United States
Environmental Protection
Agency

Preliminary Study of the Metal Finishing Category: 2015 Status Report

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ABBREVIATIONS

Acronym	**Definition**
ACS	American Chemical Society
ACWA	Association of Clean Water Administrators
AFM/AFMmm	Abrasive Flow Machining/that Incorporates a Movable/Rotatable Mandrel
APCVD	Atmospheric Pressure, Chemical Vapor Deposition
BAT	Best Available Technology Economically Achievable
BMR	Baseline Monitoring Report
BPT	Best Practicable Control Technology Currently Available
CFR	Code of Federal Regulations
CIUs	Categorical Industrial Users
CPR	Cleaner Phosphoric Recycling
CWA	Clean Water Act
DAF	Dissolved Air Flotation
DCN	Document Control Number
DDTC	Diethyldithiocarbamate
DMR	Discharge Monitoring Report
DoD	Department of Defense
DOE	Department of Energy
EDTA	Ethylenediaminetetraacetic Acid
ELGs	Effluent Limitations Guidelines and Standards
ELV	End of Life Vehicle
EPA	Environmental Protection Agency
ERG	Eastern Research Group, Inc.
ESTCP	Environmental Security Technology Certification Program
EU	European Union
FR	Federal Register
GACT	Generally Available Control Technology
GBP	Glass Bead Peening
gpm	gallons per minute
HRS	Hot Rolled Steel
HVOF	High Velocity Oxygen Fuel
IONMET	New Ionic Liquid Solvent Technology to Transform Metal Finishing Products and Processes
IP3	Integrated Profitable Pollution Prevention Technologies
IPCB	Independent Printed Circuit Board
IVD	Ion Vapor Deposition
IWC	International Water Conference
LDH	Layered Double Hydroxide
LTA	Long-term Average
MEUF	Micellar-Enhanced Ultrafiltration
MF	Microfiltration
mg/L	milligrams per Liter

ABBREVIATIONS

Acronym	**Definition**
MP&M	Metal Products and Machinery
NACWA	National Association of Clean Water Agencies
NAICS	North American Industry Classification System
NASF	National Association for Surface Finishing
NAVAIR	Naval Aviation Systems Command
NESHAP	National Emission Standards for Hazardous Air Pollutants
NF	Nanofiltration
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standards
OAR	Office of Air and Radiation
ORCR	Office of Resource Conservation and Recovery
OW	Office of Water
PAM	Polyacrylamide
PEUF	Polymer-Enhanced Ultrafiltration
PFOs	Perfluorooctane Sulfonate
POTW	Publicly Owned Treatment Works
PPI	Pollution Prevention Institute
PQAPP	Programmatic Quality Assurance Project Plan
PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources
PVD	Physical Vapor Deposition
QA	Quality Assurance
RCRA	Resource Conservation and Recovery Act
RO	Reverse Osmosis
RoHS	Restriction of Hazardous Substances
SERDP	Strategic Environmental Research and Development Program
SIC	Standard Industrial Classification
SRB	Sulfate-Reducing Bacteria
TDD	Technical Development Document
TOC	Total Organic Compounds
TOMP	Toxic Organic Management Plan
TRI	Toxic Release Inventory
TSS	Total Suspended Solids
TTO	Total Toxic Organics
UF	Ultrafiltration
UV	Ultraviolet
VOC	Volatile Organic Compounds
WAFS	Wetting Agents/Fume Suppressants
WEFTEC	Water Environment Federation’s Annual Technical Exhibition and Conference

1. INTRODUCTION

The Clean Water Act (CWA) requires Environmental Protection Agency (EPA) to review existing effluent guidelines annually. EPA reviews all point source categories subject to existing effluent guidelines and pretreatment standards to identify potential candidates for revision, consistent with CWA sections 304(b), 301(d), 304(m)(1)(A), and 304(g). The CWA also requires EPA to revise existing Effluent Limitations Guidelines and Standards (ELGs) when appropriate.

EPA promulgated ELGs for the Metal Finishing Category (Metal Finishing ELGs), codified at 40 Code of Federal Regulations (CFR) Part 433, in 1983. EPA revisited the Metal Finishing ELGs during the development of the Metal Products and Machinery (MP&M) rulemaking in the late 1990s and early 2000s. More recently, EPA conducted a preliminary category review of the Metal Finishing Category as part of its annual effluent guideline review process. In the *Final 2014 Effluent Guidelines Program Plan*, EPA announced plans to conduct a preliminary study of the Metal Finishing Category to assess the current state of the industry, including an updated industry profile, descriptions of new and traditional process technologies and techniques, potential new pollutants of concern, advances in wastewater treatment technologies, and strategies used to achieve zero liquid discharge (U.S. EPA, 2015a, 2015b). This study extends EPA's efforts beyond the 304(m) annual review to better understand changes in metal finishing operations, wastewater characteristics, and wastewater treatment technologies since EPA promulgated the 1983 ELGs. The study seeks to answer the following key questions:

- How is the metal finishing industry now different from when EPA first promulgated the Metal Finishing ELGs? Specifically:
  - What is the distribution of captive facilities and job shops that currently make up the industry?
  - Which types of facilities are conducting metal finishing operations?
  - What products are metal finishing facilities producing?
- Since the promulgation of the Metal Finishing ELGs, what process technology changes have been implemented and how have the primary sources of wastewater changed?
- Since the promulgation of the Metal Finishing ELGs, what changes to chemical formulations have been implemented and how have these changes affected the volume of wastewater and the concentrations and types of pollutants generated and discharged?
- What are the best available technologies for pollution prevention and wastewater treatment, and to what levels do they reduce discharges of pollutions of concern?
  - What are the concentrations and loadings of pollutants currently being discharged (i.e., baseline concentrations)?
  - Which pollutant discharges require additional controls?
  - How will industry discharges change if facilities implement these best available technologies/practices to control pollutants?

- What challenges do metal finishing facilities or regulatory authorities face in applying the Metal Finishing ELGs?

This interim status describes the preliminary study and presents EPA's findings to date. The remainder of the report is organized as follows:

- Section 2 summarizes the existing metal finishing regulations, the state of the industry in 1983 when the ELGs were promulgated, and a general discussion of changes to the industry since promulgation.
- Section 3 describes activities that EPA plans to conduct as part of the preliminary study and the current status of these activities.
- Section 4 details EPA's study findings (to date) in five general categories: industry profile changes, advancements in process technologies, advancements in alternative chemistries, advancements in wastewater treatment technologies, and existing regulatory issues for consideration.
- Section 5 presents EPA's next steps for the study.
- Section 6 summarizes EPA's quality assurance (QA) procedures for reviewing existing information presented in this report.
- Section 7 is the list of references cited in the report.

2. EXISTING METAL FINISHING ELGS

This section provides a brief history of the existing ELGs as background and context for EPA's continued review of the metal finishing industry. Metal finishing involves changing the surface of an object to improve its appearance and/or durability. Wastewater discharges from metal finishing operations are regulated primarily under ELGs for the Electroplating Point Source Category (40 CFR Part 413) and the Metal Finishing Point Source Category (40 CFR Part 433). 40 CFR Part 413 includes pretreatment standards for existing sources (PSES) for the Electroplating Category, and 40 CFR Part 433 include effluent limitations based on best practicable control technology currently available (BPT) and best available technology economically achievable (BAT), new source performance standards (NSPS), pretreatment standards for new sources (PSNS), and PSES for the Metal Finishing Category.[1]

EPA promulgated PSES for the Electroplating Category in 1979; limitations and standards for new sources and direct discharges were not established under this rule. The PSES apply to facilities that perform one or more of six electroplating operations and that indirectly discharge wastewater to surface water via publically owned treatment works (POTW). The pretreatment standards differ for discharges less than 10,000 gallons per day (gpd) of wastewater compared to discharges greater than 10,000 gpd of wastewater (U.S. EPA, 1979). The National Association of Metal Finishers and the Institute of Interconnecting and Packaging Electronic Circuits challenged the 1979 rule for the Electroplating Category. On March 7, 1980, EPA entered into a settlement agreement with these two organizations, and agreed to amend the final electroplating pretreatment standards. These amendments were implemented on January 28, 1981 (U.S. EPA, 1981). As a result of the agreement, EPA promulgated in 1983 a new regulation for the Metal Finishing and Electroplating Categories which established BPT, BAT, NSPS, PSNS, and PSES. Following these amendments, the applicability of the Electroplating Category ELGs (40 CFR 413) is limited to facilities (both independent (job) platers and captive operations) that apply metal coatings via electrodeposition, began operation before July 15, 1983, and discharge wastes to POTWs. All other facilities performing electroplating or metal finishing operations are subject to regulations under the Metal Finishing Category (40 CFR Part 433).[2]

During the development of the MP&M rulemaking (40 CFR Part 438, promulgated in 2003), EPA evaluated all industries involved in the "manufacture, rebuild or maintenance of metal parts, products, or machines," including facilities regulated under 40 CFR Parts 413 and 433; however, EPA did not revise the existing limitations and standards for Parts 413 and 433 in the final MP&M rule. Therefore, the 1983 regulations continue to be the guidelines set for the industry for the indirect and direct discharge of metal finishing wastewater.[3]

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[1] Discharges from facilities performing metal finishing operations may also be regulated under other ELGs (e.g., Aluminum Forming, Iron and Steel) that take precedence over the Metal Finishing ELGs.

