) were taken from the electroplating machine at the end of their service life. The process solutions were an ultrasonic degreasing solution from a 2.5 m^3 bath and a demetallisation solution from a 4.5 m^3 bath. Both solutions were taken in each case after 4 weeks of use, and thus directly before regular discharge into the PFAS- and chromium(VI)-free substream of the company's in-house wastewater treatment plant for other electroplating wastewater (acidic/alkaline). These samples were taken as simple random samples.

5.9.1.3 Description of the selected plant for decorative chromium plating

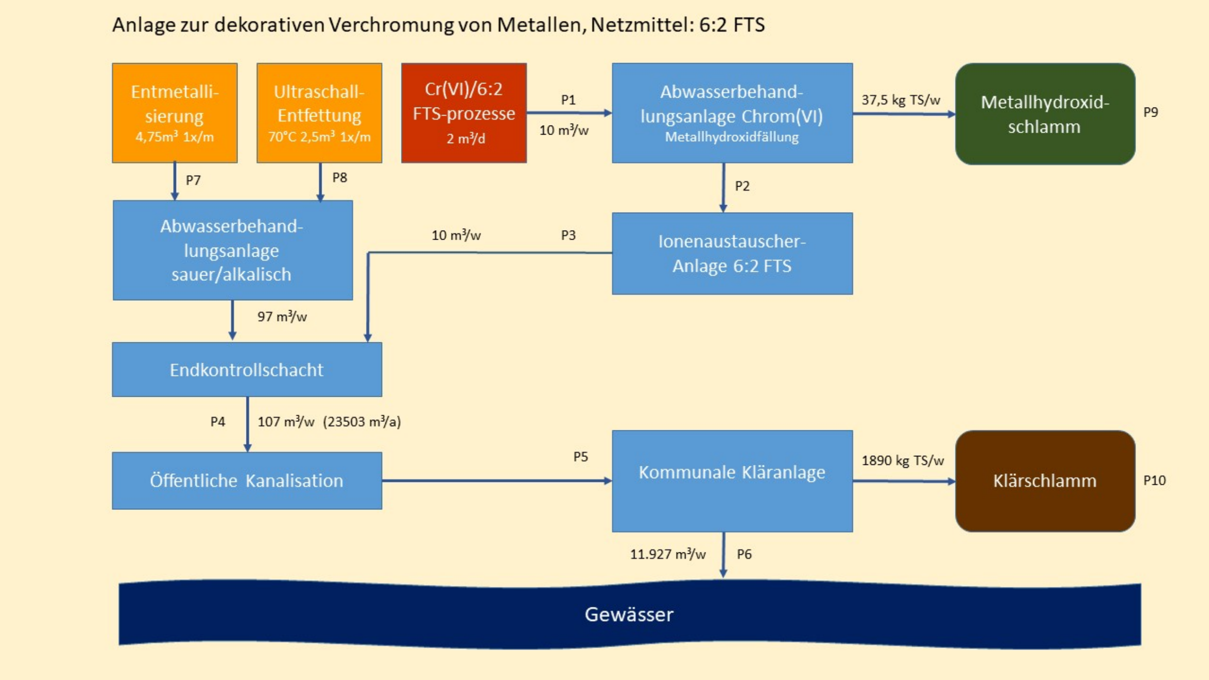
The selected plant is an automatic electroplating machine for nickel plating and decorative chromium plating of metal parts. The workpieces are first degreased in a 70 °C ultrasonic degreasing process before being electroplated in the metal-containing electrolyte after further intermediate steps. The deposited decorative layer thicknesses for chromium are 0.2 - 0.5 µm. The effective treatment vat volume of the plant is 70 m^3. The bright chromium bath has a volume of 4.5 m^3 and is operated at 45 °C. The plant has a closed chromic acid circuit and is state of the art. The plant is a so-called automatic rack plating machine in an electroplating operation with comparatively constant process conditions. For rack maintenance, the plastic-coated racks with the metallic contact points are treated in a demetallisation bath.

5.9.1.4 Sampling of the plant for decorative chromium plating of metals and the municipal wastewater treatment plant

The block diagram in Figure 17 shows which potential sources of mist suppressants were investigated in the electroplating shop and how the fate of the mist suppressant was tracked.

For a better understanding of the analytical results, it should be noted at this point that experience has shown that PFOS is still detected in the wastewater of plants where PFOS was used many years after the end of PFOS use. This is due to desorption processes from all contact surfaces (tanks, pipelines, filters, ion exchangers, etc.) that once came into contact with PFOS. This process is called "bleeding out of PFOS".

Figure 17: Simplified block diagram on mist suppressant fate for 6:2 FTS



Source: Own representation

5.9.1.4.1 Chromium(VI)/6:2 FTS processes - sampling point 1 (P1)

The following sources of 6:2 FTS-containing wastewater streams in electroplating shops are generally known:

Obvious mist suppressant sources:

- Rinsing with direct overflow into wastewater collection tanks
- Maintenance, cleaning, and draining of sinks

Hidden mist suppressant sources:

- Drainage from racks, suction shafts, and scrubber racks
- Washing water from exhaust air scrubbers
- Emergency overflows from sinks
- Hosing down of plant components contaminated with chromate
- Spillage during dosing
- Sampling for internal analyses / practical tests
- Accidents and accidents, if any

These and other sources are recorded in four wastewater sub-streams at the plant under investigation:

- Rinsing water after bright chromium electrolyte
- Regenerates from the ion exchanger plant for external metal removal in the chromium(VI) rinsing water circuit
- Wash water of the exhaust air scrubber for chromium aerosols of the chromium bath
- Cleaning and soil wastewater from maintenance work in the chromium(VI) area of the electroplating shop

These four wastewater sub-streams are summarised in Figure 17 as "chromium(VI)- or 6:2 FTS-relevant processes" of electroplating and form the known 6:2 FTS discharge into the wastewater treatment plant. These wastewaters are first treated for chromium(VI) and in a further process step for 6:2 FTS.

In the plant selected for the project for decorative chromium plating of metals, 6:2 FTS is used exclusively in a bright chromium electrolyte with an effective treatment vat volume of 4500 litres. The mist suppressant is dosed as needed according to the state of the art as a function of the measured surface tension of the electrolyte.

The 6:2 FTS-containing rinsing water from the first rinsing bath after the chromium plating bath is concentrated in an atmospheric chromic acid evaporator and returned to the chromium plating bath. In this process, an ion exchanger plant is used for external metal removal in the 6:2 FTS-containing rinse water circuit.

The wastewater substream containing chromium(VI) or 6:2 FTS is collected separately from other wastewater substreams of the electroplating shop and fed to a chromium reduction batch with a load capacity of 2 m^3. During the investigation period, 10 m^3 of this wastewater substream was produced as untreated wastewater. Sampling point 1 (P1) for untreated 6:2 FTS-containing untreated wastewater is located here.

The analytical result for P1 was 910 µg 6:2 FTS/l and 14 µg PFOS/l. This indicates that PFOS is still bleeding out. Potential degradation products of 6:2 FTS, such as PFHxA and PFPeA could not be detected in the untreated wastewater (limit of quantification: 1 µg/l).

5.9.1.4.2 Outlet of the wastewater treatment plant for chromium(VI) - sampling point 2 (P2)

In the chromium reduction batch, chromium(VI) is quantitatively reduced to chromium(III) with sodium bisulfite. Subsequently, the wastewater is alkalised with caustic soda and calcium hydroxide and the heavy metals contained are precipitated as metal hydroxides. The resulting metal hydroxide sludge is separated by means of a chamber filter press. Sampling point 2 (P2) is located at the outlet of the chamber filter press and thus in the outlet of the chromium reduction batch. During the investigation period, 10 m^3 of this pretreated wastewater substream accumulated.

The analytical result of the treated wastewater for P2 with 910 µg 6:2 FTS/l showed the same measured value as for the untreated wastewater. This finding was critically questioned, but was analytically confirmed by the TZW through two multiple measurements of P1 and P2. A sample mix-up or an evaluation error was excluded by the TZW. It must therefore be assumed that the metal hydroxide precipitation has no significant influence on the removal of 6:2 FTS from the wastewater within the scope of the measurement inaccuracy.

5.9.1.4.3 Outlet of 6:2 FTS ion exchanger plant - sampling point 3 (P3)

The wastewater pretreated in this way is passed through a gravel filter and three ion exchanger columns filled with a basic anion exchange resin specially developed for the adsorption of

PFOS/6:2 FTS. Frequently, the ion exchange resin "Lewatit® 500" is successfully used to remove 6:2 FTS from the wastewater of electroplating shops (Blepp, Willand, Weber 2016). Sampling point 3 (P3) is located in the outlet of the ion exchanger plant. The analytical result for P3 showed measured values below the detection limit in industrial wastewater: <1 µg 6:2 FTS/l and < 1 µg PFOS/l.

No PFASs were detectable in the outlet of the ion exchanger plant.

5.9.1.4.4 Outlet of the wastewater treatment plant final inspection shaft - sampling point 4 (P4)

The 6:2 FTS-containing wastewater substream is mixed with the other heavy metal-containing wastewater (wastewater substream: "acidic/alkaline") from the electroplating shop after it has been treated with the PFAS-selective ion exchange resins. The mixing ratio of 6:2 FTS-containing wastewater to other electroplating wastewater is approx. 1: 10. Sampling point P4 is called "final inspection shaft".

The analytical result for P4 showed 61 µg 6:2 FTS/l and 1.2 µg PFOS/l. This means that the "acidic/alkaline" wastewater substream, originally considered PFAS-free, obviously does contain PFAS. Multiplying the measured concentrations by the derived total wastewater flow from the electroplating shop in the observation period of 107 m^3/w results in a load of 6.53 g 6:2 FTS/w and 0.13 g PFOS/w.

5.9.1.4.5 Inflow of the municipal wastewater treatment plant - sampling point 5 (P5)

The analytical result for P5 was 0.550 µg 6:2 FTS/l and 0.019 µg PFOS/l. In the investigation period, the inflow to the municipal wastewater treatment plant was 11,297 m^3/w. Consequently, the calculated inflow loads were 6.21 g 6:2 FTS/w and 0.21 g PFOS/w. All other PFAS were not detectable in the inflow of the wastewater treatment plant.

These loads found in the inflow of the municipal wastewater treatment plant correlate quite well with the loads, derived by the company, of: 6.53 g 6:2 FTS/w and 0.13 g PFOS/w. For PFOS, sources by precursor chemicals are mostly present even in non-industrially influenced wastewater treatment plants, explaining the increased input.

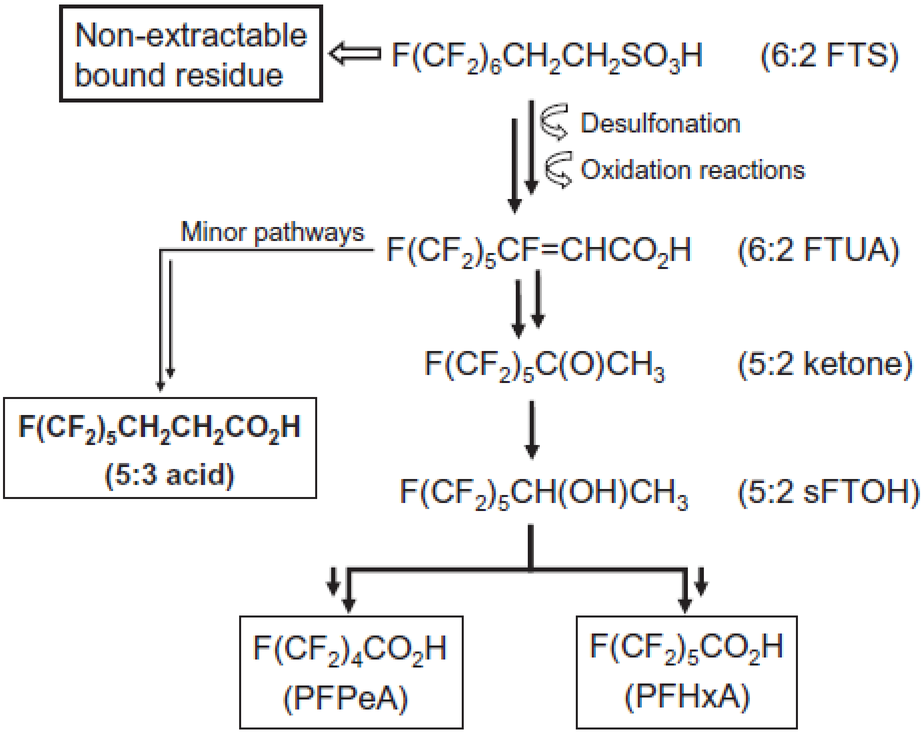
Some conclusions can be drawn from this:

- the PFAS load derived from the investigated electroplating shop was recovered in the inflow of the downstream municipal wastewater treatment plant
- there is no other relevant indirect discharger for 6:2 FTS in the catchment area of the wastewater treatment plant
- no rainwater discharge occurred during the investigation period, so the entire PFAS load derived from the electroplating shop arrived at the wastewater treatment plant
- the sewage system between the company's final inspection shaft and the municipal wastewater treatment plant does not show any significant leaks

5.9.1.4.6 Outlet of the municipal wastewater treatment plant - sampling point 6 (P6)

The analytical result for P6 was 0.060 µg 6:2 FTS/l and 0.017 µg PFOS/l. Furthermore, in order of increasing concentration, 0.007 µg/l perfluorobutanoate (PFBA), 0.012 µg/l perfluoroheptanoate (PFHpA), 0.026 µg/l perfluoropentanoate (PFPeA) and 0.033 µg/l perfluorohexanoate (PFHxA) were detected. The latter two (PFPeA and PFHxA) are described as degradation products of 6:2 FTS:

Figure 18: Possible aerobic biodegradation of 6:2 FTS



Source: Wang et al 2011

Compared to the inflow, approx. 89.1% was thus removed from the wastewater in the municipal wastewater treatment plant with respect to 6:2 FTS. This corresponds to a much higher elimination rate than would be expected based on the biodegradability found in the literature for 6:2 FTS (see Chapter 5.7.3; Ochoa-Herrera et al. 2016; Wang et al. 2011; Zhang et al. 2016). This may be due to the fact that this is a long-term adapted wastewater treatment plant, the biology of which has adapted particularly well to the regular inflowing 6:2 FTS load. On the other hand, this is only an individual measurement which certainly does not allow a more valid statement than scientific test series.

The theoretically expected degradation products PFPeA and PFHxA appear for the first time in the wastewater, which possibly confirms the biodegradation outlined above.

In the very low, two-digit nanogram range, no significant elimination rate is discernible for PFOS. However, it must be taken into account that PFOS can be formed from precursor compounds in biological wastewater treatment plants (Eriksson et al. 2017), which would explain increased levels of PFOS in sewage sludge (see 5.9.1.4.10). An additional amount of PFOS may originate from the wastewater treatment plant itself, as higher levels of PFOS were discharged into the wastewater treatment plant at the time of use in the past and walls and other surfaces were coated with PFOS. Analogous to the desorption processes in electroplating, PFOS desorption at low PFOS levels is also conceivable at the municipal wastewater treatment plant.

5.9.1.4.7 Rack demetallisation - sampling point 7 (P7)

The analytical result for P7 was 1900 µg /l for 6:2 FTS. Other PFAS were not detectable. This relatively high concentration indicates that 6:2 FTS evidently adsorbs to the plastic-coated racks to a high degree and subsequently desorbs again. Carryover through partially cracked or damaged plastic coatings in the area of the slip-on contacts is also conceivable.

It was checked whether an introduction of 6:2 FTS into the process solution with the preparation water was possible. This would be likely if water from the ion exchange circuit was used for the preparation of the demetallising solution. However, since fully demineralised municipal water is used for the preparation of the demetallisation solution, this discharge route can be excluded.

5.9.1.4.8 Ultrasonic degreasing solution - sampling point 8 (P8)

The analytical result for P8 was 2300 µg /l for 6:2 FTS. Other PFAS were not detectable. The ultrasonic degreasing thus shows a high content of 6:2 FTS in the prepared solution. This can be explained by desorption of 6:2 FTS from the plastic-coated plating racks. Increased carryover is also conceivable here due to partially detached or chipped plastic coatings in the area of the slip-on contacts.

The possibility of 6:2 FTS entering the ultrasonic degreasing with the preparation water could also be ruled out, as no water from the ion exchanger circuit is used for preparing the process solution, but fully demineralised municipal water.

5.9.1.4.9 Metal hydroxide sludge - sampling point 9 (P9)

The metal hydroxide sludge accumulated during the investigation period was collected separately from the other electroplating sludge and analysed for PFAS (P9). The analytical result for P9 was 15,000 µg 6:2 FTS /kg TS and 1,600 µg PFOS/kg TS. The analytical results for solid samples refer to dry matter. Other PFAS could only be detected in traces. During the investigation period, 107 kg of metal hydroxide sludge containing chromium(III) with a solids content of 35 % was separated from the 6:2 FTS-containing substream. This corresponds to approx. 37.5 kg dry matter per week.

Thus, only minor amounts of PFAS were removed from the wastewater by the metal hydroxide sludge during the investigation period. Through metal hydroxide precipitation, approximately 0.56 g of 6:2 FTS, equivalent to 6.16% of the total load, and 0.06 g of PFOS, equivalent to 42.9% of the total load, was removed from the treated wastewater. PFOS thus adsorbed to the metal hydroxide sludge approximately 7 times more than 6:2 FTS.

Figure19: 6:2 FTS and chromium-III-containing metal hydroxide sludge

Source: Own representation

5.9.1.4.10 Sewage sludge from the municipal wastewater treatment plant - sampling point 10 (P10)

The sewage sludge accumulated during the investigation period was collected separately and analysed for the 20 PFAS. The analytical result for the sewage sludge showed 32 µg 6:2 FTS/kg TS, 96 µg PFOS/kg TS. The 6:2 FTS degradation products PFHxA and PFPeA were detected in the sludge at 25 µg/kg TS and 9 µg /kg TS, respectively. Other PFASs were found only in trace amounts.

The results confirm previous findings that PFOS adsorbs much more strongly to the sewage sludge and can thus be removed from the wastewater through municipal wastewater treatment plants much better than 6:2 FTS.

5.9.1.4.11 Wastewater treatment on 6:2 FTS using ion exchange technology

The facility under investigation has an ion exchange plant to separate PFOS from the wastewater. After the use of PFOS was discontinued in the year 2010 and replaced by 6:2 FTS, the existing PFOS ion exchange plant was used to remove 6:2 FTS from the wastewater. All wastewater sub-streams known to contain 6:2 FTS and chromium(VI) are collected together and, after chromium(VI) reduction and metal hydroxide precipitation with sludge separation step, are fed to an ion exchange plant (IAT) for the separation of 6:2 FTS.

The facility has an atmospheric evaporator for the recovery of the chromium electrolyte from the rinsing water with a recovery rate of over 90%. The mist suppressant used is also recovered in this process. As a result, the ion exchangers in the wastewater substream could be dimensioned smaller by a factor of 10 than would be the case in a comparable plant without recovery (closed loop technology).

The IAT plant has a gravel filter (KF) for the separation of suspended matter as a pre-filtration stage and subsequently three ion exchange columns for the separation of 6:2 FTS. Typically, only two ion exchange columns are used. Since the analytics to monitor a 6:2 FTS breakthrough is relatively costly and therefore should only be carried out every 2 months, a third column was installed for safety. Commercially available basic anion exchangers are used. For the removal of 6:2 FTS, weakly basic anion exchange resins have proven successful, if necessary in combination with strongly basic anion exchange resins.

To determine the loading status of the three ion exchanger columns S1, S2 and S3 connected in series, wastewater samples are regularly taken and analysed for PFAS. The analytics for PFAS is comparatively cost-intensive and can only be carried out by specialised external laboratories. To determine the service life of the three ion exchangers (IAT) connected in series, the PFAS concentrations were therefore initially analysed monthly and, after empirical values were available, since the beginning of 2017 every 2 months before, between and after the three columns. Analytical results are available from the period 01.01.2017 to 30.05.2018. below Table 24 shows the analytical results found for 6:2 FTS and PFOS.

Table 24: Decorative chromium plating: PFAS ion exchanger self-monitoring measurement results

Datum	**vor KF**	**nach S1**	**nach S2**	**nach S3**	**EKS**	**vor KF**	**nach S3**	**EKS**
	6:2 FTS (µg/l)	**6:2 FTS (µg/l)**	**6:2 FTS (µg/l)**	**6:2 FTS (µg/l)**	**6:2 FTS (µg/l)**	**PFOS (µg/l)**	**PFOS (µg/l)**	**PFOS (µg/l)**
25.01.2017	120	58	< BG	< BG	12	< BG	< BG	< BG
07.03.2017	100	290	< BG	< BG	32	< BG	< BG	< BG
09.05.2017	63	68	< BG	< BG	10	< BG	< BG	< BG
19.07.2017	79	130	< BG	< BG	10	< BG	< BG	< BG
07.09.2017	93	150	10	< BG	21	< BG	< BG	< BG
22.11.2017	180	58	< BG	< BG	65	< BG	< BG	11
03.01.2018	5000	110	34	< BG	26	< BG	< BG	< BG
22.03.2018	240	< BG	< BG	< BG	73	< BG	< BG	< BG
30.05.2018	340	< BG	< BG	< BG	35	7,7	< BG	10

Note: after chromium (VI) reduction, hydroxide precipitation and desludging, 3 ion exchange columns are used for PFAS removal

KF = gravel filter of the PFAS ion exchange plant = untreated wastewater

S1-3 = Ion exchange columns 1-3

EKS = final inspection shaft = after mixing with other electroplating wastewater

BG = limit of quantification for PFOS and 6:2 FTS each 5 µg/l

Source: Own representation

5.9.1.4.12 Disposal of the loaded ion exchange resins

High-temperature incineration was chosen as the disposal route for the PFAS-loaded ion exchange resins, as this is the only economic way, given the current status, to finally destroy PFAS and remove them from the material cycles.

In a study by the Japanese Ministry of the Environment, it was shown that PFOS is 99.999% destroyed in a waste incinerator at 1100°C and a residence time of 8 seconds, without any evidence of the formation of other fluorinated carbon compounds (Ministry of the Environment of Japan 2013).

To date, no waste treatment facility for external regeneration of these loaded ion exchange resins exists in Germany.

5.9.1.5 Discussion of the results

5.9.1.5.1 Removal of 6:2 FTS in wastewater to concentrations < 5 µg/l

The measurement results in Table 24 show that the PFAS ion exchangers function reliably. They remove both 6:2 FTS, as well as the still bleeding PFOS in a quantitative, permanent and safe manner from the treated electroplating wastewater substream to concentrations < 5 µg/l (limit of quantification). No other PFAS were found in the wastewater of the electroplating shop.

During the investigation period, "breakthrough" of the 2nd column occurred twice, but was completely adsorbed by the 3rd column in each case. The loaded ion exchange resins were always replaced and disposed of in good time.

Occasionally, PFOS concentrations of around 10 µg/l are still found in the untreated water - this is the currently discussed limit value for PFOS in Appendix 40 of the Waste Water Ordinance - although PFOS has not been used in the facility for 9 years. This PFOS does not originate from the substream treated for PFAS but is due to bleeding from plant components that do not drain into the chromium(VI) partial flow.

Due to the cost-intensive self-monitoring analysis, the use of a 3rd column is a reasonable safety measure (see breakthrough of column 2 on 03.01.2018) to avoid having to perform too frequent self-monitoring analyses. As for the frequency of the self-monitoring measurements, every 2 months seems sufficient.

The very high measured value for 6:2 FTS in the untreated wastewater on 03.01.2018 (5000 µg/l) is probably due to an overdose of the mist suppressant after cleaning work during the year-end break.

Other electroplating shops, which remove 6:2 FTS adsorptively from the wastewater via ion exchangers, currently only achieve concentrations in the upper two-digit or even three-digit µg-range, according to concurring statements by Dr. Zimmer, ZVO and Mr. Bauer, Aquaplus. In the present case, the conditions for adsorptive removal of 6:2 FTS are very good.

Favourable conditions in the present case are:

- it is an electroplating operation for decorative chromium plating with comparatively constant operating conditions
- more than 90% of the dragged-out 6:2 FTS is recirculated through a combination of an atmospheric evaporator with external metal removal via ion exchangers. This allows the ion exchangers to be relatively small in size.
- only the substream containing chromium(VI) is treated. As a result, there are no other mist suppressants or organic substances in the treated wastewater that could trigger competing reactions during adsorption

5.9.1.5.2 Previously unknown discharge routes of 6:2 FTS into wastewater

The chromium(VI)-containing wastewater substream is treated for chromium(VI) and 6:2 FTS. The chromium(VI)-free, but also heavy metal-containing wastewater substream from all other wastewater generation points of the electroplating shop is treated in a separate wastewater batch. In the so-called final inspection shaft, the two wastewater substreams are mixed and discharged from here into the public sewage system. Sampling point 4 (P4) is located in the final inspection shaft.

