December 2022

# PFAS in the metal plating and finishing industry

An inventory of information about PFAS use, environmental release pathways, and source reduction strategies.







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# Abbreviations

6:2 FTS	6:2 Fluorotelomer sulfonic acid
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
CalEPA	California Environmental Protection Agency
ECTFE	Ethylene chlorotrifluoroethylene
EPA	Environmental Protection Agency
FEP	Fluorinated ethylene propylene
FEVE	Fluoroethylene vinyl ether
GAC	Granulated activated carbon
HDPE	High density polyethylene
МРСА	Minnesota Pollution Control Agency
NAICS	North American Industrial Classification System
NESHAP	National Emission Standards Hazardous Air Pollutants
PVDF	Polyvinylidene fluoride
PFAAs	Perfluoroalkyl acids
PFAS	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutanesulfonate
PFCAs	Perfluoroalkyl carboxylic acids
PFECHS	Perfluoroethyl cyclohexyl sulfonate
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPE	Perfluoropolyether
PFSA	Perfluoroalkyl sulfonate
PTFE	Polytetrafluoroethylene

PVC	Polyvinyl chloride
SIC	Standard Industrial Classification System
SNUR	Significant new use rule
TCEQ	Texas Commission on Environmental Quality
TSCA	Toxic Substances Control Act
UNEP	United Nations Environment Programme
WA/FS	Wetting agent/fume suppressant
WWTP	Wastewater treatment plant

# Overview

Metal plating and finishing processes serve to add resistance to wear, corrosion, and heat, as well as to add lubricity, electrical conductance, and aesthetic properties to base materials. Per- and polyfluoroalkyl substances (PFAS) have been used across this industry sector as wetting agents, fume suppressants, dispersion products, coating additives, corrosion inhibitors, and more. The chrome plating industry in particular has received considerable regulatory and scientific attention as a source of PFAS to the environment, since perfluorooctanesulfonic acid (PFOS) and other PFAS have been used for decades as agents to suppress emissions of hexavalent chromium (Cr(VI)), a known carcinogen. Source identification studies conducted by the U.S. Environmental Protection Agency (EPA) and state agencies have concluded that the metal finishing industry represents a significant source of PFOS emissions to wastewater treatment plants (WWTPs), and that within the metal finishing industry, facilities performing chrome plating and associated operations represent the dominant sources (EPA, 2009; EPA, 2021a; MI EGLE, 2020b). However, PFAS are associated with several finishing processes for chromium and other metals, including electroplating, electroless plating, anodizing, coating, etching, and cleaning. Examples include the use of polytetrafluoroethylene (PTFE) in electroless nickel plating and powder coating, PFAS-based deposition aids in copper plating, PFAS-based wetting agents in metal plating on plastics, and fluorochemical blocking agents in aluminum foil production.

The primary pathway for PFAS release to the environment from metal finishing facilities is through wastewater. PFAS are used as agents in chemical baths in which metal finishing operations are performed. When the baths are replaced, toxics such as Cr(VI) are removed, and the remaining water, including the PFAS, is discharged. Air emissions are also significant, due to the potential of PFAS aerosolization from finishing tanks and subsequent release through facility vents. PFAS may also be present in waste sludge and in certain metal plated or coated products. An EPA rule effective 2015 banned PFOS use in wetting agents/fume suppressants (WA/FS) in chrome plating and chromium anodizing operations. However, other PFAS are still used in WA/FS and in other metal finishing processes. The primary PFAS replacement in WA/FS formulations is 6:2 fluorotelomer sulfonic acid (6:2 FTS, also abbreviated 6:2 FTSA), which degrades in the environment to several compounds including perfluorohexanoic acid (PFHxA).

There are alternatives to PFAS use in this industry sector. Nonfluorinated WA/FS are commercially available and viable for plating without Cr(VI) and for etching plastics in preparation for electroplating. Moreover, some metal finishing facilities have adopted mechanical controls for suppressing chromium emissions that do not require the use of WA/FS, presenting an alternative for hard chrome plating. Despite this progress, emissions of PFAS from metal finishing facilities, including PFOS, continue to occur. This is likely due to the ongoing use of PFAS-containing products as well as persistence of PFAS in the equipment when PFAS-free alternatives are adopted. Source reduction strategies include limiting use of PFAS-based agents in metal finishing processes, cleaning and replacing contaminated equipment, and installing waste pre-treatment technologies at discharging facilities.

The remainder of this report provides information on the metal finishing operations that use PFAS and discusses the specific applications of PFAS, pathways for environmental release, and opportunities to reduce PFAS emissions from metal finishing facilities. This information is intended to be useful to regulators, environmental professionals, and industry workers in conducting mitigation, cleanup, and programmatic efforts around PFAS. Supplementary information tables are included as part of this report which detail information about specific chemistries and known trade names for PFAS-containing products used in metal finishing processes. These lists draw on sources including the scientific literature, chemical industry, and government reports, but they are not exhaustive. Many PFAS-containing

products are associated with numerous trade names, and information on specific products and chemicals is often considered proprietary information. A definitive list of products is therefore outside the scope of this report; however, the information provided here may be used as a basis for further investigation.

# Metal plating and finishing in Minnesota

## **Industry classification**

Several industrial processes falling under the metal plating and finishing sector are associated with PFAS use. These include the core operations subject to EPA's *Metal Finishing Effluent Guidelines* for industrial wastewater: electroplating, electroless plating, anodizing, coating, chemical etching and milling, and printed circuit board manufacture (Metal Finishing Point Source Category, 1983). These processes are therefore covered in this report, with the exception of printed circuit board manufacture. Printed circuit boards contain PFAS as part of their construction; fluoropolymers including PTFE and perfluoroalkoxy alkane (PFA) form a fiber-reinforced layer underlying laminates of copper (PSD, 2019; Brown, 2022; Gaines, 2022). While their manufacture falls under a regulatory point source category, from an industrial standpoint, it may be best categorized as part of the electronics and electrical components industry (e.g. Glüge et al., 2020; Gaines, 2022). PFAS use in printed circuit board manufacture is included in this report as part of discussions on plated products; however, further discussion is outside the scope of this report.

To assess the presence of the metal plating and finishing industry in Minnesota, businesses that may perform the metal finishing processes likely to use PFAS were identified on the basis of North American Industrial Classification System (NAICS) codes. NAICS is the standard system used by the federal government in classifying businesses for the purpose of statistical data collection, analysis, and publication related to the U.S. business economy. It was implemented to replace the Standard Industrial Classification (SIC) system and was most recently updated in 2022 (U.S. Census Bureau, 2022). NAICS codes describing industries that are known to use PFAS have been utilized by government agencies, research groups, and other organizations to identify potential industrial PFAS sources (e.g. Andrews et al., 2021; MPCA, 2022a; Salvatore et al., 2022).

The metal finishing operations that are associated with PFAS use and covered in this report are encompassed by three NAICS codes (Table 1). Minnesota businesses that may perform these operations were identified by using these NAICS codes in a search of the *U.S. Businesses* module of Data Axle's Reference Solutions database, an annually updated repository of detailed business information in the United States available for government use (Data Axle, 2022). This search yielded 566 unique facilities listed with one or more of the metal finishing-relevant NAICS codes (Figure 1). Facilities may have more than one of these NAICS codes listed in this database, since up to ten codes may be included for each business. Therefore, any duplicate facilities yielded by the data aggregation process were removed based on location information. Additionally, business records designated "closed/out of business" were excluded.

Table 1. Metal finishing industry classes encompassing business operations representing potential sources of PFAS. The table columns represent a) NAICS codes and titles encompassing metal finishing processes, b) select index entries for metal finishing operations associated with PFAS use, c) inclusion on MPCA's criteria for inclusion in the PFAS Monitoring Plan (MPCA, 2022a), and d) number of facilities with the NAICS code listed in the Reference Solutions database (Data Axle, 2022).