[2] Facilities include electroplaters discharging to surface water, electroplaters that began operation after July 15, 1983, and metal finishers that do not perform one or more of six electroplating operations.

[3] EPA promulgated the Electroplating Point Source Category regulation in 1974 and amended it in 1977, 1979, 1981, and 1983. The 1983 amended rule continue to regulate facilities in the Electroplating Point Source Category in operation prior to July 15, 1983 and that discharge wastes to POTW. Therefore, all other facilities operating on or after that date that discharge wastewater (indirect and/or direct discharge) are subject to the Metal Finishing Point Source Category.

This remainder of section describes the existing 1983 Metal Finishing ELGs, a profile the industry at the time of promulgation (section 2.1), metal finishing process operations (section 2.2), wastewater treatment of metal finishing wastewater (section 2.3), and the applicability of the existing ELGs to current metal finishing operations (section 2.4).

2.1 Metal Finishing Industry Profile at Promulgation

The applicability of the Metal Finishing Category is defined by process operations rather than by industry sectors; therefore, a facility subject to the Metal Finishing ELGs may belong to one or more of a variety of metal processing and metal forming industry classifications. The industries covered by the Metal Finishing ELGs perform one of 46 unit operations, discussed in section 2.2 below, and are generally included in the following two-digit Standard Industrial Classification (SIC) codes (U.S. EPA, 1983a):[4]

- 34: Fabricated Metal Products, Except Machinery and Transportation.
- 35: Machinery, Except Electrical.
- 36: Electrical and Electronic Machinery, Equipment and Supplies.
- 37: Transportation Equipment.
- 38: Measuring, Analyzing and Controlling Instruments: Photographic, Medical, and Optical Goods; Watches and Clocks.
- 39: Miscellaneous Manufacturing Industries.

Metal finishing facilities are categorized as either captive facilities or job shops, which EPA defined as follows (U.S. EPA, 1984):

- *Captive facility.* A facility that in a calendar year owns more than 50 percent (by surface area) of the materials undergoing metal finishing. Captive facilities were categorized as integrated or non-integrated to characterize the wastewater discharges generated. Integrated facilities are those which, prior to treatment, combine electroplating waste streams with significant process waste streams not covered by the Electroplating Point Source Category. Non-integrated facilities are those which have significant wastewater discharges only from operations addressed by the Electroplating Point Source Category.

- *Job shop.* A facility that in a calendar year owns less than 50 percent (by surface area) of the materials undergoing metal finishing. During development of the regulation, approximately 97 percent of job shops were found to be non-integrated.

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[4] Although facilities performing metal finishing operations generally fall under these SIC codes, not all facilities under the codes are subject to the Metal Finishing ELGs. For example, the Metal Finishing ELGs are not applicable to facilities that do not perform any of the six electroplating operations. Instead, these facilities may be subject to other metal ELGs that take precedence over the Metal Finishing ELGs.

At promulgation of the 1983 Metal Finishing ELGs, the Metal Finishing and Electroplating Categories included a total of 13,470 facilities, consisting of 10,000 captive facilities and 3,470 job shops and independent printed circuit board (IPCB) manufacturers[5] (U.S. EPA, 1984). The facilities varied greatly in size, age, number of employees, and number and type of operations performed, ranging from small shops with less than 10 employees to large facilities employing thousands of employees (U.S. EPA, 1983a).

During the Metal Finishing rulemaking development, EPA identified 10,561 out of 13,470 facilities (78 percent) that indirectly discharged to surface water via POTWs. These facilities were evenly distributed between job shops, non-integrated captive facilities, and integrated captive facilities. The remaining 2,909 facilities (22 percent) discharged directly to surface water, with captive facilities (both integrated and non-integrated) predominantly performing this practice (U.S. EPA, 1983a). The 1983 rule did not capture the number of facilities in the industry that reused wastewater.

2.2 Metal Finishing Process Operations at Promulgation

Metal finishing is the process of changing the surface of an object by creating a thin layer of metal or metal precipitate on its surface to impart the desired surface characteristics to the final product, such as corrosion resistance, wear resistance, and hardness. The operations performed and the sequence of operations at a metal finishing facility can vary and depend on numerous factors (e.g., raw materials used, industry sector, product specifications), and may generate significant volumes of wastewater (U.S. EPA, 2000a).

The Metal Finishing ELGs regulate wastewater discharges from six primary metal finishing operations. Additionally, at facilities where at least one of these primary operations is being conducted, the ELGs also cover wastewater discharges resulting from 40 additional metal finishing operations. If a facility does not perform any of the six primary metal finishing operations, it is not subject to the Metal Finishing ELGs (U.S. EPA, 1984). The six primary operations and associated waste streams are described below (U.S. EPA, 1983a).

- *Electroplating*. The application of a thin surface coating of one metal upon another by electrodeposition. This surface coating is applied to provide corrosion protection, wear or erosion resistance, or anti-frictional characteristics, or for decorative purposes. Cathodic surfaces are plated by reducing metal ions in either acid, alkaline, or neutral solutions. Metal ions in the plating solution are replenished by the dissolution of metal from anodes, small pieces contained in inert wire or metal baskets, or metal salts. Hundreds of different electroplating solutions have been adopted commercially, but only two or three types are used widely for a specific metal or alloy. Electroplating baths contain metal salts, acids, alkalines, and various bath control compounds which contribute to the wastewater stream through dragout, batch dumping, or floor spills. The waste

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[5] Indirect discharging job shops and IPCB manufacturers that existed under Part 413 continued to comply with Part 413 Electroplating Pretreatment Standards and were exempt from the Part 433 Metal Finishing ELGs (U.S. EPA, 1984).

from the electroplating process can include common metals, precious metals, chromium (hexavalent), and cyanide.

- *Electroless plating*. A chemical reduction process that depends on the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of metal without the use of external electrical energy. Electroless plating has several advantages over electroplating. It provides a uniform plating thickness on all areas of a part, and a dense and virtually non-porous plate on properly prepared surfaces. Copper and nickel electroless plating are the most common. Electroless plating baths can contain precious metals, complexed metals, and cyanide, which can enter the wastewater stream through dragout or batch dumping of process baths. The basic ingredients in an electroless plating solution are:
  - A source of metal, usually a salt.
  - A reducer, to reduce the metal to its base state.
  - A complexing agent, to hold the metal in solution.
  - Various buffers and other chemicals designed to maintain bath stability and increase bath life.
- *Anodizing*. An electrolytic oxidation process that converts the surface of the metal to an insoluble oxide. These oxide coatings provide corrosion protection, decorative surfaces, a base for painting and other coatings, and special electrical and mechanical properties. Aluminum is the most frequently anodized material, while some magnesium and limited amounts of zinc and titanium are also treated. For aluminum parts, the formation of oxide occurs when the parts are made anodic in dilute sulfuric acid or dilute chromic acid solutions. The oxide layer begins formation at the extreme outer surface, and as the reaction proceeds, the oxide grows into the metal. The last-formed oxide, the boundary layer, is at the interface between the base metal and the oxide. The boundary layer is extremely thin and nonporous. The wastewater from anodizing processes can contain the base material being anodized (typically aluminum or magnesium) and constituents of the processing baths (such as sulfuric or chromic acid). It is also common to dye or color anodized coatings. Many of the dyes contain chromium and other metals which can enter the wastewater stream.
- *Coating*. The process of chromating, phosphating, metal coloring, and passivating. These coatings are applied to previously deposited metal or basis material (i.e., the materials onto which metal finishes are applied) for increased corrosion protection, lubricity, and preparation of the surface for additional coatings or formulation of a special surface appearance. In chromating, a portion of the base metal is converted to a component of the film by reaction with aqueous solutions containing hexavalent chromium and active organic or inorganic compounds. Most coatings are applied by chemical immersion although a spray or brush treatment can be used.