Measurements in the run-up to the investigation had shown that 6:2 FTS in not insignificant concentrations and occasionally PFOS in low concentrations had been found again and again in the final inspection shaft, although the facility had not used PFOS for nine years and no known wastewater substreams containing PFAS were discharged into the final inspection shaft. It was therefore obvious that there must still be previously unknown sources for this PFAS input.

At the beginning of the project, it was suspected that PFOS and 6:2 FTS adsorb to the PVC-coated plating racks and are desorbed again during their subsequent use. The racks, along with the workpieces suspended on them, first pass through a 70°C ultrasonic degreasing bath. The aim was to determine whether adsorbed PFAS desorb from the racks in this treatment step. Therefore, such an ultrasonic bath with a volume of 2.5 m^3 was sampled at the end of its service life after 4 weeks (P8).

Furthermore, it was suspected that PFAS can also desorb from the racks during the so-called rack maintenance, the chemical demetallisation of the plating racks. Therefore, a demetallisation bath with a volume of 4.75 m^3 was sampled at the end of its service time of 4 weeks in (P7).

Both process solutions are prepared with demineralised municipal water and not with water from the ion exchange recirculation system, so that a 6:2 FTS input with the preparation water can be ruled out.

The high concentrations and contents of 2300 µg 6:2 FTS /l (corresponding to 5.7 g 6:2 FTS/w) found in the ultrasonic degreasing bath and 1900 µg 6:2 FTS /l (corresponding to 9.0 g 6:2 FTS/w) in the rack demetallisation bath confirm the above assumption. It can be assumed that PFAS is desorbed even from plating racks, which may be stored temporarily for a long time and in some cases are only used again after months or years, according to the order. These effects explain the 6:2 FTS concentrations found in the "actually" PFAS-free main wastewater flow from the electroplating shop.

Thus, there are discharge routes for 6:2 FTS (and possibly also for PFOS) into the metal electroplating wastewater that are not covered by the substream treated with PFAS ion exchangers. Therefore, 6:2 FTS is regularly found in the final inspection shaft at average concentrations, as they occur, at worst, after the 2nd ion exchange column in the treated substream.

Ultrasonic degreasing and demetallisation could be proven as sources (cf. 5.9.1.4.7 and5.9.1.4.8).

Due to customary desorption processes, which are customary in the industry but cannot always be explained in detail, PFOS still occurs sporadically in wastewater even many years after the use of PFOS has ceased. In the present case, however, PFOS is then quantitatively removed by the ion exchangers in the treated substream, as e.g. on 30.05.2018.

Currently, the company is working to completely eliminate the use of PFAS as a mist suppressant in the decorative chromium bath. The use of the fluorine-free substitute product "Saphir WA 2020" from the company Kiesow is being investigated. The active component is sodium dodecyl sulfate in 2.5-5% solution. It will be interesting to see how long 6:2 FTS continues to bleed. The process would be significantly accelerated by a complete exchange of the process solutions containing 6:2 FTS and a thorough cleaning of the plant including the exhaust air systems and an exchange of the ion exchange resins in the rinsing water circuit containing chromium.

In order to avoid PFOS bleeding, all piping and tanks downstream of the PFOS ion exchanger used were replaced at some facilities.

Conclusion:

From the factors mentioned above, with regard to the design of future plants for the elimination of PFAS from the wastewater of electroplating shops, it appears that a pure substream treatment of only the chromium(VI) substream for PFAS is not sufficient to prevent the wastewater emissions of PFAS from electroplating shops. Treatment of the entire wastewater substream from the electroplating shop appears necessary.

5.9.1.5.3 Mass balance for 6:2 FTS in the electroplating shop

During the investigation period, 4 litres of the product "Proquel OF" from the company Kiesow Dr. Brinkmann were added into the process solution containing chromium(VI). According to company information, the product contains c.a. 1.5 % 6:2 FTS. Accordingly, 60g of 6:2 FTS was added to the system per week.

During this period, 910 µg/l in 10 m^3 were recovered in the untreated chromium(VI) wastewater, corresponding to 9.1 g 6:2 FTS or 15.2 % of the 6:2 FTS quantity used.

If one also takes into account the wastewater substream originally thought to be PFAS-free with 97 m^3 in the investigation period and 61 µg 6:2 FTS/l, a further 5.9g 6:2 FTS were found. Together, therefore, 15 g 6:2 FTS or 25 % of the 6:2 FTS quantity used.

Conversely, this means that 35 g or 75%, of the 6:2 FTS used was not recovered in the wastewater of the electroplating shop. This is a facility with relatively steady production, whose equipment has been used for years under constant operating conditions. It would therefore be reasonable to assume that a steady state of adsorbed and desorbed 6:2 FTS has been established. The extent to which new racks were used during the investigation period, to which 6:2 FTS could adsorb in a more intensified manner, could no longer be clarified.

The following possibilities can be considered as potential reasons for the above-mentioned lower finding:

5.9.1.5.3.1 Use of newly coated plastic racks

As described under 5.9.1.5.2, 6:2 FTS evidently adsorbs to the PVC-coated plating racks to a considerable extent. It is possible that a larger number of such newly coated racks were used at the time of the investigation, which additionally removed mist suppressant from the system by adsorption. This could not be verified afterwards.

5.9.1.5.3.2 Electrochemical degradation

A publication on the topic "Electrochemical PFT degradation in electroplating industry wastewater" concludes: "In 500 litre batches, both reduced (chromium (III)-containing) and unreduced chromium wastewater were treated and very good and reproducible degradation values around 99% for partially fluorinated PFT (H4PFOS) were achieved within 2-3 hours." (Fath 2011).

This raises the question of the degradation reaction and the degradation products. No PFHxA and PFPeA were detected in the rinsing water after the chromium electrolyte, which would be expected from oxidative degradation of the hydrogen-substituted carbon atoms analogous to biochemical degradation (see Figure 18). Although these degradation products were found at the wastewater treatment plant, they may also be due to degradation of other PFASs (Section 5.9.1.4.6). Thus, the partial degradation of 6:2 FTS in the chromium bath results in other degradation products. In this context, it has not yet been clarified beyond doubt on a technical scale whether the electrochemical degradation involves complete mineralisation of the 6:2 FTS (Fath 2011), whether there are volatile fluorinated degradation products that evaporate, or whether there are undetected degradation compounds in the electrolyte.

5.9.1.5.3.3 Electrosorption at the anodes

The partial electrosorption of 6:2 FTS on anodes was investigated and demonstrated under laboratory conditions by Prof. Dr. Marzinkowski in the Galvarec project. In the experimental setup chosen there, a reduction of the 6:2 FTS content by about 80% was observed during electrolysis after 4 hours. "At the end of the experiment, the entire apparatus was thoroughly rinsed and the collected rinsing waters were again analysed for the 6:2 FTS content. 81% of the initial amount could be recovered thereby (Marzinkowski 2011)." Electrochemical degradation probably occurred here as well, supplemented by the effect of electrosorption.

The findings obtained under laboratory conditions can only be transferred to the industrial scale to a limited extent. In a chromium electrolyte in an electroplating shop, 6:2 FTS is subject to electrochemical degradation not just for hours, but for several days. A "thorough rinsing of the entire apparatus" naturally does not take place in an electroplating shop. Nevertheless, electrosorption of 6:2 FTS can also play a role here. However, this cannot explain the large amount of additional dosage of 6:2 FTS, but is only part of the adsorption and desorption process in the plant.

Conclusion on the mass balance of 6:2 FTS

The extent to which electrochemical degradation, adsorption of 6:2 FTS onto PVC-coated plating racks and electrosorption were causal factors in the fact that only 26% of the 6:2 FTS used was recovered in the wastewater could not be determined within the scope of this study.

However, since the aforementioned issues are important both for the disposal of waste from electroplating shops and for the evaluation of 6:2 FTS emissions and possibly emissions of fluorine-containing degradation products from electroplating shops, further research is needed in this area.

5.9.2 Fate of PFOS using the example of a plastic electroplating plant

IUW Integrierte Umweltberatung has already carried out[7] its own research on the possibilities of retaining or treating PFOS, and has accompanied corresponding research projects[8]. The results of these projects are partly included here.

In 2008, IUW Integrierte Umweltberatung was commissioned by the Thuringian Ministry of Agriculture, Nature Conservation and Environment to conduct an investigation into the prevention and reduction of PFOS in a plastic electroplating plant (Willand 2008). The facility investigated still exists today. It was a plastic electroplating plant in which a process technology that minimised material losses was already in use, in which a recovery rate of 85% for chromium trioxide and PFOS was achieved by combining two titanium vacuum evaporators and ion exchangers. This explains the comparatively low annual consumption or emissions of PFOS of about 3.5 kg/a. Since the agricultural use of the sludge from the downstream municipal sewage treatment plant was nevertheless no longer possible due to its high PFOS content, the two-stage activated carbon adsorption plant recommended in the above-mentioned study was installed in the wastewater substream.

In the untreated wastewater of the electroplating shop investigated, which had been using PFOS for many years; 496 µg/l PFOS were detected in the monthly composite sample. In the same

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[7] e.g. "Investigation of an electroplating shop regarding the avoidance/reduction of PFT in wastewater", Willand, W. for the Ministry of Agriculture, Forestry, Environment and Nature Conservation of the Free State of Thuringia (TMLFUN)

[8] e.g. "Minimisation of PFT input into electroplating wastewater" and "Electrochemical PFT degradation in electroplating industry wastewater and development of a PFT recycling plant"; Ministry of the Environment Baden-Württemberg

period, a monthly composite sample of the wastewater treated exclusively by classical metal hydroxide precipitation yielded 50.1 µg/l PFOS. Here, no adsorption step for PFOS was used yet. The proportion of PFOS load removed from the wastewater by adsorption processes to the metal hydroxide sludge is unknown because sludge analyses were not considered at that time.

The annual PFOS input in the plastic electroplating plant was 3,480 kg. The annual PFOS load found in the untreated wastewater, i.e. before metal hydroxide precipitation, was of the same order of magnitude at 3.506 kg. It can be concluded that almost all of the PFOS used in the production enters the wastewater path and that emissions via exhaust air or products were negligible.

For the operation of the adsorption plant, the PFOS-containing wastewater substreams were separated and, after chromium(VI) reduction, passed through a 2-column plant in the effluent via a specially selected activated carbon (suitable ion exchangers were not yet known at that time).

Schwarz summarises the results for continuous operation as follows: "The practical results demonstrate that it is possible to reliably maintain residual PFOS concentrations of < 10 µg/l with the activated carbon adsorber system designed as a transitional solution. Based on an average feed concentration of 500 µg/l in the PFOS-containing wastewater substream, an elimination output of approx. 98% is thus achieved. This positive result is not diminished by the fact that in exceptional cases there were still inexplicable upward concentration outliers. Finally, PFOS concentrations well below 10 µg/l up to the analytical determination limit (1 µg/l) could be determined over longer operating phases. Considering the system solution of material loss minimisation (recovery rate: approx. 85%) and a PFOS retention rate, already at present for the plastic electroplating plant, of more than 99% is confirmed in practical operation (Schwarz et al. 2011)."

From today's point of view, it can be said that maintaining a concentration of < 1 µg/l for PFOS in the wastewater of an electroplating shop can be regarded as part of a closed loop.

5.9.3 Recommendation for treatment of electroplating wastewater for PFAS

Due to the carryover of the fluorine-containing mist suppressants in the electroplating machine as shown above, it must be assumed that a pure substream treatment of the chromium(VI)-containing wastewater substream for PFAS is not sufficient. It is therefore recommended to treat the total wastewater flow of the electroplating shop for PFAS. For a possible determination of a limit value, the determination of a monitoring value for PFOS/PFAS in part D of annex 40 of the Waste Water Ordinance would therefore be preferable.

For the adsorptive removal of PFOS and long-chain PFAS from electroplating wastewater, basic anion exchange resins can be considered in addition to some activated carbon types. These can include: “Lewatit ® MP 62, a weakly basic, macroporous anion exchanger with tertiary amino groups, Lewatit ® MP 64 a weakly basic, macroporous anion exchanger based on a styrene-divinylbenzene copolymer, Lewatit ® Monoplus MP 500 a strongly basic, macroporous anion exchanger, and Lewatit ® Monoplus MP 600 a strongly basic, macroporous anion exchanger from Lanxess Deutschland GmbH and Amberlite® or Duolite® from Dow Chemical (patent specification 2012).”

6 New processes for fluorine-free chromium plating and plastic etching

This chapter describes innovative physico-chemical processes that can be used to eliminate the need for PFOS or chromium(VI).

The alternative methods are differentiated into PFOS substitution:

1. by using other fluorine-containing or fluorine-free mist suppressants in the same processes
2. by using other wet-chemical processes (e.g. chromium(VI)-free process solutions)
3. by using technological alternatives (e.g. use of other physical processes)

The application opportunities and limitations of these processes or new technological developments, some of which are not yet operated on a broad industrial scale in Germany, are reflected in this chapter.

Possible adverse environmental effects of these processes are highlighted.

The implementation obstacles to the use of innovative processes and possibilities for supporting the spread of more environmentally friendly processes are presented.

Consideration is given not only to the results of the literature review but also, among other things, to the relevant papers presented at the industry's most important conference in this context, the Oberflächentage in Berlin in 2015 and Leipzig in 2019.

According to the Stockholm Convention's BAT/BEP Guidance on the Use of PFOS (BAT/BEP Guidance 2015), there is currently a lack of information regarding the processes for which these alternatives can be used, and when and why they are not used. This information gap will be further addressed by this report.

6.1 PFOS substitution by using other mist suppressants

6.1.1 Other mist suppressants in functional chromium plating

Although the use of PFOS in the field of functional chromium plating, i.e. "non-decorative hard chromium plating" in closed loop systems is still permitted in specific exceptional cases according to the POP Regulation, status as of July 2019, the substitution of PFOS by 6:2 FTS in Germany has been completed on the basis of the presently available information. On the part of the ZVO, there were therefore no longer any objections to deleting the general exemption for the use of PFOS for "non-decorative hard chromium plating" in the Stockholm Convention, which was still valid in 2018, and converting it into a specific exemption. This means that PFOS could still be used in functional chromium plating in justified exceptions in individual cases where a closed loop exists. However, such a case is currently not known in Germany.

There are facilities that do not use mist suppressants at all in functional chromium plating.

6.1.2 Other mist suppressants in decorative chromium plating

As shown under point 5.3.4, the substitution of PFOS has also been completed in decorative chromium plating. According to the survey, about 60% of the facilities use 6:2 FTS as a substitute and about 40% use fluorine-free mist suppressants.

6.1.3 Other mist suppressants in plastic etching

In chromium(VI)-based plastic etching, PFOS has been consistently replaced by 6:2 FTS. In individual cases, ABS plastic parts are pre-dipped in aqueous solutions of fluorine-free mist suppressants before etching. In these cases, the use of fluorine-containing mist suppressants in the plastic etching can be dispensed with. PFOS substitution through the use of modified wet chemical processes

6.2 PFOS substitution through the use of modified wet chemical processes

6.2.1 Decorative chromium plating - PFOS substitution by replacing chromium VI with chromium III processes

If chromium VI is replaced by chromium III in decorative chromium plating, perfluorinated or polyfluorinated compounds can be dispensed with as mist suppressants, since the conditions in the process solution are no longer so aggressive or strongly oxidative.

The slow but steady progress in the development and application of chromium(III)-based chromium plating processes in decorative chromium plating in Germany can be illustrated quite well by the publications of the ZVO on the subject. As recently as 2012, the ZVO wrote in a position paper: “From today’s perspective, trivalent chromium plating cannot fully replace hexavalent chromium plating on an equivalent basis. The industry has committed itself to further development work, which will, however, take further time (ZVO 2012)." The industry association stated the following in 2018: "Research into substitutes for chromium(VI)-free coatings poses major challenges for developers. Nevertheless, chromium deposition from chromium(III) electrolytes has been successfully pursued and is already available and feasible for numerous applications, especially in the decorative sector (ZVO 2018b).” An example is given in the ZVO-report of March 2019: "Subsequently, the use of chromium(III) for decorative chromium plating of automotive exterior parts was discussed. Apparently, the development here is positive and substitution is possible. However, there are numerous disadvantages to consider, for example, in process control and wastewater treatment (ZVO 2019)."

The disadvantages mentioned are dealt with under 6.2.1.4.

Chemical formulators in the electroplating industry already took a more optimistic view in 2014: "Decorative chromium plating with chromium(III) electrolytes can now be regarded as the state of the art (Kiesow 2014)". In 2018, Galvanotechnik wrote the following on the state of chromium deposition from chromium(III) systems: "These have already proven themselves in contract operations, particularly in Asia, the USA and neighbouring European countries. With them, high performance requirements can already be met in a process-safe manner, bright chromium plating in trivalent chromium electrolytes will therefore find its way more and more into surface finishing in the future (Suchentrunk 2018):"

However, a trivalent chromium electrolyte requires significantly more maintenance than the previous chromium(VI)-based electrolytes. The chromium(III)-based electrolytes are more sensitive to contamination, e.g. by foreign metals, than previous chromium(VI)-based electrolytes. Ion exchangers usually have to be used for external metal removal (WOMAG 2019b).

In addition to the serious advantages in occupational safety, a further advantage of chromium III electrolytes is that a significantly less aggressive medium is used and therefore less corrosion occurs in the environment of the process. In individual cases, there may be lower safety and administrative requirements for the facility, if the substitution means that the company is no longer subject to the scope of the Hazardous Incident Ordinance or only has to meet the lower requirements of the lower class.

The significantly better layer thickness distribution is cited as an advantage of the chromium(III) process. "In the meantime, this technology is also used for coating plastic parts for vehicles (Käszmann 2019a)."

"However, in the area of corrosion resistance, for example in the CASS test, trivalent chromium platings in combination with a microporous nickel layer show no disadvantages and are successfully used in the field. For example, CASS tests are passed with a test time of 48 hours according to DIN EN ISO 9227. This means that an application in both the interior and exterior is possible and is the state of current applications (Heinzler 2019)."

Meanwhile, trivalent electrolytes correspond to a very similar appearance compared to hexavalent chromium-plated components. In addition, the colour of the chromium layer can be specifically adjusted by admixtures.

Another advantage of the chromium(III) process is its insensitivity to power failures. Unlike the chromium(VI) electrolytes, no disturbing passivation layer forms and production can continue immediately after the power failure (Büker 2019).

An example of successful conversion to the chromium(III) process is reported from the furniture manufacturing sector, although here deviations in the chromium colour between the chromium(VI) and chromium(III) processes and the associated possible darkening for the products were also unacceptable due to at least 5-year subsequent delivery guarantees (Bohnet 2019).

6.2.1.1 Decorative chromium-III based chromium plating in plastic electroplating

The substitution of chromium(VI)-containing electrolytes by chromium(III)-containing electrolytes in decorative chromium plating is also basically possible in plastic electroplating. The substitution process here is somewhat slower than in decorative chromium plating of metals. One reason for this is that there is currently no production-ready substitute for chromium(VI) in plastic etching, so for the time being, the facilities continue to rely on the use of chromium(VI) and the associated REACH approval.

"Individual FGK member companies are already using trivalent chromium processes in series production or have installed test procedures. The task now is to plan and schedule the plant modifications, some of which are substantial. This will take several years, depending on the company, but will in any case be achieved by 2024 (FGK 2019)."

Currently, chromium surfaces in plastic metallisation are still predominantly deposited from chromium(VI) electrolytes. The corrosion resistance of layers deposited from chromium(III) electrolytes is equivalent to that of a microporous nickel layer. The colour of the chromium layer can now be specifically adjusted by the addition of admixtures.

A market-leading supplier to the automotive sector writes: "This can be used to adapt the vehicle's ambience in a manufacturer-specific manner to a warmer, friendlier colour, for example. Design studies are already showing this trend toward a feel-good ambience corresponding to a third living space, the vehicle. Here, real metal surfaces and a valuable impression continue to play a major role, enhanced by trivalent chromium plating as a design element (BIA 2019)."

6.2.1.2 Decorative chromium plating with sulfate-based chromium(III)

In sulfate-based chromium (III) electrolytes, chromium (III) sulfate is usually used. In these sulfate-based chromium (III) electrolytes, insoluble so-called titanium-based MMO (mixed metal oxide) anodes are often used to prevent the anodic oxidation of chromium (III) to chromium (VI) (Kiesow 2014).

Large amounts of hydrogen and oxygen are evolved in sulfate chromium(III) electrolytes (Jimenez 2017).

Weak acid cation exchangers are used to eliminate foreign metals such as nickel, iron, copper, or zinc from the base materials, which are used continuously and regenerated with dilute sulphuric acid. Alternatively, complexing agents are added to the complexation of foreign metals, but these can cause difficulties in the treatment of the wastewater. Under certain circumstances, the limit value for total chromium according to Appendix 40 of the Waste Water Ordinance can no longer be complied with. The use of per- or polyfluorinated mist suppressants is not necessary in chromium(III) electrolytes, since the same strongly oxidative conditions do not prevail in them as in chromium(VI) electrolytes. In most cases, conventional surfactants, such as those used in nickel electrolytes, can be used (Disse 2018).

6.2.1.3 Decorative chromium plating with chromium (III) on chloride basis

In chloride-based chromium (III) electrolytes, chromium (III) chloride or ammonium chloride are usually used. There are also mixed processes containing sulfates and chlorides.

With regard to the danger of chlorine gas formation when chloride-based chromium(III) electrolytes and chromium(VI)-based electrolytes are used simultaneously, reference is made to chapter 4.2.6 .

6.2.1.4 Limits of chromium(III) processes for decorative chromium plating

In conventional chromium VI electrolytes, the chromium surface is deposited with a purity of up to 99.99% based on the chromate anion (CrO^{2-}). In chromium III electrolytes, the chromium surfaces are deposited from the trivalent chromium cation (Cr^{3+}). Foreign metals that are also cationic, such as typically cations of iron, nickel, zinc or copper, lead to competitive reactions during electrolytic deposition. Even minor impurities from other metals, which cannot be completely avoided due to the process, therefore lead to alloy deposition, which can cause colour variations of the surface. For example, impurities due to iron already produce significantly darker coatings from about 30 ppm.

As a result, chromium III electrolytes are considerably more sensitive in the decorative sector and require more personnel-intensive bath maintenance measures than the more robust and easier-to-handle chromium VI-based electrolytes used in the past.

Cost-intensive mixed oxide anodes (e.g. iridium-tantalum) are required for chromium deposition. Foreign metals must be removed by ion exchange resins. Chromium III deposition thus involves higher investment costs compared to chromium VI deposition.

Nevertheless, chromium III surfaces can nowadays also be safely deposited on plastic surfaces. They also meet the high quality requirements of many well-known automotive manufacturers (Schütte 2019).

Organic impurities, current density, component geometry and the concentration of metal impurities have an influence on the colour tone of the deposited chromium layers. Therefore, bath maintenance measures, such as the use of filter pumps with activated carbon precoating, may be necessary.

Chromium III electrolytes usually require more additives (up to 8 additives) than chromium(VI)-based electrolytes, which increases the analytical effort.

The most cost-intensive investment when converting to the chromium(III) process is said to be the adaptation of the anodes to iridium-tantalum mixed oxide anodes .

The use of chromium(III) processes in plastic metallisation is currently being intensively tested, but progress is slow, particularly in the automotive sector.

"For the deposition of chromium, the available chromium(III) processes are currently being tested with the following results: Abrasion, corrosion behaviour, cleaning behaviour, gloss, and colour have different properties than the coatings from chromium(VI) processes. In order to be able to realise a changeover here, on the one hand, a corresponding acceptance must be achieved among the automobile manufacturers. On the other hand, the required delivery time must be guaranteed for ten to twelve years. Finally, the strong fragmentation of supplier companies poses a challenge, as different manufacturers supply the parts that are combined in a vehicle. Moreover, the workload of the companies is so high at present that hardly any manufacturer has the possibility to rebuild production facilities. On the part of the OEMs (note: OEM: Original Equipment Manufacturer, in the automotive sector the vehicle manufacturer itself is referred to as OEM), it has yet to be approved that parts may be coated with the new chromium(III) processes - the first manufacturers are now moving toward accepting coatings made of chromium(III) electrolytes (Käszmann 2019a)."