NAICS code <sup>a</sup> NA	AICS title <sup>a</sup>	Illustrative index entries <sup>b</sup>	On MP list? <sup>c</sup>	MN facility count <sup>d</sup>
Ma En Jev Silv	etal Coating, ngraving (except welry and verware), and lied Services to	<ul> <li>Aluminum coating of metal products for the trade</li> <li>Etching metals and metal products (except printing products) for the trade</li> <li>Powder coating metals and metal</li> </ul>		
332812 Ma	anufacturers	products for the trade	No	219
		<ul> <li>Anodizing metals and metal products for the trade</li> <li>Chrome plating metals and metal products for the trade</li> </ul>		
Ele Pla	ectroplating, ating, Polishing,	Electroplating metals and formed     products for the trade		
An 332813 Co	nodizing, and oloring	<ul> <li>Plating metals and metal products for the trade</li> </ul>	Yes	110
All Mi Fa Pro	l Other iscellaneous bricated Metal oduct	<ul> <li>Bathroom fixtures, metal, manufacturing</li> <li>Foil not made in rolling mills</li> </ul>		
332999 Ma	anufacturing	<ul> <li>Plated ware manufacturing</li> </ul>	Yes	284

#### Data considerations

Importantly, the Reference Solutions dataset contains information about known businesses in Minnesota performing activities ascribed to the selected NAICS codes. These codes are not selfreported, but rather assigned by Data Axle. The dataset may include facilities that are not currently operating under any environmental permits. It may also include businesses performing one or more operations captured by the NAICS codes beyond the metal finishing processes associated with PFAS that are included in this report. For example, code 332812 contains index entries for both powder coating (included in this report) and metal engraving (not included in this report). Further, businesses may be captured who perform one of the metal finishing operations of interest as a minor portion of business, even if the major business operations do not involve metal finishing. Relatedly, corporate offices for companies involved with metal finishing may be captured, even if no metal finishing is performed onsite. Finally, the list may include duplicates that were not captured by removal based on coordinates, in the case of multiple listings with differing geographic information.

These limitations may apply to other datasets relying on industrial classification systems to determine the potential for PFAS use. The maps and facility data included here should not be interpreted as a definitive list of PFAS users, but rather a visualization of the geographic spread of potential PFAS sources within the metal plating and finishing industry category.

Figure 1. Potential metal finishing facilities in Minnesota. Facilities have been identified based on NAICS codes encompassing the metal finishing operations described in this report. Facility location data was retrieved from the *U.S. Businesses* module of Data Axle's Reference Solutions database (Data Axle, 2022).



# **Timeline of important dates**

- Early 1920s: Chrome plating became commercially available (Rudy, 2022).
- **1954:** Use of PFAS-based WA/FS in the chrome plating industry was first reported. These were PFAS with amino functional groups. This "second generation" class of WA/FS followed the hydrocarbon-based "first generation" WA/FS (Gaines, 2022).
- **Early 1970s:** Trivalent chromium (Cr(III)) was introduced as a commercially viable alternative to Cr(VI) in decorative chrome plating (Snyder, 2022).
- Late 1980s/early 1990s: "Third generation" WA/FS begun to be used. These utilized PFAS with a sulfonate functional group, namely PFOS (Gaines, 2022).
- **1995:** EPA finalized a rule limiting Cr(VI) and Cr(III) emissions from metal finishing facilities under the Clean Air Act (NESHAP, 1995).
- **2007:** EPA amended a significant new use rule (SNUR) under the Toxic Substances Control Act (TSCA) to require reporting of PFAS. The SNUR contained an exception for the use of the ammonium salt of PFOS as a "fume/mist suppressant in metal finishing and plating baths. Examples of such metal finishing and plating baths include: hard chrome plating; decorative chromium plating; chromic acid anodizing; nickel, cadmium, or lead plating; metal plating on plastics; and alkaline zinc plating" (PFOS SNUR, 2007).
- **2012:** EPA finalized a rule to phase out the use of PFOS in WA/FS for hard and decorative chromium electroplating and anodizing tanks. This rule applied to PFOS only; no other PFAS were mentioned (NESHAP, 2012).
- **2015:** Compliance began for PFOS phase-out as part of the updated National Emission Standards Hazardous Air Pollutants (NESHAP) requirements (NESHAP, 2012).

## **Chrome plating**

#### **Key points**

- PFAS have been used for decades in wetting agents/fume suppressants in chrome plating baths to suppress chromium-bearing mist emissions.
- Historically, several PFAS compounds have been associated with chrome plating.
- PFOS was commonly used as an ingredient in wetting agents/fume suppressants up until its regulatory phase-out beginning in 2012. Since then, 6:2 FTS has been its primary replacement.
- There are alternatives to PFAS-based wetting agents/fume suppressants, including the use of non-fluorinated surfactants and mechanical controls to suppress fumes.
- In the US, chrome plating represents the most significant source of PFAS to the environment within the broader category of metal finishing industry.

PFAS compound	Processes	Products	Time period of concern	Potential media impacted
Potassium or amine perfluoroalkyl sulfonate (PFSA)	Chrome plating and associated processes	WA/FS	1954 – late 1980s	Wastewater, air, solid waste, groundwater, soil
Potassium perfluoroethyl cyclohexyl sulfonate (PFECHS)	Chrome plating and associated processes	WA/FS	1954 – late 1980s	Wastewater, air, solid waste, groundwater, soil
Ammonium perfluorohexylethyl sulfonate (6:2 FTS-NH4)	Chrome plating and associated processes	WA/FS	1954 – late 1980s	Wastewater, air, solid waste, groundwater, soil
Perfluorooctane sulfonic acid and derived salts (PFOS)	Chrome plating, plating on plastics, etching, anodizing	Wetting agents, mist suppressants, WA/FS	Late 1980s - 2015	Wastewater, air, solid waste, groundwater, soil
Perfluorobutanesulfonate (PFBS)	Chrome plating	Mist suppressants	Unknown (registered product in EU)	Wastewater, air, solid waste, groundwater, soil
Fluorotelomer sulfonic acids (6:2 FTS and 6:4 FTS)	Chrome plating, plating on plastics, etching, anodizing	Wetting agents, mist suppressants, WA/FS	2000s – present	Wastewater, air, solid waste, groundwater, soil

# Table 2. Summary of key PFAS used in chrome plating and adjacent operations. For a more detailed list, seeSupplementary Table S1.

#### Overview

There are two main types of chrome plating: hard and decorative chrome plating. Hard chrome plating describes the process of electrochemically applying a relatively thick layer of chromium to base metals to provide hardness, corrosion resistance, lubricity, and heat and chemical resistance (NESHAP, 2012). It is widely applied in the automotive industry, aircraft construction, shipbuilding and engineering, railroad industry, and mold manufacturing for the plastic and rubber industries (ECHA, 2021). Decorative chrome plating describes the process of plating base materials including brass, steel, aluminum or plastic with layers of copper and nickel, followed by a relatively thin layer of chromium (NESHAP, 2012). This serves to provide a bright, decorative finish and a surface resistant to tarnish and wear. Decorative chrome plating is associated with the manufacture of bathroom and kitchen appliances, car and truck bumpers, motorcycle parts, and more (ECHA, 2021).