  Phosphate coatings are used to provide a good base for paints and other organic coatings, to condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and to provide corrosion resistance to the metal surface (by the coating itself or by providing a suitable base for rust-preventative oils or waxes). Phosphate conversion coatings are formed by the immersion of iron, steel, or zinc-plated steel in a dilute solution of phosphoric acid plus other reagents. Metal coloring by chemical conversion converts the metal surface into an oxide or similar metallic compound, producing a variety of decorative finishes. Passivation refers to forming a protective film on metals by immersion in an acid solution. Numerous pollutants may enter the wastewater through coating operations by rinsing and batch dumping of process baths. The baths usually contain metal salts, acids, bases, and dissolved basis materials and various additives.

- *Chemical Etching and Milling*. Methods of producing specific design configurations and tolerances on metal parts by controlled dissolution with chemical reagents or etchants. This classification includes chemical milling, chemical etching, and bright dipping. Chemical etching is the same process as chemical milling, but with much lower rates and depths of metal removal. Typical solutions for etching and chemical milling include ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride, hydrochloric acid, and combinations of these reagents. Bright dipping is a specialized form of etching, used to remove oxide and tarnish from ferrous and nonferrous materials, and can produce a range of surface appearances from bright clean to brilliant. This unit operation also includes the stripping of metallic coatings. The wastewater from etching and chemical milling operations mainly contains dissolved basis materials, such as stainless steel, aluminum, and copper. Zinc and cadmium, frequently subjected to bright dipping, may also be present in wastewater.
- *Printed Circuit Board Manufacturing*. The formation of a circuit pattern of conductive metal (usually copper) on nonconductive board materials such as plastic or glass. It usually involves cleaning and surface preparation, catalyst and electroless plating, pattern printing and masking, electroplating, and etching. There are three main production methods for printed circuit boards: additive, which uses pre-sensitized, unclad material as the starting board; semi-additive, which uses unclad, unsensitized material as the starting board; and subtractive, which begins with copper clad, unsensitized material. Wastewater is generated in the manufacturing of printed circuit boards primarily from rinsing and cleaning during surface preparation, electroless plating, pattern plating, etching, tab plating, and immersion plating. Additionally, rinsing away spills, air scrubbing water, equipment washing, and dumping spent process solutions can contribute to the wastewater. The most common constituents of the waste streams are suspended solids, copper, fluorides, phosphorus, tin, palladium, and chelating agents.

As stated above, if any of the six core electroplating operations is present at a facility, the Metal Finishing ELGs also apply to wastewater discharges from 40 additional unit operations (listed in Table 2-1). Appendix A further describes the 40 additional metal finishing operations.

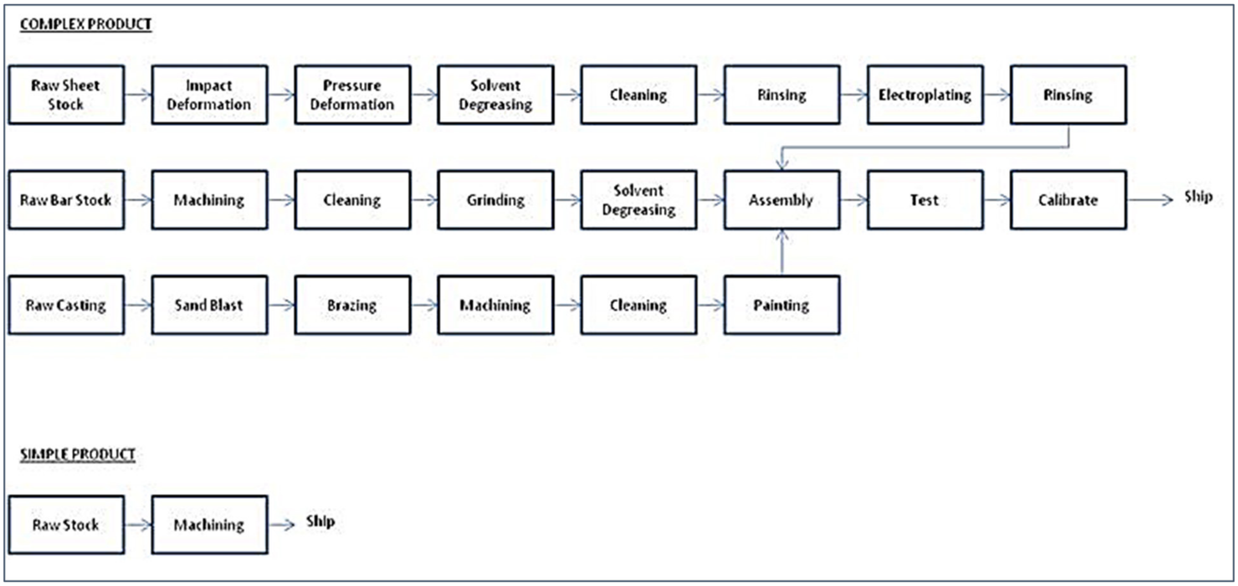
Table 2-1. Unit Operations Regulated by ELGs for the Metal Finishing Category

Six Primary Operations	40 Additional Metal Finishing Unit Operations	
• Electroplating • Electroless plating • Anodizing • Coating • Etching and chemical milling • Printed circuit board manufacturing	• Cleaning • Machining • Grinding • Polishing • Barrel finishing • Burnishing • Impact deformation • Pressure deformation • Shearing • Heat treating • Thermal cutting • Welding • Brazing • Soldering • Flame spraying • Sand blasting • Abrasive jet machining • Electrical discharge machining • Electrochemical machining • Electron beam machining	• Laser beam machining • Plasma arch machining • Ultrasonic machining • Sintering • Laminating • Hot dip coating • Sputtering • Vapor plating • Thermal infusion • Salt bath descaling • Solvent degreasing • Paint stripping • Painting • Electrostatic painting • Electropainting • Vacuum metalizing • Assembly • Calibration • Testing • Mechanical plating

Source: 40 CFR Part 433.

As discussed in supporting documentation for the Metal Finishing ELGs, metal finishing operations usually begin with raw stock materials (rods, bars, sheets, castings, forgings, etc.) which can progress through the simplest or most sophisticated surface finishing operations. Production facilities vary in size and processes, and are custom-tailored to the specific needs of each individual plant. Figure 2-1 illustrates the variation in the number of unit operations that can be performed in facilities within the metal finishing industry, depending upon the complexity of the product. A complex product could require the use of nearly all unit operations, while a simple product might require only a single operation (U.S. EPA, 1983a). The Metal Finishing ELGs would apply to wastewater discharges from the complex product in Figure 2-1 because at least one of the six core electroplating operations is taking place; they would not apply to wastewater discharges from the simple product as shown, because none of the six primary operations are performed.

Many different raw materials are used by facilities in the Metal Finishing Category. During the development of the 1983 Metal Finishing ELGs, the basis materials were almost exclusively metals which range from common copper and steel to extremely expensive high grade alloys and precious metals, but may also include glass, plastic, and other non-conductive materials. The raw materials used in metal finishing unit operations to coat these basis materials can contain acids, bases, cyanide, metals, complexing agents, organic additives, oils, and detergents. All of the basis materials and raw materials used in metal finishing can potentially enter wastewater streams during production and subsequently be discharged as metal finishing wastewater (U.S. EPA, 1983a).



