Report summary metal plating and manufacturing of metal products

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1. Uses / Applications

PFAS are used in metal plating processes and in the manufacture of metal products. In metal plating PFAS are used to lower the surface tension of the plating solution and to decrease aerosol emissions (wetting agent, mist suppressing agent) (Blepp et al., 2017; UNEP, 2018; Willand et al., 2020). In the manufacture of metal products PFAS are used to e.g. lower the surface tension, to promote the flow of metal coatings or inhibit the formation of acid mist, to inhibit corrosion on steel and to improve the life of baths. The PFAS uses and applications are described in table 1.

Table 1: uses and applications of PFAS in metal plating processes and in the manufacture of metal products

Process	Examples
Metal plating	Mist suppressant
Metal plating	Lowering surface tension of plating solution (Glüge et al., 2020; Willand et al., 2020)
Metal plating	Nickel-plating: non-foaming surfactant - increasing the strength of the nickel electroplate by eliminating pinholes, cracks, and peeling (European Commission, 2006; Kissa, 2001)
Metal plating	Copper plating: preventing haze by regulating foam and improving stability while improving brightness and adhesion (Brunn Poulsen et al., 2005; European Commission, 2006)
Metal plating	Tin plating: produce a plate of uniform thickness (European Commission, 2006; Kissa, 2001)
Metal plating	Supporting the deposition of fluoropolymers onto steels for surface protection (European Commission, 2006). For this purpose, cationic and amphoteric fluorinated surfactants are used to impart a positive charge to fluoropolymer particles which facilitates the electroplating of the fluoropolymer (Kissa, 2001).
Manufacture of metal products	Inhibit the formation of acid mist or spray over metal electrowinning tanks (Glüge et al., 2020)
Manufacture of metal products	Treatment of coatings of metal surfaces (Glüge et al., 2020), lowering the surface tension and thus promoting the flow of metal coatings and the prevention of cracks in the coating during drying.
Manufacture of metal products	Use as corrosion inhibitor on steel (Kissa, 2001).
Manufacture of metal products	Coatings on metal (Glüge et al., 2020)
Manufacture of metal products	Used for processing of aluminium e.g. during etching of aluminium to improve the efficient life of alkali baths or in the phosphating process of aluminium to dissolve the oxide layer of the aluminium (Glüge et al., 2020; Kissa, 2001).
Manufacture of metal products	Cleaning of metal surfaces (Glüge et al., 2020; Kissa, 2001). The fluorinated surfactants disperse scum in molten-salt baths, speed runoffs of acid when metal is removed from the bath and increase the bath life.
Manufacture of metal products	Solvent displacement drying (e.g. for water removal prior to plating, coating, and other surface treatments) (Glüge et al., 2020).

2. Main PFAS substances

<u>Metal plating</u>

The fluorinated substances used mainly consist of C6 fluorinated substances (as alternative for already regulated C8 substances). Detailed information on the use of other fluorinated substances is hardly available. Only limited information is available on the use of other PFAS (beside PFOS and 6:2 FTS) in chrome plating processes.

Identification of PFOS as persistent organic pollutant (POP) and the inclusion in Annex B of the POP regulation (EU 2019/1021) led to the substitution of PFOS with 6:2 fluorotelomer sulfonate (6:2 FTS also known as H4-PFOS) in chrome plating processes (UNEP, 2018). Based on the PFHxA restriction dossier an annual use tonnage of 30 (central estimate, range 2-57 t/a) for 6:2 FTS in the EU was estimated.

A survey conducted by the German Environment Agency (Willand et al., 2020) showed that in functional chrome plating and plastic electroplating only 6:2 FTS-containing wetting agents were used (30 facilities participated in the survey). In decorative chrome plating 6:2 FTS-containing (60%) as well as fluorine-free (40%) wetting agents were used. The use of fluorinated substances other than 6:2 FTS was not noted.

Manufacture of metal products

Glüge et al. (2020) estimated that around 900 t PFAS (fluoropolymers) were used in the manufacture of metal products in Sweden, Finland, Norway and Denmark between 2000 and 2017. With the assumption that the four countries account for about 5.2% of the EEA population it was estimated that on average around 960 t of PFAS are used in the manufacture of metal products in the EEA per year.

PFAS substances used in metal plating processes and in the manufacture of metal products are described in table 2.