Hard chrome plating has historically been associated with aerosol emissions of hexavalent chromium (Cr(VI)), which is highly toxic and carcinogenic. Chromium-bearing mist is generated as a byproduct of the electroplating process, resulting from hydrogen and oxygen evolution of chromic acid leftover in the chrome tanks after plating operations (Baral & Engelken, 2002). To suppress these fumes, wetting agents are applied to the chrome baths. These lower the surface tension of the plating solution, which lowers the size and energy of process gas bubbles and thus reduces the likelihood of mist emission to the air (ECHA, 2021). EPA has regulated emissions of chromium compounds from the metal plating industry since 1990 (NESHAP, 1995), although PFAS-containing surfactants have been used as ingredients in WA/FS since the 1950s (Paulson et al., 2004). Due to their efficiency in controlling Cr(VI) emissions, their inclusion in WA/FS for hard chrome plating is ubiquitous today.

Decorative chrome plating has also historically employed Cr(VI) and thus PFAS-based WA/FS. However, since hard plating involves the application of a thicker layer of chromium than decorative plating (10 to > 300 µm vs. 0.25 µm), decorative plating is associated with significantly lower levels of potential chromium emissions (Baral & Engelken, 2002). Additionally, in the 1970s, decorative plating with Cr(III) emerged as commercially available option (Rudy, 2022). In addition to greater industrial efficiency, Cr(III) has generally low human toxicity compared to Cr(VI) (Baral & Engelken, 2002). The widespread adoption of Cr(III) over Cr(VI) in decorative chrome plating generally renders the use of PFAS-based WA/FS unnecessary for this purpose (Gaines, 2022), although it is not disallowed (NESHAP, 2012). Notably, the shift toward Cr(III) use in decorative chrome plating is relatively recent, and Cr(VI) has still been commonly used within the past two decades. In 2009, an EPA Region 5 study of Cr(VI)-based decorative chrome plating facilities found that all the facilities emitted PFOS and other PFAS in their effluent wastewater (EPA, 2009). A more recent study of PFOS sources in Michigan identified Cr(VI) use by decorative chrome plating facilities, indicating that PFAS-based WA/FS are likely still employed by decorative chrome platers (MI EGLE, 2020b).

Chrome plating has historically been associated with many distinct PFAS, although in the past couple of decades, PFOS has been dominant. In conversation with metal finishing industry representatives, EPA Region 5 found that PFOS-based WA/FS use had become the industry standard in complying with Cr(VI) emission regulations (EPA, 2009). A 2007 EPA SNUR regulating PFOS included an exception for the compound's use as a WA/FS in metal finishing operations (PFOS SNUR, 2007). However, a 2012 rule banned the use of products containing greater than 1% PFOS by weight in chrome plating and anodizing operations by 2015 (NESHAP, 2012). The primary PFAS replacement in WA/FS for chrome plating has been 6:2 FTS (Ritter, 2010), although 6:4 FTS has also been discovered in fume suppressants (MI EGLE, 2020a). Notably, 6:2 FTS degrades in the environment to PFHxA, which is a PFAS with known toxicity (ECHA, 2021).

Although several metal finishing operations are associated with PFAS use, state agencies and EPA have concluded that within this industry category, chromium plating is the most significant source of PFAS to the environment, primarily via wastewater (MI EGLE, 2020b; EPA, 2021a). Notably, however, not all chrome plating facilities use PFAS today. WA/FS that do not contain PFAS appear to be on the market and in use by some facilities. Mechanical controls for suppressing chromium emissions are also possible, reducing the need for surfactants in the plating baths (MI EGLE, 2020a; MI EGLE, 2020b). Furthermore, while EPA has not found any current permits requiring treatment or evaluation for PFAS, some facilities are proactively removing PFAS from effluent wastewater using granulated activated carbon (GAC) technology (EPA, 2021a).

#### Anodizing

Anodizing refers to the process of using an acid to form an oxide layer on a metal surface, forming a nanoporous coated surface. Anodizing may be performed using chromic acid, sulfuric acid, or a combination of acids (Stevenson, 1994; NESHAP, 2012; AlumiPlate, 2022). Chromium anodizing specifically is associated with PFAS use and is discussed here due to its similarity to chrome electroplating with regards to PFAS applications and regulatory framework.

The term "anodizing" refers to the fact that the part to be coated becomes the anode during the electrolytic processes, as distinct from electroplating, in which it becomes the cathode (Stevenson, 1994). While aluminum and its alloys are most commonly subject to anodizing, other nonferrous metals, such as magnesium and titanium, can also be anodized. Unlike metal plating, anodizing fully integrates the metal oxide layer with the underlying substrate, meaning there is no possibility of chipping or peeling. The resultant surface is porous and can be further processed (AAC, 2022a). Anodizing serves several purposes, including to increase corrosion and abrasion resistance, provide a decorative appearance, increase paint and bonding adhesion, improve lubricity, provide electrical insulation, and to facilitate further plating (Stevenson, 1994). Anodizing is used to strengthen components such as aircraft parts and underlying materials in architectural structures that are subject to high stress and corrosive conditions (NESHAP, 2012).

Sulfuric acid anodizing is not suitable for all applications, particularly in anodizing parts that are subject to the highest levels of stress, such as aircraft parts, or in anodizing parts from which removing all of the acid may be difficult. This is due to the particularly corrosive nature of sulfuric acid (Stevenson, 1994; AnoPlate, 2022). However, according to industrial sources—including the Aluminum Anodizers Council—sulfuric acid is generally preferred over chromic acid anodizing (e.g. AAC, 2022b; AnoPlate; 2022).

Where chromium anodizing is performed, PFAS are used similarly as they are in chrome plating: as WA/FS to minimize chromium misting (EPA, 2021b). Chromium anodizing is regulated in the same way as decorative chrome plating. Though EPA had less data on chromium anodizing facilities compared to chrome plating facilities during the rulemaking process, it was determined that the two processes were similar enough that the same emissions limits for chromium were used (NESHAP, 2012). Furthermore, chromium anodizing operations and chromium electroplating are collectively the more significant sources of PFAS to wastewater treatment plants in the metal finishing category due to the use of PFAS-based WA/FS to control Cr(VI) emissions (EPA, 2021a).

## **Processes associated with PFAS**

#### Chrome plating and anodizing baths

In both hard and decorative chrome plating as well as chromium anodizing, PFAS are primarily used to suppress chromium fumes from the plating baths. PFAS-based surfactants are included as active ingredients in WA/FS added to the electrolytic baths used to deposit layers of chromium on base materials, which can include various metals or plastics. The WA/FS lie on the surface of the chrome tank, lowering the kinetic energy of gas bubbles produced as a byproduct of chromic acid reactions and thus preventing the escape of chromium-bearing droplets (ECHA, 2021; Finishing.com, 2021). Fume suppressants may be added to chromium baths by the tank owner (i.e. the facility performing chrome plating), or purchased by the chrome plater as part of a pre-mixed bath package. There are some differences between how Cr(VI) and Cr(III) suppressed by a wetting agent are regulated with regards to work practice and continuous monitoring requirements. EPA's 2012 rule expanding on emissions requirements for chrome platers states that in Cr(III)-based decorative plating baths, if a wetting agent is used, it must be part of a pre-made bath mixture (NESHAP, 2012).

Decorative chrome plating typically takes advantage of chromic acid baths containing chromium in the trivalent form Cr(III), which is less toxic than the hexavalent form ((CrVI)) (Baral and Engelken, 2002) and, as mentioned previously, subject to fewer regulations (NESHAP, 2012). PFAS may still be used in decorative chrome plating, although alternatives to PFOS-based fume suppressants were more readily available and adopted for decorative compared to hard chrome plating by the time PFOS began to be phased out of the industry (UNEP, 2010). In hard and decorative chrome plating operations taking advantage of chemical WA/FS, 6:2 FTS has been the primary replacement for PFOS. In a recent study of Michigan chrome plating facilities, about half of the inspected facilities subject to chromium emission regulations used PFAS-based surfactants (mostly 6:2 FTS-based) in their operations (MI EGLE, 2020b).