Adapted from (U.S. EPA, 1983a)

Figure 2-1. Metal Finishing Process Application

2.3 Treatment of Metal Finishing Wastewater at Promulgation

As described in Section 2.2, Metal Finishing ELGs apply to wastewater discharges from the six primary electroplating operations, including any discharges from the additional metal finishing unit operations listed in Table 2-1. At promulgation, 78 percent of facilities indirectly discharged metal finishing wastewater to receiving water via POTWs and 22 percent directly discharged to surface waters (U.S. EPA, 1984). The Metal Finishing ELGs established one set of concentration-based discharge limits that apply across a single subpart (Subpart A: Metal Finishing), summarized in Table 2-2. Direct dischargers comply with BPT/BAT discharge limitations and NSPS, whereas indirect dischargers comply with PSES and PSNS. As the table shows, the limitations and standards are the same for new and existing sources of metal finishing wastewater discharges, except for cadmium, which has a lower NSPS and PSNS discharge standard (U.S. EPA, 1983a).

Table 2-2. Regulated Pollutants and ELG Limits for the Metal Finishing Category

Process Operations Covered	Pollutant	BPT/BAT/PSES Daily Max (Monthly Average) (mg/L)	NSPS/PSNS Daily Max (Monthly Average) (mg/L)
See Table 2-1, for the list of 46 unit operations[a]	Cadmium (T)	0.69 (0.26)	0.11 (0.07)
	Chromium (T)	2.77 (1.71)	2.77 (1.71)
	Copper (T)	3.38 (2.07)	3.38 (2.07)
	Lead (T)	0.69 (0.43)	0.69 (0.43)
	Nickel (T)	3.98 (2.38)	3.98 (2.38)
	Silver (T)	0.43 (0.24)	0.43 (0.24)
	Zinc (T)	2.61 (1.48)	2.61 (1.48)
	Cyanide (T)[b]	1.20 (0.65)	1.20 (0.65)
	Total Toxic Organics (TTO)[c]	2.13	2.13
	Oil and Grease[d]	52 (26)	52 (26)
	Total Suspended Solids (TSS)[d]	60 (31)	60 (31)
	pH[d]	Within 6.0 to 9.0	Within 6.0 to 9.0
For industrial facilities with cyanide treatment, and upon agreement between a source subject to those limits and the pollution control authority, the following amenable cyanide limit may apply in place of the total cyanide limit.	Cyanide amenable to alkaline chlorination	0.86 (0.32)	0.86 (0.32)

Source: 40 CFR Part 433.

[a] The provisions of this subpart apply to discharges from six electroplating operations on any basis material: electroplating, electroless plating, anodizing, coating (chromating, phosphating, and coloring), chemical etching and milling, and printed circuit board manufacturing. If any of these six operations are present, the provisions of this subpart also apply to discharges from 40 additional metal finishing operations, listed in Table 2-1. These limits do not apply to (1) metallic platemaking and gravure cylinder preparation conducted within or for printing and publishing facilities or (2) existing indirect discharging job shops and independent printed circuit board manufacturers, which are covered by 40 CFR Part 413.

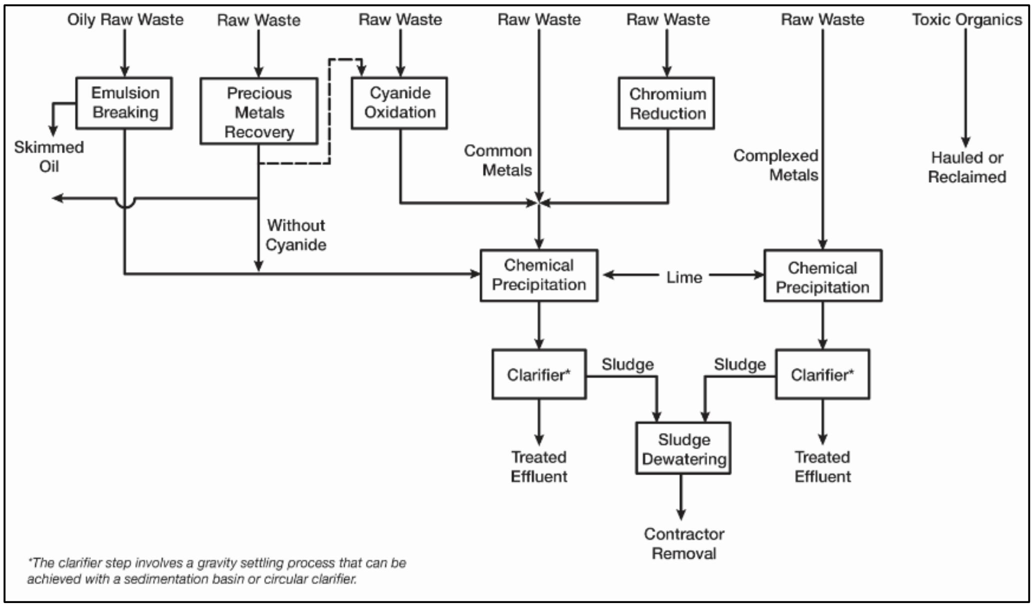
[b] Anti-dilution provisions are stipulated in 40 CFR Part 433, which require self-monitoring for cyanide after cyanide treatment and before dilution with other waste streams. In general, the practice of diluting rinse water as a partial or total substitute for adequate treatment to achieve compliance with discharge limits is in violation of the National pretreatment standards: Categorical standards (40 CFR Part 403.6(d)).

[c] No monthly average TTO limitation.

[d] Parameter is regulated for BPT and NSPS only.

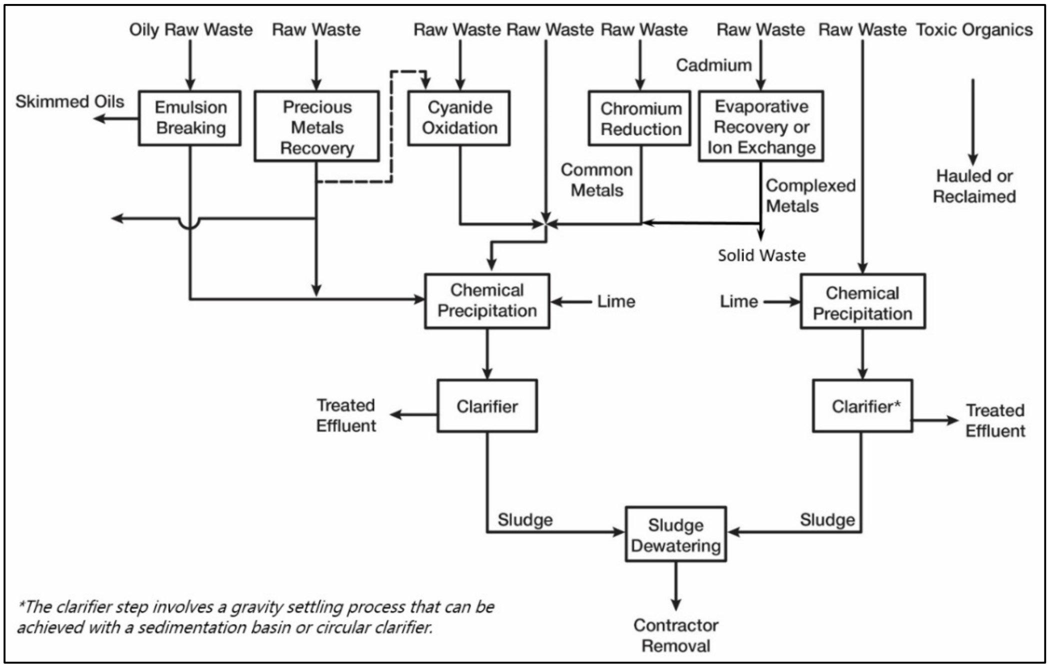
EPA based BPT, BAT, and PSES on the treatment of metal finishing wastewater using hydroxide precipitation, clarification, and sludge dewatering for common metals treatment, with pretreatment steps for chromium reduction, cyanide oxidation, complexed metals removal, and oil and grease removal, where the wastewater contains these components. This wastewater treatment technology is depicted in Figure 2-2 (U.S. EPA, 1983a).

EPA based NSPS and PSNS on the BPT/BAT/PSES technology, adding in-process treatment modifications for controlling the discharge of cadmium, as illustrated in Figure 2-3. The modifications for controlling cadmium employ evaporative recovery or ion exchange on cadmium-bearing wastewater before it mixes with other wastewater (U.S. EPA, 1983a). The following subsections discuss in detail the technology basis for BPT/BAT/PSES and NSPS/PSNS.