Table 2: PFAS substances used (or patented) in metal plating processes and in the manufacture of metal products

Group/substance	EU market for metal plating (Tpa)	Source
Metal plating		
N,N,N,-triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (derivate of PFBS)	1-10 (registration dossier)	Norwegian Environment Agency, 2017
Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo)ethane sulfonate (F-53)	Unknown – not registered.	Nordic Council of Ministers, 2020; Swedish Chemicals Agency, 2015
Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate (F-53B)		
Perfluoroalkyl phosphinic acids	1-10 (registration dossier)	Glüge et al., 2020
Perfluorohexanesulfonamides	Unknown	
1-Alkanesulfonamide, N,N'-bis(2,3-dihydroxy propyl)-perfluoro-	Unknown	
Tridecafluoroheptanamide	Unknown	
Alkanamide, N,N-bis(2,3-dihydroxy propyl)-perfluoro	Unknown	
N-Alkyl perfluoroalkane sulfonamides	Unknown	
1-Alkanesulfonamide, N,N'-[phosphonicobis(oxy-2,1,ethanediyl)]bis[perfluoro-N-methyl)	Unknown	
Fluorinated (meth)acrylate polymers	Unknown	
Manufacture of metal products		
Potassium perfluorohexane-1-sulponate	Unknown	Glüge et al., 2020; European Chemicals Agency, 2021
Potassium undecafluorocyclohexanesulphonate	Unknown	
1-Propanaminium, 3-[[(perfluoroalkyl)sulfonyl]amino]-N,N,N-trimethyl-, chloride (1:1)	Unknown	
1-Propanaminium, N-ethyl-3-[[(perfluoroalkyl)sulfonyl]amino]-N,N-dimethyl-, ethyl sulfate (1:1)	Unknown	
N-[3-(Dimethylamino)propyl]-N-[(perfluoroalkyl)sulfonyl]-β-alanine	Unknown	

Group/substance	EU market for metal plating (Tpa)	Source
Cyclohexanecarboxamide, N-[3-(dimethyl amino)propyl]-1,2,2,3,3,4,4,5,5,6,6-undecafluoro-	Unknown	
1-Propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[[(1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexyl)carbonyl]amino]-, inner salt	Unknown	
1-Propanaminium, N-(2-carboxyethyl)-3-[[[1,2,2,3,3,4,5,5,6, 6-decafluoro-4-(trifluoromethyl)cyclohexyl]carbonyl] amino]-N,N-dimethyl-, inner salt	Unknown	
Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(perfluoroalkyl) sulfonyl]amino]ethyl]-ω-hydroxy	Unknown	
N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo-2-[[2-(trifluoromethyl)phenyl]azo] butyramide	100-1000 (registration dossier)	
6:2 FTS	10-100 (registration dossier)	
3,3'-[(2-chloro-5-methyl-p-phenylene)bis[imino(1-acetyl-2-oxoethylene)azo]]bis[4-chloro-N-[2-(4-chlorophenoxy)-5-(trifluoromethyl)phenyl]benzamide]	10-100 (registration dossier)	
Reaction mass of ammonium(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) hydrogen phosphate and ammonium bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphate	1-10 (registration dossier)	
Polytetrafluoroethylene (PTFE)	Unknown	
Poly(vinylidene fluoride) (PVDF)	Unknown	
Siloxanes and silicones, di-Me, Me 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl	Unknown	
Siloxanes and silicones, di-Me, Me 3-(1,1,2,2-tetra fluoro ethoxy)propyl, Me 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl	Unknown	
Hexafluoropropylene polymer (HFP)	Unknown	
Polychlorotrifluoroethylene	Unknown	
Ethylene tetrafluoroethylene copolymer	Unknown	
Fluorinated ethylene propylene (FEP)	Unknown	
Chlorotrifluoroethylene-ethylene copolymer	Unknown	
Perfluoralkoxy polymer	Unknown	
Ethylene-tetrafluoroethylene-hexafluoro propylene copolymer	Unknown	
Hexafluoropropylene-tetrafluoroethylene-vinylidene fluoride copolymer	Unknown	
Ethylene-hexafluoropropylene-perfluoropropyl vinyl ether-tetrafluoroethylene copolymer	Unknown	
Hexafluoropropylene-perfluoropropyl vinyl ether-tetra fluoroethylene-vinylidene fluoride copolymer	Unknown	
Ethane, 1,1,2,2-tetrafluoro-1-(2,2,2-trifluoro ethoxy-)	Unknown	
Pentane, 1,1,1,2,2,3,4,5,5,5-decafluoro-	Unknown	
Cyclopentane, 1,1,2,2,3,3,4-heptafluoro-	1-10 (registration dossier)	

3. Manufacturing & Market price + market development

Information, e.g. on the concentration of PFAS, the annual production volume or annual import and export volumes of this PFAS relating to the specific use in chrome/metal plating processes and processes for manufacture of metal products, is only scarcely available. Information on the concentration of PFAS per use, annual production tonnages volumes/ import volumes of all used PFAS for metal plating/ manufacture of metal products, information on annual emissions/release and future emissions and information on costs is not available.