#### **Plastic etching**

PFAS may also be applied to etching baths to facilitate plastic electroplating. This is performed in conjunction with decorative chrome plating, whereby plastic base materials are plated with layers of copper and nickel followed by a thin layer of chromium. Plating on plastics is becoming popular in the decorative chrome plating industry as a cost-efficiency measure and to create lighter-weight final products (MI EGLE, 2020). Plastics are made electrically conductive by etching microscopic pores into the plastic surface to prepare them for chrome electroplating. They are etched in a bath of highly concentrated chromo-sulfuric acid (ECHA, 2021). Since the acid baths contain Cr(VI), PFAS may be used as fume suppressants to control air emissions, as in chrome plating on metal base materials (MI EGLE, 2020). PFAS may also be used as stable surfactants added to the acid etch bath to achieve wettability of the hydrophobic plastic surface (Blepp et al., 2017). Polyfluorinated wetting agents, including those based on 6:2 FTS, are predominantly used today as an alternative for PFOS (Willand et al., 2022).

#### **Pre-treatment processes**

Several pretreatment steps are required to clean aluminum surfaces prior to anodizing. These include alkaline soaking, etching, vapor degreasing, and/or removal of leftover solvents from the cleaning and etching processes (TCEQ, 2007). PFAS can be used in the alkaline baths to improve the efficiency and thus extend the lifetime of the bath (Glüge et al., 2020). They may also be used as wetting agents in the aluminum etch baths (Gaines, 2022). Pickling with acid or molten-salt baths may be used as a step in the aluminum cleaning process (Stevenson, 1994). PFAS-based surfactants can be added to pickling baths to disperse scum, increase bath life, and prevent hydrogen formation and embrittlement (Kissa, 2001).

## **PFAS in products**

PFOS was commonly used in hard chrome plating from the late 1980s to 2010s, beginning with its inclusion as a surfactant in third generation wetting agents/fume suppressants and ending with its regulatory phase-out in the United States and Europe. It has most commonly been used in its salt forms (Glüge et al., 2020). Quaternary tetraethylammonium perfluorooctane sulfonate has been frequently used in hard chrome plating (Gaines, 2022), although other PFOS derivatives, such as potassium perfluorooctane sulfonate, have been used for this purpose as well (Glüge et al., 2020). These WA/FS exist under several trade names, including Fluorotenside-248, SurTec 960, and Fumetrol 140 (Gaines, 2022), the latter of which was originally developed for the purpose of compliance with EPA chromium emission standards (Paulson et al., 2004) and found to be used by a majority of Cr(VI) electroplating facilities included in a 2003 survey by the California Air Resources Board (CalEPA, 2006). Most WA/FS serve the general purpose of suppressing chromium emissions from plating and/or etching baths, but a subset are used for a more specific purpose. PFAS dispersion products, which have been manufactured since 1951, create foam to suppress acid mists and to reduce bath material drag (Gaines, 2022). Some examples of these include Dupont's (now Chemours) Zonyl FSN and Chemguard's fluorosurfactants tested for use in metal plating (Chemguard, 2007; Gaines, 2022).

Earlier generations of chrome bath WA/FS either did not use a fluorosurfactant or used other polyfluorinated or perfluorinated compounds. The first generation of WA/FS were hydrocarbon-based, although these posed fire and health risks and would lead to oxidation, forming Cr(III) as a byproduct. The second generation of WA/FS were introduced in 1954. These utilized a polyfluorinated or perfluorinated chain in place of the hydrocarbon. Some active ingredients included potassium perfluoroalkyl sulfonate (PFSA), amine perfluoroalkyl sulfonate (PFSA), potassium perfluoroethyl cyclohexyl sulfonate (PFECHS), and ammonium perfluorohexylethyl sulfonate. These WA/FS were more stable and less prone to oxidation, but their low solubility posed functional issues for the final chromium plate, leading to the development of the third generation of more highly soluble perfluorinated WA/FS (including PFOS-based). These are not associated with adverse effects on the final chromium plate (Paulson et al., 2004).

Presently, fluorotelomer-based substances, perfluoroalkyl acids (PFAAs), and perfluoropolyether (PFPE)based substances are used instead of PFOS (Glüge et al., 2020). The primary replacement for PFOS has been 6:2 FTS, which degrades to PFAS including PFHxA in the environment. In Europe, there is one perfluorobutanesulfonate (PFBS)-based spray mist inhibitor registered for use in industrial chrome plating, Bayowet FT 248. Since this product consists of a mixture of PFBS and PFOS, however, it is likely no longer in use in the US or EU (Lassen et al., 2017). A 2020 study of PFAS at chrome plating facilities in Michigan found a suite of PFAS present in effluent wastewater, including PFOS and 6:2 FTS in addition to PFBS, perfluorooctanoic acid (PFOA), other perfluoroalkyl carboxylic acids (PFCAs), and more. The study concluded that PFOS detections were a product of historical PFOS-based fume suppressant usage (MI EGLE, 2020b). Many of these compounds have either been historically used or patented for use as WA/FS in chrome plating. Their presence in emissions from chrome plating facilities could therefore indicate the historical usage of WA/FS based on these compounds.

A list of PFAS compounds used and/or patented for use in chrome plating operations is included as Supplementary Information Table S1.

## Non-chromium metal plating

#### **Key points**

- Copper and nickel are the most commonly plated metals and serve in a wide variety of engineering and decorative applications.
- PFAS can be used as surfactants in nickel, copper, and tin electro- and electroless plating to reduce foaming, improve bath stability, and ensure uniform thickness of the final plate
- In certain electroless plating operations, PFAS are incorporated into the final coating or plate.

# Table 3. Summary of key PFAS used in non-chromium metal plating. For a more detailed list, see SupplementaryTable S2.

PFAS compound	Processes	Products	Time period of concern	Potential media impacted
Perfluorooctane sulfonic	Copper, nickel, and tin electroplating on metals or plastics; etching plastics in preparation for copper and nickel	Products that regulate foam, improve bath stability, aid in metal deposition, and improve the quality of the final plate; wetting agents	1980s - 2015	Wastewater, air, solid waste, groundwater, soil
6:2 Fluorotelomer sulfonic acids (6:2 FTS)	Copper, nickel, and tin electroplating on metals or plastics; etching plastics in preparation for copper and nickel plating	Products that regulate foam, improve bath stability, aid in metal deposition, and improve the quality of the final plate; wetting agents	2000s – present	Wastewater, air, solid waste, groundwater, soil
Polytetrafluoroethylene (PTFE)	Nickel electroless plating	Nickel coating additives	1985 – present	Wastewater, solid waste, groundwater, soil, final plated products

## Overview

PFAS are used for a variety of applications in both electroplating and electroless plating with metals other than chrome. Electroplating describes a process by which a material is coated with a layer of a metal by means of electrolysis. To accomplish this, a charge is applied to the object to be plated by immersing it in a metal salt solution (Makhlouf & Gajarla, 2020). Electroless plating, or chemical plating, refers to non-galvanic metal plating performed on a material without the use of an electric current (Makhlouf & Rodriguez, 2020). Instead, the reactions are forced by the use of a chemical reducing agent or by the material being plated (Makhlouf & Gajarla, 2020). Electroplating is typically used to deposit thicker layers of metal (Zhang & Hoshino, 2019), but both electro- and electroless plating serve to improve corrosion resistance of base materials (Makhlouf & Rodriguez, 2020).