Source: (U.S. EPA, 1983a)

Figure 2-2. BPT/BAT/PSES Technology Basis



Source: (U.S. EPA, 1983a)

Figure 2-3. NSPS/PSNS Technology Basis (Equivalent to BPT/BAT/PSES with Additional Cadmium Reduction)

2.3.1 Common Metals Treatment

BAT is based on BPT of metal finishing wastewater, which reflects treatment and control practices at metal finishing plants of various sizes, ages, and manufacturing processes. Pollutant control focuses on end-of-pipe treatment rather than process changes or internal controls, except where such are common industry practice. The control technologies for treatment of common metals include hydroxide precipitation, clarification, and sludge dewatering, discussed in the subsections below. Treatment modifications for controlling the discharges of cadmium (as required for NSPS/PSNS), including evaporative recovery and ion exchange, are also discussed.

2.3.1.1 Hydroxide Precipitation

Hydroxide precipitation is used to remove dissolved metals and phosphates from metal finishing wastewater by converting the dissolved pollutants into solid form (precipitates) and coagulating suspended precipitates into larger, faster settling particles. Precipitation is achieved by adding lime, caustic, sodium carbonate, or acid to reach a favorable pH (typically 8.8 – 9.3). Any recovery of precious metals, reduction of hexavalent chromium, removal of oily wastes, or destruction of cyanide must be performed before metals and phosphates are removed via hydroxide precipitation.

2.3.1.2 Clarification

Following precipitation, the waste streams flow through a clarifier, where solids are removed by gravity. Clarifiers are used for sedimentation to reduce space requirements and retention time, making solids removal more efficient. Coagulants or flocculants are typically added to the waste stream to enhance solids settling (U.S. EPA, 1983a).

2.3.1.3 Sludge Dewatering

Precipitation and clarification generate large quantities of sludge requiring disposal. These sludges are dewatered prior to disposal to reduce their volume. Sludge dewatering techniques include gravity sludge thickening, pressure filtration, vacuum filtration, centrifugation, and sludge bed drying. Once the sludge is dewatered, it is generally disposed of at an onsite landfill or hauled away by a contractor to an off-site landfill or reclamation facility. Other less common disposal options include chemical containment, encapsulation, fixation, and thermal conversion, all of which require landfilling, but reduce the potential for groundwater contamination (U.S. EPA, 1983a).

2.3.2 In-process Cadmium Reduction

In addition to the BPT technology of hydroxide precipitation followed by clarification described above, NSPS/PSNS limitations require in-process treatment modifications for controlling the discharge of cadmium. The in-process cadmium reduction technologies may include ion exchange or evaporative recovery to provide near zero discharge of heavy metals from the raw waste stream. Although both ion exchange and evaporation are used in treatment of metal finishing wastewaters for removing a variety of precious metals from bath concentrates and rinse waters, the technology basis for NSPS and PSNS specifically uses these techniques for removing of cadmium before mixing with other metal-bearing wastewater for common metals treatment (U.S. EPA, 1983a).

The ion exchange process consists of ions, held by electrostatic forces to charged functional groups on the surface of the ion exchange resin, exchanged for ions of similar charge from the solution in which the resin is immersed. It is a sorption process because the exchange occurs on the surface of the resin. The cadmium is adsorbed onto the resin and exchanged for the harmless ions of the resin. Eventually, when the resin cannot exchange any more cadmium ions, it must be regenerated. The ion exchange resin is regenerated with regenerant solution containing hydrochloric or sulfuric acid. The regenerant flows through the ion exchange resin and replaces each cadmium ion with one or more hydrogen ions. The used regenerant solution is then treated, reused, and/or disposed.

Evaporation of water from a solution increases the concentration of solute in the remaining solution. Evaporation techniques include atmospheric evaporation (boiling the liquid) and vacuum evaporation (the evaporation pressure is lowered to cause the liquid to boil at reduced temperature). The vaporized water resulting from these processes humidifies the air in the system and is either blown out of the system as hot air or collected, condensed, and reused as waste process heat source for the system. The concentrate may be hauled off-site for recovery and resale or further processed on site for recovery and reuse.

2.3.3 Treatment of Complexed Metals, Cyanide-Bearing and Chromium-Bearing Wastewaters, and Wastewater Containing Oily Wastes

The following subsections discuss additional treatment requirements for facilities generating complexed metals, cyanide-bearing, chromium-bearing, or oily wastewaters. Complexed metals wastewater requires separate treatment using high pH chemical precipitation. Cyanide-bearing, chromium-bearing, or oily wastewaters require pretreatment using cyanide oxidation, chromium reduction, or emulsion breaking prior to common metals treatment. These constituents in the wastewater may hinder hydroxide precipitation, clarification, and sludge dewatering.

2.3.3.1 High pH Chemical Precipitation

High pH precipitation is particularly applicable to waste streams containing complexing agents (or chelating agents), which hinder conventional precipitation. These agents are used during metal finishing operations to maintain heavy metals in solution. The complexing agent produces a stable composition of non-metal molecules or ions that are covalently bonded to metal atoms or ions, which keeps the metal atoms or ions in solution during metal finishing operations, but also hinders their precipitation during wastewater treatment. Waste streams containing complexing agents (or complexed metals) are segregated and treated separately. Precipitation of complexed metals is characteristically accomplished at a high pH (11.6 – 12.5) to induce a shift in the complex dissociation equilibrium. This produces uncomplexed metal ions which can then be precipitated out of solution by available hydroxide ions. The pH is adjusted by the addition of chemicals such as calcium hydroxide, lime, calcium chloride, or calcium sulfate (U.S. EPA, 1983a).

2.3.3.2 Cyanide Oxidation

Waste streams containing cyanide are segregated for separate treatment prior to common metals treatment. Cyanides are introduced through metal salts for plating and conversion coatings, and plating and cleaning baths. Cyanide is generally destroyed by oxidation, and chlorine is typically used as the oxidizing agent. If the cyanide is not removed before further treatment, it will prevent efficient removal of metals during common metals treatment (U.S. EPA, 1983a).

2.3.3.3 Chromium Reduction

Waste streams containing hexavalent chromium are segregated for separate treatment prior to common metals treatment. Hexavalent chromium-containing wastewaters are generated in several ways including chromium electroplating and chromate conversion coatings. Chemical reduction requires the addition of a chemical such as sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate, which form strong reducing agents in aqueous solutions that reduce hexavalent chromium to trivalent chromium. Trivalent chromium can then be removed from wastewater using precipitation in common metals treatment (U.S. EPA, 1983a).

2.3.3.4 Emulsion Breaking

Metal finishing wastewater may contain oily wastes from process coolants and lubricants, wastes from cleaning operations, wastes from painting processes, and machinery lubricants. If oily wastes are generated, they should be separated and pretreated to remove the oils before commingling for common metals treatment. Emulsion breaking removes emulsified oils from oil/water mixtures. Chemicals such as acids, salts, or polymers are added to the wastewater and agitated to break the oil/water emulsion bond. The oily residue rises to the surface where it is skimmed off or decanted from the remaining wastewater. The skimmed oily residue is typically stored in tanks for further processing or removal by a contractor, and the remaining wastewater is sent to common metals treatment (U.S. EPA, 1983a).

2.3.4 Control and Treatment of Toxic Organics

The Metal Finishing ELGs also establish discharge limitations and pretreatment standards on TTO. EPA defines TTO as the sum of the masses or concentrations of a specific list toxic organic compounds detected exist in the industrial user’s process discharge at a concentration higher than 0.01 mg/L.[6] The primary source of TTO is from waste solvents. Although TTO may be present in combined wastewater and concentrated oily wastes generated during metal finishing operations, EPA determined that TTO concentrations from these sources were small and generally treatable by the technology basis for common metals treatment and the treatment of oily wastes (see Sections 2.3.1 and 2.3.3). The established TTO limit in the Metal Finishing ELGs was intended to prevent the dumping of concentrated toxic organic wastes from waste solvents, such as solvent degreasers and paint strippers. In addition to the TTO limit, EPA also established monitoring requirements for TTO in the Metal Finishing ELGs (U.S. EPA, 1983a, 1983b).

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[6] As listed at 40 CFR 433.11.