4. Emissions

Emissions of PFAS during plating processes originate e.g. from the rinsing steps between the electrolytes and from replacement of used solutions (Blepp et al., 2017). According to the ZVO in the case of Germany 20% of the applied surfactant is lost in the plating processes over time (Brunn Poulsen et al., 2011). The dossier submitter assumes that this share can be generalized for all manufacturers in the EU.

Release of PFAS from chrome plating processes into the environment is possible via wastewater and air and also via waste (e.g. metal hydroxide sludge, ion exchange resins). Short-chain PFAS have a low adsorption potential and are difficult to remove during water treatment processes and will be released in receiving waters. PFAS with higher adsorption potential will be bound to the metal hydroxide sludge and also removed via active carbon or ion exchangers (Blepp et al., 2017; Willand et al., 2020).

A survey in Switzerland found that most fluorosurfactants (only PFOS and 6:2 FTS used) are not retained in in-house WWTPs, but are carried to municipal WWTPs (Hauser et al., 2020). The following pathways for the fluorosurfactants were quantified: 50-85% in wastewater, 0.1-24% in filter sludge and < 0.1% in exhaust air. Based on information from the PFHxA dossier a current annual release of 6 tonnes (central estimate, range 0.5-11.4 t/a) into the environment was estimated for 6:2 FTS in Europe.

A further source of PFAS-emissions is de-chroming plating of defective batches and product carriers. Due to adsorption and desorption processes on plastic coated plating parts, PFAS could also get to other partial streams of the electroplating plant. Used process solutions from degreasing baths could also release PFAS. The degreasing solutions and their rinse waters are normally not treated for PFAS (Willand et al., 2020). Due to the lack of information, a quantification of the PFAS release by dechroming is not possible.

Chromate solutions containing mist suppressing agents have a limited usage lifetime and have to be changed regularly. The used solutions are treated as chemical waste, where chromium is isolated. The rest is disposed of with the risk of long-term leaching of PFAS to the groundwater or emission of PFAS-contaminated wastewater (Norwegian Environment Agency, 2017).

It is not possible to derive sufficiently representative numbers from the literature to calculate use quantities and emissions for the industry as a whole or for individual metal plating baths.

5. Alternatives

Chrome plating

Fluorine-free alternatives (substances as well as technologies) are available and already in use. Non-fluorinated surfactants seem feasible for decorative as well as functional chrome plating (UNEP, 2019). They are not considered equally effective to fluorinated surfactants. Furthermore, additional risks with respect to occupational safety, process stability and device preservation are mentioned by German electroplating industry association (UNEP, 2018). Nevertheless, these substances have been partly used successfully in bright (decorative) chrome electrolytes (Blepp et al., 2017). The use in functional chrome plating is also possible, but according to the current state of knowledge the substances should be used on a case-by-case basis. Furthermore, fluorine-free surfactants oxidatively decompose very rapidly in the process solutions and chromium (III) compounds are formed. This impairs the functional efficiency of the process solution (Blepp et al., 2017).

Fluorine-free wetting agents contain higher concentrations of active substances (fluorine-free 1 – 50 %; 6:2 FTS 1 – 10 %). Reasons for this are, for example: a) these alternative substances reduce surface tension only at higher concentrations and b) higher consumption due to more or less rapid oxidation. Fluorine-free products often require a higher technical effort compared to the previous application with PFOS. In contrast to fluorinated products the fluorine-free products often have to be added diluted and in smaller dosages throughout the day. To achieve comparable surface tensions higher amounts of wetting agents are necessary. Nevertheless, compared to PFAS, fluorine-free wetting agents are expected to have a lower impact on the aquatic environment due to rapid oxidation and biodegradation (Willand et al., 2020).

From a technical perspective, most probably there is no one-fits-all solution. For some industrial applications closed reactors will be an option whereas others will have to switch to non-fluorinated wetting agents or mist suppressants. Some surface treatments will have to even switch to a completely different process such as laser metal deposition or plasma processes. This all requires further intensive research and development work, but approaches show that there will be PFAS-free alternatives for all applications which today require the use of PFAS.

Fluorine-free alternatives (substances as well as technologies) for chrome plating processes are described in table 3.