#### Nickel

Nickel is the most commonly plated metal and has both decorative and engineering applications. It is valuable for its high level of corrosion resistance and is often used to provide protection to steel parts (Zangari, 2018). Nickel electroplating can be performed as a standalone coating or as an undercoat onto which other metals are subsequently plated; for example, decorative nickel plating can be covered by a thin layer of chromium for applications requiring brilliance. This kind of plating can be found on automobiles, hardware, and home fixtures. Non-decorative engineering applications include plating parts used by the aerospace industry, coins, jewelry, and circuit boards (Arnold, 2022). Electroless nickel plating is performed using chemical nickel plating baths consisting of phosphorous-containing acid and the nickel substrate. This type of coating provides a low friction surface and wear- and corrosion-resistance, and it is commonly used in plating fixtures and doorknobs (McKeen, 2016).

In nickel electroplating, PFAS, including PFOS, have been used to improve stability of the electroplating bath and enhance overall performance (Cheremisinoff, 2017; Gaines, 2022). PTFE powder can be added to electroless nickel plating baths to provide stability and is incorporated into the final plate (McKeen, 2016). Fluorosurfactants are not specifically mentioned in the *Nickel Plating Handbook* published by the Nickel Institute, but anionic surfactants are typically used as wetting agents to lower the surface tension of bath solutions during nickel electroplating (Nickel Institute, 2014). Information provided by manufacturers of commercial organic additives commonly used in nickel electroplating confirmed the use of alkyl or lauryl ether sulfate sodium salt as wetting agents, but the reference study does not specifically mention fluorosurfactants (Schmitz et al., 2016).

#### Copper

Copper is the second most commonly plated metal and, like nickel, can be used for decorative or engineering purposes. A copper plate can provide corrosion resistance, enhanced conductivity, and improved surface adhesion. It can be coated underneath other metal plates to provide enhanced rust resistance in highly corrosive environments. Copper plating is considered advantageous over other metal plating for the low cost of copper and its high thermal and electrical conductivity, ductility, and plating efficiency (Snyder, 2022). Due to these properties, copper plating is used extensively in the electronics manufacturing industry, including printed circuit boards, semiconductors, and electrical cabling, where copper is plated onto wire made of steel or other metals (Miura & Honma, 2003; SPC, 2022). It is also commonly applied to parts used in the oil and gas industry (Electro-Coatings, 2022). Decorative copper electroplating may be used in the automotive and domestic appliance industries (Horner, 1999; Weimer, 2017).

Electroless copper plating involves the deposition of copper from solution onto a base material without the use of an electric current. This requires use of a copper salt, a reducing agent, and stability of the plating solution. Additives are required to maintain the latter and are considered proprietary ingredients of the copper plating baths. Electroless copper plating is slower and more expensive than electroplating, but its high performance in surface uniformity and ability to coat non-conductive surfaces make it useful for certain applications. Notable examples are circuit manufacture and decorative and functional plating on plastics (Deckert, 1995).

Acidic sulfate baths are typically used in copper electroplating and have generally included a variety of organic additives as constituents to improve the final copper deposit (e.g. Passal, 1959; Volov, 2012; Marro et al., 2017). PFAS are known to be used in copper electroplating to prevent haziness in the final plate. These are included as ingredients in chemical additives to copper baths for their ability to regulate foam and improve the stability of the plated copper (Cheremisinoff, 2017). Furthermore, PFAS can aid in the deposition of copper during the electroplating process by reducing hydrogen evolution and the formation of metal oxides. One study demonstrated that the fluorosurfactant Zonyl FSN enhanced deposition of a copper-tin alloy onto base metals by adsorbing onto the surface of the metal and becoming incorporated into the final deposit (Pewnim & Roy, 2015). In copper electroless plating, PFAS are added to the plating solution to disperse free fluoride generated in the acid baths and to improve the quality of the final plate (Glüge et al., 2020; Gaines, 2022).

## **Processes associated with PFAS**

PFAS use is associated with the metal deposition process in electro- and electroless plating baths. In copper, nickel, and tin electroplating PFAS can serve as surfactants in acid bath formulations to regulate foam, reduce the surface tension and increase the stability of the baths, and improve the quality of the final plate (Cheremisinoff, 2017). In copper electroplating specifically, fluorosurfactants can aid in the adhesion of the copper to the base material being plated (Pewnim & Roy, 2015; Gaines, 2022). In nickel electroplating, fluorinated surfactants can be used to prevent foaming and increase the strength of the final plate by eliminating pinholes, cracks, and peeling (Kissa, 2001). In nickel electroless plating, PTFE powder is included as an ingredient in chemical bath formulations to enhance lubrication of the final surface while retaining the mechanical properties of a non-fluorinated hard nickel coating (Ebdon, 1985; McKeen, 2016; Atotech, 2022a).

In addition to base metal materials, copper and nickel can be electroplated or chemically plated onto plastics (DuPont, 2022). As a first step, the underlying plastics must be made electrically conductive by etching with chromic and/or sulfuric acids (ECHA, 2021; DuPont, 2022). Stable surfactants containing PFOS, 6:2 FTS, or other PFAS alternatives may be added to the acid etching baths to achieve wettability of the hydrophobic plastic surface (Blepp et al., 2017; Willand et al., 2022).

# **PFAS in products**

PFAS are used as ingredients in baths used to perform copper, nickel, tin, and zinc electroplating, as well as copper and nickel electroless plating. The PFAS-containing products are added to baths to ensure even thickness in the final plate, prevent foaming in the bath, and increase the stability of the bath by reducing surface tension (Cheremisinoff, 2017; Gaines, 2022). PFOS has specifically been cited for use in these applications historically (Cheremisinoff, 2017), although other PFAS replacements may be used today. In copper electroplating, the use of PFAS-containing products in the plating bath can help the copper better adhere to the base material being plated. Zonyl FSN is an example of a fluorosurfactant that has been shown to be useful for this purpose (Pewnim & Roy, 2015); however, Zonyl

fluorosurfactant products were discontinued between 2009 and 2014. They have been replaced by a line of fluorosurfactants called Capstone, which are described to be "based on short-chain molecules that cannot break down to PFOA or PFOS in the environment" (ChemPoint, 2022). PTFE, the polymeric PFAS compound commonly known as Teflon, is used as a surfactant in nickel electroless plating baths to provide lubricating properties to the final plate. The availability of this technology, termed "Niflor," has been reported since at least the 1980s (Ebdon, 1985) and is still marketed for use today (e.g. Atotech, 2022a).

A list of PFAS compounds used and/or patented for use in non-chromium metal plating is included as Supplementary Information Table S2.

#### Metal coating and treatment

#### **Key points**

- PFAS can be used in various types of metal coating, either as WA/FS--as in plating—or as ingredients in the final coat
- PFAS are often used as cleaning, etching, and other metal surface treatment agents associated with a variety of metal finishing processes
- PFAS-coated and PFAS treatment products can be found in a wide range of industries, including the chemical manufacture and architecture industries

# Table 4. Summary of select PFAS used in metal coating and treatment operations. For a more detailed list, seeSupplementary Table S3.