2.3.4.1 Monitoring Requirements

Facilities choosing to measure ongoing compliance with the TTO limit via self-monitoring need to report the results in the baseline monitoring report (BMR) and 90-day compliance report, which are submitted to the Control Authority.[7] In lieu of self-monitoring for TTO, facilities can choose the certification alternative discussed in Section 2.3.4.2. Subsequent self-monitoring for TTO is required following the guidelines outlined in the General Pretreatment Regulations (40 CFR Part 403) for indirect dischargers and National Pollutant Discharge Elimination System (NPDES) permitting requirements for direct dischargers. If self-monitoring is required to measure compliance with the limit, the facility needs to report analytical data only those for pollutants reasonably expected to be present in the wastewater (U.S. EPA, 1983b, 1985). Ongoing TTO monitoring is generally performed by those facilities that continue to dump waste solvents in the wastewater as a disposal practice. As indicated in the 1983 Metal Finishing ELGs, EPA anticipated very few facilities with these practices because waste solvents have sufficient reclaim value to be recovered, and thus, EPA anticipated few facilities that would need to conduct periodic self-monitoring to comply with the regulations (U.S. EPA, 1983a).

2.3.4.2 Toxic Organic Management Plan and Certification Process

As an alternative option to self-monitoring, a facility may be allowed to comply with the requirements through the certification process, which requires that the discharger submit a Toxic Organic Management Plan (TOMP).[8] Indirect dischargers certify in their semi-annual compliance reports to the control authority that they are implementing the TOMP and are not dumping toxic organics into the wastewater since the previous filing. For direct dischargers, the TOMP is incorporated as a condition of the NPDES permits and is reported in the comment section of the Discharge Monitoring Reports (DMRs) (U.S. EPA, 1983b, 1985).

To determine whether a TOMP is a feasible alternative to TTO monitoring, the facility is required to complete a process engineering analysis to identify potential sources of TTO and then evaluate pollution control options to reduce or eliminate TTO in wastewater discharge. The facility may decide whether a TOMP is a feasible alternative to TTO monitoring after weighing the costs for implementing the pollutant control options with those for monitoring. If the TOMP is feasible, the facility can make a request to the control or permitting authority to implement the TOMP and certification process in lieu of the monitoring requirements. Specifically, the TOMP must generally include (U.S. EPA, 1985):

- Identification of all the toxic organic compounds used by the facility.[9]
- Method of disposal for all wastes associated with TTO (e.g., reclamation, incineration, and/or contract hauling).

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[7] The Control Authority is considered the POTW, if it has an approved pretreatment program. Otherwise, the reports are submitted to the state, if it has an approved state pretreatment program, or to the EPA Region.

[8] Also referred to in the Metal Finishing ELGs as the solvent management plan.

[9] As defined in 40 CFR 433.12.

- Procedures followed by facility to assure that toxic organic compounds do not routinely spill or leak into any process wastestream that may be discharged.

The TOMP is submitted to the facility's control or permitting authority with baseline monitoring report to meet the requirements of the certification process (U.S. EPA, 1985).

2.4 Applicability of the Existing ELGs to Current Operations

The Metal Finishing ELGs reflect facilities, process operations, and wastewater management practices in 1983. Over the ensuing 32 years, process technologies and chemistries of metal finishing operations have evolved, and the industry has implemented more advanced treatment technologies than those described in Section 2.3. Additionally, many Metal Finishing facilities have developed waste minimization techniques leading to zero discharges or to the recovery/reuse of metal finishing wastewater. With these changes, stakeholders have raised questions regarding the applicability of certain operations to the Metal Finishing ELGs. These advances are discussed further in the following subsections.

2.4.1 Changes to Industry Profile

There is uncertainty regarding how the industry profile has changed since 1983. Based on a 2008 National Center for Manufacturing Sciences review of the surface finishing industry (including metal finishing) and additional discussions with industry representatives, EPA believes the industry has moved towards a more global market over the years. In addition, some U.S. firms may have more recently attempted to concentrate the industry (i.e., incorporate the smaller job shops into larger companies) to achieve economies of scale, expand niche markets, and provide a larger range of finishing services in a global market. Many firms may have also shifted surfacing operations to non-U.S. locations (such as Asia, India, Mexico, Canada, and Europe) to further reduce costs. Outsourcing metal finishing operations has generally been more cost effective than operating captive metal finishing facilities; therefore, EPA anticipates a shift in the number of captive facilities versus job shops as well as a decrease in the number of domestic job shops (ERG, 2016; U.S. EPA, 2015a).

2.4.2 Scope of Metal Finishing Operations

EPA has received comments from the Association of Clean Water Administrators (ACWA) urging it to consider the applicability of the Metal Finishing ELGs to current metal finishing operations (U.S. EPA, 2015c). Specifically, stakeholders identified a need for clarifying descriptions of metal finishing operations listed in the ELGs, including:

- Guidance to distinguish between metal finishing operations in which the same acid is used for different functions, such as etching and chemical milling, acid cleaning, chemical conversion coating, and similar cases.
- Clarification of how the Metal Finishing ELGs apply to current industry practices, including metal finishing processes or chemical alternatives that are not specifically identified in the ELGs.

- Clarification of how the Metal Finishing ELGs apply to newer manufacturing operations that use metal finishing processes not identified in the ELGs, such as solar panel manufacturing and cell phone manufacturing.

2.4.3 Process Technology Modifications and Alternative Chemistries

Since 1983, numerous modifications and process alternatives have been developed for processes conducted at metal finishing facilities such as cleaning and rinsing operations, coating and plating processes, and polishing. These modifications may impact the overall wastewater volume generated (and subsequently treated) as well as the general wastewater characteristics of metal finishing wastewater. Section 4.2 of this report further discusses updates to metal finishing process technologies. Additionally, alternatives to traditional chemistries used in the metal finishing operations have been developed, primarily alternatives to chemistries using cadmium, hexavalent chromium, phosphate, and cyanide. See Section 4.3 of this report for further discussion on alternative chemistries.

2.4.4 Technological Advances in Wastewater Treatment

At promulgation, it was evident that other treatment technologies, while not widespread in the industry, did exist and could be used to meet the discharge limitations. Since then, advanced treatment technologies and zero-discharge or reuse practices have emerged within the industry for the treatment and/or recycling of metal finishing wastewater.

Based on more recent observations from the regional EPA pretreatment coordinators and industry sources, emerging technologies are being used to some extent, but are still not widespread within the industry (U.S. EPA, 2015a). Some improvements are being applied to the technologies identified in the 1983 rule, including new chemical additives for improved precipitation and sludge generation, and alternative filtration techniques to replace or supplement clarification. Section 4.4 of this report further discusses treatment technologies that have emerged in the industry.

Waste minimization technologies for reuse and zero discharge strategies have a small footprint within the metal finishing industry. Vendors have described potential application of closed-loop processes for metal finishing operations to collect, treat, and return process wastewater for reuse (U.S. EPA, 2015a). Section 4.2 of this report further describes waste minimization technologies and practices available to reduce the volume of wastewater discharged from metal finishing operations and to recover other process waste streams to be reused in the process.

3. STUDY ACTIVITIES AND PROGRESS

This study seeks to answer the key questions described in Section 1. Historically, EPA has used various approaches for collecting information to further inform Agency actions and decisions related to effluent guidelines development and revision for select industries. Typically, a preliminary study profiles an industry category, gathers information about the hazards posed by its wastewater discharges, collects information about availability and cost of treatment and pollution prevention technologies, assesses the financial status of the facilities in the category, and investigates other factors to determine whether revisions to the current effluent guidelines are warranted. As the study evolves, EPA may decide to conduct a more detailed study, which is a more rigorous examination of the industry and its practices, and may include primary data collection activities (such as industry questionnaires and wastewater sampling and analysis) to fill data gaps (U.S. EPA, 2015a).

As part of this study, EPA is evaluating facilities that make up the metal finishing industry, their size, and the major markets they serve; the types of metal finishing operations and alternative chemistries used that may potentially introduce new pollutants of concern that are not currently regulated; new sources of metal finishing wastewater that contribute to the overall wastewater characteristics, such as wet air pollution controls or new operations in metal finishing; and advanced technologies that facilities employ for the treatment and subsequent recycle or discharge of metal finishing wastewater. The study initially focuses on examining existing information that EPA collected or will collect through literature reviews, technical conferences, and discussions with industry experts and stakeholders. EPA also plans to conduct site visits at metal finishing facilities, analyze current available discharge data, and review information collected on the industry during the MP&M Rulemaking development. This section describes these activities planned for the preliminary study of the Metal Finishing Category and the current status of those planned activities. Section 4 of this report further details EPA's preliminary findings, which will lay the foundation for EPA's decisions on how to proceed with the study.