Chromium(III) electrolytes usually contain boric acid, and thus a substance that is also being increasingly criticised in chemical regulation. Chromium(III) electrolytes are more sensitive and must be operated more mindfully than conventional chromium electrolytes. For example, if excessively high current densities are used (above the specification limits of the electrolyte suppliers), this can lead to dissolution of the MMO anodes and chromium(VI) formation in the electrolyte (Büker 2019).

The original problems with colour deviations and "yellowish" chromium surfaces deposited from chromium(III) electrolytes have now been largely resolved (see 4.2.2.1).

6.2.1.5 Problems with the treatment of wastewater from chromium(III) electrolytes

Even when modern chromium(III) electrolytes are used in decorative chromium plating, rinsing water continues to be produced, which is usually treated in the facility's existing wastewater pretreatment system. Because of the complexing agents they often contain, serious problems can arise in some cases when treating these wastewater substreams containing chromium(III) with the classic methods for treating wastewater containing heavy metals. However, there are many applications where no problems at all occur in wastewater treatment.

With regard to the problems in the treatment of wastewater from chromium(III) electrolytes, Dr. Anke Walter from the company Atotech stated at the 40th expert discussion in Ulm in 2018: "While Cr(VI) deposition is carried out with catalysts, in Cr(III) deposition, it is the complexing agents to which attention must be paid. The latter baths are comparatively more sensitive to impurities; current densities, bath temperature and deposition rates, however, are comparable (ZVO 2018c)."

"Instead of chromic acid, chromium (III) compounds are now used, which are operated in sulfate- or chloride-based baths. The pH values range from 2.5 to 4.0, depending on the type of bath, and are mixed with organic acids to stabilise the solution, which function as complexing agents.

In practice, these organic hydroxy acids (e.g. malic acid) increasingly lead to massive exceedances of the limit values of/for chromium. The two carboxyl groups and one hydroxyl group available in malic acid tend to form chelate complexes. First stable complexes with Cr, Ni and Cu are formed already at pH 2.5. Compliance with the required limit of 0.5 mg/l "total chromium" in the wastewater to be treated is not only becoming increasingly difficult with current detoxification methods, but is often impossible." (Schmid 2014)

"Common detoxification methods" here refers to the proven methods such as metal hydroxide precipitation followed by sludge separation and removal of residual concentrations of heavy metals using cation exchangers, or precipitation of heavy metals using organosulfides followed by sludge separation by fine filtration.

6.2.1.5.1 Summary - decorative chromium plating based on chromium(III) or chromium(VI)

Advantages and disadvantages of chromium(III)- or chromium(VI)-based decorative chromium plating are summarised in the following table:

Table 25: Comparison: decorative chromium(III) and chromium(VI)-based chromium plating

Process parameters	Chromium(III) electrolyte	Chromium(VI) electrolyte
Use of PFOS / PFAS	not required	predominantly required
Anodes	iridium-tantalum mixed oxide anodes, expensive, non-toxic, longer service life when used correctly	lead anodes, cheap, toxic. substitution requirement, service life 2-3 years
Anode sludge / disposal	there is no anode sludge formation	leaded anode sludge must be disposed of
Chromic acid content	0 g/l	180 – 300 g/l
Boric acid content	approx. 50 g/l	0 -2 g/l
Electrolyte additives	4-8	2-3
Analytical requirements	complex and personnel-intensive	little complex and little personnel-intensive
Corrosiveness and toxicity of the electrolytes	low	high
Electrolyte composition	complex, maintenance-intensive	simple, robust
Power interruption	no problems	problems due to formation of passivation layer
Requirements for mist suppressants and extraction	moderate and usual in electroplating plants	very high
Hydrogen generation / explosion protection requirements	moderate and usual in electroplating plants	very high
Requirements for occupational safety	moderate and usual in electroplating plants	very high
Power consumption for chromium deposition	moderate	high
Bath circulation/filtration	required	not required
Sensitivity to enrichment of foreign metals	very high, from approx. 10 mg/l	low, from approx. 3 g/l
Foreign metal removal by ion exchange	continuously required	mostly only required for electrolyte return and evaporator (= closed circuit)
Wastewater treatment	mostly complex splitting and heavy metal precipitation	chemical reduction and heavy metal precipitation
Authorisation according to REACH	not required	required
Seveso III-relevant	No	Yes
Market acceptance	increasing	decreasing

Source: Own representation

6.2.2 Functional chromium plating – wet chemical PFOS substitution

6.2.2.1 PFOS substitution by replacing chromium VI with chromium III processes

In functional chromium plating, the state of development in replacing chromium VI processes with chromium III processes is significantly less advanced than in decorative chromium plating. So far, these are still isolated cases and niche applications.

It is still difficult to produce hard chromium coatings from chromium(III) electrolytes in greater layer thicknesses. The limit is currently around 200 µm, and in some processes even 20 µm.

As part of the 40th discussion in Ulm in 2018, alternatives for chromium(VI) in functional chromium plating were presented in the forum. "A number of alternatives have emerged for hard chromium in the application area of corrosion protection and abrasion resistance, such as for bearings, in accordance with the REACH regulation, explained Dr. Nikolay Podgaynyy of Schaeffler AG. These represented a toolbox, so to speak. For some applications, such as plain bearings or needle bearings, coatings deposited from trivalent electrolytes are proving to be quite suitable. With sufficient hardness, inhomogeneous layer thicknesses and nodule formation could be a problem here for thick layers (ZVO 2018c)."

The Finnish company Savroc Oy has developed a chromium(III)-based hard chromium process, which, according to the company, has been used successfully for years in Spain and Finland for wear parts, ball valves and hydraulic rods. However, it has not yet become established in Germany.

Usage:

According to the developers, the process is already being tested by 50 users. It is used for brake parts in vehicles, for shock absorbers, weapons systems or valves, rollers and hydraulic elements. The achievable hardness is 1500 HV to 1800 HV.

"One of the advantages cited is the low layer thickness required, which is less than 20 µm. For the comparison of properties, three types of TriplHard Coating were considered:

- 2 µm - 30 µm nickel-phosphorus + 5 µm - 100 µm chromium
- 1 µm - 3 µm nickel + 5 µm - 100 µm chromium
- Chromium as the sole layer.

The process has been used for about three years at the Spanish coating company Tecnocrom Industrial S. A., and is used there for functional surfaces on 20MnV6 steel, for example for mining (WOMAG 2019a)."

Limitations of the process:

The process requires heating (annealing) of the workpieces at temperatures above 400 - 700°C, which limits the use of the technology. The wear resistance of the surfaces is increased compared to classic hard chromium(VI)-based coatings, and they do not shine in the same way.

"Pure elementary chromium is not deposited from chromium(III) electrolytes, but coarse-grained chromium compounds. Primarily, these are compounds with carbon, phosphorus and/or sulphur. It is therefore not surprising that the coatings have different properties. The coatings are extremely cracked and brittle and offer no corrosion protection under load. Another problem is the often extremely weak coating adhesion. In addition, the process control cannot be realised safely and stably. The author himself has developed and tested various chromium(III) electrolytes (Hekli 2016).

6.2.2.2 PFOS substitution by replacing chromium layers with nickel-combination layers

6.2.2.2.1 Nickel-tungsten alloy deposition (with finely dispersed diamond-carbon deposits, if necessary)

"Duratec NiW" is a process for the deposition of nickel-tungstenalloy layers with an alloy composition 65/35 percent Ni/W, ± 5 percent. The deposited layers exhibit high abrasion and corrosion resistance. The easy-to-conduct process can replace hard chromium in many cases (ZVO 2018d)."

"A particular advantage is the ductility of the alloy with up to 10% expansion. This makes such nickel-tungsten coatings an alternative to functional chromiumcoatings as well as nickel-phosphorus coatings. According to the supplier, these coatings perform significantly better under wear stress than hard chromium coatings, especially at higher operating temperatures (Meyer 2018)."

Limitations of the process: Due to the high costs of tungsten, this is a technology that can only be used economically in niches. With all nickel alloy deposits, problems can basically arise in wastewater treatment due to complexing agents contained in the process solution. Due to nickel emissions, the process is not suitable for the food industry - (e.g. separators) and the production of medicines.

6.2.2.2.2 Electroless nickel with dispersion layers

In dispersion nickel plating, particles are incorporated into the nickel layer. The particles are in suspension in the electrolyte solution during metal deposition. For example, particles of diamond or boron nitride can be co-deposited, consequently producing wear-resistant coatings that can replace hard chromium coatings in individual cases (Mayer 2016).

"Dispersion coatings based on chemically deposited nickel with embedded hard material particles such as diamond, boron carbide or silicon carbide have now been proven for many years in various industrial applications. Mainly, the excellent wear resistance of these coating systems, combined with the advantageous properties of chemically deposited nickel coatings such as uniform coating thickness distribution and corrosion resistance, is used (Meyer 2018)"

Usage: Textile machinery industry and in mechanical engineering

Limitations of the process: due to the nickel emissions from the surfaces, the deposited surfaces are not used in the food and pharmaceutical industries. With all electroless nickel processes, problems can basically arise in wastewater treatment due to complexing agents contained in the process solution.

6.2.2.2.3 Electroless nickel coatings with embedded phosphorus or nanoparticles

The so-called "electroless nickel coating" is deposited without externally applied current in a chemical process, hence the process is also referred to as electroless nickel plating to distinguish it from galvanic nickel plating. In sub-areas, functional chromium layers can be replaced by electroless nickel, especially when nanoparticles are incorporated into the layer. 6- 13% phosphorus is also incorporated in the coatings, which is why the coatings are also called nickel-phosphorus coatings, or NiP for short.

"NiP coatings," Dr. Podgaynyy continued, also behaved acceptably, but did not exhibit overrolling resistance, at least without suitable nanoparticles. In many cases, the NiP/DLC coating system represents a very good alternative to conventional hard chromium (ZVO 2018c)."

Usage:

The process offers high wear and corrosion resistance. It is applicable for complex geometries and for many applications, from the automotive industry to the electrical industry and mechanical engineering. The base materials steel, stainless steel and non-ferrous metals (brass, copper, etc.) as well as sintered metals and aluminium can be electroless nickel plated (Holzapfel 2019). Ni-P coatings are mainly used for small components and for increased corrosion protection requirements.

Limitations of the process:

The process is not applicable in the food and pharmaceutical industries due to the nickel emissions of the coatings . The achieved hardness of the surface usually reaches only 470 -600 HV and can only be increased to that of hard chromium surfaces (1000 HV) by heat treatment (Candel-Ruiz A. 2019). In all electroless nickel plating processes, problems can basically arise in wastewater treatment due to contained complexing agents in the process solution.

6.2.2.2.4 Nickel alloy deposits (NiL35)

This nickel alloy deposit is a combination layer of two alloys of the metals copper, tin and nickel, more precisely a nickel-tin layer and an intermediate layer of bronze (Kölle 2018). The layers exhibit high corrosion resistance and are resistant to seawater. The maximum achievable hardness of about 600HV is far below the hardness levels achievable by hard chromium coatings.

Usage:

The coatings are resistant to sea salt. Therefore, the process is used in wind power-off-shore plants or for hydraulic cylinders of harbour cranes (Candel-Ruiz A. 2019).

Limitations of the process:

One factor that limits the use of this process is that the repair of incorrectly surfaces is not successful with conventional methods.

Due to the possible nickel emissions from the surfaces, the deposited surfaces are not used in the food and pharmaceutical industries. There are manufacturers who have withdrawn the process from their range of products due to quality problems in long-term use. With all nickel alloy deposits, problems can basically arise in wastewater treatment due to complexing agents contained in the process solution.

6.2.2.3 Functional chromium plating from ionic liquids

The deposition of hard chromium coatings from anhydrous ionic liquids based on chromium(III) salts has been tested on an industrial scale in a pilot plant. Dr. Franz Hörzenberger reported at the Oberflächentage 2017 on coatings with properties of conventional hard chromium surfaces. "The deposition is done on steel as well as other metals. The layer hardnesses are 1,000 HV001 to 1,300 HV001 and abrasion values below those of conventional hard chromium coatings. Improvement still needs to be achieved in terms of precipitable coating thicknesses (ZVO 2017b).

The processes are at the development stage. Currently, there are no known processes for hard chromium plating from ionic liquids used on a large scale. Possible problems in the treatment of the rinsing waters are therefore also not yet known.

6.2.3 Plastic etching - PFOS substitution by using other oxidising agents

For several years, various Cr(VI)-free processes for etching of ABS plastics have been developed by part of chemical distributors.

There are peracetic acid-based processes (Lehmann et al 2018), permanganate-based processes, and processes based on manganese in various oxidation states (including manganese II/III), which are being tested at laboratory scale, pilot plant scale, and in series production.

“In principle, nitric acid and trichloroacetic acid mixtures have been successfully tested as other alternative immersion processes for etching plastics with chromic acid. However, the following turned out to be disadvantages: Problems with wastewater treatment due to halogen-organic compounds contained, problems finding suitable rack insulation, risk of nitrous gas formation when using nitric acid, and problems with brownstone formation and fire protection issues when using permanganate solutions (Blepp, Willand, Weber 2016)."

Since these alternative processes are mostly also based on the use of very strong acids in a strongly oxidising environment, the use of perfluorinated or polyfluorinated mist suppressants will also be necessary according to the current state of knowledge, so that progress can be expected from these processes with regard to the substitution of chromium(VI), but not necessarily also with regard to the substitution of PFAS.

What these processes have in common is that they have not yet been developed to full market maturity, so that it is not yet possible to speak of a state of the art for the substitution of chromic acid in the etching of plastics.

"The switch to chromium(VI)-free processes in pretreatment can only be implemented in series production once the process reliability for the commonly used plastics has been assured. Intensive trials are currently underway to this end (FGK 2019b).” However, the alternatives available on the market to date are not yet capable of meeting the defined requirements on an industrial scale.

Therefore, only a cursory description of some of the processes currently under development will be given in the following:

6.2.3.1 Plastic etching with potassium permanganate and phosphoric acid

Processes for activating ABS and acrylonitrile-butadiene-styrene copolymer/polycarbonate (ABS/PC) with potassium permanganate and phosphoric acid are under development.

"The surface of ABS plastic shows an almost identical appearance with the new process as with the classic process using chromic acid; the additional step of conditioning can be integrated into existing plants relatively easily in this case. In addition to pure ABS, ABS/PC can also be treated.

When using the racks, somewhat closer attention must be paid to damage, as this can lead to rack coating. By using a reoxidation cell and filtration, a long service life of the etching solution can be achieved. Treatment of the resulting wastewater is possible without major problems (Lemke 2014)."

"Subsequently, Ms. D. Lemke from the company Conventya reported on the development of a "chromium-free plastic etching - experiences from application". The electrochemical regeneration is also possible without problems with this plastic etching on the basis of potassium permanganate-phosphoric acid and good adhesion properties, according to the automotive standards, are achieved. Before the palladium activator, this process requires the parts to be immersed in two neutralisation solutions to prevent carryover of the etching solution. According to Ms. Lemke, even better results are achieved with this etching process, e.g. with 3D-printed ABS, than with the classic chromium-sulphuric acid etching process. (Willand 2015)."

6.2.3.2 Plastic etching with manganese (III) base

Plastic etchings are being developed not only on a potassium permanganate basis (oxidation state +7), but also on the basis of manganese compounds with a lower oxidation state.

"As a replacement for the previous chromium(VI)-containing plastic etching, Dr. Scheybal presented a new manganese(III)-sulphuric acid-based etching that is relatively tolerant to contamination by heavy metals. Electrochemical regeneration from Mn(II) to Mn(III) is possible without any problems, he said. The requirements of adhesion tests in the automotive industry are met. Currently, for the industrial scale-up, some pilot tests are already being run by European customers (Willand 2015)."

Some manganese(III)-based processes require different pretreatments for different types of plastics. "The pretreatment of ABS is done by means of a pre-sweller as a pre-etch. For ABS/PC, two different swellers are required. The process is suitable for many types of plastics and gives good coating results, but not for polyamide (Willand 2019).

The progress of the development can be seen from certain communication of the ZVO or the Fachverband Galvanisierte Kunststoffe e.V. (FGK):

"In mid-2017, the FGK had called on process suppliers to test chromium(VI)-free conditioned coated plastic components. At the end of August 2018, the FGK working group met with the participants in Solingen to discuss the results.

The FGK has set itself the goal of evaluating the alternatives to chromium-sulphuric acid conditioning for plastics that are available on the market. To this end, it has asked process suppliers to participate in a test. By April 2018, four of the six process suppliers contacted had resubmitted the selected sample sheets and components with the different pretreatment stages and coating variants.

The test results varied widely, especially in the climate change and temperature stress tests. In parts, especially with the ABS coating, some processes showed very good results. However, the PC/ABS coating remains critical. In some cases, there were detached areas between the coating and the substrate. In addition, the two-component parts demonstrated overchroming. None of the processes presented completely passed all the tests carried out. Overall, however, significant progress can be seen.

During the project meeting, further starting points and opportunities for improvement emerged, which will be taken up by the process suppliers. A second evaluation round with series components is now to start at the beginning of 2019 on (FGK 2018)."

"The FGK was involved in the evaluation of trivalent chromium plating at an early stage. Over several years, the systems available on the market were put through their paces. The development of the processes was significantly influenced by the knowledge thus gained. "Individual FGK member companies are already using trivalent chromium processes in series production or have installed test procedures (FGK 2019)."

6.2.3.3 ABS plastic activation by microporous foaming

In this process, the plastic surface is temporarily softened by the use of strong acids and the butadiene component within the ABS plastic is oxidised in the interior of the surface. The resulting gases create an open pore structure in which the subsequent conventionally deposited metal layer can be anchored. The process is also called the Biconex process after the company that intends to introduce it to the market.

The advantages of this process are pretreatment at low temperature (40 °C) and short process times of a few minutes. In individual cases, according to the information provided by the process developers, the process line in the machine is even shorter than when chromosulphuric acid is used. The halogen-free oxidant is only required in low concentrations and is generated electrochemically alongside the process in an electrolysis cell. According to the process developers, the adhesive strengths of the coatings are consistently high and meet all the relevant requirements of automotive standards.

Based on current information, the process does not use PFAS. It is currently (December 2019) at pilot plant scale and is soon expected to be implemented at production scale. The chromic acid-free etching processes based on alternative inorganic acids are suitable for coating of special plastics, such as polyetherimide, polyphenylene sulfide, and various polyamides (Hoflinger 2019).

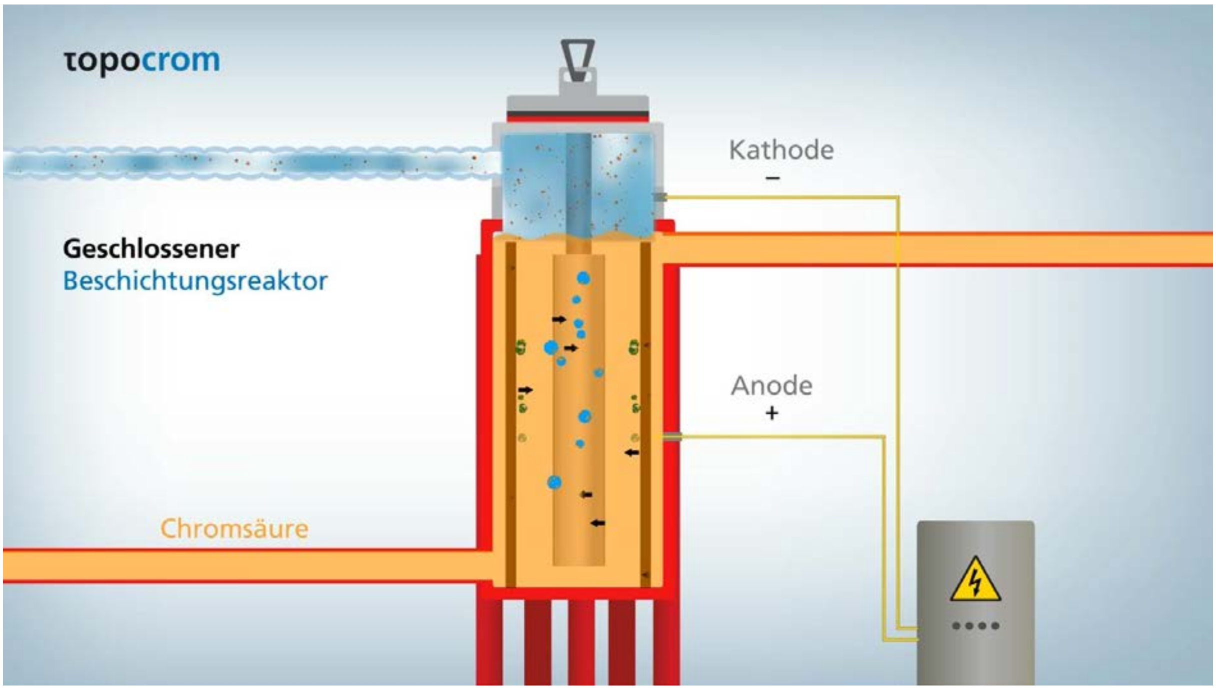
Since all the above-mentioned alternative processes continue to work with strong acids and oxidising agents in an aqueous environment, it can be assumed that oxidation-resistant, i.e. fluorinated, mist suppressants will continue to have to be used.

6.2.4 Functional chromium plating in a closed reactor at negative pressure

In contrast to conventional electroplating, which works with open baths and extraction of the aerosols, there are also electroplating processes in closed reactors which follow the so-called "chemistry-to-part" technology.

A proven long-standing example of this is the so-called TOPOCROM® process technology. Here, the coating of workpieces, e.g. pressure rollers or tubes, is carried out in a closed reactor. By changing and controlling the physical process parameters, the topography and roughness of the chromium surfaces can be precisely controlled.

Figure 20: Principle of a TOPOCROM® reactor

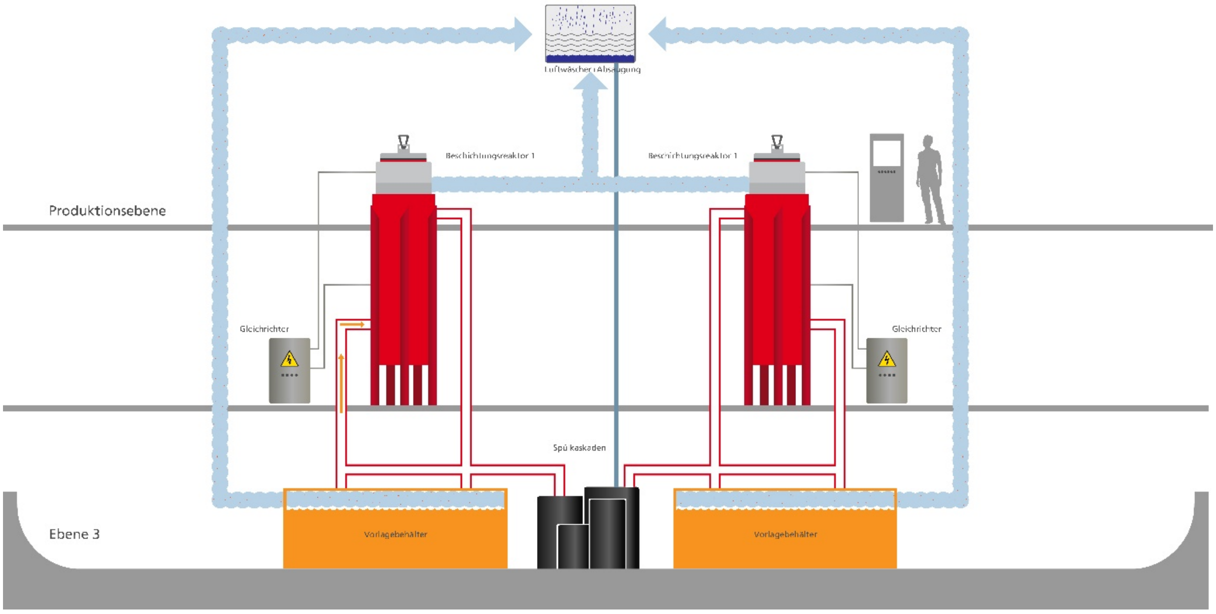


Source: Topocrom

The electric current is transmitted from the rectifier via a copper bar to the lead anodes in the reactor. During the chromium plating process, the component, which is connected as a cathode, is inserted vertically into the reactor and concentrically surrounded by insoluble anodes. Apertures protect the areas of the component not to be plated during the plating process. During the process, the component is rotated to achieve consistent and best possible quality.