PFAS compound	Processes	Products	Time period of concern	Potential media impacted
Perfluorooctane sulfonic acid and derived salts	Chromate			Wastewater, air, solid waste,
(PFOS)	conversion coating	WA/FS	Late 1980s – 2015	groundwater, soil
6:2 Fluorotelomer sulfonic acids (6:2 FTS)	Chromate conversion coating	WA/FS	2000s – present	Wastewater, air, solid waste, groundwater, soil
Polyvinylidene fluoride (PVDF)	Powder coating	Weathering- resistant coatings for products such as pipelines; coatings for steel building materials	1965 - present	Wastewater, air, solid waste, groundwater, soil, final coated products
Ethylene chlorotrifluoroethylene (FCTFF)	Powder coating	Coatings for the surfaces of vessels, reactors, chemical storage tanks, piping, and semiconductors	1960s/70s –	Wastewater, air, solid waste, groundwater, soil, final coated products

PFAS compound	Processes	Products	Time period of concern	Potential media
Fluoroethylene vinyl ether (FEVE)	Powder coating	Coatings for aluminum window frames and curtain walls of buildings	1970s – present	Wastewater, air, solid waste, groundwater, soil, final coated products
Perfluorooctanoic acid (PFOA)	Unknown	Nonstick aluminum oil	? – present	Final products, other media unknown
Perfluorobutane sulfonic acid (PFBS)	Unknown	Nonstick aluminum oil	? – present	Final products, other media unknown

### Overview

The terms "coating" and "plating" are sometimes used interchangeably, but coating refers to metal finishing operations meant to provide a durable outer surface that are distinct from electroplating or electroless plating and can be performed in conjunction with plating for added durability. Cleaning and other forms of metal treatment are also usually performed in conjunction with other metal finishing operations. Conversion coating, powder coating, metal cleaning operations, and various specialized metal treatment operations have been associated with PFAS usage.

#### Conversion Coating

Conversion coating refers to the process of "converting" the surface properties of the underlying substrate to those of the metal providing the coating. Unlike plating, where the coating is applied as a layer on top of the base material, conversion coating alters the base material itself to provide the desired properties (AST, 2022). Aluminum is a particularly common substrate, although conversion coating may also be applied to magnesium, zinc, and cadmium. The two principal coating methods are chromate and phosphate conversion coating, which pickle the surface of the base metal with chromate or phosphate salt solutions. The reaction with the metal oxide at the surface of the substrate produces a protective "coating" that is resistant to corrosion and stress and can act as a primer for further coatings. It can be performed as an alternative to or in conjunction with anodizing (Hughes, 2018; MI EGLE, 2020b).

Importantly, chromate conversion coating can be performed using Cr(VI) and/or Cr(III) solutions (AST, 2022). PFOS has been historically used as a WA/FS for chromate conversion coating. In MI EGLE's recent study of PFAS in chrome plating facility effluent, they found that chromate conversion coating, along with chrome plating, was one of the dominant sources of PFOS to WWTPs within the metal finishing category, due to use of WA/FS to suppress Cr(VI) fumes. The report notes, however, that facilities performing chromate conversion coating alone were associated with lower PFOS emissions than those performing chrome plating. Additionally, as with chrome plating, PFOS emissions appeared to be associated with historical use, although 6:2 FTS may currently serve as a replacement agent (MI EGLE, 2020b).

PFAS are also associated with phosphate conversion coating, as additives to the phosphating solutions to help dissolve the oxide layer of aluminum substrates (Glüge et al., 2020).

#### Powder coating

Powder coating, unlike conversion coating, does not contribute additional properties to the underlying metal being coated. Rather, the powder is applied externally to the base material to provide surface protection and a durable finish (ProPlate, 2022). Powder coatings can be applied either by spraying or dipping followed by curing with UV or visible light. Polymeric PFAS are often used in powder coating due to their thermal, fire, and corrosion resistance properties. These coatings may be used on non-metal surfaces but can be used in metal finishing as well, particularly in coating aluminum and steel. Powder coating has numerous applications in the architectural and chemical industries, providing protection to the exterior surfaces of metal bridges and building structures and lining metal tanks and reaction vessels (OECD, 2022). Within the chrome plating industry, it is considered best practice to use heating and cooling tanks with PTFE incorporated into the surface (Pullara & Gardner, 2022). Note that only fluoropolymers, rather than any short- or long-chain PFAS, have been identified for use in powder coating, products based on high density polyethylene (HDPE), polyvinyl chloride (PVC), and epoxy, although these may not provide the same degree of thermal and fire resistance as fluoropolymers (OECD, 2022).

#### Metal treatment and cleaning

PFAS are associated with various treatment and cleaning processes that are performed as steps in the metal finishing operations discussed in previous sections. In order to plate plastics—and oftentimes steel and aluminum—the base materials must be electrolyzed via a chemical etching process. PFAS are often used as agents in these baths to promote wettability of the substrate being etched and/or to suppress fumes from chromic acid used in the wetting process (Gaines, 2022). PFAS may also be used in cleaning solutions for plating tanks and other reaction vessels, as well as to pre-treat base metals before they are further processed by anodizing, conversion coating, or plating (Kissa, 2001). There is documented use of PFAS as anti-blocking agents for aluminum foil production (Gaines, 2022). Finally, fluorinated surfactants can be used to promote the flow of metal coatings, prevent cracks during the drying process, and treat steel surfaces to inhibit corrosion (Kissa, 2001; Glüge et al., 2020; Gaines, 2022).

## **Processes associated with PFAS**

In both chromate and phosphate conversion coating, PFAS use is associated with the process of applying the base metal to a crystalline salt bath to chemically transform its surface. PFAS-based WA/FS are applied to chromate baths to suppress Cr(VI) fumes, while PFAS are included in phosphating solutions as an additive to break down aluminum oxides, in the case of phosphating on an aluminum substrate (Glüge et al., 2020; MI EGLE, 2020b).

In powder coating, PFAS are incorporated into the final coat and therefore the finished metal product, as opposed to facilitating the coating process as in conversion coating, anodizing, and plating. PFAS are included as ingredients in free-flowing powders which are applied via spraying or dipping the base object, depending on its size and application (OECD, 2022).

Etching is performed on materials with low or no electrical conductivity to create microscopic pores that enable current flow during electroplating (ECHA, 2021). PFAS-based surfactants may be added to etch baths to achieve wettability of hydrophobic base materials, in the case of plating on plastics, or to suppress Cr(VI) emissions when chromic acid is used for etching (Blepp et al., 2017; Gaines, 2022). They may also be added to alkali aluminum etch baths to improve the efficiency and thus extend the lifetime of the bath (Glüge et al., 2020). PFOS-based solutions have historically been used to clean machine parts following nickel plating operations. Further, PFAS-based surfactants can be used as anti-blocking additives in aluminum foil production, which reduce the tendency of sheets to stick together (Murphy, 2001; Gaines, 2022).

The use of PFAS-based surfactants in improving the quality of metal coating and inhibiting corrosion on steel has been documented, which may apply to several operations within the scope of metal finishing.

## **PFAS in products**

PFAS are included as WA/FS in baths used to perform chromate conversion coating. Fluorosurfactants serve the same purpose for this application as in chromium electroplating—which is to suppress chromium-bearing fumes—implying that similar products are available and viable for use in chromate conversion coating. For further discussion, see Section 5.1.3. For a list of PFAS compounds used and/or patented for use in chrome plating, see Supplementary Information Table S1. Specific PFAS-containing products for aluminum phosphating have not been named in the referenced literature (Kissa, 2001; Glüge et al., 2020).

Polymeric PFAS are used in powder coatings broadly applied in the oil and gas industry and chemical processing and manufacturing. Polyvinylidene fluoride (PVDF) coatings are one of the most commonly used industrial coatings, originally developed in 1965 under the trademark Kynar (Fonnov, 2018). The fluoropolymer resin is highly inert and stable, providing protection for weathering. The product Solef, manufactured by Solvay, is a PVDF-based coating used for internal and external surface coating of pipelines (OECD, 2022). Ethylene chlorotrifluoroethylene (ECTFE)-based coatings have been in use for decades and can provide anti-corrosion, chemical resistance, and fire resistance (Solvay, 2019; Solvay, 2022). Halar, also manufactured by Solvay, is an ECTFE-based coating designed for application to the surfaces of vessels, reactors, chemical storage tanks, and piping (OECD, 2022). Within the electronics industry, it can also be used to coat semiconductors (Solvay, 2022). Similar fluoropolymers are used in powder coatings for the architectural industry to provide durability and weather resistance. Fluoplast, Kynar, and Koflux are PVDF- and hydrocarbon-based coatings marketed as coatings for steel and other building materials. Fluoroethylene vinyl ether (FEVE)- and fluorinated ethylene propylene (FEP)-based coatings have been in use for several decades and are reported as coating ingredients in aluminum window frames and aluminum curtain walls of buildings (Blankenship, 2020; Chemours, 2022; OECD, 2022).