3.1 Literature Review

As an initial step in answering the key study questions, EPA collected and reviewed technical literature about the metal finishing industry. Using a defined list of key words, listed in Appendix B, EPA identified technical papers and reports, studies, peer-reviewed journal articles, and industry publications on metal finishing operations and wastewater management. EPA used several research collections and search engines[10] to identify over 130 documents that were subject to EPA's quality assurance standards and procedures for inclusion in a literature review (these standards are described in Section 6 of this report). EPA categorized the documents into three topic areas:

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[10] Research collections and search engines used include Kirk-Othmer Encyclopedia of Chemical Technology, Google Scholar, Dialog, The Strategic Environmental Research and Development Program (SERDP)-Environmental Security Technology Certification Program (ESTCP), Rowan Technology Group, Science Direct, ACS Publications, Academic Search, Directory of Open Access Journals, and PLOS One.

- *Process technology* documents*,* addressing improvements in metal finishing process techniques and technologies that lower air emissions, reduce chemical use, or decrease wastewater pollutant discharges.
- *Alternative chemistries* documents discuss innovative metal finishing chemistries that can be used to reduce toxicity, wastewater volume, and pollutant discharges.
- *Wastewater treatment technology* documents discuss innovative technologies to reduce wastewater pollutant concentrations and strategies to achieve zero liquid discharge at metal finishing facilities.

A significant portion of the preliminary findings of this study to date (presented in Section 4 of this report) is based on the data and information gathered from the literature review.

3.2 Technical Conferences

EPA attended the Water Environment Federation's Annual Technical Exhibition and Conference (WEFTEC) on September 26-30, 2015. WEFTEC provides water quality education and training by offering technical sessions and workshops on a variety of topics and provides access to information from exhibitors on water management technologies and services. EPA attended presentations and obtained papers from proceedings relevant to the general categories listed in Section 3.1. EPA plans to review publications from WEFTEC regarding metal finishing wastewater management practices, to support the preliminary study of the industry.

EPA also attended the Engineers' Society of Western Pennsylvania's International Water Conference (IWC) on November 15-19, 2015. IWC discusses the most recent scientific advances and practical applications for treatment, use, and reuse of water for engineering purposes, industry or otherwise. Presenters and attendees of the IWC include researchers, practicing engineers, managers, educators, suppliers, contractors, government workers, and end users. EPA plans on reviewing IWC presentations and papers relevant to the metal finishing industry in support of the preliminary study.

EPA plans to continue seeking other technical conferences to further inform the Agency on current industry practices.

3.3 Industry Experts

EPA contacted a variety of experts to improve its understanding of the metal finishing industry and to gain different perspectives on the 1983 regulations and current industry operations.

3.3.1 Metal Finishing Facilities and Technology Vendors

EPA contacted personnel from metal finishing facilities and technology vendors advertising zero discharge systems for the treatment of metal finishing wastewater (ERG, 2016). EPA identified and selected facilities and vendors based on: recommendations by other industry experts and trade groups; directories and/or marketing databases; information from previous EPA data collection efforts; and other publicly available information on metal finishing operations and wastewater treatment technologies of interest to the study. Information collected from vendor and facility contacts fulfilled several objectives of the preliminary study: 1) to obtain information that helps answer key study questions; 2) to identify potential candidate facilities for future EPA site visits; 3) to obtain industry perspectives on the existing 1983 Metal Finishing ELGs; and 4) to initiate assessment of the technical and economic feasibility of waste minimization practices. EPA plans to continue calling additional metal finishing facilities and technology vendors to pursue these objectives further.

3.3.2 Pretreatment Coordinators

As discussed in Section 2, the majority of metal finishing facilities are indirect dischargers subject to pretreatment standards under the Metal Finishing ELGs. As part of the Metal Finishing Category Review under EPA's annual review process (CWA §304m), EPA had discussions with the federal pretreatment coordinator and regional pretreatment coordinators who have direct experience with metal finishing wastewater issues at POTWs. These personnel provided insight on the applicability of the Metal Finishing ELGs. The coordinators described key issues encountered by POTWs receiving metal finishing wastewater, primarily from new or modified metal finishing processes. Issues included misapplication of limits in permit applications, applicability of the 46 metal finishing unit operations, and new source criteria development (U.S. EPA, 2015a). As part of the preliminary study, EPA will continue to have discussions with the coordinators to identify metal finishing scenarios for which the applicability of the regulations is unclear.

3.3.3 Other Stakeholders

EPA held meetings with the Association of Clean Water Administrators (ACWA) and several pretreatment coordinators in November 2015 to gather different perspectives on the metal finishing category (U.S. EPA, 2015d). EPA also plans to initiate discussions with other organizations, such as the National Association of Clean Water Agencies (NACWA), to understand their perspective on the implementation of the 1983 regulations.

3.4 Industry and Trade Organizations

In response to EPA's published plans to further review the Metal Finishing Category under CWA §304m authority, the National Association for Surface Finishing (NASF) reached out to EPA to support EPA's information gathering efforts for the preliminary study (U.S. EPA, 2015b, 2015c). NASF is a trade association representing the interests of the North American surface finishing industry, including metal finishing. At NASF's invitation, EPA spoke at the NASF Washington Forum on April 14-16, 2015, to discuss the Agency's plans to review the metal finishing industry. EPA also met with NASF in August and November 2015 to discuss the preliminary study of the Metal Finishing Category (NASF, 2015; U.S. EPA, 2015e, 2015f). EPA and NASF will continue discussions on approaches for collecting information on the industry to answer key study questions and to explore potential opportunities to collaborate with industry and provide additional outreach activities.

3.5 Site Visits to Metal Finishing Facilities

To date, EPA has accompanied pretreatment coordinators on visits to the Bureau of Printing and Engraving (Washington, D.C.), Bethesda (Maryland) Art Metal Works, and Metro Plating and Polishing (Kensington, Maryland).

EPA will continue site visits to metal finishing facilities to observe operations and wastewater management practices. EPA may also request information, such as historical data on raw and treated wastewater samples, general process design, and typical operating conditions. EPA may also obtain information on the wastewater treatment technologies and treatment chemicals used on site. EPA will use information gathered through industry experts (as described in Section 3.3) to identify potential site visit candidates for the coming year.

3.6 Metal Products and Machinery (MP&M) Rulemaking

EPA will continue to review supporting documentation from the MP&M proposed rulemaking (proposed in 2000), which evaluated facilities covered under the Metal Finishing ELGs in the 1980's and 1990's. As part of that proposed rulemaking, EPA extensively reviewed the changes to the metal finishing industry, process and wastewater technology improvements made by the industry, and metal finishing wastewater characteristics. EPA will evaluate any significant changes to the industry since its review during the MP&M proposed rulemaking of 2000, which will further define the scope of this study.

4. PRELIMINARY STUDY FINDINGS

This section describes the information EPA gathered to date for the preliminary study of the Metal Finishing Category, which will help answer the key study questions outlined in Section 1 of this report. EPA summarized the findings into five main categories that are presented in the following subsections:

- Changes in the metal finishing industry profile (Section 4.1),
- Process technologies (Section 4.2),
- Alternative chemistries (Section 4.3),
- Wastewater treatment technologies (Section 4.4), and
- Applicability and other regulatory considerations (Section 4.5).

4.1 Changes in the Metal Finishing Industry Profile

As discussed in Section 2.1, at promulgation of the 1983 Metal Finishing ELGs, the Metal Finishing and Electroplating Categories included a total of 13,470 facilities, consisting of 10,000 captive facilities and 3,470 job shops and IPCB manufacturers. The existing captive facilities ultimately fell into the Metal Finishing Category (after the final compliance date) and the 3,470 job shops and IPCB manufacturers remained in the Electroplating Category (U.S. EPA, 1984). EPA has not fully evaluated the changes to the number of facilities in the metal finishing industry as part of this preliminary study. However, several EPA efforts have collected recent information on this population.