The chromium electrolyte circulates between the reactor and the storage tank, maintaining its concentration and temperature. After the chromium electrolyte has been pumped back, the rinsing process is initiated. Here, the component is rinsed in the circulation process via a 3-fold cascade and the cascade is changed via valves after a preset time. In addition, a water spraying system is installed in the reactor to clean the component as the final rinsing process. This supplied water is used to compensate for evaporation losses in the electrolyte storage tank. The process therefore operates with low wastewater and has been industrially proven for years. Due to the closed reactor technology, the use of mist suppressants can be completely avoided.

Figure21: TOPOCROM® Process technology



Source: Topocrom

The compact design and the construction of the reactors allow for good accessibility for maintenance and cleaning work despite the multi-storey structure.

Since hydrogen and oxygen are also released during chromium plating in closed reactors, special attention must be paid to explosion protection with this process technology .

It must be taken into account that the rinsing water requirement for this process is fundamentally higher than for conventional electroplating, since in addition to the workpieces, the entire piping and the reactor must also be rinsed during each rinsing operation.

Another example of a process in which hard chromium plating is carried out in closed reactors comes from the automotive industry. Here, injection nozzles, inlet and exhaust valves and components for brake cylinders and shock absorbers are hard chromium plated.

"In high-speed coating, in contrast to the conventional electroplating bath, the coating is carried out in relatively small, closed cells. For this coating technique, article-specific anodes adapted to the component are produced. This ensures a very uniform and reproducible coating thickness distribution and thus also a high coating quality (Holzapfel 2018)."

The process can also be used to coat complex and design-intensive components. However, it is designed for high quantities due to the high degree of automation.

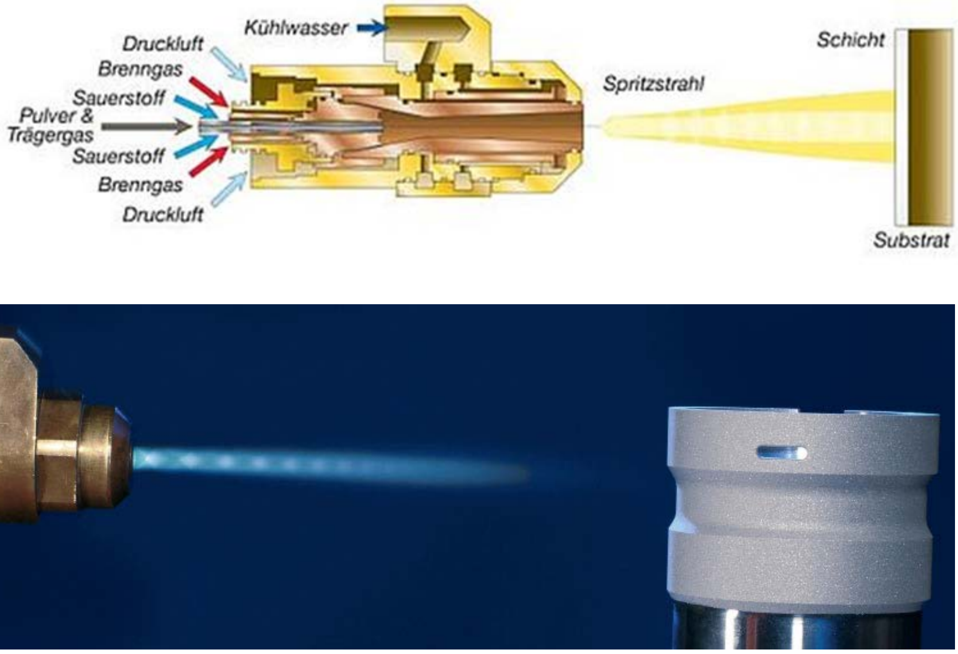
6.3 Substitution of PFOS by using technological alternatives to wet chemical chromium plating

6.3.1 High-speed flame spraying (HVOF process)

High-velocity flame spraying (HVOF, derived from **high-velocity oxygen fuel**process) is the most common form of thermal spraying. In this process, continuous gas combustion takes place at high pressures within a combustion chamber, in the central axis of which the powdered spray additive is fed. The high pressure of the fuel gas-oxygen mixture generated in the combustion chamber and the usually downstream expansion nozzle produce the desired high flow velocity in the gas jet. This accelerates the spray particles to the high particle velocities of up to 600 m/sec (i.e. almost twice the speed of sound), resulting in enormously dense spray coatings with excellent adhesive properties.

Propane, propene, ethylene, acetylene and hydrogen can be used as fuel gases.

Figure22: Sketch and photo of high velocity flame spraying



Source: Linde AG / Gemeinschaft Thermisches Spritzen e.V. (GTS)

The HVOF process can be used to produce extremely thin coatings and coatings from approx. 50 µm to 0.5 mm thick coatings with high corrosion resistance, wear resistance and dimensional accuracy (www.gts-ev.de 2019). Other advantages of the process include the possibility of on-site repairs using mobile equipment and that, unlike electroplated chromium plating, there is no limit to component size. The process is already widely used in Germany and industrially proven in many applications.

Usage:

As an alternative process for hard chromium plating, high velocity flame spraying (HVOF process) of chromium coatings is used, for example, for pressure rollers. This process can also be used, for example, to deposit tungsten carbide coatings (WC Co Cr), which are even harder than hard chromium coatings and also have very good corrosion resistance due to the chromium content. Tungsten carbide and chromium carbide in a cobalt or nickel/chromium matrix achieve particularly good corrosion and wear resistance and are used to replace hard chromium. Alternatively, chromium carbide nickel chromium (CrC NiCr) coatings are also used, which are about 1100 HV in hardness and have very good corrosion resistance (GTS 2019).

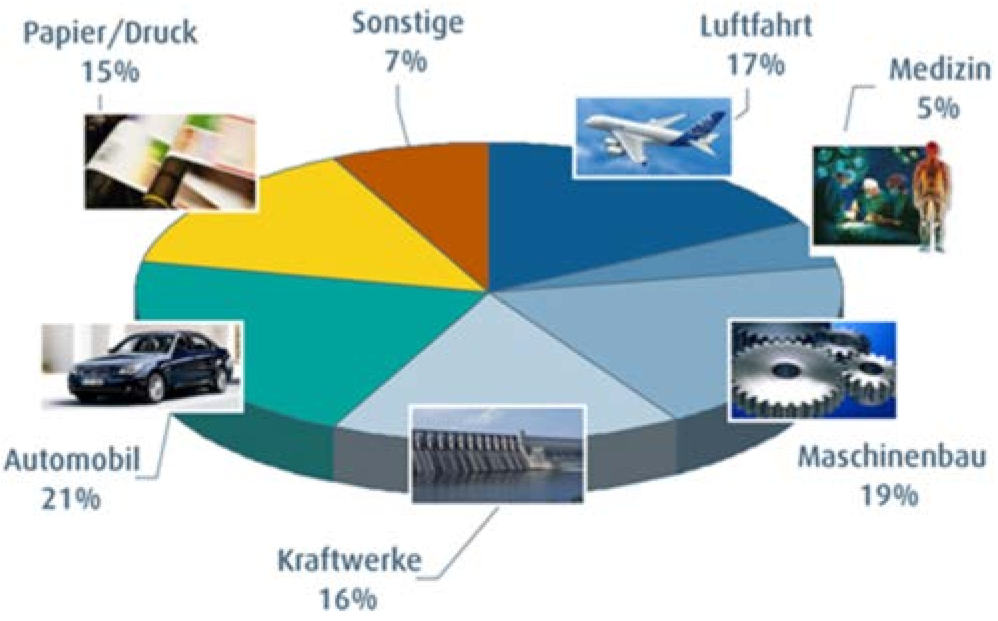
Other applications include aircraft landing gear, pistons and rollers, hydraulic pistons and piston rods, sliding surfaces of steam irons, rollers for the photographic industry, parts for petrochemical and chemical machines, e.g. pumps, slide valves, ball valves, mechanical seals, repair and increase in service life for agricultural machines, etc.

"Cylinders in particular, for example for paper production, are increasingly coated with thermally sprayed layers as protection against corrosion and wear. In addition to iron, the corresponding coatings contain chromium boride, tungsten carbide and cobalt (Käszmann 2018)."

According to the Gemeinschaft Thermisches Spritzen e.V. announcement in August 2019 (GTS 2019), the HVOF process is currently used in 450 facilities in Germany, of which 250 facilities use the process only for their in-house products. The association estimates that more than 2000 plants are in operation in Europe.

Here, the current market distribution of the HVOF process is as follows:

Figure23: Market distribution of HVOF process



Source: GTS e.V.

The coatings show higher corrosion resistance and wear resistance than electric arc wire spraying.

Limitations of the process:

The HVOF process can be used for coating rotationally symmetrical or flat components. Internal coatings are possible up to a diameter of 100 mm. It is not suitable for complex geometries, workpieces with indentations and for internal coatings.

Disadvantages of the process are the required sound insulation and the sometimes complex preparation of the components. If the process parameters for high-temperature flame spraying of chromium are not kept within the optimum range, the formation of chromium(VI) compounds is possible in conjunction with atmospheric oxygen.

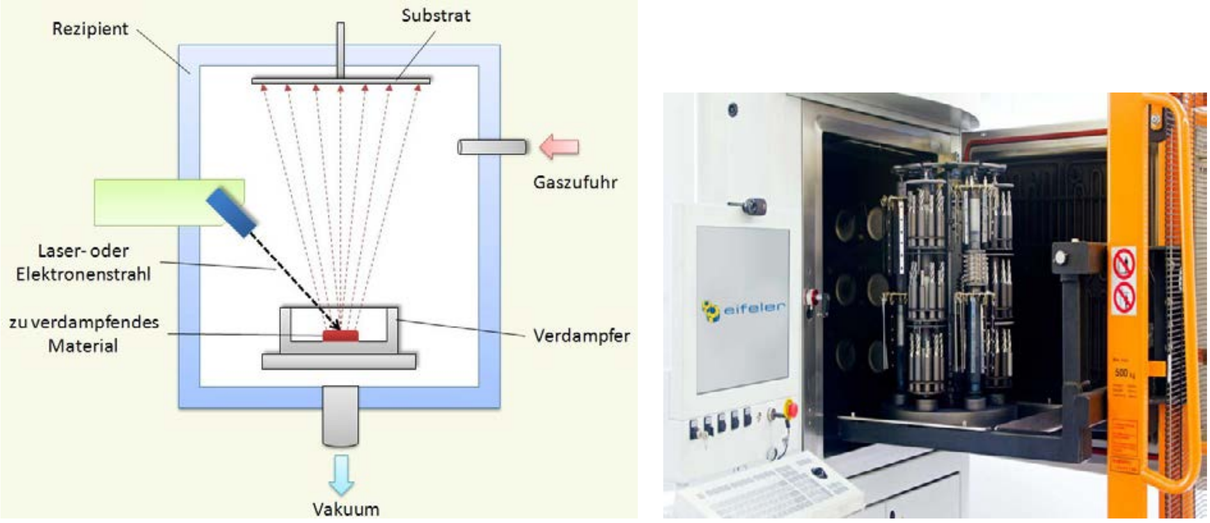
"High amounts of chromium(VI) compounds, in the form of chromium trioxide (CrO_3), are also formed during thermal spraying with spray additives containing high levels of chromium. However, special thermal spray processes in the field of metallurgical special metal production must be excluded from this (Szameitat 2018)."

However, according to GTS, chromium(VI) formation can be easily avoided if HVOF technology is used properly.

6.3.2 Physical vapor deposition (PVD)

In physical vapour deposition (PVD), the starting material is converted into the gas phase in a vacuum by means of physical processes by evaporation or atomically from solids, e.g. by laser bombardment . It is then deposited again on the colder workpiece (substrate) by condensation.

Figure24: Sketch and photo of physical vapour deposition



Source: Wikimedia Commons; Eifeler

In principle, PVD processes differ from CVD processes in that the temperature load occurring during deposition of the layer does not exceed a maximum of 500°C (Müller 1996). In order to increase the deposition rate, the gas particles are often accelerated by electric fields and shot onto the substrate as a stream of particles at 160 -500°C. The cathode sputtering is called sputtering. If all surfaces are to be coated as homogeneously as possible, the workpieces must be rotated during coating. Common process gases are nitrogen, methane and ethylene.

In the PVD process, comparatively thin layers of up to max. 10µm are deposited. The process is generally cost-efficient for series production. "PVD options include several carbon-based coating processes that offer a unique combination of extreme surface hardness, low coefficient of friction and corrosion protection (Galvanotechnik 9/2019)."

Today, hard material coatings based on titanium nitride (TiN), titanium carbonitride (TiCN), titanium aluminium nitrite (TiAlN) or diamond (DLC) are mainly used as coatings. For die-castparts made of aluminium and magnesium, chromium-based coating systems such as chromium nitride (CrN), chromium vanadium nitride (CrVN) and chromium aluminium nitride (CrAlN) are mainly used.

Usage:

Physical vapour deposition coatings are used for tools made of coated cutting materials. Rolling bearings, chassis parts, actuators, balls in ball bearings, bearing races and cylinders, flap systems and pumps are also manufactured using the process (Galvanotechnik 9/2019).

"Airbus had previously granted PVD coating approval for steel, titanium and Inconel substrates. According to the manufacturer, the coating offers stronger adhesion to metallic substrates than hard chromium, high load-bearing capacity and abrasion resistance (adhesive wear), and a low coefficient of friction; it reduces pitting and fretting corrosion on sliding or moving parts of an aircraft, making it suitable for low-lubrication and lubrication-free applications. (Kecht 2019)"

"With the increasing use of PVD coatings by industry leaders such as Airbus, hard chromium will most likely be displaced from the aerospace industry in the long term (MO 2019)"

Limitations of the process:

The PVD coating process is relatively inexpensive. The processes are only suitable for small parts in non-corrosion-sensitive installation areas. Large parts such as hydraulic rods in aircraft construction or rollers in the printing industry can hardly be coated in high vacuum.

"These coating technologies offer good tribological properties, but they are dependent on prior hardening of the base material or coating of hard metal to realize their potential. If base material of insufficient hardness is used, the hard coatings will be pressed into the coated soft base material under load or even sheared off.
Therefore, primarily high-quality hardened steels or expensive hard metal (WC-Co) are coated. The necessary hardening process for the steel as well as the subsequent gas phase coating produce distortion in the vast majority of cases. During hardening, it should be noted that the hardening depth as well as the achievable hardness depends on the steel alloy used and is not solely an adjustable variable of the coating. Thin-film technology is further restricted by the limited size of the coating that can be applied. In addition, narrow, deep internal bores cannot be coated in a cost-efficient manner.
The aspects listed mean a limited selection of sensible base materials for thin-film technology and thus a restriction of possible areas of application as well as costs that should not be underestimated (Hekli 2015)."

If high-purity chromium is used as a sputtering material, it must be taken into account that "chromium(VI) also plays a decisive role in the production of input materials for non-galvanic processes, for example for physical vapour deposition (PVD). For the production of high-purity chromium sputtering targets, via corresponding aluminothermic processes, for use in PVD technologies, only electrolytically produced chromium metal, from electrolytes containing chromium(VI), can be used (Szameitat 2018).

The surface temperature of the workpieces to be coated is approx. 250 °C, which may limit usability in individual cases.

6.3.3 Plasma Nitriding

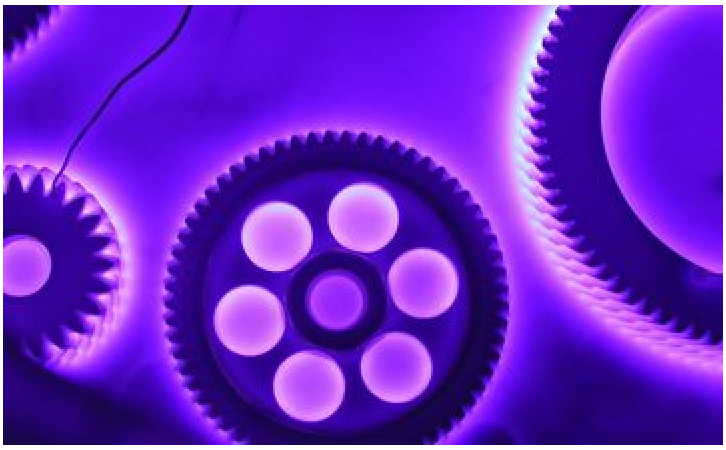
Plasma nitriding works with a nitrogen-hydrogen mixture which is ionised in a closed vacuum furnace at negative pressure by applying a voltage between the container wall and the charge. The process creates a discernible glow edge on the tool. This allows the gas ions to react with the iron of low- to high-alloy steels and form a hard nitriding zone.

The plasma parameters such as pulse height, duration and cycle frequency are freely adjustable in the treatment processes. To avoid the formation of electric arcs, the voltage is interrupted in microseconds and pulse repetition times of up to 20 kHz are applied.

Plasma nitriding is not a surface coating but a diffusion process. The ionised gas atmosphere diffuses into the peripheral zone of steel components . The process is used to impart a higher surface hardness to functional surfaces (up to 1000 HV). It increases wear resistance and reduces corrosion behaviour.

Surface temperatures are in the range of 350 - 600 °C.

Figure25: Plasma Nitriding



Source: Rübig, Marchtrenk, Austria www.rubig.com

Usage:

Typical applications include transmissions, crankshafts, camshafts, cam followers, valve components, extruder screws, pressure die casting tools, forging dies, tools for cold forming, injection nozzles, plastic injection tools, long shafts, axles, clutches and engine parts.

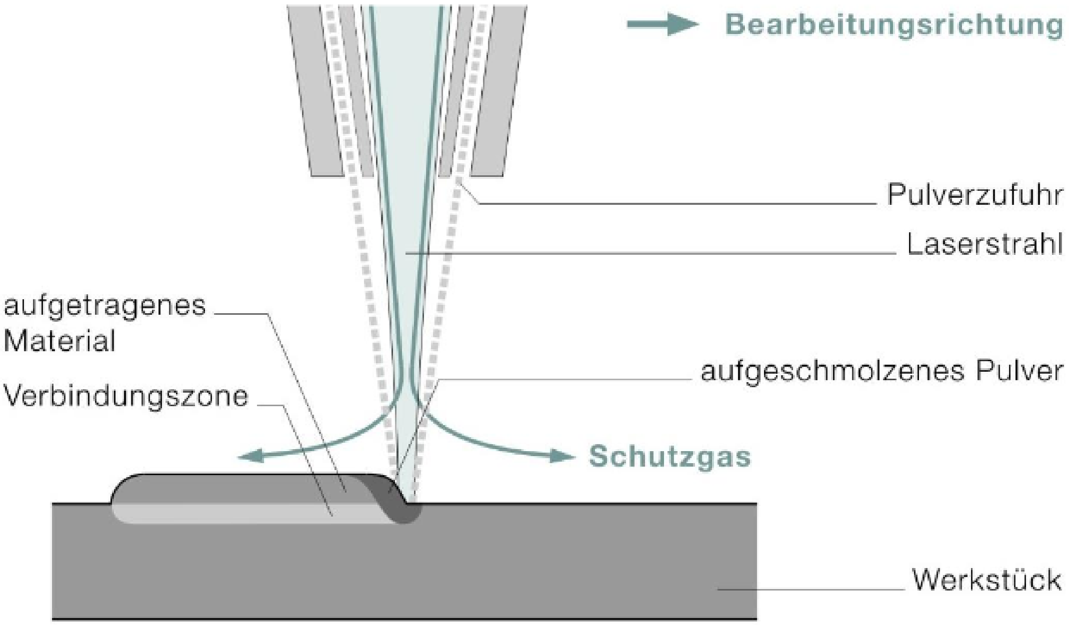
The process is also suitable for very large steel or cast iron parts. Plasma nitriding can be applied to all major cast iron and cast steel variants used in automotive tools. In this area, it has completely replaced the hard chromium process for some manufacturers (Horschig 2019).

"Plasma nitriding results in coatings with hardnesses of about 1000 HV, with the surface having a transition zone from maximum hardness to base hardness. The process by slow heating and slow cooling prevents the occurrence of stress cracks. Challenges for the production of an optimum surface consist in the adaptation of the base material, usually cast steel. Another criterion is the creation of a minimum roughness of the applied coating to ensure lubrication with minimum quantities. With the introduction of the new process to replace the hard chromium plating previously carried out, a 25% increase in productivity was achieved. As a result, it was possible to achieve service lives for some tools that no longer require intermediate reconditioning, thus naturally making the new process technology highly cost-effective. In the meantime, individual plant technologies have been developed for coating such tools and have been put into operation at all major automotive locations (Käszmann 2019a)."

6.3.4 Laser Metal Deposition (LMD)

In laser metal deposition, metal powders are applied to the surface of a base material and melted by laser. The principle of this process is shown in Fig. 26.

Figure26: Sketch of laser metal deposition



Source: TRUMPF Laser-und Systemtechnik GmbH

"The laser beam creates a melting bath on the component surface. A powdery coating material is introduced into this melting bath with the aid of a nozzle. The filler material melts and metallurgically bonds with the base material. After solidification, individual welding beads are formed, which are placed next to each other for flat coatings. The welding process can also be carried out in a stable manner in constrained positions, which makes it possible to coat complexly shaped surfaces. This allows a wide variety of coatable tool geometries. The process is also suitable for precise tools or for filigree geometries (Graf et al 2014)."

The achievable coating thicknesses are 500 µm.

6.3.5 Extreme high-speed laser metal deposition (LMD)

In extreme high-speed laser deposition welding (high-speed LMD or EHLA process), a powdered filler material already meets the laser light above the melting bath, which heats it almost up to the melting point while still on its way to the component.

Since the original technology of conventional laser deposition welding operates relatively slowly, the technology has been further developed into high-speed laser deposition welding. While the conventional process is around 2 m/min, high-speed laser deposition welding reaches over 100 m/min.

The use of material combinations is possible, e.g. metal matrix composite materials and/or sandwich structures to increase component lifetime. Tungsten carbide, titanium and chromium carbides, but also iron-, nickel- and cobalt-based powders are used, depending on the requirements concerning the wear layer.

The deposition rate is up to 1000 cm^2/min, coating thicknesses are 10-250 µm and the feed rate is >100 m/min.

The process is more economical than hard chromium plating for brake discs, for example. "Advantages of the process are the low energy consumption, the absence of environmentally harmful chemicals or the extensive selection of filler materials, and excellent linking of the coating to the substrate. The composition of a corresponding coating can be adjusted very well to the different applications or the different desired properties. Good wear protection is achieved, for example, by incorporating tungsten carbide, titanium carbide or chromium carbide, while high thermal stress is achieved by using nickel or cobalt as the base material (Käszmann 2019a)."

Possible fields of application: Brake discs, valves, piston rings, shafts in the automotive industry, metering rollers, printing cylinders, plate cylinders in the printing industry, hydraulic cylinders, rollers, pistons, rods in mechanical engineering

Limitations of the process: The process can only be used for rotationally symmetrical workpieces. Complex geometries and workpieces with undercuts, blind holes, etc. cannot be coated. (Candel-Ruiz A. 2019). The laser-based surface processes such as laser metal deposition (LMD:) and extreme high-speed laser deposition welding (EHLA) are currently being developed as an alternative in the field of hard chromium plating. “To be an alternative to hard chromium, productivity, process stability and automation must be further optimised (Käszmann 2019a).“

6.3.6 Sulfonation of plastics with sulphur trioxide in the gas phase

In the conditioning of plastics prior to electroplating, chromium(VI) can be replaced by gas phase activation with sulphur trioxide (sulfonation) at room temperature in the area of special plastics in niche applications since 20 years.

With this process, the use of PFAS can be completely eliminated.

As Dr. S. Henne explained at the Oberflächentage 2017, the process has advantages in terms of flexibility, energy costs, wastewater treatment, occupational health and safety, and in terms of application technology by shortening the process steps.

"The activation of plastics with sulphur trioxide takes place through a targeted modification of the plastic chains in the form of the formation of functional groups as well as mechanical roughening. Subsequent nucleation with palladium shows a very uniform palladium distribution with relatively small nuclei. According to the speaker, adhesion promotion takes place as a combination of several types of interactions: Interfacial interaction, chemical interaction, mechanical anchoring, and electrostatic attraction. Because of the different properties here, the subsequent coating sequence can be shortened slightly by reducing the processing times by about 30 % and the process can be carried out at room temperature - compared with about 40 °C to 70 °C for the conventional approach. This reduces energy consumption and increases the throughput. Despite these advantages, Dr. Henne believes that conditioning is currently not an alternative to the activation with chromic acid that has been previously used, especially due to the fact that ABS and ABS/PC account for about 90% of the total amount of plastic processed (Henne 2017)."