Fluorinated surfactants can be used to treat metal surfaces to provide resistance to physical and chemical wear. Zonyl FSN and Zonyl FSP have been used to provide water and solvent repellency to underlying metal surfaces. The fluorosurfactant Atsurf F-21 has been used to inhibit corrosion in steel surfaces. Various PFAS-based agents can be added to pickling baths used to clean metals for the purposes of dispersing scum, accelerating acid runoff when the metal article is removed from the bath, and increase the lifetime of the bath. PFAS are also used in anti-blocking agents, such as Monflor 91, to prevent sticking of aluminum foil sheets during manufacture (Kissa, 2001). While these agents are generally not incorporated into the final aluminum foil product, foil marketed as "nonstick" has been found to contain PFOA and PFBS (Rodowa et al., 2020).

A list of PFAS compounds used and/or patented for use metal coating and treatment applications is included as Supplementary Information Table S3.

# **Potential PFAS release pathways**

There are four life cycle stages described for the wetting agents/fume suppressants—which may contain PFAS—generally used in metal finishing baths:

- 1. The manufacture of the WA/FS
- 2. The production of the etching, anodizing, or plating agents and baths
- 3. The industrial use of these agents for metal finishing operations
- 4. The disposal of the metal finishing bath (Lassen et al., 2017).

The production of fluorosurfactants and bath formulations are typically performed by distinct parties from those performing the metal finishing operations. Therefore, this discussion focuses on life cycle stages (3) and (4).

## Wastewater

The primary pathway for PFAS release to the environment from metal finishing operations is via wastewater. The acid baths used to perform plating and other metal finishing operations have a limited usage lifetime (Lassen et al., 2017). Once they can no longer be used, the liquid is treated to remove chromium and other metals and discharged to the sewer system. Common treatment technologies include electrochemical reduction of Cr(VI) to Cr(III), chemical precipitation, and ion exchange. Use of adsorptive media such as activated carbon can be used to treat relatively low concentrations of chromium, and membrane filtration may be used by facilities that reclaim chromium, although this method is less common and more costly (SAMCO, 2020). Granular activated carbon, ion exchange resins, and high-pressure membrane systems are the three treatment technologies currently known to effectively remove PFAS (EPA, 2021c); the traditional metal treatment methods alone will likely not remove them. At facilities using PFAS-based WA/FS or baths containing PFAS ingredients, absent any targeted treatment technologies, PFAS likely remain present in the effluent wastewater (NESHAP, 2012). Furthermore, facilities that are not currently using PFAS-based agents may still discharge PFAS via wastewater if products containing PFAS were used historically. A 2020 study of chrome finishing facilities in Michigan found that PFOS was present in effluent wastewater from nearly every facility included in the study, although no facilities were actively using PFOS-based fume suppressants. It was concluded that the PFOS discharge was associated with historical usage (MI EGLE, 2020a). A larger Michigan study of PFAS sources to wastewater treatment plants found that two thirds of metal finishers were sources of PFOS, despite compliance with the phase-out of these products. One decorative chrome plating facility built after the 2015 PFOS ban was not a PFOS source to WWTPs, further supporting the conclusion that historical use can lead to ongoing discharge (MI EGLE, 2020b).

# Solid waste

It has been suggested that PFAS may be present in solid waste generated by chrome plating facilities due to their use as WA/FS in the plating baths (Lu et al., 2017). After removing spent plating baths and before discharging to the sewer, chromium is removed from the baths by reducing the chromium and then precipitating the metal hydroxides. This process generates a sludge that is highly concentrated in heavy metals (de Souza e Silva et al., 2005; Wang et al., 2022). If PFAS-based surfactants are included in the bath, then treatment of associated wastewaters may result in PFAS-bearing sludge (HRP, 2022). Sludge containing Cr(VI) is classified as hazardous waste and discharged to hazardous waste management facilities. Sludge containing primarily Cr(III), however, is not considered hazardous waste

and is discharged to nonhazardous industrial or municipal waste landfills (Identification and Listing of Hazardous Waste, 1980).

## Air

Air emissions of PFAS may be associated with metal finishing operations. Generally, PFAS can be released to air by either evaporation or aerosolization. In the metal finishing industry, PFAS may be released from open vessels and air ventilation canals (Lassen et al., 2017). These could include open etching, anodizing, and plating baths containing PFAS-based agents as well as facility vent systems. Air emissions tend to be of greater concern with regards to short-chain PFAS such as PFBS and 6:2 FTS, since they are both more volatile and water-soluble, enabling gas- and aqueous-phase air transport (Danish EPA, 2015; Lassen et al., 2017; Riedel et al., 2021). However, long-chain PFAS such as PFOS more easily adsorb to particles, so they are capable of atmospheric transport via particulate matter (Danish EPA, 2015). Both PFOS and its primary replacement in metal finishing operations, 6:2 FTS, will likely therefore have an air pathway for environmental release if there are open reactors on site (rather than a closed reactor system). An illustrative example of this pathway is the case of Douglas Corporation, a chrome finishing facility in St. Louis Park, MN. PFOS contamination in a nearby lake, Bde Maka Ska (formerly known as Lake Calhoun), was traced to concentrations in snow and stormwater runoff from the roof of the facility. PFOS had been accumulating there by way of fumes vented to the roof from the chromic acid etch tanks inside the facility. After the facility switched to a 6:2 FTS based mist suppression product, elevated levels of 6:2 FTS were observed downwind from the facilities in ambient air monitors (MPCA, 2022b).

## Products

In general, PFAS wetting agents/fume suppressants remain in the baths used to perform metal plating and other finishing operations. This is specifically noted for chrome electroplating, which comprises the dominant operation in the broader metal finishing industry category (Lassen et al., 2017). In some cases, however, PFAS may be incorporated into the final metal product. PTFE is used in electroless nickel plating as an ingredient in the final coat. Roughly 20-25% of the final nickel plate in products manufactured via this method will be PTFE (McKeen, 2016). It has also been shown that fluorosurfactants used in copper electroplating adhere to the base surface onto which the copper is deposited (Pewnim & Roy, 2015), although it is unclear how much PFAS ultimately remains in the final product. In powder-coated materials, fluoropolymers comprise a significant portion of the coating. Therefore, although waste and fumes produced during the manufacturing process of metal plated articles are the dominant sources of PFAS to the environment, use and disposal of metal plated or powder coated products may represent a minor source. When there are both industrial and consumer users of PFAS, however, consumer product use has been found to be an insignificant source PFAS to WWTPs compared to industrial processes. In a study of PFOS release to wastewater treatment plants, MI EGLE found that plants with no significant industrial PFOS source received influent water with PFOS concentrations similar to the background level (MI EGLE, 2020b).