Table 3: Non-PFAS alternatives for chrome plating (Willand et al., 2020, Müller et al., 2020; UNEP, 2015; UNEP, 2016; UNEP, 2018; Blepp et al., 2017)

Non-PFAS alternative	**Function**	**Advantage / disadvantage *(note: potential hazards of alternatives not mentioned here)***
Alkane sulfonates	Functional and decorative chrome plating	Disadvantages: not resistant to functional chrome plating; less effective in decorative chrome plating
Amines, C12-C14 alkyl, ethoxylated	Functional and decorative chrome plating	
Oleo amine ethoxylates (e.g. mixtures with (Z)-octadec-9-enylamine, ethoxylated	Functional and decorative chrome plating, plastic etching	
3-[dodecyl(dimethyl) ammonio]propan-1-sulfonate (mixture with 3-hydroxypropane-1-sulfonic acid and amines, coco alkyldimethyl, N-oxides)	Decorative chrome plating	
Paraffin oils, sulfochlorinated, saponified	Functional and decorative chrome plating	
Isodecanol, ethoxylated	Plastic etching	
Chromium (III) plating	Decorative chrome plating (functional chrome plating in individual cases and niche applications)	Advantages: process does not require the use of fluorinated mist suppressants or wetting agents; original problems with colour deviations have been largely solved Disadvantages: potential for conversion of Cr(III) to Cr(VI) during plating process is unclear; potential contamination with other metals;

Non-PFAS alternative	**Function**	**Advantage / disadvantage *(note: potential hazards of alternatives not mentioned here)***
		potential formation of complexing agent
Add-on air pollution control devices e.g. packed bed scrubbers	Functional and decorative chrome plating	
Thermal spraying, e.g. HVOF (high velocity oxygen fuel) process	Functional and decorative chrome plating	Advantages: process is globally available and is considered effective (high deposition efficiency and good quality finish); extremely thin layers with high corrosion resistance, wear resistance and high dimensional accuracy Disadvantages: requiring high temperature application; partly complex preparation of components; geometric restrictions (only rotationally symmetric parts can be coated); interior machining not possible
Physical vapour deposition (PVD)	Functional chrome plating; decorative chrome plating on plastics (in combination with one or more lacquer coatings)	Advantages: high wear-resistance Disadvantages: limited areas of application because of application in vacuum chambers and therefore limitation to the size of the components and required relative hardness of the base materials; low corrosion resistance
Case hardening process, e.g. plasma nitriding	Functional chrome plating	In the field of automotive tools this process has already completely replaced functional chrome plating; closed system process.
Laser metal deposition (LMD), Extreme high-speed LMD	Functional chrome plating	Advantages: no processing chemicals or solvents are used (only the applied metal alloys); process is more economical than functional chrome plating; Depending on material composition a higher corrosion and wear resistance than for chromium plating can be achieved (e.g. for off-shore applications); possible applications in automotive industry and mechanical engineering Disadvantages: productivity, process stability and automation have to be further optimized
Anhydrous ionic liquids based on chromium (III)salts	Functional chrome plating	Still in development
Closed coating reactors	Functional and decorative chrome plating	Advantages: no surfactants (either fluorine-free or fluorinated) are necessary; limited aerosol emission to room air. Due to highly diversified chrome plating processes it is impossible to

Non-PFAS alternative	Function	Advantage / disadvantage ***(note: potential hazards of alternatives not mentioned here)***
		describe a universal closed loop process technology for all of the various uses and process combinations
Nickel-based coatings	Functional chrome plating	Disadvantages: possible nickel emission from the surface (not suitable for food and pharmaceutical industries)
Sulfonation of plastics with sulfur trioxide in the gas phase	Plastic etching	Advantages: e.g. in terms of flexibility, energy costs or wastewater treatment; no PFAS necessary
Acidic permanganate solutions, nitric acid and trichloroacetic acid mixtures.	Plastic etching	Disadvantages: problems with wastewater treatment due to organohalogen compounds; problems when searching for suitable rack insulation; risk of formation of nitrous gases during the use of nitric acid; and problems with the formation of manganese dioxide and fire safety issues when using permanganate solutions

6. Economic impacts in case of a full PFAS ban

For metal plating processes mainly C6 PFAS are used. Information on the use of other PFAS for metal plating and manufacture of metal products are hardly available. Several C6 PFAS (e.g. 6:2 FTS) are already in scope of the PFHxA restriction proposal. Most likely no other PFAS alternatives are availabale. Therefore substitution will take place in case the restriction on PFHxA and related substances enters into force within the next years and in that case no further economic impacts are expected to result from the PFAS restriction.