Work is currently underway to extend the application of the process to ABS plastics.

6.3.7 Plasma etching as an alternative etching process for the pretreatment of ABS plastics

This very innovative process for pretreating of ABS plastics dispenses entirely with hazardous or toxic chemicals. It was presented for the first time at the Oberflächentage 2018.

"Subsequently, David Zapf from Hansgrohe reported on a completely new and very interesting, albeit purely physical etching process for ABS under the title: "Development of alternative etching processes for ABS plastics for subsequent metallisation." Plasma etching is a non-galvanic process for etching and activating ABS in oxygen plasma and subsequent removal of the etching products with sodium hydroxide solution. In principle, it is conceivable to install such a relatively inexpensive plasma etching system decentrally behind each plastic injection moulding machine. The existing process chemistry can continue to be operated unchanged (Willand 2019)."

The limitations of the process are the slower throughput rates compared to the previous chromic acid-based etching process, the investment costs for the closed reactors and the additional space required. On the other hand, there are the advantages of flexibility and the complete absence of hazardous chemicals.

6.4 Conclusion and Outlook

PFOS was largely substituted by 6:2 FTS in the electroplating shop. The fate of 6:2 FTS could be determined in the investigated facility to a certain extent in the chromium(VI)-containing wastewater substream, but also partly in the chromium(VI)-free wastewater substream through the identification of previously unknown discharge routes. However, the fate of the 6:2 FTS used could not be determined quantitatively, since only about 25% of the amount used was found in the total wastewater of the facility. Further research is needed in this area.

Due to the determined carryover of the 6:2 FTS in the electroplating machine by adsorption and desorption processes, it must be assumed that a substream treatment of the chromium(VI)-containing wastewater substream for 6:2 FTS alone is not sufficient. It is therefore recommended that, if necessary, the total wastewater flow of an electroplating plant should also be treated for 6:2 FTS. For a possible determination of a limit value, the determination of a monitoring value for PFOS/PFAS in part D of annex 40 of the Waste Water Ordinance would therefore be preferable.

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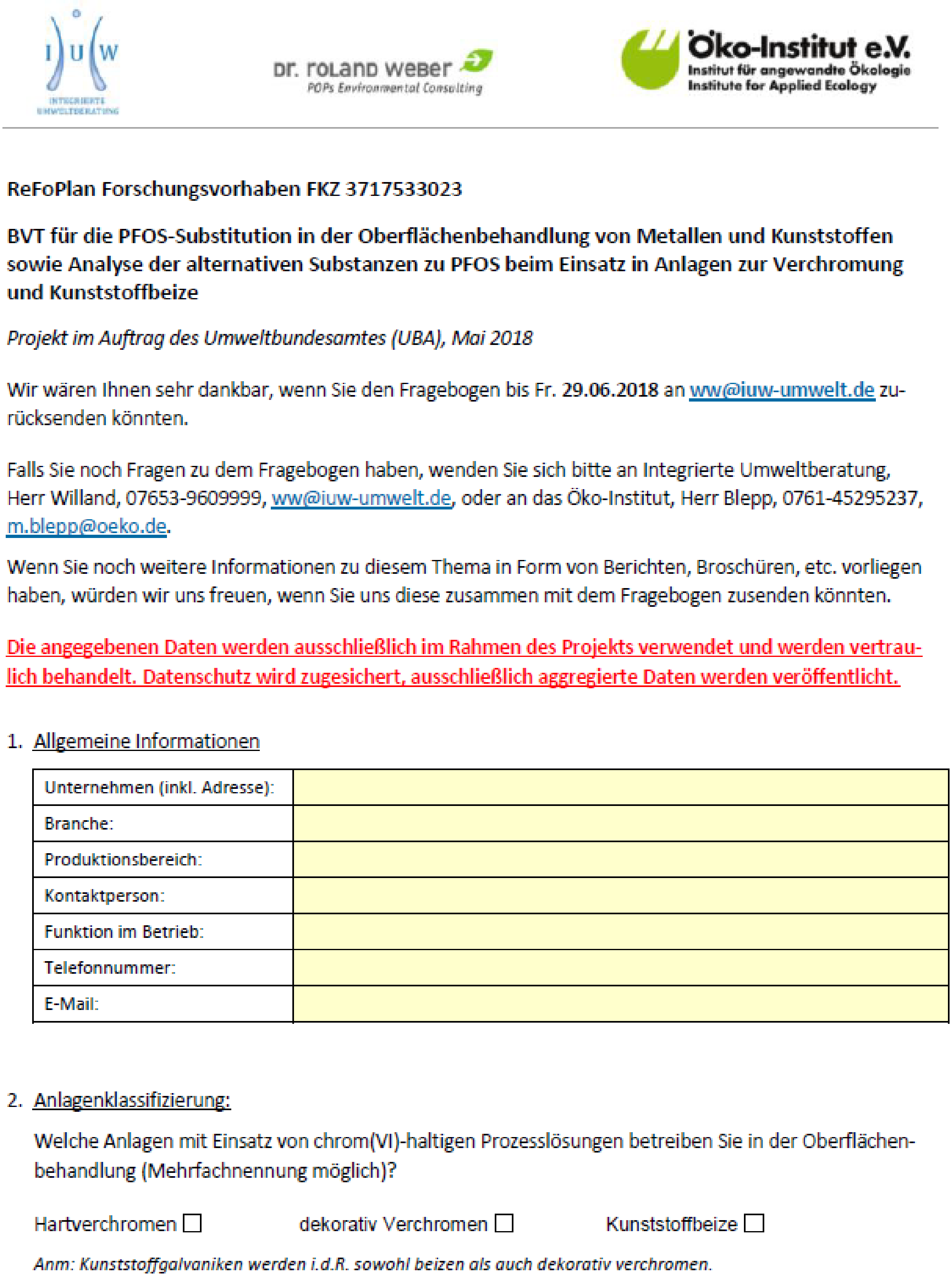
A Appendix 1: Questionnaire on the survey of mist suppressant users



IUW INTEGRIERTE UMWELTBERATUNG

Dr. Roland Weber POPs Environmental Consulting

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Institute for Applied Ecology

ReFoPlan Forschungsvorhaben FKZ 3717533023

BVT für die PFOS-Substitution in der Oberflächenbehandlung von Metallen und Kunststoffen sowie Analyse der alternativen Substanzen zu PFOS beim Einsatz in Anlagen zur Verchromung und Kunststoffbeize

Projekt im Auftrag des Umweltbundesamtes (UBA), Mai 2018

Wir wären Ihnen sehr dankbar, wenn Sie den Fragebogen bis Fr. **29.06.2018** an ww@iuw-umwelt.de zurücksenden könnten.

Falls Sie noch Fragen zu dem Fragebogen haben, wenden Sie sich bitte an Integrierte Umweltberatung, Herr Willand, 07653-9609999, ww@iuw-umwelt.de, oder an das Öko-Institut, Herr Blepp, 0761-45295237, m.blepp@oeko.de.

Wenn Sie noch weitere Informationen zu diesem Thema in Form von Berichten, Broschüren, etc. vorliegen haben, würden wir uns freuen, wenn Sie uns diese zusammen mit dem Fragebogen zusenden könnten.

Die angegebenen Daten werden ausschließlich im Rahmen des Projekts verwendet und werden vertraulich behandelt. Datenschutz wird zugesichert, ausschließlich aggregierte Daten werden veröffentlicht.

1. Allgemeine Informationen

Unternehmen (inkl. Adresse):	
Branche:	
Produktionsbereich:	
Kontaktperson:	
Funktion im Betrieb:	
Telefonnummer:	
E-Mail:	

2. Anlagenklassifizierung:

Welche Anlagen mit Einsatz von chrom(VI)-haltigen Prozesslösungen betreiben Sie in der Oberflächenbehandlung (Mehrfachnennung möglich)?

Hartverchromen ☐ dekorativ Verchromen ☐ Kunststoffbeize ☐

Anm: Kunststoffgalvaniken werden i.d.R. sowohl beizen als auch dekorativ verchromen.

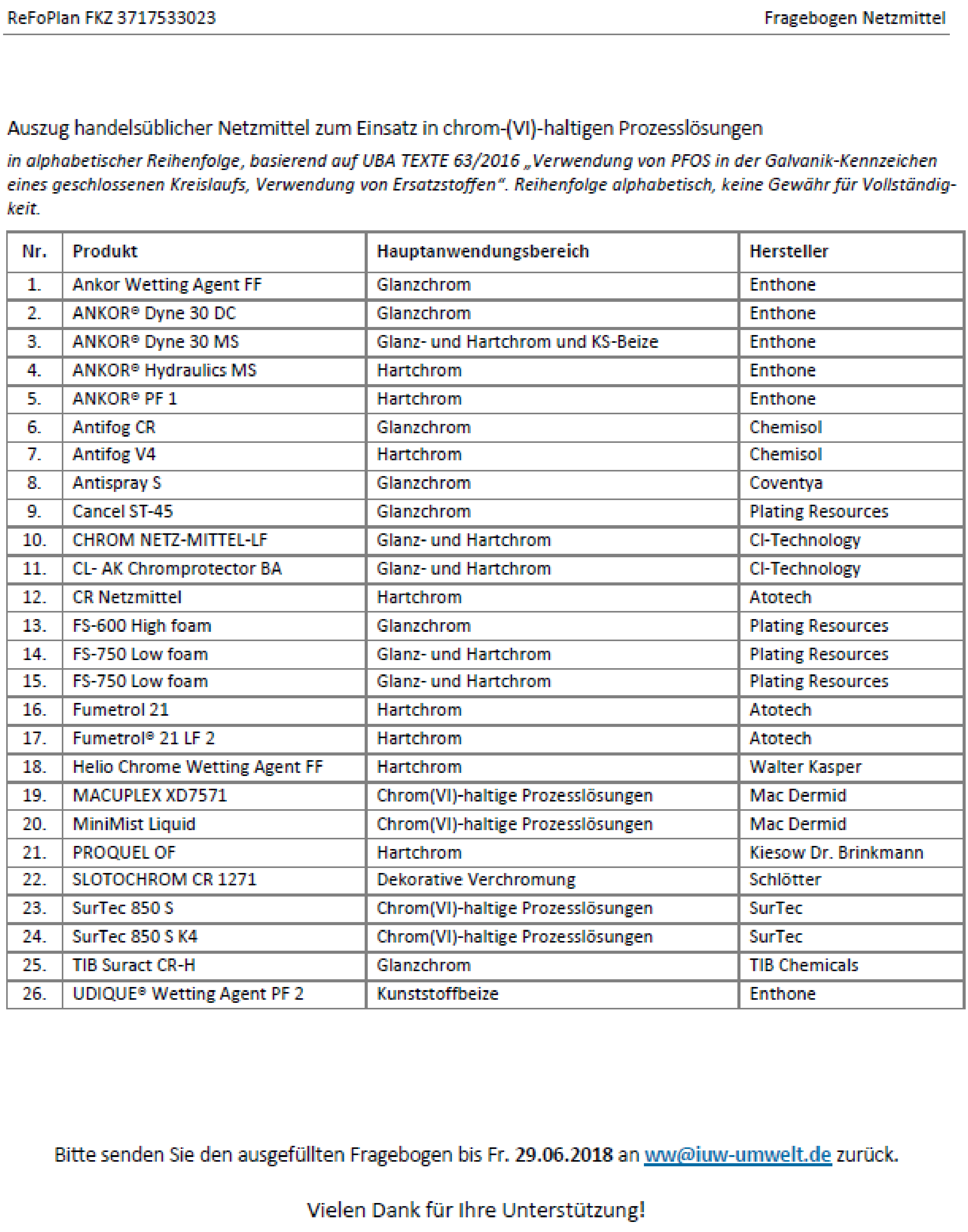
3. Einsatzort und Netzmittelverbrauch:

Falls Sie mehrere der unter Frage 2 genannten Anlagentypen betreiben, beantworten Sie bitte die folgenden Fragen mehrfach für den jeweiligen Anlagentyp, getrennt durch / .

Anlagenart:		
Wirkbadvolumen mit chrom(VI)-haltigen Prozesslösungen [m³]:		
Gesamtwirkbadvolumen der Anlage gemäß der 4.BImschV [m³]:		
Anlagen-Baujahr:		
Welche(s) Netzmittel verwenden Sie in den chrom(VI)-haltigen Prozesslösungen und wie hoch ist der Jahresverbrauch (wenn möglich Bezugsjahr 2017)?		
Name der verwendeten Netzmittel (**Auswahl siehe beiliegende Beispielliste auf Seite 3**):	Bezeichnung des Bades/des Verfahrens (bitte genaue Angaben, wie z.B. KS-Beize; Glanzchrombad etc.):	Verbrauch in kg/a (2017)
Anderes:		
Anderes:		
Werden Reduzierungs-/Behandlungsmaßnahmen bzgl. des Netzmittels werden durchgeführt?		
Falls ja, welche Maßnahmen werden durchgeführt (z.B. bedarfsabhängig gesteuerte Dosierung, Abwasserbehandlung mit Aktivkohle / Ionenaustauschern etc.)?		
Sind die eingesetzten Maßnahmen zur Kreislaufführung und/oder Rückhaltung von Netzmitteln grundsätzlich auch bei anderen, vergleichbaren Betrieben realisierbar?		
Falls die Konzentration des Netzmittels, bzw. Wirkstoffs im Abwasser der Anwendung bekannt ist, bitte angeben [µg/l]:		
Kommentare:		

4. Alternativverfahren:

Werden Alternativverfahren zur Oberflächenbehandlung mit Chrom(VI) werden eingesetzt (z.B. Chrom(III)-Verfahren, PVD etc.)? Nennen Sie die Verfahren und deren Einsatzgrenzen.	



ReFoPlan FKZ 3717533023 Fragebogen Netzmittel

Auszug handelsüblicher Netzmittel zum Einsatz in chrom-(VI)-haltigen Prozesslösungen

in alphabetischer Reihenfolge, basierend auf UBA TEXTE 63/2016 „Verwendung von PFOS in der Galvanik-Kennzeichen eines geschlossenen Kreislaufs, Verwendung von Ersatzstoffen". Reihenfolge alphabetisch, keine Gewähr für Vollständigkeit.

Nr.	**Produkt**	**Hauptanwendungsbereich**	**Hersteller**
1.	Ankor Wetting Agent FF	Glanzchrom	Enthone
2.	ANKOR® Dyne 30 DC	Glanzchrom	Enthone
3.	ANKOR® Dyne 30 MS	Glanz- und Hartchrom und KS-Beize	Enthone
4.	ANKOR® Hydraulics MS	Hartchrom	Enthone
5.	ANKOR® PF 1	Hartchrom	Enthone
6.	Antifog CR	Glanzchrom	Chemisol
7.	Antifog V4	Hartchrom	Chemisol
8.	Antispray S	Glanzchrom	Coventya
9.	Cancel ST-45	Glanzchrom	Plating Resources
10.	CHROM NETZ-MITTEL-LF	Glanz- und Hartchrom	CI-Technology
11.	CL- AK Chromprotector BA	Glanz- und Hartchrom	CI-Technology
12.	CR Netzmittel	Hartchrom	Atotech
13.	FS-600 High foam	Glanzchrom	Plating Resources
14.	FS-750 Low foam	Glanz- und Hartchrom	Plating Resources
15.	FS-750 Low foam	Glanz- und Hartchrom	Plating Resources
16.	Fumetrol 21	Hartchrom	Atotech
17.	Fumetrol® 21 LF 2	Hartchrom	Atotech
18.	Helio Chrome Wetting Agent FF	Hartchrom	Walter Kasper
19.	MACUPLEX XD7571	Chrom(VI)-haltige Prozesslösungen	Mac Dermid
20.	MiniMist Liquid	Chrom(VI)-haltige Prozesslösungen	Mac Dermid
21.	PROQUEL OF	Hartchrom	Kiesow Dr. Brinkmann
22.	SLOTOCHROM CR 1271	Dekorative Verchromung	Schlötter
23.	SurTec 850 S	Chrom(VI)-haltige Prozesslösungen	SurTec
24.	SurTec 850 S K4	Chrom(VI)-haltige Prozesslösungen	SurTec
25.	TIB Suract CR-H	Glanzchrom	TIB Chemicals
26.	UDIQUE® Wetting Agent PF 2	Kunststoffbeize	Enthone

Bitte senden Sie den ausgefüllten Fragebogen bis Fr. **29.06.2018** an ww@iuw-umwelt.de zurück.

Vielen Dank für Ihre Unterstützung!

B Appendix 2: Portfolio fiches - Characterisation of the individual mist suppressants

B.1 Overview

	Anonymous formulator	Anonymous brand name	Substitute	CAS
1	Formulator E	Mist suppressants E1	(Z)-Octadec-9-enylamine, ethoxylated	26635-93-8
2	Formulator Aa	Mist suppressants A1	Oleylamine ethoxylate+1,2-propylene glycol	26635-93-8, 57-55-6
3	Formulator D	Mist suppressants D1	Oleylamine ethoxylate	26635-93-8, 111-77-3
4	Formulator J	Mist suppressants J1	Amines, C12-C14 alkyl, ethoxylated	61791-14-8
5	Formulator K	Mist suppressants K1	Tallow alkylamine ethoxylate	61791-26-2, 26635-93-8
6	Formulator B	Mist suppressant B1	6:2 FTS	27619-97-2
	Formulator D	Mist suppressant D2		27619-97-2
	Formulator La	Mist suppressant La1		27619-97-2
	Formulator La	Mist suppressant La2		27619-97-2
	Formulator E	Mist suppressant E2		27619-97-2
	Formulator E	Mist suppressant E3		27619-97-2
	Formulator E	Mist suppressant E4		27619-97-2
	Formulator Ca	Mist suppressant Ca1		27619-97-2
	Formulator Cb	Mist suppressant Cb2		27619-97-2
	Formulator Cb	Mist suppressant Cb3		27619-97-2
	Formulator G	Mist suppressant G1		27619-97-2
7	Formulator E	Mist suppressant E5	6:2 FTS + Methyl dipropylene glycol	27619-97-2; 34590-94-8
8	Formulator F	Mist suppressant F1	6:2 FTS + Methanol	27619-97-2, 67-56-1
9	Formulator Lb	Mist suppressant L3	6:2 FTS + Maleic acid + Methanol	27619-97-2, 110-16-7, 67-56-1
	Formulator Lb	Mist suppressant L4		27619-97-2, 110-16-7
10	Formulator B	Mist suppressant B2	Sodium dodecyl sulfate	151-21-3
11	Formulator H	Mist suppressant H1	Dodecyl(dimethyl)ammonio_propane	68201-55-8, 15909-83-8; 61788-90-7
12	Formulator Cb	Mist suppressant C4	Isodecanol ethoxylated	61827-42-7
13	Formulator M	Mist suppressant M1	Paraffin oils	68188-18-1
14	Formulator N	Mist suppressant N1	Mist suppressant N1	No CAS
15	Formulator Ab	Mist suppressant A2	Mist suppressant A2	No CAS

B.3 Portfolio fiche - Mist suppressant E1

Substance data		
Product name:	**Mist suppressants E1**	
Manufacturer	**Formulator E**	
CAS:	26635-93-8	
Synonym:	(Z)-Octadec-9-enylamine, ethoxylated	
	Oleylamine ethoxylate	
	Polyoxyethylene(5) Oleylamine Ether	
	Oleylamine ethoxylate	
Molecular formula:	R-N(CH2CH2O)Hm(CH2CH2O)Hn	
Main application area	decorative chromium plating and plastic etching according to user questionnaire	
Note	Fluorine-free To maintain performance, it must be added continuously. However, it can only be used for decorative chromium, not for hard chromium plating	
Safety data sheet		
SDS is available	Yes	
Link	no longer available	
Supplier	Formulator E	
Issue date	16.04.2015	
Concentration	>10-25%	
Classification of the substance		
Physical hazards	**Hazard class and category**	**Coding**
Health hazards	ACUTE TOXICITY (Oral) - Category 4	H302 Harmful to health if swallowed
	CORROSIVE/IRRITANT EFFECT ON SKIN - Category 2	H315 causes skin irritation
	SEVERE EYE DAMAGE/EYE IRRITATION - Category 1	H318 causes severe eye damage
Dangerous to the environment	ACUTELY HAZARDOUS TO THE AQUATIC ENVIRONMENT - Category 1	H400 Very toxic to aquatic organisms
Other hazards	-	

GHS pictograms	
Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance (colour)	Yellow
Smell	Amine-like
Thickness	1.005 g/cm³ at 20 °C
Melting point	not available
Boiling point	not available
Combustion point	not available
Vapour pressure	not available
pH value	11.4
Water solubility	not available
Other chemical characterisation	not available
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	LD50 Oral; <2000 mg/kg (rat) ATE value 2010 mk/kg (ATE = Estimated value of acute toxicity)
Chronic toxicity	not available
Carcinogenicity	not available
Mutagenicity	not available
Reproduction toxicity	not available
Metabolism and depletion	not available
Additional toxicological information:	not available
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	not available
Bio-accumulation	not available

Toxicity	not available
PNEC: Predicted No-Effect Concentration (REACH)	not available
Ecotoxicological effects	No particular effects or hazards known
Mobility	
Name	**Value**
log Koc	not available
Long-distance transport	not available
Substance lists	
Name	**Record**
REACH, Appendix XIV	Substance not listed
REACH, Appendix XVII	Not applicable
INTL Stockholm Agreement, Appendix B, Restriction, Manufacture	None of the components is listed.
INTL Stockholm Agreement, Appendix B, Restriction, Use	None of the components is listed.
Other (e.g. degradation products, by-products, monitoring, etc.)	
Decomposition products may include the following materials:	
Carbon dioxide Carbon monoxide Nitrogen oxide	

B.4 Portfolio fiche - Mist suppressant A1

Substance data		
Product name:	**Mist suppressants A1**	
Manufacturer	**Formulator Aa**	
CAS:	26635-93-8	57-55-6
Synonym:	Oleylamine ethoxylate	1,2-propylene-glycol
	(Z)-Octadec-9-enylamine, ethoxylated	
	Polyoxyethylene(5) Oleylamine Ether	
Molecular formula:		
Main application area	decorative chromium plating, bright chromium, hard chromium	
Note	PFOS- and completely halogen-free. Consumption is largely determined by the degree of drag-out and is normally (as concentrate) approx. 1.5 - 3 litres / 10,000 Ah.	
Safety data sheet		
SDS is available	Yes	
Link		
Supplier	Formulator Aa	
Issue date	06.03.2017	
Concentration	10-<25%	0.1-≤ 2.5%
Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards		
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Eye Dam. 1	H318 causes severe eye damage
Dangerous to the environment		
Other hazards	-	
GHS pictograms		

Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance (colour)	Light yellow
Smell	Noticeable
Thickness	1.005 g/cm³ at 20 °C
Melting point	
Boiling point	100°C
Combustion point	Not applicable
Vapour pressure	23 hPa at 20 °C
pH value	11.4
Water solubility	Fully miscible
Other chemical characterisation	Solvent content: Organic solvent: 2.2%; VOC (EU) 2.20%
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Based on available data, the classification criteria are not met
Chronic toxicity	
Carcinogenicity	Based on available data, the classification criteria are not met
Mutagenicity	Based on available data, the classification criteria are not met
Reproduction toxicity	Based on available data, the classification criteria are not met
Metabolism and depletion	
Additional toxicological information:	
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	No further relevant information available
Bio-accumulation	No further relevant information available
Toxicity	No further relevant information available.
PNEC: Predicted No-Effect Concentration (REACH)	
Ecotoxicological effects	Water hazard class 1 (Self-assessment): slightly hazardous to water. Do not allow undiluted or in large quantities into groundwater, in the watercourse or in the sewage system. Must not be discharged undiluted or un-neutralised into wastewater or receiving waters.

Mobility	
Name	**Value**
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P101	If medical advice is needed, have packaging or identification label at hand.
P102	Keep out of the reach of children.
P103	Read identification label before use.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician.
Substance lists	
Name	**Record**
REACH, Appendix XIV	
REACH, Appendix XVII	Conditions of restriction: 3
INTL Stockholm Agreement, Appendix B, Restriction, Manufacture	
INTL Stockholm Agreement, Appendix B, Restriction, Use	
Other (e.g. degradation products, by-products, monitoring, etc.)	