# Accidental releases

In addition to the waste streams highlighted above, PFAS may be discharged from metal finishing facilities by way of leaks, cracks, and corrosion of equipment or facility flooring. The baths used to perform plating, etching, anodizing, and conversion coating operations are strongly acidic and therefore corrosive to certain materials. At a chrome plating facility in Minnesota, chromo-sulfuric acid corrosion

of a steel POP etch tank and subsequent corrosion of the underlying concrete led to a release of Cr(VI) and other bath chemicals to the groundwater (Carlson McCain, 2020). Bath chemicals—including PFAS— may also be released to soil and groundwater via spills and leaks from piping, sumps, and other equipment, as well as from spills occurring during raw material handling (CalEPA, 2011). The possibilities for accidental PFAS release are numerous, and in many cases, likely to be facility-specific. Further discussion of these possibilities is outside the scope of this report.

# Source reduction considerations

Fluorinated surfactants are widely used as wetting agents throughout the metal plating and finishing industry to suppress harmful fumes, stabilize plating baths, and ensure high quality of the final product. These chemical agents are financially costly; therefore, they are typically used only when alternative surfactants cannot deliver the required performance (Knepper & Lange, 2012). The original WA/FS used by the metal plating industry were based on hydrocarbons rather than fluorocarbons; however, associated health and safety issues as well as process inefficiencies led to the adoption of fluorinated surfactants (Paulson et al., 2004).

Following emerging evidence regarding the toxicity and persistence of long-chain PFAS and subsequent regulatory action, PFOS in metal plating surfactants was replaced with 6:2 FTS. Based on information available to date, 6:2 FTS is considered less bioaccumulative and less toxic than PFOS, but it can be nearly as persistent in the environment. Its environmental persistence is of concern due to the potential for continuous exposure, which prevents elimination from organisms despite shorter tissue and serum half-lives (Lu et al., 2017; Brendel et al., 2018). Additionally, there is comparatively little health risk data available for 6:2 FTS, and it degrades in the environment to several intermediate PFAS whose toxicities are not all well-known (Hoke et al., 2015; Sheng et al., 2016). One degradate of 6:2 FTS is PFHxA, which is associated with toxic effects on development, reproduction, and the endocrine and neurological systems (MDH, 2021; MDH, 2022).

There is a growing consensus that nonfluorinated WA/FS may be a viable alternative in chrome plating based on Cr(III), and that transitioning from Cr(VI) to Cr(III) is generally feasible for decorative chrome plating and plating on plastics. Source reduction efforts may therefore include using the trivalent form of chromium wherever technically possible, although it has been noted that some facilities may face logistical and economic challenges surrounding such a transition. Cr(III) is not a feasible substitute in hard chrome plating, as the level of hardness, corrosion- and wear-resistance provided is insufficient given the performance conditions of hard chrome-plated parts. In some decorative chrome plating applications requiring a high level of technical performance, Cr(III) may not be feasible either. The viability of non-fluorinated surfactants in hard chrome plating applications requires further research and testing. There are greater safety concerns with the performance of non-fluorinated surfactants in suppressing Cr(VI)-bearing fumes, since these surfactants are reportedly not as effective (ECHA, 2021). Notably, however, there is at least one WA/FS product marketed for use in plating with Cr(VI) that is advertised as "PFAS-free" (e.g. Atotech, 2022b). Additionally, a Michigan study of WA/FS used by chrome plating facilities found one product containing no detectable PFAS when analyzed using existing targeted and non-targeted methods, although it was not specified whether this product was used for hard or decorative chrome plating (MI EGLE, 2020a).

Fluorinated surfactants are often used in electroplating on plastics, in the process of etching to enable electrical conductivity of the underlying plastic. However, nonfluorinated surfactants are viable as non-toxic and easily biodegradable alternatives. Acid permanganate solutions, nitric acid, and trichloroacetic acid mixtures have been tested as alternative immersion techniques. Additional safety and technological controls may be required when using these alternatives, as there is risk of forming nitrous gases with use of nitric acid, fire risk with permanganate solutions, and the potential for organohalogen compound formation (ECHA, 2021).

Mechanical controls present an alternative to the use of surfactants in suppressing metal plating fumes. Performing metal finishing operations inside closed coating reactors would eliminate the need for surfactants and, by extension, the need for fluorosurfactants (ECHA, 2021). Due to the complexity in metal finishing processes, there is no single describable way to accomplish a closed system. Different technological and safety controls would be required for each combination of possible operations (e.g. plating, anodizing, etching, cleaning, etc.) (Blepp et al., 2017). Moreover, a closed system presents unique safety concerns that would need to be addressed, such as the explosion hazard of hydrogen gas produced during electroplating processes (UNEP, 2021). Nevertheless, enclosures and physical controls are in use today in the chrome plating industry. In a survey conducted by MI EGLE, about half of chrome plating facilities regulated for chromium emissions used mechanisms other than chemical fume suppression, including scrubbers, physical fume suppression methods, and non-fluorinated chemicals. In the same study, approximately one third of chrome platers were not sources of PFOS to wastewater treatment plants—despite the potential for legacy emissions based on historical use—indicating that mechanical controls were likely used by those facilities in the past as well (MI EGLE, 2020b).

Chromate conversion coating relies on fluorosurfactants as WA/FS due to the risk posed by Cr(VI) emissions. However, advances in conversion coating technology that do not rely on hard chromate may alleviate the need for this usage. Conversion coatings based on Cr(III), permanganate, rare earth elements, vanadium, heteropolymolybdate, and others have been tested, although these do not appear to have been commonly adopted in industry and present drawbacks in durability compared to surfaces converted with Cr(VI) (Minevski et al., 2002; NCMS, 2002; Pommier et al., 2014). Ongoing research and development of Cr(VI)-free alternatives to conversion coating and protective coatings for aluminum has been reported, although these efforts are generally in their early stages, and technical limitations have been identified for the most demanding applications, such as in the aerospace industry (Henkel, 2017). There are a number of commercially available non-fluorinated alternatives to powder coatings based on materials including HDPE, PVC, and epoxy. These may be suitable for some applications, but in applications requiring a high degree of thermal resistance, such as chemical manufacturing, fluoropolymers provide higher degrees of thermal resistance.

The potential for PFAS emissions based on historical use invites an opportunity for source reduction efforts beyond the shift away from using PFAS-based agents at metal finishing facilities. In MI EGLE's study, approximately two thirds of chrome plating facilities included were emitting PFOS to wastewater treatment plants, despite not actively using baths or bath agents containing PFOS. Five of these facilities were the single industrial PFOS source to their respective wastewater treatment plants. After installing GAC pretreatment technologies, PFOS concentrations in effluent wastewater were reduced by orders of magnitude, and there were improvements in solid waste concentrations as well. Extensive cleaning of metal finishing equipment resulted in some PFOS reduction, but pretreatment technologies were still required to achieve dischargeable levels. EGLE noted that since PFOS may persist in many surfaces and conduits—including various tanks, parts, ducts, etc.—cleaning in and of itself is likely not an adequate source reduction method (MI EGLE, 2020b).

Importantly, there are limits to the capability of treatment technologies in reducing sources of PFAS to the environment. Though treatment of 6:2 FTS in wastewater is generally more feasible than treatment of PFOS, there is little known about the destruction or decomposition of fluorotelomers from solid waste, including chrome-plating sludge (Lu et al., 2017). Other short-chain PFAS such as PFHxA, which is a degradation product of 6:2 FTS, have low adsorption potential and cannot be as readily removed from water using granular activated carbon technology (Brendel et al., 2018). Furthermore, removal of any PFAS in wastewater or solid waste does not necessarily reduce the possibility of aerosol or particulate-bound air emissions. A combination of minimized PFAS use, equipment cleaning and/or replacement, and waste pretreatment would likely produce the most significant outcomes with regards to PFAS reduction from metal finishing sources.

# **Supplementary information**

Supplementary information tables can be found online as report number gp3-05a, "PFAS in the metal plating and finishing industry: Supplementary information."

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