Availability of alternatives:

- Hard Chrome Plating: within 5 years (medium uncertainty). Users will face very varying costs, mainly depending on characteristics of the current manufacturing sites (high uncertainty);
- Decorative plating: Regarding Cr(VI) the shift to Cr(III) is affordable (certain). For some applications the switch to Cr(III) is uncertain. Costs and availability of other alternatives are not clear (high uncertainty).
- Plastic Electroplating: Regarding Cr(VI) there is an ongoing substitution process to Cr(III) which suggests affordability.

Cost information:

Only a qualitative assessment is possible. Some information is available (e.g. substitution of Cr(VI) to Cr(III)), but other important information is missing (e.g. number/size of chrome baths in EU/EEC, variance/distribution of size of manufacturing sites, etc.). Although it is not possible to calculate the overall costs, the available information suggests general affordability. However, considering that no one-fits-all solution exists a better understanding is needed on how many and which kind of manufacturing sites would face difficulties with regard to substitution.

A study by the Danish Ministry of Environment from 2011 focussing on PFOS "suggests that the price of the PFOS products used as mist suppressant for non-decorative hard chrome plating is around 100 to 200 DKK (13 EUR to 27 EUR) per kg/liter. The price is dependent on the concentration of PFOS in the chemical. […] The price is not fully comparable as no information was received on the amounts to be used compared to a PFOS product. […] Other information about the price of the non-PFOS alternatives was sparse. One supplier informed that their non-PFOS alternative is more expensive than PFOS (but not how much more expensive)" (UNEP, 2013).

It has to be considered that in contrast to fluorinated products the fluorine-free products often have to be added diluted and in smaller dosages throughout the day. To achieve comparable surface tensions, higher amounts of wetting agents are necessary (Willand et al., 2020). Therefore, it is possible that production processes need to be changed.

If an alternative is used where the goods have to be dipped into the surfactant liquid, an additional bath has to be installed into the production facility. This means additional costs for the procurement of equipment as well as costs related to a reorganization of the production facilities for some companies. Information from industry suggests that 'the costs of phasing-in alternatives varies per company. Tests with alternative products may cost a company €50,000 to €150,000 per test and a test cycle has a minimum length of at least 1 year. However, the representatives indicate that the costs are mainly related to the costs of phasing in the alternative in practice and not in the costs of testing. Most relevant for the cost is whether the alternative is a drop-in alternative or that new installations (tanks, baths, etc.) are required' (Hauzenberger et al., 2016).

For decorative plating a shift to other electrolytes that are Cr(III) based is an available alternative. This would mean that the demand on surfactants and process fluids is considerably lower, and that PFAS are not required. The Norwegian association of electroplaters (NGLF) has estimated the cost of replacing Cr(VI) in plating baths with Cr(III) to be approximately NKR 100,000 (€ 10,000) per bath (UNEP, 2013). It is not clear whether this estimate would be lower for a bath replacement where the Cr(VI) in use is due for replacement at the moment of substitution.

According to the German central association for surface technology (Zentralverband Oberflächentechnik e.V. - ZVO), about 200 companies are working in the sector of functional chrome plating, about 800 in the sector of decorative chrome plating and about 30 in the sector of plastic products chrome plating in Germany (evaluation from 2018/2019 (Willand et al., 2020)).

One main missing information to derive costs for the chrome / metal plating industry is the number of baths per manufacturer. The chrome / metal plating industry is characterized by heterogeneity and a large share of small and medium enterprises. Large production facilities might use considerably more than 100 baths of different sizes. Small and medium enterprises might use single- to double-digit number of baths.

The cost estimate from the Norwegian association of electroplaters suggests that substitution of Cr(VI) with Cr(III) is affordable. Substitution costs mainly consist of one-time replacement costs that amount to less than 1000 €/a (750-800 €/a) per bath.

7. Methods used & uncertainties

It is unknown whether data for German industry, provided by the German ZVO, and from the Norwegian association of electroplaters is representative for the EU.

The information on further costs is uncertain: Implementation costs might be a heavy burden especially for the large number of SMEs in the market.

No additional transitional periods are needed for decorative chrome plating and plastic electroplating. Alternatives are available. For hard chrome plating a longer transitional period might be necessary to avoid high economic costs in case alternatives could not be installed successfully in time.

Some stakeholders claim that for decorative chrome plating the use of alternatives like Cr(III) will lead to limitations with regard to the aesthetic qualities of the final product. The dossier submitter has no information regarding the resulting magnitude of impacts for the various articles affected.

As mentioned before: A lot of information (production volume , import and export volumes, PFAS concentrations, emissions) is not available.

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