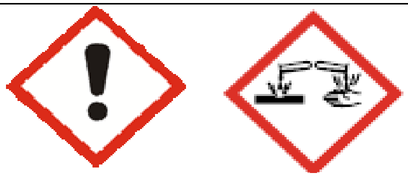
B.5 Portfolio fiche - Mist suppressant D1

Substance data		
Product name:	**Mist suppressants D1**	
Manufacturer	**Formulator D**	
CAS:	26635-93-8	111-77-3
Synonym:	Oleylamine ethoxylate	2-(2-METHOXYETHOXY)ETHANOL
Molecular formula:		
Main application area	Mist suppressant: Products for the treatment of metal surfaces, including electroplating and galvanising products; PFOS-free liquid additive for chromium baths; decorative chromium plating	
Note		
Safety data sheet		
SDS is available	yes	
Link		
Supplier	Formulator D	
Issue date	11.10.2016	
Concentration	≥ 25 - < 50%	≥ 3 - < 10 %
Classification of the substance		
Physical hazards	**Hazard class and category**	**Coding**
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Eye Dam. 1	H318 causes severe eye damage
	Repr. 2	H361d is likely to cause harm to the unborn child
Dangerous to the environment	Aquatic Acute 1	H400 Very toxic to aquatic organisms
Other hazards		
GHS pictograms		

Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance	light red
Thickness	1.0 - 1.02 g/cm³
Melting point	not determined
Boiling point	100°C
Combustion point	not applicable
Vapour pressure	not determined
pH value	8 to 10
Water solubility	miscible
Other chemical characterisation	No further relevant information available.
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Parameters: ATEmix calculated Exposure route: Oral Effective dose: 1111.1 mg/kg Parameter: LD50 (2-(2-METHOXYETHOXY)ETHANOL; CAS no. : 111-77-3) Exposure route: Oral Species: Rat Effective dose: 9210 mg/kg
Chronic toxicity	
Carcinogenicity	
Mutagenicity	
Reproduction toxicity	
Metabolism and depletion	
Additional toxicological information:	
Hazardousness to the environment / ecotoxicity	
Name	Value
Persistence	No information is available.
Bio-accumulation	No information is available.

Toxicity	No information is available.
PNEC: Predicted No-Effect Concentration (REACH)	
Ecotoxicological effects	
Mobility	
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P201	Obtain special instructions before use
P202	Read and understand all safety instructions before use
P264	After use ... wash thoroughly
P310	Immediately call POISON INFORMATION CENTRE/physician/...
P330	Rinse out mouth
P405	Keep under lock and key
Substance lists	
Other (e.g. degradation products, by-products, monitoring, etc.)	

B.6 Portfolio fiche - Mist suppressant J1

Substance data		
Product name:	**Mist suppressants J1**	
Manufacturer	**Formulator J**	
CAS:	61791-14-8	
Synonym:	Amines, C12-C14 alkyl, ethoxylated	
Molecular formula:		
Main application area	Mist suppressant: Hard chromium; bright chromium	
Note	PFOS- and halogen-free	
Safety data sheet		
SDS is available	yes	
Link		
Supplier	Formulator J	
Issue date	20.06.2016	
Concentration	10-25%	
Classification of the substance		
Physical hazards	**Hazard class and category**	**Coding**
Health hazards	Eye Dam. 1	H318 causes severe eye damage
	Acute Tox. 4	H302 Harmful to health if swallowed
Dangerous to the environment	-	
Other hazards		
GHS pictograms		
Physico-chemical properties		
Name	Value	
Molecular weight	-	
Physical state	liquid	

Appearance	light yellow
Thickness	0.99-1.02 g/cm³
Melting point	approx. 0 °C
Boiling point	100°C
Combustion point	> 100°C
Vapour pressure	not determined
pH value	approx. 10
Water solubility	fully miscible with water
Other chemical characterisation	-
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Classification-relevant LD/LC50 values: 61791-14-8 amines, C12-C14 alkyl, ethoxylated Oral LD50 >500-<2000 mg/kg (rat)
Chronic toxicity	?
Carcinogenicity	Based on available data, the classification criteria are not met.
Mutagenicity	Based on available data, the classification criteria are not met.
Reproduction toxicity	Based on available data, the classification criteria are not met.
Metabolism and depletion	-
Additional toxicological information:	
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	No further relevant information available.
Bio-accumulation	No further relevant information available.
Toxicity	Aquatic toxicity: 61791-14-8 amines, C12-C14 alkyl, ethoxylated EC50 >10-<100 mg/kg (daphnia)
PNEC: Predicted No-Effect Concentration (REACH)	
Ecotoxicological effects	
Mobility	

log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician.
Substance lists	
Other (e.g. degradation products, by-products, monitoring, etc.)	

B.7 Portfolio fiche - Mist suppressant K1

Substance data		
Product name:	**Mist suppressants K1**	
Manufacturer	**Formulator K**	
CAS:	61791-26-2	26635-93-8
Synonym:	Tallow alkylamine ethoxylate	Oleylamine ethoxylate
Molecular formula:		
Main application area	Bright chromium	
Note		
Safety data sheet		
SDS is available	yes	
Link		
Supplier	Formulator K	
Issue date	01.07.2015	
Concentration	5-<-10%	1-<-3%
Classification of the substance		
Physical hazards	**Hazard class and category**	**Coding**
Health hazards	Acute Tox. 3	H301 Toxic if swallowed
	Eye Dam. 1	H318 causes severe eye damage
Dangerous to the environment	Aquatic Acute 1	H400 Very toxic to aquatic organisms
	Aquatic Chronic 1	H410 Very toxic to aquatic organisms with long lasting effects
	Aquatic Chronic 2	H411 Toxic to aquatic organisms, with long lasting effects
	Aquatic Chronic 3	H412 Harmful to aquatic organisms, with long lasting effects
Other hazards	Results of the PBT and vPvB assessment PBT: Not applicable. vPvB: Not applicable.	

GHS pictograms	
Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance	yellow
Thickness	0.990 - 1.030 g/cm3
Melting point	Not determined.
Boiling point	> 100 °C (> 212 °F)
Combustion point	Not applicable.
Vapour pressure	Not determined.
pH value	6 - 10
Water solubility	Fully miscible in/with water
Other chemical characterisation	No further relevant information available.
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	61791-26-2 Tallow alkylamine ethoxylate Oral LD50 200-2000 mg/kg (rat) 26635-93-8 Oleylamine ethoxylate Oral: LD50 300 - 2000 mg/kg (rat) 7778-50-9 potassium dichromate Oral: LD50 190 mg/kg (mouse) 57 mg/kg (rat) Dermal LD50 1640 mg/kg (rabbit) Inhalative LC50 AEROSOL 0.094 mg/l (rat) 4 Heures/hours
Chronic toxicity	?
Carcinogenicity	-

Mutagenicity	
Reproduction toxicity	
Metabolism and depletion	-
Additional toxicological information:	Other toxicological information: General information: Water hazard class 2 (self-classification): hazardous to water Do not allow into groundwater, in the watercourse or in the sewage system. Hazardous to drinking water even if small quantities leak into the subsurface. Harmful to aquatic organisms 12.5 Results of PBT and vPvB assessment PBT: Not applicable. vPvB: Not applicable. 12.6 Other adverse effects No further relevant information available.
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	No further relevant information available
Bio-accumulation	No further relevant information available
Toxicity	Aquatic toxicity: 61791-26-2 Tallow alkylamine ethoxylate EC50 180 mg/kg (Bacterium) 4 Heures/Hours EC50/48H 1.7 mg/l (Daphnia) LC50/96H/fresh water 1.3 mg/l (ttr) 26635-93-8 Oleylamine ethoxylate EC50/48H 0.88 mg/l (Daphnia) Daphnia magna IC50/72H 1.1 - 10 mg/l (algae) LC50/96H/fresh water 1.3 mg/l (ttr) 7778-50-9 potassium dichromate Sensitisation EC50/24H 0.53 mg/L (Daphnia) 0.53 Cr/l EC50/72H 0.30 mg/l (algae) 0.30 mg Cr/l LC50/96H/fresh water 37.1 mg/l (fish) 37.1 mg Cr/l - Pimephales promelas

PNEC: Predicted No-Effect Concentration (REACH)	
Ecotoxicological effects	Note: Hazardous for fish.
Mobility	
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P280	Wear protective gloves/protective clothing/eye protection/face protection
P273	Avoid release into the environment
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician
P501	Dispose of contents / container in accordance with local / regional / national / international regulations
Signal word	Hazard
Hazardous components of labelling	Tallow alkylamine ethoxylate oleylamine ethoxylate
Hazard warnings	H318 causes severe eye damage.; H412 Harmful to aquatic organisms, with long lasting effects
Substance lists	
Other (e.g. degradation products, by-products, monitoring, etc.)	
Other hazards Results of the PBT and vPvB assessment PBT: Not applicable. vPvB: Not applicable.	

B.8 Portfolio fiche - Mist suppressant B1 und variations 1-4

Substance data			**Variation 1**		**Variation 2**		**Variation 3**		**Variation 4**	
Product name:	**Mist suppressant B1**		**Mist suppressant D2**		**Mist suppressant La1**		**Mist suppressant La2**		**Mist suppressant E2**	
Manufacturer	**Formulator B**		**Formulator D**		**Formulator La**		**Formulator La**		**Formulator E**	
CAS:	27619-97-2		27619-97-2		27619-97-2		27619-97-2		27619-97-2	
Synonym:	Tridecafluorooctane sulphonic acid		Tridecafluoro octane sulphonic acid		3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octane sulphonic acid		3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octane sulphonic acid		3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octane sulphonic acid	
	H4PFOS		H4PFOS						H4PFOS	
Molecular formula:										
Main application area	Mist suppressant - hard chromium								Bright and hard chromium and plastic etching	
Note									-	
Link										
Safety data sheet										
SDS is available	yes		yes		yes		yes		yes	
Link			-		-		-		-	
Supplier	Formulator B		Formulator D		Formulator La		Formulator La		Formulator E	
Issue date	07.12.2015		05.06.2018		27.10.2017		27.10.2017		29.03.2018	
Concentration	1-2.5%		≥ 1 - < 5 %		<3%		<3%		>-1-<3 %	

Classification of the substance										
	Hazard class and category	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**
Physical hazards										
Health hazards	Eye Dam. 1	H318 causes severe eye damage	Acute Tox. 4	H302 Harmful to health if swallowed	ACUTE TOXICITY (oral) - Category 4	H302 Harmful to health if swallowed.	Acute Tox. 4	H302 Harmful to health if swallowed	Acute Tox. 4	H302 Harmful to health if swallowed
	Acute Tox. 4	H302 Harmful to health if swallowed	Skin Corr. 1B	H314 Causes severe skin burns and eye damage	Skin. Corr. 1B	H314 Causes severe skin burns and eye damage	Skin. Corr. 1B	H314 Causes severe skin burns and eye damage	Eye Dam. 1	H318 causes severe eye damage
			Eye Dam. 1	H318 causes severe eye damage	Skin Irrit. 2	H315 causes skin damage	Skin Irrit. 2	H315 causes skin damage	Eye Irrit. 2	H319 causes severe eye irritation
					Eye Irrit. 2	H319 causes severe eye damage	Eye Irrit. 2	H319 causes severe eye damage		
Dangerous to the environment	-	-			-	-	-	-	-	-
Other hazards		-	-	-	-		-	-	Other hazards that do not lead to a classification: None known.	

GHS pictograms					
Physico-chemical properties					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Molecular weight	-	-	-	-	-
Physical state	liquid	liquid	liquid	liquid	liquid
Appearance	light brown	colourless	yellowish	colourless to pale yellow	yellowish
Smell				No odour	Onion
Thickness	1.0075g/cm³	0.98 - 1.02 g/cm³	1,005 g/cm³	1,008 g/cm³	1.005g/cm³
Melting point	not determined	not determined	0°C	not available	0°C
Boiling point	100°C	100°C	100°C	not available	100°C
Combustion point	not applicable	none	not applicable	not available	not available.
Vapour pressure	23 hPa	not determined			not available.
pH value	approx. 2-3 (concentrate)	2 to 3	<2.5	<2.5	<2.5
Water solubility	fully miscible in/with water	miscible	fully miscible with cold water	fully miscible with water	easily soluble in cold water
Other chemical characterisation	-	No further relevant information available	No further relevant information available	No further relevant information available	no further information

Hazardousness to humans /Human toxicity					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Acute toxicity	Classification-relevant LD/LC50 values: Oral LD50 > 2000 mg/kg (rat)	Parameters: LD50 (TRIDECAFLUOROOCTANE SULFONIC ACID ; CAS no. : 27619-97-2) Exposure route: Oral; Species: Rat; Effective dose: 1800 mg/l	Oral 30665.4 mg/kg	ATE - Oral 28001.8 mg/kg	ATE value 30665.4mg/kg
Chronic toxicity	?		?	?	not available.
Carcinogenicity	Based on available data, the classification criteria are not met.		not available	not available	no particular effects or hazards known.
Mutagenicity	Based on available data, the classification criteria are not met.		not available	not available	not available
Reproduction toxicity	Based on available data, the classification criteria are not met.		not available	not available	not available
Metabolism and depletion			-	-	not available

Additional toxicological information:			The product is not subject to labelling according to the calculation methods of the General Classification guideline for preparations of the EC in the latest valid version. According to our experience and the information available to us, the product does not cause any harmful effects when handled and used as intended.	The product is not subject to labelling according to the calculation methods of the General Classification guideline for preparations of the EC in the latest valid version. According to our experience and the information available to us, the product does not cause any harmful effects when handled and used as intended.	Percentage of components in the mixture with unknown hazard to the aquatic environment: 1.6%
Hazardousness to the environment / ecotoxicity					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Persistence	easily biodegradable	No information is available.	No further relevant information available.	No further relevant information available.	not available
Bio-accumulation	No further relevant information available.	No information is available.	No further relevant information available.	No further relevant information available.	not available
Toxicity	No further relevant information available.	No information is available.	No further relevant information available.	No further relevant information available.	not available
PNEC: Predicted No-Effect Concentration (REACH)				not available	not available
Ecotoxicological effects	Water hazard class 1 (Self-assessment): slightly hazardous to water Do not allow undiluted or in large quantities into groundwater, in the				no particular effects or hazards known

	watercourse or in the sewage system.									
Mobility										
log Koc									not available	
Long-distance transport									not available	
Safety instructions and workplace labels										
P280	Wear protective gloves/protective clothing/eye protection/face protection.		P264	Wash thoroughly after use.	P280	Wear protective gloves: < 1 hour (breakthrough time): Fluorinated rubber, thickness: 0.5 mm. Wear eye protection or face shield	P280	Wear protective gloves: < 1 hour (breakthrough time): Fluorinated rubber, thickness: 0.5 mm. Wear eye protection or face shield	Prevention	Wear eye protection or face shield. Wash hands thoroughly after use.

P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.		P280	Wear protective gloves/protective clothing/eye protection/face protection.	P264	Wash hands thoroughly after use.	P264	Wash hands thoroughly after use.	Reaction	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician.	P337+P313	If eye irritation persists: Seek medical advice/consult medical assistance.	P305 + P351 + P338	IF ON THE EYES: Rinse carefully with water for a few minutes. Remove contact lenses, if present and easy to remove. Continue rinsing.	P305 + P351 + P338	IF ON THE EYES: Rinse carefully with water for a few minutes. Remove contact lenses, if present and easy to remove. Continue rinsing.	Storage	Not applicable.	
P301+P312	UPON INGESTION: If you feel unwell, call a POISON INFORMATION		P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water					Disposal	Not applicable.

	CENTRE/physician.			for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.						
P330	Rinse out mouth.								Hazardous ingredients	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid
P501	Dispose of contents / container in accordance with local / regional / national / international regulations.								Additional labelling elements	Not applicable.
									Signal word	Warning
									Hazard warnings	causes severe eye irritation
Substance lists										
REACH Appendix XVII							Appendix XIV: none of the components is listed		not applicable	

INTL Stockholm Agreement, Appendix B, Restriction, Manufacture						Appendix XVII: not applicable	none of the components is listed
INTL Stockholm Agreement, Appendix B, Restriction, Use						INTL Stockholm Agreement: not listed	none of the components is listed
European inventory							not determined
Other (e.g. degradation products, by-products, monitoring, etc.)							
						Decomposition products may include the following materials: Carbon dioxide Carbon monoxide Sulphur oxide halogenated compounds	Decomposition products may include the following materials: Carbon dioxide Carbon monoxide Sulphur oxide halogenated compounds

B.9 Portfolio fiche - Variations 5-8 of the mist suppressant B1

Substance data	**Variation 5**		**Variation 6**		**Variation 7**		**Variation 8a**		**Variation 8b**	
Product name:	**Mist suppressant E3**		**Mist suppressant E4**		Mist suppressant Ca1		Mist suppressant Cb2		Mist suppressant Cb3	
Manufacturer	**Formulator E**		**Formulator E**		Formulator Ca		Formulator Cb		Formulator Cb	
CAS:	27619-97-2		27619-97-2		27619-97-2		27619-97-2		27619-97-2	
Synonym:	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid		3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid		Polyfluorosulphonic acid		1H,1H,2H,2H-Perfluoroctane sulphonic acid		1H,1H,2H,2H-Perfluorooctanesulphonic acid	
			H4PFOS				6:2 FTS		6:2 FTS	
							H4PFOS		H4PFOS	
							Polyfluorosulphonic acid		Polyfluorosulphonic acid	
Molecular formula:										
Main application area	Hard chromium		Hard chromium		Hard chromium		Hard chromium; chemical coating of metals / surface technology		Hard chromium; chemical coating of metals / surface technology	
Note										
Link										
Safety data sheet										
SDS is available	yes		yes		yes		yes		yes	
Link	-		-		-		-		-	
Supplier	Formulator E		Formulator E		Formulator Ca		Formulator Cb		Formulator Cb	

Issue date	27.10.2017		16.04.2015		15.04.2013		01.06.2015		01.04.2014	
Concentration	<3%		>-3-<5 %		2.5-5%		1-2.5%;		5-10%	
Classification of the substance										
	Hazard class and category	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**	**Hazard class and category**	**Coding**
Physical hazards										
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed	Acute Tox. 4	H302 Harmful to health if swallowed	Acute Tox. 4	H302 - Harmful to health if swallowed	Acute Tox. 4	H302 - Harmful to health if swallowed	Acute Tox. 4	H302 - Harmful to health if swallowed
	Eye Dam. 1	H318 causes severe eye damage	Eye Dam. 1	H318 causes severe eye damage	Eye Dam. 1	H318 - causes severe eye damage	Eye Dam. 1	H318 - causes severe eye damage	Eye Dam. 1	H318 - causes severe eye damage
	Eye Irrit. 2	H319 causes severe eye irritation								
Dangerous to the environment	-	-			-	-	-	-	-	-
Other hazards	Other hazards that do not lead to a classification: None known.		Other hazards that do not lead to a classification: None known.							

GHS pictograms					
Physico-chemical properties					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Molecular weight	-	-	-	-	-
Physical state	liquid	liquid	liquid	liquid	liquid
Appearance	yellowish	red	colourless, brown	colourless, yellow, light brown	light yellow, light brown
Smell	Onion			No information available	No information available
Thickness	1,005g/cm³	1,015 g/cm³	0,995 - 1,025	0,995 - 1,021	1,010 - 1,040
Melting point	0 °C	not available.	No information available	No information available	No information available
Boiling point	100°C	not available.	> 100	No information available	> 100
Combustion point	not available.	not available.	not applicable	not applicable	not applicable
Vapour pressure		not available.	approx. 23 hPa	approx. 23 hPa	approx. 23 hPa
pH value	<2.5	<2.5	0.0- 2.5	0.0- 3.0	0.000- 2.500
Water solubility	easily soluble in cold water	easily soluble in cold water	miscible	miscible	completely soluble

Other chemical characterisation	no further information	no further information	VOC content (%)**:< 0.1 Solubility in other solvents: No information available Bulk density: No information available Ignition temperature (°C): No information available Solidification point (°C): Not required	VOC content (%)**: 0.5	VOC content (%)**: 0.5
Hazardousness to humans /Human toxicity					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Acute toxicity	ATE oral value 30665.4mg/kg	Oral 12467.3 mg/kg, Dermal 245298.4 mg/kg, Inhalation (vapours) 2453 mg/l		causes severe eye irritation; may be harmful if swallowed;	causes severe eye damage; may be harmful if swallowed
Chronic toxicity	not available.	not available.	?	Prolonged skin contact may cause skin irritation	Prolonged skin contact may cause skin irritation
Carcinogenicity	not available.	not available.	-	No information available	No information available
Mutagenicity	not available	not available	No information available	No information available.	No information available.
Reproduction toxicity	not available	not available	No information available	No information available.	No information available.

Metabolism and depletion	not available	-	-	-	-
Additional toxicological information:	not available	not available			
Hazardousness to the environment / ecotoxicity					
Name	**Value**	**Value**	**Value**	**Value**	**Value**
Persistence	not available	not available	No information available	No information available	No information available
Bio-accumulation	not available	not available	indefinite	No information available	indefinite
Toxicity	not available			In case of intended use, no adverse effects on the environment are known or expected	In case of intended use, no adverse effects on the environment are known or expected
PNEC: Predicted No-Effect Concentration (REACH)	not available	not available			
Ecotoxicological effects	no particular effects or hazards known. 1.6% - Percentage of components in the mixture with unknown hazard to the aquatic environment	3.4% - Percentage of components in the mixture with unknown hazard to the aquatic environment			

Mobility										
log Koc	not available		not available							
Long-distance transport	not available		not available				Not a hazardous material in the sense of ADR, IMDG, IATA.		Not a hazardous material in the sense of ADR, IMDG, IATA.	
Safety instructions and workplace labels										
P280	Prevention	Wear eye protection or face shield. Wash hands thoroughly after use.	Prevention	Wear eye protection or face shield. Wash hands thoroughly after use.	P280	Wear protective gloves/eye protection/face protection	P280	Wear eye protection / face shield	P280	Wear eye protection / face shield
P305+P351+P338	Reaction	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	Reaction	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove existing contact lenses, if possible. Continue rinsing	P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove existing contact lenses, if possible. Continue rinsing	P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove existing contact lenses, if possible. Continue rinsing

P310	Storage	Not applicable.	Storage	Not applicable.	P337+P313	If eye irritation persists: Seek medical advice / seek medical assistance	P337+P313	If eye irritation persists: Seek medical advice / seek medical assistance	P310	Immediately call POISON INFORMATION CENTRE or physician
P301+ P312	Disposal	Not applicable.	Disposal	Not applicable.						
P330	Hazardous ingredients	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid	Hazardous ingredients	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid						
P501	Additional labelling elements	Not applicable.	Additional labelling elements	Contains formaldehyde. May cause allergic reactions.						
	Signal word	Warning	Signal word	Hazard						
	Hazard warnings	causes severe eye irritation	Hazard warnings	Causes severe eye damage						
Substance lists										
REACH Appendix XVII	not applicable		Appendix XIV, List of substances subject to authorisation: none of the components is listed							

INTL Stockholm Agreement, Appendix B, Restriction, Manufacture	none of the components is listed	Appendix XIV: Substances of Very High Concern: none of the components is listed			
INTL Stockholm Agreement, Appendix B, Restriction, Use	none of the components is listed	Appendix XVII: not applicable			
European inventory	not determined	INTL, Appendix B, Restriction, Manufacture: None of the components is listed			
		INTL, Appendix B, Restriction, Use: None of the components is listed			
		European inventory: All components are listed or excluded			
Other (e.g. degradation products, by-products, monitoring, etc.)					

		Decomposition products may include the following materials: Carbon dioxide Carbon monoxide Sulphur oxide halogenated compounds			In case of fire, the following hazardous decomposition products may be formed: Carbon dioxide Sulphur oxide

B.10 Portfolio fiche - Variation 9 of the mist suppressant B1

Substance data	**Variation 9**	
Product name:	**Mist suppressant G1**	
Manufacturer	**Formulator G**	
CAS:	27619-97-2	
Synonym:		
Molecular formula:		
Main application area	Hard chromium	
Note	May cause respiratory tract irritation, may cause skin irritation, symptoms (if swallowed) include abdominal pain/nausea/vomiting, lachrymatory effect.	
Link		
Safety data sheet		
SDS is available	yes	
Link		
Supplier	Formulator G	
Issue date	10.06.2015	
Concentration	1-<3%	
Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards		
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Eye Dam. 1	H318 causes severe eye damage
	Eye irrit. 2	H319 causes severe eye irritation

	-	-
Dangerous to the environment		
Other hazards	-	-
GHS pictograms		
Physico-chemical properties		
Name	**Value**	
Molecular weight	-	
Physical state	liquid	
Appearance	yellowish	
Smell	peculiar	
Thickness	not determined	
Melting point	not determined	
Boiling point	approx. 100	
Combustion point	not determined	
Vapour pressure	not determined	
pH value	acidic	
Water solubility	miscible	
Other chemical characterisation	none	
Hazardousness to humans /Human toxicity		
Name	**Value**	
Acute toxicity	ATE-mix, oral, > 2000 mg/kg.	
Chronic toxicity	?	
Carcinogenicity	not determined	

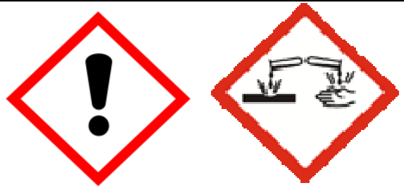
Mutagenicity	not determined	
Reproduction toxicity	not determined	
Metabolism and depletion	-	
Additional toxicological information:		
Hazardousness to the environment / ecotoxicity		
Name	**Value**	
Persistence		
Bio-accumulation	Biodegradability: not determined	
Toxicity		
PNEC: Predicted No-Effect Concentration (REACH)		
Ecotoxicological effects	Behaviour in environmental compartments: not determined; Behaviour in wastewater treatment plants: not determined;	
Mobility		
log Koc		
Long-distance transport		
Safety instructions and workplace labels		
	P280	Wear eye protection / face shield
	P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.

	P337+P313	If eye irritation persists: Seek medical advice / seek medical assistance
Substance lists		
REACH Appendix XVII		
INTL Stockholm Agreement, Appendix B, Restriction, Manufacture		
INTL Stockholm Agreement, Appendix B, Restriction, Use		
European inventory		
Other (e.g. degradation products, by-products, monitoring, etc.)		
	Risk of formation of toxic pyrolysis products Carbon monoxide (CO) Carbon dioxide (CO2) Sulphur oxide (SOx) Fluorinated compounds	

B.11 Portfolio fiche - Mist suppressant B1; mist suppressant D2; mist suppressant La1; mist suppressant La2; mist suppressant E2; mist suppressant E3; mist suppressant E4; mist suppressant Ca1; mist suppressant Cb2; mist suppressant Cb3; mist suppressant G1

Substance data	
Product name:	**Mist suppressant B1; mist suppressant D2; mist suppressant La1; mist suppressant La2; mist suppressant E2; mist suppressant E3; mist suppressant E4; mist suppressant Ca1; mist suppressant Cb2; mist suppressant Cb3; mist suppressant G1**
Manufacturer	**Formulator B; Formulator D; Formulator La; Formulator La; Formulator E; Formulator E; Formulator E; Formulator Ca; Formulator Cb; Formulator Cb; Formulator G**
CAS:	27619-97-2
Synonym:	Tridecafluorooctane sulphonic acid
	H4PFOS
	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane sulphonic acid
	1H,1H,2H,2H-Perfluoroctanesulphonic acid
	6:2 FTS
	Polyfluorosulphonic acid
Molecular formula:	
Main application area	Hard and bright chromium and plastic etching;
Note	
Safety data sheet	
SDS is available	yes
Link	
Supplier	Formulator B; Formulator D; Formulator La; Formulator E; Formulator Ca; Formulator Cb; Formulator G
Issue date	15.04.2013-05.06.2018
Concentration	1-2.5% (3 indications); >-1-<3 % (2 indications); ≥ 1 - < 5 %; <3% (3 indications); >-3-<5 %; 5-10%;

Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards		

Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Skin Corr. 1B	H314 Causes severe skin burns and eye damage
	SKIN CORROSION/IRRITATION - Category 2	H315 causes skin damage.
	Eye Dam. 1	H318 causes severe eye damage
	SERIOUS EYE DAMAGE/EYE IRRITATION - Category 2	H319 causes severe skin damage.
Dangerous to the environment	-	-
Other hazards	Other hazards that do not lead to a classification: None known.	
GHS pictograms		
Physico-chemical properties		
Name	Value	
Molecular weight	-	
Physical state	liquid	
Appearance	colourless; colourless to pale yellow; colourless, yellow; colourless, brown; yellowish (4 indications); red; light brown (2 indications); light yellow, light brown;	
Smell	Odourless; No information available (2 indications); Onion (2 indications) Peculiar	

Thickness	1.0075g/cm³; 1,005 g/cm³ (3 indications); 1,008 g/cm³ 1,015 g/cm³; 0,995 - 1,021; 0,995 - 1,025; 0.98 - 1.02 g/cm³; 1,010 - 1,040 not determined;
Melting point	not determined (3 indications); not available (5 indications); 0°C (3 indications);
Boiling point	100°C (6 indications); > 100 (2 indications); No information available (3 indications);
Combustion point	not applicable (2 indications); not available (4 indications); not applicable (3 indications); not determined; none;
Vapour pressure	23 hPa (4 indications); not determined (2 indications); not available (2 indications);
pH value	Approx. 2-3 (concentrate) 2 to 3; <2.5 (5 indications); 0.0- 2.5 (2 indications); 0.0- 3.0; acidic;
Water solubility	completely miscible in/with water (2 indications; lightly soluble in cold water (3 indications); completely miscible with cold water; completely soluble; miscible (4 indications);

Other chemical characterisation	"VOC content (%)**: < 0.1; "VOC content (%)**: 0.5" ;
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Parameters: LD50 (TRIDECAFLUOROOCTANE SULFONIC ACID ; CAS no. : 27619-97-2) Exposure route: Oral; Species: Rat; Effective dose: 1800 mg/l; ATE-mix, oral, > 2000 mg/kg; Classification-relevant LD/LC50 values: Oral LD50 > 2000 mg/kg (rat); ATE - Oral 28001.8 mg/kg; ATE-Oral Value 30665.4mg/kg (3 indications); Oral 12467.3 mg/kg, Dermal 245298.4 mg/kg, Inhalation (vapours) 2453 mg/l; Causes severe eye irritation; May be harmful if swallowed; Causes severe eye damage; May be harmful if swallowed;
Chronic toxicity	not available (3 indications); Prolonged skin contact may cause skin irritation (2 indications);
Carcinogenicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.
Mutagenicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.
Reproduction toxicity	Based on available data, the classification criteria are not met / not available; no particular effects or hazards known.
Metabolism and depletion	not available.
Additional toxicological information:	According to our experience and the information available to us, the product does not cause any harmful effects when handled and used as intended; Percentage value of components in the mixture with unknown hazard for the aquatic environment: 1.6%; not available;
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	easily biodegradable; No information is available;
Bio-accumulation	No further relevant information available; indefinite;
Toxicity	No further relevant information available; In case of intended use, no adverse effects on the environment are known or expected;

PNEC: Predicted No-Effect Concentration (REACH)	not available.
Ecotoxicological effects	no particular effects or hazards known. 1.6% - Percentage value of components in the mixture with unknown hazards for the aquatic environment 3.4% - Percentage value of components in the mixture with unknown hazards for the aquatic environment Water hazard class 1 (self-classification): slightly hazardous for water. Do not allow undiluted product or large quantities of it to reach groundwater, watercourse or sewage system; Behaviour in environmental compartments: not determined; Behaviour in wastewater treatment plants: not determined;
Mobility	
log Koc	
Long-distance transport	not available; not a hazardous material in the sense of ADR, IMDG, IATA;
Safety instructions and workplace labels	
P264	After use ... wash thoroughly.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P337+P313	If eye irritation persists: Seek medical advice/consult medical assistance.
P310	Immediately call POISON INFORMATION CENTRE/physician.
P301+P312	UPON INGESTION: If you feel unwell, call a POISON INFORMATION CENTRE/physician.
P330	Rinse out mouth.
P501	Dispose of contents / container in accordance with local / regional / national / international regulations.
Prevention	Wear eye protection or face shield. Wash hands thoroughly after use.
Reaction	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
Storage	Not applicable.
Disposal	Not applicable.
Hazardous ingredients	3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctane sulphonic acid
Additional labelling elements	Not applicable.
Signal word	Warning
Hazard warnings	causes severe eye irritation

Substance lists	
REACH Appendix XIV, List of substances subject to authorisation	none of the components is listed
REACH Appendix XIV, Substances of Very High Concern	none of the components is listed
REACH Appendix XVII	not applicable
INTL Stockholm Agreement, Appendix B, Restriction, Manufacture	none of the components is listed
INTL Stockholm Agreement, Appendix B, Restriction, Use	none of the components is listed
European inventory	All components are listed or excluded
Other (e.g. degradation products, by-products, monitoring, etc.)	

B.12 Portfolio fiche - Mist suppressant E5

Substance data			
Product name:	**Mist suppressant E5**		
Manufacturer	**Formulator E**		
CAS:		34590-94-8	27619-97-2
Synonym:	ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctyl and/or hydropoly(oxyethylene)] phosphate	(2-Methoxymethylethoxy) propanol Dipropylene glycol methyl ether DPM Methyl dipropylene glycol	3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctane sulphonic acid H4PFOS
Molecular formula:		$C_7H_{16}O_3$	
Concentration	≥5 - <8	≥1 - <3	≥1 - <3
Note	fluorinated		
Main application area	Hard chromium; plastic etching, bright chromium		

Safety data sheet	
SDS is available	Yes
Link	no longer available
Supplier	Formulator E
Issue date	20.04.2015.

Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards		-
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Eye Dam. 1	H318 causes severe eye damage
	Eye Irrit. 2	H319 causes severe eye irritation
	Acute Tox. 2	H330 Danger to life if inhaled
	Acute Tox. 3	H331 Toxic if inhaled
Dangerous to the environment	Aquatic Chronic 3	H412 Harmful to aquatic organisms, with long lasting effects

Other hazards	Other hazards that do not lead to a classification: None known.
GHS pictograms	
Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance	yellowish, sweetish
Thickness	1.025 g/cm^3
Melting point	0 °C
Boiling point	100°C
Combustion point	not available
Vapour pressure	not available
pH value	6.2
Water solubility	easily soluble in cold water
Distribution coefficient: n-Octanol/water	not available
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Oral, ATE value 12897 mg/kg Inhalation (vapours); 2.56 mg/l
Chronic toxicity	no information
Carcinogenicity	not available
Mutagenicity	not available
Reproduction toxicity	not available
Metabolism and depletion	not available

Additional toxicological information:	Irritation/burns: (2-Methoxymethylethoxy) propanol Eyes - Mild irritant for humans; 8 mg- Eye - Mild irritant for rabbits; 24 hours; 500 mg Skin - Mild irritant for rabbits; 500 mg 66.8% - Percentage of components in mixture with unknown toxicity
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	not available
Bio-accumulation	not available
Toxicity	not available
PNEC: Predicted No-Effect Concentration (REACH)	not available
Ecotoxicological effects	68.1% - Percentage of components in the mixture with unknown hazard to the aquatic environment
Mobility	
Name	Value
log Koc	not available
Long-distance transport	not available
Safety instructions and workplace labels	
Eye contact	Immediately rinse eyes with plenty of water and lift upper and lower eyelids time and again. Check for contact lenses and remove if present. Rinse continuously for at least 10 minutes. Notify a physician.
Inhalation	Expose affected person to fresh air and keep at rest in a position that facilitates breathing. If presence of vapours is still suspected, the rescuer must wear an appropriate respiratory mark or self-contained breathing apparatus. If breathing is absent or irregular, or if respiratory arrest occurs, artificial respiration or oxygen administration shall be initiated by trained personnel. It may be dangerous for the person providing first aid to perform mouth-to-mouth resuscitation. Notify a physician. If necessary, call a poison information centre or a physician. If unconscious, place in recovery position and seek immediate medical attention. Keep airways open. Loosen tight-fitting clothing (e.g. collar, tie, belt or waistband).
Skin contact	Rinse contaminated skin with plenty of water. Remove contaminated clothing and shoes. Seek medical attention if symptoms occur. Wash clothing before reuse. Clean shoes thoroughly before reuse.

Ingestion	Rinse the mouth with water. Remove dentures if present. Expose affected person to fresh air and keep at rest in a position that facilitates breathing. If the substance was swallowed and the affected person is conscious, give small amounts of water to drink. If nauseous, do not allow to continue drinking as vomiting can be dangerous. Do not induce vomiting unless specifically instructed to do so by medical personnel. If vomiting occurs, keep head low to prevent vomit from entering lungs. Notify a physician. Never administer anything by mouth to an unconscious person. If unconscious, place in recovery position and seek immediate medical attention. Keep airways open. Loosen tight-fitting clothing (e.g. collar, tie, belt or waistband).
Substance lists	
Name	Record
REACH, Appendix XIV	Substance not listed
REACH, Appendix XVII	Not applicable
INTL - Stockholm Agreement - Appendix B - Restriction - Manufacture	None of the components is listed.
INTL - Stockholm Agreement - Appendix B - Restriction - Use	None of the components is listed.
Other (e.g. degradation products, by-products, monitoring, etc.)	
Decomposition products may include the following materials: Carbon dioxide Carbon monoxide Sulphur oxide halogenated compounds	

B.13 Portfolio fiche - Mist suppressant F1

Substance data		
Product name:	**Mist suppressant F1**	
Manufacturer	**Formulator F**	
CAS:	27619-97-2	67-56-1
Synonym:	Tridecafluorooctane sulphonic acid	Methanol
Molecular formula:		
Main application area	Electroplating auxiliary Decorative chromium plating	
Note	Fluorine-free, PFOS-free, chromium(VI)-resistant, surface-active mist suppressant	
Safety data sheet		
SDS is available	yes	
Link	-	
Supplier	Formulator F	
Issue date	03.02.2016	
Concentration	25 - <50%; to form a dense foam blanket on the chromium bath, about 0.1 - 0.2 ml/l of mist suppressant F1 (= dilution 9:1) is sufficient	
Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards	Flam. Liq. 2	H225 Highly flammable liquid and vapour
Health hazards	Acute Tox. 3	H301 Toxic if swallowed
	Acute Tox. 4	H302 Harmful to health if swallowed
	Acute Tox. 3	H311 Toxic upon skin contact
	Skin Corr. 1A	H314 Causes severe skin burns and eye damage
	Eye Dam. 1	H318 causes severe eye damage
	Acute Tox. 3	H331 Toxic if inhaled
	STOT SE 1	H370 Causes damage to organs (through inhalation/skin contact/ingestion)
	STOT SE 2	H371 can damage the organs
Dangerous to the environment	-	-
Other hazards		

GHS pictograms	
Physico-chemical properties	
Name	Value
Molecular weight	-
Physical state	liquid
Appearance	colourless to yellow
Thickness	1.15 g/cm³
Melting point	not determined
Boiling point	100°C
Combustion point	not applicable
Vapour pressure	23 hPa
pH value	< 2
Water solubility	fully miscible with water
Other chemical characterisation	-

Hazardousness to humans /Human toxicity		
Name	**Value**	
Acute toxicity	Classification-relevant LD/LC50 values: 27619-97-2 tridecafluorooctane sulphonic acid Oral LD50 500 mg/kg (Acute Toxicity Estimates)	67-56-1 Methanol: Oral LD50 100 mg/kg (Acute Toxicity Estimates) Dermal LD50 300 mg/kg (Acute Toxicity Estimates) Inhalative LC50/4h 3 mg/l (Acute Toxicity Estimates) AGW: Long-term value: 270 mg/m³, 200 ml/m³ 4(II);DFG, EU, H, Y DNEL: Dermal: exposure long term - systemic effects 40 mg/kg bw/day (workers); exposure short term - systemic effects 40 mg/kg bw/day (workers) DNEL: Inhalative: exposure long term - systemic effects 260 mg/m³ (workers); exposure long term - local effects 260 mg/m³ (workers); exposure short term - systemic effects 260 mg/m³ (workers); exposure short term - local effects 260 mg/m³ (workers) PNEC: 100 mg/l (wastewater treatment plant); 15.4 mg/l (seawater); 1540 mg/l (sporadic release); 23.5 mg/kg (soil); 570.4 mg/kg (Sediment fresh water)

		BGW: 30 mg/l; test material: Urine; time of sample: in case of long-term exposure: After several previous shifts; end of exposure or end of shift; parameters: Methanol
Chronic toxicity	?	
Carcinogenicity	Based on available data, the classification criteria are not met.	
Mutagenicity	Based on available data, the classification criteria are not met.	
Reproduction toxicity	Based on available data, the classification criteria are not met.	
Metabolism and depletion	-	
Additional toxicological information:	PBT: Not applicable. vPvB: Not applicable.	
Hazardousness to the environment / ecotoxicity		
Name	**Value**	
Persistence	No further relevant information available.	
Bio-accumulation	No further relevant information available.	
Toxicity	Aquatic toxicity: LC50/96h >107 mg/l (Oncorhynchus mykiss - rainbow trout) EC50/48h >109 mg/l (Daphnia magna - water flea) ErC50/72h >96 mg/l (Pseudokirchneriella subcapitata) 6 7-56-1 methanol LC50/96h 15900 mg/l (Daphnia magna - water flea) (ECHA) 12700 mg/l (Lepomis macrochirus-bluegill sunfish) (ECHA).	
PNEC: Predicted No-Effect Concentration (REACH)		
Ecotoxicological effects	The classification into the water hazard class was made according to the Administrative Regulation on the Classification of Substances Hazardous to Water (VwVwS) of 17.05.1999. Water hazard class 3 (self-classification): highly hazardous to water The product does not contain EDTA The product contains 30 % AOX. Do not allow into groundwater, in the watercourse or in the sewage system, not even in small quantities. Collect contaminated extinguishing water separately, must not enter the sewage system. Must not be discharged undiluted or un-neutralised into wastewater or receiving waters. Danger to drinking water even in the event of leakage of the smallest quantities into the subsurface. The product is free from organic complexing agents.	

Mobility	
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P260	Do not breathe dust/fume/gas/mist/vapour/aerosol.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P303+P361+P353	IN CASE OF CONTACT WITH SKIN (or hair): Remove all contaminated clothing immediately. Wash skin with water/shower.
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician.
P501	Dispose of contents / container in accordance with local / regional / national / international regulations.
Substance lists	
Other (e.g. degradation products, by-products, monitoring, etc.)	
In the event of a fire, the following may be released: Hydrogen fluoride (HF) Carbon monoxide (CO) Sulphur dioxide (SO2) Carbon dioxide (CO2)	

B.14 Portfolio fiche - Mist suppressant L3 und L4

Substance data				**Variation 1**		
Product name:	**Mist suppressant L3**			**Mist suppressant L4**		
Manufacturer	**Formulator Lb**			**Formulator Lb**		
CAS:	27619-97-2,	110-16-7;	67-56-1			
Synonym:	Tridecafluorooctane sulphonic acid	Maleic acid	Methanol			
	Tridecafluorooctane sulphonic acid					
Molecular formula:						
Main application area	Chromium(VI)-containing process solutions			Preparation for use in surface technology. Additives for the reduction of surface tension in etchings		
Note						
Safety data sheet						
SDS is available	yes					
Link	-					
Supplier	Formulator Lb			Formulator Lb		
Issue date	16.03.2015					
Concentration	1 - <3%	1 - <3%	0.1 - <1%			

Classification of the substance						
	Hazard class and category	**Coding**		**Hazard class and category**	**Coding**	
Physical hazards	Inflammation Fl. 2	H225 Highly flammable liquid and vapour	CAS no.: 67-56-1	Inflammation Fl. 2	H225 Highly flammable liquid and vapour	67-56-1
Health hazards	Acute Tox. 3	H301 Toxic if swallowed	CAS no.: 67-56-1	Acute Tox. 3	H301 Toxic if swallowed	67-56-1
	Acute Tox. 4	H302 Harmful to health if swallowed	CAS no.: 27619-97-2; 110-16-7	Acute Tox. 4	H302 Harmful to health if swallowed	27619-97-2; 110-16-7
	Acute Tox. 3	H311 toxic in case of contact with skin	CAS no.: 67-56-1	Acute Tox. 3	H311 Toxic upon skin contact	67-56-1
	Skin irritation 2	H315 causes skin irritation	CAS no.: 110-16-7;	Acute Tox. 4	H312 Harmful to health in case of skin contact	110-16-7;
	Sens. Skin 1	H317 may cause allergic skin reactions	CAS no.: 110-16-7;	Skin corrosivity 1A	H314 Causes severe skin burns and eye damage	27619-97-2; 110-16-7
	Eye damage 1	H318 causes severe eye damage	CAS no.: 27619-97-2	Skin irritation 2	H315 causes skin irritation	Mixture
	Eye irritation 2	H319 causes severe eye irritation	CAS no.: 110-16-7;	Sens. Skin 1	H317 may cause allergic skin reactions	Mixture; 110-16-7
	Acute Tox. 3	H331 Toxic if inhaled	CAS no.: 67-56-1	Eye damage 1	H318 causes severe eye damage	Mixture; 110-16-7
	STOT, one-time 3	H335 May cause irritation of the respiratory system	CAS no.: 110-16-7;	Acute Tox. 3	H331 Toxic if inhaled	67-56-1
	STOT, one-time 1	H370 Causes damage to organs	CAS no.: 67-56-1	STOT, one-time 1	H370 Causes damage to organs	67-56-1

				STOT, repeated 2	H373 Causes damage to organs in case of longer or repeated exposure	27619-97-2
				STOT, one-time 3	H335 May cause irritation of the respiratory system	110-16-7;
Dangerous to the environment				-	-	
Other hazards	-	-			-	
GHS pictograms						
Physico-chemical properties						
Name	**Value**			**Value**		
Molecular weight	-			-		
Physical state	liquid			liquid		
Appearance	colourless			colourless		
Thickness	0.97 - 1.07 g/ml (20 °C)			0.97 - 1.07 g/ml (20 °C)		
Melting point	no data available					
Boiling point	(760 mm Hg) ~ 110°C			~ 110 °C (760 mm Hg)		
Combustion point	not applicable					
Vapour pressure	no data available					
pH value	< 3			< 3		
Water solubility	miscible with water			miscible with water		
Other chemical characterisation	Volatile organic compounds (VOC) < 1 %w/w			Decomposition temperature (°C) > 200 °C Volatile organic compounds (VOC) < 1 %w/w		

				Volatile organic compounds (VOC -CH) < 1 %w/w	
Hazardousness to humans /Human toxicity					
Name	**Value**			**Value**	
Acute toxicity	Based on the available data, the classification criteria are not met.			Based on the available data, the classification criteria are not met	
Chronic toxicity	?			?	
Carcinogenicity	Contains no substances known or suspected to be carcinogenic.			Contains no substances known or suspected to be carcinogenic.	
Mutagenicity	Contains no substances known or suspected to be mutagenic.			Contains no substances known or suspected to be mutagenic.	
Reproduction toxicity	Contains no substances known or suspected to be teratogenic.			Contains no substances known or suspected to be teratogenic.	
Metabolism and depletion	-			-	
Additional toxicological information:	Methanol: Occupational limit value: 200 ppm 270 mg/m3; Resorptive active substances; No risk of foetal damage need be feared if the occupational exposure limit value and the biological limit value (BGW) are complied with; Skin resorptive	Methanol: DNEL Industry Dermal Short-term Systemic effect 40 mg/kg/day Industry Inhalation. Short-term Systemic effect 260 mg/m3 Industry Inhalation. Short-term local effects 260 mg/m3 Industry Dermal long-term systemic effect 40 mg/kg/day Industry Inhalation.		Methanol: Resorptive active substances; Skin resorptive; AGW 200 ppm 270 mg/m3 Methanol: DNEL Industry Dermal Short-term Systemic effect 40 mg/kg/day Industry Inhalation. Short-term Systemic effect 260 mg/m3 Industry Inhalation. Short-term local effects 260 mg/m3 Industry Dermal long-term systemic effect 40 mg/kg/day Industry Inhalation. Long-term Systemic effect 260 mg/m3 Industry Inhalation. Long-term local effects 260	AGW - Occupational limit value

		Long-term Systemic effect 260 mg/m3 Industry Inhalation. Long-term local effects 260 mg/m3		mg/m3 Maleic acid: DNEL DNEL Industry Inhalation. Long-term Systemic effect3 mg/m3 Industry Inhalation. Short-term Systemic effect3 mg/m3	
Hazardousness to the environment / ecotoxicity					
Name	**Value**			**Value**	
Persistence	Biodegradability: As expected, the product is difficult to biodegrade.			As expected, the product is difficult to biodegrade.	
Bio-accumulation	Bio-accumulation potential: The product does not contain any substances that are expected to be bioaccumulative. Distribution coefficient: No data available.			The product does not contain any substances that are expected to be bioaccumulative.	
Toxicity	Based on the available data, the classification criteria are not met.			Based on the available data, the classification criteria are not met.	
PNEC: Predicted No-Effect Concentration (REACH)				Methanol: Fresh water 154 mg/l Saltwater 15.4 mg/l Periodic release 1540 mg/l STP 100 mg/l Deposition (freshwater 570.4 mg/kg Soil 23.5 mg/kg Maleic acid	

				Fresh water 0.1 mg/l Salt water 0.01 mg/l STP 44.6 mg/l Deposition (fresh water 0.334 mg/kg Deposition (seawater 0.033 mg/kg Soil 0.042 mg/kg	
Ecotoxicological effects	This product does not contain any PBT or vPvB substances. The product is not expected to be harmful to the environment. The constituents of the product are classified as not harmful to the environment. However, this does not exclude the possibility that large or frequent quantities may have a harmful or damaging effect on the environment. The product may affect the pH value in water and have harmful effects on aquatic organisms.	PNEC Fresh water 154 mg/l Saltwater 15.4 mg/l Periodic release 1540 mg/l STP 100 mg/l Deposition (freshwater 570.4 mg/kg Soil 23.5 mg/kg Methanol: PNEC Fresh water 154 mg/l Saltwater 15.4 mg/l Periodic release 1540 mg/l STP 100 mg/l Deposition (freshwater 570.4 mg/kg Soil 23.5 mg/kg		This product does not contain any PBT or vPvB substances The product is not expected to be harmful to the environment. The constituents of the product are classified as not harmful to the environment. However, this does not exclude the possibility that large or frequent quantities may have a harmful or damaging effect on the environment. The product may affect the pH value in water and have harmful effects on aquatic organisms.	
Mobility					
log Koc					
Long-distance transport	The product is water soluble and can be dispersed in aqueous systems.			The product is water soluble and can be dispersed in aqueous systems.	

Safety instructions and workplace labels						
P261	Avoid inhalation of vapour/aerosol				P261	Avoid inhalation of vapour/aerosol
P280	Wear protective clothing, gloves, eye and face protection				P280	Wear protective clothing, gloves, eye and face protection
P302+352	IN CASE OF CONTACT WITH SKIN: Wash with water and soap				P302+352	IN CASE OF CONTACT WITH SKIN: Wash with water and soap
P305+351+338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove existing contact lenses, if possible. Continue rinsing				P333 + P313	For skin irritation or rash: Seek medical advice/consult medical assistance
P333+313	For skin irritation or rash: Seek medical advice/consult medical assistance				P305+351+338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove existing contact lenses, if possible. Continue rinsing
P337+313.	If eye irritation persists: Seek medical advice/consult medical assistance				P315	Seek medical advice/consult medical assistance immediately
P403+233	Keep container tightly closed in a well-ventilated place				P403+233	Keep container tightly closed in a well-ventilated place

P501a	Dispose of the contents / container in accordance with local, regional, national or even international official regulations.				P501	Dispose of the contents / container in accordance with local, regional, national or even international official regulations.
Substance lists						
Authorisations (Title VII Regulation 1907/2006)	No special approvals are required for this product			Not regulated. Not subject to international regulations concerning transport of dangerous goods (IMDG, ICAO/IATA, ADR/RID		
restrictions (Title VIII Regulation 1907/2006)	No special approvals are required for this product			Authorisations (Title VII Regulation 1907/2006): No special approvals are required for this product. Restrictions (Title VIII Regulation 1907/2006): No special restrictions are applicable for this product. Water hazard class: WHC 1		
Other (e.g. degradation products, by-products, monitoring, etc.)						
None under normal conditions. Thermal decomposition or combustion may release carbon oxides and other toxic gases or vapours. Fire or high temperatures produce: Sulfurous gases (SOx). Hydrofluoric acid(HF). Fluorides.				Thermal decomposition or combustion may release carbon oxides and other toxic gases or vapours. Fire or high temperatures produce: Sulfurous gases (SOx). Hydrofluoric acid(HF). Fluorides.		

B.15 Portfolio fiche - Mist suppressant B2

Substance data		
Product name:	**Mist suppressant B2**	
Manufacturer	**Formulator B**	
CAS:	151-21-3	
Synonym:	Sodium dodecyl sulfate	
Molecular formula:		
Main application area	Metal surface treatment	
Note	-	
Safety data sheet		
SDS is available	yes	
Link	-	
Supplier	Formulator B	
Issue date	13.12.2017	
Concentration	2.5-5%	
Classification of the substance		
	Hazard class and category	**Coding**
Physical hazards		
Health hazards	Eye Dam. 1	H318 causes severe eye damage
	Acute Tox. 4	H302 Harmful to health if swallowed.
	Skin Irrit. 2	H315 causes skin irritation.
Dangerous to the environment	Aquatic Chronic 3	H412 Harmful to aquatic organisms, with long lasting effects.
Other hazards		

GHS pictograms	
Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance	colourless
Thickness	1 g/cm^3
Melting point	not determined
Boiling point	100°C
Combustion point	not applicable
Vapour pressure	23 hPa (at 20°C)
pH value	6 (at 20°C)
Water solubility	fully miscible
Other chemical characterisation	-
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Based on available data, the classification criteria are not met.
Chronic toxicity	?
Carcinogenicity	Based on available data, the classification criteria are not met.
Mutagenicity	Based on available data, the classification criteria are not met.
Reproduction toxicity	Based on available data, the classification criteria are not met.
Metabolism and depletion	-
Additional toxicological information:	
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	No further relevant information available.
Bio-accumulation	No further relevant information available.

Toxicity	No further relevant information available.
PNEC: Predicted No-Effect Concentration (REACH)	
Ecotoxicological effects	PBT: Not applicable; vPvB: Not applicable; Water hazard class 1 (Self-assessment): slightly hazardous to water Do not allow undiluted or in large quantities into groundwater, in the watercourse or in the sewage system.
Mobility	
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P280	Wear eye protection / face shield.
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.
P310	Immediately call POISON INFORMATION CENTRE/physician.
Substance lists	
Regulation (EC) No. 1272/2008	The product is classified and labelled according to CLP regulation.
Directive 2012/18/EU	APPENDIX I None of the ingredients are included.
REGULATION (EC) No. 1907/2006	APPENDIX XVII Conditions of restriction: 3
Water hazard class:	WHC 1 (Self-assessment): slightly hazardous to water.
Other (e.g. degradation products, by-products, monitoring, etc.)	

B.16 Portfolio fiche - Mist suppressant H1

Substance data			
Product name:	**Mist suppressant H1**		
Manufacturer	**Formulator H**		
CAS:	68201-55-8	15909-83-8	61788-90-7
Synonym:	3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate;	3-Hydroxypropane-1-sulphonic acid;	Dimethyl coco alkylamine

	3-(Decyldimethylammonio)propane-1-sulfonate;
	N-Decyl-N,N-dimethyl-3-ammonio-1-propanesulfonate; Sulfobetaine 10; Caprylyl sulfobetaine;
	3-(Decyldimethylammonio)propanesulfonate ;
		3-Hydroxypropane-1-sulfonic acid;
		3-Hydroxypropanesulfonic Acid;
		1-Propanesulfonic acid, 3-hydroxy-;
		3-Hydroxy-1-propanesulfonic acid;
		1-Propanesulfonic acid,3-hydroxy-
			Amine, Kokos-alkyldimethyl-, N-Oxide
			Barlox(R) 12;
			COCAMINE OXIDE;COCO DIMETHYLAMINE OXIDE;
			coconutdimethylamineoxide;
			alkyl(c10-16)dimethylamine;
			N,N- Dimethylcocoamino oxide;
			alkyl(c10-16)dimethylamineoxide;
			Amine oxides, cocoalkyldimethyl;
			Amines,cocoalkyldimethyl,N-oxides;
			N-(Cocoalkyl)-dimethylamine oxide

	Betaine, Coco-alkyldimethyl(3-sulfopropyl) from ECHA Information on Chemicals		
Molecular formula:			
Main application area	Electroplating auxiliary - Decorative chromium plating		
Note	Fluorine-free		
Safety data sheet			
SDS is available	Yes		
Link	not available		
Supplier	Formulator H		
Issue date	27.07.2016		
Concentration	25-50%	2.5-<5%	1-≤2.5%

Classification of the substance			
	Hazard class and category	**Coding**	
Physical hazards	Met. Corr.1	H290 may be corrosive to metals	CAS: 15909-83-8
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed	Dimethyl coco alkylamine
	Skin Corr. 1A,	H314 Causes severe skin burns and eye damage	CAS: 15909-83-8
	Skin Corr. 1B	H314 Causes severe skin burns and eye damage	Dimethyl coco alkylamine
	Skin Irrit. 2	H315 causes skin irritation	CAS: 68201-55-8; Mixture
	Eye Dam. 1,	H318 causes severe eye damage	CAS: 15909-83-8
	Eye Irrit. 2	H319 causes severe eye irritation	CAS: 68201-55-8; Mixture
Dangerous to the environment	Aquatic Acute 1	H400 Very toxic to aquatic organisms	Dimethyl coco alkylamine
	Aquatic Chronic 1	H410 Very toxic to aquatic organisms with long lasting effects	Dimethyl coco alkylamine
	H412	H412 Harmful to aquatic organisms, with long lasting effects	Mixture
Other hazards			
GHS pictograms	 GHS07		

Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	Liquid

Appearance (colour)	Light yellow	
Smell	Soap-like	
Thickness	approx. 1.02 - 1.03 g/cm³ at 20 °C	
Melting point	not determined	
Boiling point	approx. 100 °C	
Combustion point	> 110 °C (DIN 51758)	
Vapour pressure	not determined	
pH value	7 - 8 (tel quel)	
Water solubility	Fully miscible	
Other chemical characterisation	Solidification temperature/range: approx. 0-<4 °C Solubility in / Miscibility with organic solvents: Soluble in methanol; Soluble in ethanol Distribution coefficient (n-octanol/water): 2.24 log POW (calc. KOWWIN 1.67)	
Hazardousness to humans /Human toxicity		
Name	**Value**	
Acute toxicity	Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data) Oral LD50 > 2000 mg/kg (rat) (Limit test) Based on available data, the classification criteria are not met	Dodecyl(dimethyl)ammonio]propane-1-sulfonate 3-hydroxypropane-1-sulphonic acid
Chronic toxicity	No information	
Carcinogenicity	Based on available data, the classification criteria are not met	
Mutagenicity	Based on available data, the classification criteria are not met	
Reproduction toxicity	Based on available data, the classification criteria are not met	
Metabolism and depletion		
Additional toxicological information:	causes skin irritation causes severe eye irritation	
Hazardousness to the environment / ecotoxicity		
Name	**Value**	
Persistence	Not easily biodegradable calculated BIOWIN 4.10	
Bio-accumulation	The bioaccumulation potential is considered to be low. BCF : 71, log BCF 1.85, calculated, BCFWIN 2.15).	

Toxicity	[Dodecyl(dimethyl)ammonio]propane-1-sulfonate - Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data); 3-Hydroxypropane-1-sulphonic acid- Oral LD50 > 2000 mg/kg (rat) (Limit test)	
PNEC: Predicted No-Effect Concentration (REACH)	EC50/96h > 100 mg/L (algae) (calculated ECOSAR 1.00) LC50/14d ≥ 100 mg/L (fish) (calculated ECOSAR 0.99h) LC50/48h > 100 mg/L (Aquatic invertebrates - Daphnia magna) (calculated ECOSAR 1.00) LC50/96h > 100 mg/L (fish) (calculated ECOSAR 1.00) EC10/16h 180 mg/L (bacteria - Pseudomonas putida) (LTWS No. 1, ISO 10712)	Dodecyl(dimethyl)ammonio]propane-1-sulfonate
	EC50/96h > 100 mg/L (algae) (calculated ECOSAR 0.99h) LC50/96h 420 mg/L (fish - Leuciscus idus) (OECD 203)	3-Hydroxypropane-1-sulphonic acid
Ecotoxicological effects	Water hazard class 2 (self-classification): hazardous to water (VwVwS dated 17.05.1999, Appendix 4) Do not allow into groundwater, in the watercourse or in the sewage system. Harmful for aquatic organisms. PBT: Not applicable; vPvB: Not applicable Aquatic toxicity	
Mobility		
Name	**Value**	
log Koc	Distribution coefficient (n-Octanol/water): 2.24 log POW (calc. KOWWIN 1.67)	
Long-distance transport	not available	
Substance lists		
Name	**Record**	
REACH, Appendix XIV	No information	
REACH, Appendix XVII	Conditions of restriction: 3	
Safety instructions and workplace labels		
P280	Wear protective gloves/protective clothing/eye protection/face protection	
P273	Avoid release into the environment	
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	
P302+P352	IN CASE OF CONTACT WITH SKIN: Wash with a lot of water	
P332+P313	In case of skin irritation: Seek medical advice/consult medical assistance.	
P337+P313	If eye irritation persists: Seek medical advice/consult medical assistance	
Other (e.g. degradation products, by-products, monitoring, etc.)		
Special hazards arising from the substance or mixture		

In the event of a fire, the following may be released: Nitrogen oxides (NOx), hydrogen cyanide (HCN), sulphur oxides (SOx), carbon monoxide (CO), carbon dioxide (CO2), risk of formation of toxic pyrolysis products	
Possibility of hazardous reactions	
Reactions with strong acids.	
Reactions with alkalis (lyes).	
Reactions with oxidising agents.	

B.17 Portfolio fiche - Mist suppressant H1

Substance data			
Product name:	**Mist suppressant H1**		
Manufacturer	**Formulator H**		
CAS:	68201-55-8	15909-83-8	61788-90-7
Synonym:	3-[Dodecyl(dimethyl)ammonio]propane-1-sulfonate;	3-Hydroxypropane-1-sulphonic acid;	Dimethyl coco alkylamine

	3-(Decyldimethylammonio)propane-1-sulfonate;
	N-Decyl-N,N-dimethyl-3-ammonio-1-propanesulfonate; Sulfobetaine 10; Caprylyl sulfobetaine;
	3-(Decyldimethylammonio)propanesulfonate ;
		3-Hydroxypropane-1-sulfonic acid;
		3-Hydroxypropanesulfonic Acid;
		1-Propanesulfonic acid, 3-hydroxy-;
		3-Hydroxy-1-propanesulfonic acid;
		1-Propanesulfonic acid,3-hydroxy-
			Amine, Kokos-alkyldimethyl-, N-Oxide
			Barlox(R) 12;
			COCAMINE OXIDE;COCO DIMETHYLAMINE OXIDE;
			coconutdimethylamineoxide;
			alkyl(c10-16)dimethylamine;
			N,N- Dimethylcocoamino oxide;
			alkyl(c10-16)dimethylamineoxide;
			Amine oxides, cocoalkyldimethyl;
			Amines,cocoalkyldimethyl,N-oxides;
			N-(Cocoalkyl)-dimethylamine oxide

	Betaine, Coco-alkyldimethyl(3-sulfopropyl) from ECHA Information on Chemicals		
Molecular formula:			
Main application area	Electroplating auxiliary - Decorative chromium plating		
Note	Fluorine-free		
Safety data sheet			
SDS is available	Yes		
Link	not available		
Supplier	Formulator H		
Issue date	27.07.2016		
Concentration	25-50%	2.5-<5%	1-≤2.5%

Classification of the substance			
	Hazard class and category	**Coding**	
Physical hazards	Met. Corr.1	H290 may be corrosive to metals	CAS: 15909-83-8
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed	Dimethyl coco alkylamine
	Skin Corr. 1A,	H314 Causes severe skin burns and eye damage	CAS: 15909-83-8
	Skin Corr. 1B	H314 Causes severe skin burns and eye damage	Dimethyl coco alkylamine
	Skin Irrit. 2	H315 causes skin irritation	CAS: 68201-55-8; Mixture
	Eye Dam. 1,	H318 causes severe eye damage	CAS: 15909-83-8
	Eye Irrit. 2	H319 causes severe eye irritation	CAS: 68201-55-8; Mixture
Dangerous to the environment	Aquatic Acute 1	H400 Very toxic to aquatic organisms	Dimethyl coco alkylamine
	Aquatic Chronic 1	H410 Very toxic to aquatic organisms with long lasting effects	Dimethyl coco alkylamine
	H412	H412 Harmful to aquatic organisms, with long lasting effects	Mixture
Other hazards			
GHS pictograms	 GHS07		

Physico-chemical properties	
Name	**Value**
Molecular weight	-
Physical state	Liquid

Appearance (colour)	Light yellow	
Smell	Soap-like	
Thickness	approx. 1.02 - 1.03 g/cm³ at 20 °C	
Melting point	not determined	
Boiling point	approx. 100 °C	
Combustion point	> 110 °C (DIN 51758)	
Vapour pressure	not determined	
pH value	7 - 8 (tel quel)	
Water solubility	Fully miscible	
Other chemical characterisation	Solidification temperature/range: approx. 0-<4 °C Solubility in / Miscibility with organic solvents: Soluble in methanol; Soluble in ethanol Distribution coefficient (n-octanol/water): 2.24 log POW (calc. KOWWIN 1.67)	
Hazardousness to humans /Human toxicity		
Name	**Value**	
Acute toxicity	Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data) Oral LD50 > 2000 mg/kg (rat) (Limit test) Based on available data, the classification criteria are not met	Dodecyl(dimethyl)ammonio]propane-1-sulfonate 3-hydroxypropane-1-sulphonic acid
Chronic toxicity	No information	
Carcinogenicity	Based on available data, the classification criteria are not met	
Mutagenicity	Based on available data, the classification criteria are not met	
Reproduction toxicity	Based on available data, the classification criteria are not met	
Metabolism and depletion		
Additional toxicological information:	Causes skin irritation causes severe eye irritation	
Hazardousness to the environment / ecotoxicity		
Name	**Value**	
Persistence	Not easily biodegradable calculated BIOWIN 4.10	
Bio-accumulation	The bioaccumulation potential is considered to be low. BCF : 71, log BCF 1.85, calculated, BCFWIN 2.15).	

Toxicity	[Dodecyl(dimethyl)ammonio]propane-1-sulfonate - Oral LD50 6000-9000 mg/kg (rat) (50 % solution, external data); 3-Hydroxypropane-1-sulphonic acid- Oral LD50 > 2000 mg/kg (rat) (Limit test)	
PNEC: Predicted No-Effect Concentration (REACH)	EC50/96h > 100 mg/L (algae) (calculated ECOSAR 1.00) LC50/14d ≥ 100 mg/L (fish) (calculated ECOSAR 0.99h) LC50/48h > 100 mg/L (Aquatic invertebrates - Daphnia magna) (calculated ECOSAR 1.00) LC50/96h > 100 mg/L (fish) (calculated ECOSAR 1.00) EC10/16h 180 mg/L (bacteria - Pseudomonas putida) (LTWS No. 1, ISO 10712)	Dodecyl(dimethyl)ammonio]propane-1-sulfonate
	EC50/96h > 100 mg/L (algae) (calculated ECOSAR 0.99h) LC50/96h 420 mg/L (fish - Leuciscus idus) (OECD 203)	3-Hydroxypropane-1-sulphonic acid
Ecotoxicological effects	Water hazard class 2 (self-classification): hazardous to water (VwVwS dated 17.05.1999, Appendix 4) Do not allow into groundwater, in the watercourse or in the sewage system. Harmful for aquatic organisms. PBT: Not applicable; vPvB: Not applicable Aquatic toxicity	
Mobility		
Name	**Value**	
log Koc	Distribution coefficient (n-Octanol/water): 2.24 log POW (calc. KOWWIN 1.67)	
Long-distance transport	not available	
Substance lists		
Name	**Record**	
REACH, Appendix XIV	No information	
REACH, Appendix XVII	Conditions of restriction: 3	
Safety instructions and workplace labels		
P280	Wear protective gloves/protective clothing/eye protection/face protection	
P273	Avoid release into the environment	
P305+P351+P338	IN CASE OF CONTACT WITH EYES: Rinse gently with water for a few minutes. Remove any existing contact lenses, if possible. Continue rinsing.	
P302+P352	IN CASE OF CONTACT WITH SKIN: Wash with a lot of water	
P332+P313	In case of skin irritation: Seek medical advice/consult medical assistance.	
P337+P313	If eye irritation persists: Seek medical advice/consult medical assistance	
Other (e.g. degradation products, by-products, monitoring, etc.)		
Special hazards arising from the substance or mixture		

In the event of a fire, the following may be released: Nitrogen oxides (NOx), hydrogen cyanide (HCN), sulphur oxides (SOx), carbon monoxide (CO), carbon dioxide (CO2), risk of formation of toxic pyrolysis products	
Possibility of hazardous reactions	
Reactions with strong acids.	
Reactions with alkalis (lyes).	
Reactions with oxidising agents.	

B.18 Portfolio fiche - Mist suppressant M1

Substance data		
Product name:	**Mist suppressant M1**	
Manufacturer	**Formulator M**	
CAS:	68188-18-1	
Synonym:	Paraffin oils, sulfochlorinated, saponified	
Molecular formula:		
Main application area	Electroplating auxiliary - Bright chromium, hard chromium, black chromium	
Note	General information: Do not allow undiluted or in large quantities into groundwater, in the watercourse or in the sewage system	
Safety data sheet		
SDS is available	yes	
Link	-	
Supplier	Formulator M	
Issue date	25.02.2019	
Concentration	<2.5%	
Classification of the substance		
	Hazard class and category	Coding
Physical hazards	Not specified	
Health hazards	Acute Tox. 4	H302 Harmful to health if swallowed
	Skin Irrit. 2	H315 causes skin irritation
	Skin Corr. 3	H316 causes mild skin irritation
	Eye irrit. 2A	H319 causes severe eye irritation
	Acute Tox 5	H313 may be harmful in case of contact with skin
Dangerous to the environment	Aquatic chronic 3	H412 Harmful to aquatic organisms, with long lasting effects
Other hazards		
GHS pictograms		
Physico-chemical properties		

Name	**Value**
Molecular weight	-
Physical state	liquid
Appearance	Clear blue green solution
Thickness	1 g/cm³
Melting point	not determined
Boiling point	>100°C
Combustion point	not applicable
Vapour pressure	57 hPa at 20 °C
pH value	2.5
Water solubility	fully miscible
Other chemical characterisation	Solvent content: Organic solvent: 0.2%; water (EU) 97.9%
Hazardousness to humans /Human toxicity	
Name	**Value**
Acute toxicity	Oral LD50 1,271 mg/kg (rat) (Acute oral toxicity) Dermal LD50 >2,000 mg/kg (rat)
Chronic toxicity	
Carcinogenicity	Not classified according to the available information
Mutagenicity	Not classified according to the available information
Reproduction toxicity	Not classified according to the available information
Metabolism and depletion	-
Additional toxicological information:	The product is not subject to labelling according to the calculation methods of the General Classification guideline for preparations of the EC in the latest valid version. According to our experience and the information available to us, the product does not cause any harmful effects when handled and used as intended.
Hazardousness to the environment / ecotoxicity	
Name	**Value**
Persistence	No further relevant information available.
Bio-accumulation	No further relevant information available.
Toxicity	No further relevant information available.

PNEC: Predicted No-Effect Concentration (REACH)	EC50/24h 9.48 mg/l (Daphnia magna (water flea))(Daphnia sp. Acute Immobilisation Test) EC50/48h 4.72 mg/l (Daphnia magna (water flea))(Daphnia sp. Acute Immobilisation Test) LC50/96h 4.16 mg/l (Brachydanio rerio (zebrafish))(Fish, Acute toxicity Test) NOEC 96 mg/l (Brachydanio rerio (zebrafish))(Fish, Acute toxicity Test) 48 mg/l (Daphnia magna (water flea))(Daphnia sp. Acute Immobilisation Test) EC50 (static) 94 mg/l (Scenedesmus subsicatus (algae))(Alga Growth Inhibition Test)
Ecotoxicological effects	PBT: Not applicable; vPvB: Not applicable
Mobility	
log Koc	
Long-distance transport	
Safety instructions and workplace labels	
P332+P313	In case of skin irritation: Seek medical advice/consult medical assistance.
Substance lists	
Name	Record
REACH, Appendix XIV	Not applicable.
REACH, Appendix XVII	Not applicable.
Other (e.g. degradation products, by-products, monitoring, etc.)	
The formation of toxic gases may occur in case of fire or heating:	
Carbon monoxide (CO)	
Carbon dioxide (CO2)	
Sulphur dioxide (SO2)	