In the MP&M proposed rulemaking (published in 2000), EPA estimated that approximately 12,700 facilities performed metal finishing operations. EPA classified the facilities into four subcategories: general metals, metal finishing job shops, non-chromium anodizing, and printed wiring boards (U.S. EPA, 2000a). The general metals category may have included facilities that did not conduct any of the six primary metal finishing operations that define the applicability of the Metal Finishing ELGs and, therefore, the number of facilities may be an overestimation of those covered under 40 CFR Part 433. These estimates were primarily based on responses to industry surveys sent to MP&M facilities in 1989 and 1996 (U.S. EPA, 2000a).

In 2012, EPA revised the National Emission Standards for Hazardous Air Pollutant (NESHAP) Emissions: Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks (Subpart N).[11] EPA estimated 1,339 existing U.S. facilities performing metal finishing operations that involved chromium. Outside California, there were 188 large and 394

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[11] EPA also revised the NESHAP for Steel Pickling-HCl Process Facilities and Hydrochloric Acid Regeneration Plants (Subpart CCC) in 2012; however, steel pickling facilities (estimated at 100 facilities) are subject to the Iron and Steel Category (under 40 CFR Part 420) and therefore, would not be regulated under the Metal Finishing Category (40 CFR Part 433).

small hard chromium electroplating facilities.[12] The distribution of large and small facilities was unknown in California, but there are approximately 70 additional hard chromium electroplating facilities there. There are an estimated 170 chromium anodizing plants and the 517 decorative chromium electroplating facilities in the U.S. (77 FR 58220). These estimates are a subset of the facilities comprising the metal finishing industry but provide a more recent look at the population of chromium electroplaters.

As part of EPA's 2014 Annual Effluent Guidelines Review, EPA searched for recent data to determine the number of facilities that currently fall into the Metal Finishing Category. The 2007 Economic Census provides a general industry description for each North American Industry Classification System (NAICS) code under which these facilities may fall; however, it does not detail facility-specific process operations or wastewater discharge practices, which form the basis for determining whether the Metal Finishing ELGs would apply to specific facilities. In the 2011 Annual Effluent Guidelines Review, EPA identified 166,356 facilities included in the 2007 Economic Census for the 200 NAICS codes. However, this number includes establishments that are distributors or sales facilities, not just manufacturers (U.S. EPA, 2012a). It may also include facilities that do not conduct any of the six primary operations and thus, would not be regulated under the Metal Finishing ELGs. In previous annual reviews, EPA has identified the number of facilities submitting discharge monitoring reports (DMRs) and reporting to EPA's Toxic Release Inventory (TRI). However, EPA determined that these data sources include only a fraction of the facilities that would fall under the Metal Finishing Category ELGs, due to the limitations of the data sets. Therefore, these data sources do not adequately provide a complete picture of the metal finishing industry (U.S. EPA, 2015a).

After discussions with regional and state pretreatment coordinators, EPA learned that some EPA regions and states have maintained lists of industrial users that discharge metal finishing wastewater to POTWs and are subject to pretreatment standards under 40 CFR Part 433; however, a national inventory of metal finishing facilities does not exist (U.S. EPA, 2015a). As discussed in Section 2.4.1, there is uncertainty in how the metal finishing industry profile has changed. EPA suspects that the industry has trended toward a wider market since 1983, with market share dispersed among many companies. Recent discussions with metal finishing facilities also suggest some growth of the U.S. metal finishing industry due to increased product quality demands in certain markets that cannot be met elsewhere (ERG, 2016).

Six Primary Metal Finishing Operations

40 CFR Part 433 applies to discharges from metal finishing facilities conducting any of the six primary operations: electroplating, electroless plating, anodizing, coating (chromating, phosphating, and coloring), chemical etching and milling, and printed circuit board manufacturing. If any of these six operations are conducted at a facility, then the provisions also apply to any of the 40 ancillary processes (which include cleaning and polishing) listed in 40 CFR Part 433, if any are also being conducted at the facility.

4.2 Process Technologies

EPA identified papers reporting advances in metal finishing process

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[12] As defined in the NESHAP, large hard chromium electroplating facilities are any facility with a cumulative annual rectifier capacity equal to or greater than 60 million ampere-hours per year (amp-hr/yr). Small hard chromium electroplating facilities are defined as any facility with a cumulative annual rectifier capacity less than 60 million amp-hr/yr.

techniques and technologies. The papers cover cleaning and rinsing operations, coating and plating processes, and polishing. Numerous modifications and process alternatives have been developed for these processes since the 1983 Metal Finishing ELGs were promulgated. The following subsections discuss the technological advancements in each process category.

4.2.1 Cleaning and Rinsing Operations

Most metal finishing operations require surface preparation including cleaning and rinsing. Cleaning and rinsing remove oil and dirt to ensure that the finishes applied during coating or plating properly adhere to the surface and meet performance expectations. Surface preparation can range from simple mechanical techniques, such as spray cleaning, abrasive blasting, buffing, or grinding, to more complex chemical techniques, such as acid washes and multi-stage acid/alkaline cleaning processes.[13] These techniques may be used alone or in combination to remove dust, grease, oils, oxides, base metal, and other materials from the surface of the object (U.S. EPA, 1979).

Acidic or alkaline chemicals are used as cleaning agents. According to studies done at the Rochester Institute of Technology and Wayne State University (Fister, 2010; Xiao, et al., 2012), cleaning and subsequent rinsing are the primary sources of wastewater from metal finishing facilities. However, alternative methods of cleaning and rinsing are increasingly used to reduce water use and chemical consumption (Fister, 2010; Xiao & Huang, 2012). In recent discussions with industry, EPA learned that cleaning and rinsing operations may be conducted over other rinse tanks or plating baths to collect and reuse the wastewater. Facilities have also implemented countercurrent rinse cycles to reduce the replacement frequency of the rinsewater used in rinsing operations (ERG, 2016).

The Wayne State study reviewed the growing use of "integrated profitable pollution prevention" (IP3) techniques by metal finishers to reduce water use and chemical consumption (Xiao & Huang, 2012). That study identified the following five IP3 technologies:

- A cleaning and rinse process control method that uses a two-layered hierarchical dynamic optimization technology to conserve chemical and water use. The lower layer adjusts local control variables, such as chemical concentration and water flow rate, to optimal settings. The upper layer uses the optimal processing time in all the cleaning and rinse tanks to achieve the desired surface characteristics. The two layers, when used together, maximize cleaning and rinsing efficiency, thereby minimizing chemical use and conserving water.
- Re-designing water flow patterns through a rinsing system to optimize flow rates. The water flow patterns can be switched during operation (based on current use) to maximize water reuse while maintaining rinse water quality.
- A sludge reduction method to classify sludge as avoidable or unavoidable. The method determines the amount of avoidable sludge and reduces it by altering the chemical use and identifying unnecessarily long cleaning times.

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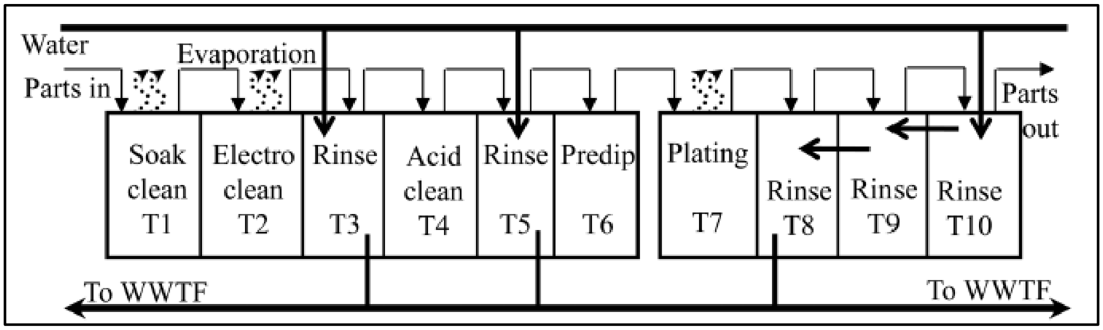
[13] Acid washes are subject to Metal Finishing ELGs (U.S. EPA, 2004).

- A model-based design and operation strategy to derive an optimal reversed drag-out network system to recover chemical losses from cleaning and plating systems.
- A dynamic hoist scheduling algorithm to generate a production schedule based on waste generation, chemical consumption, and energy use.

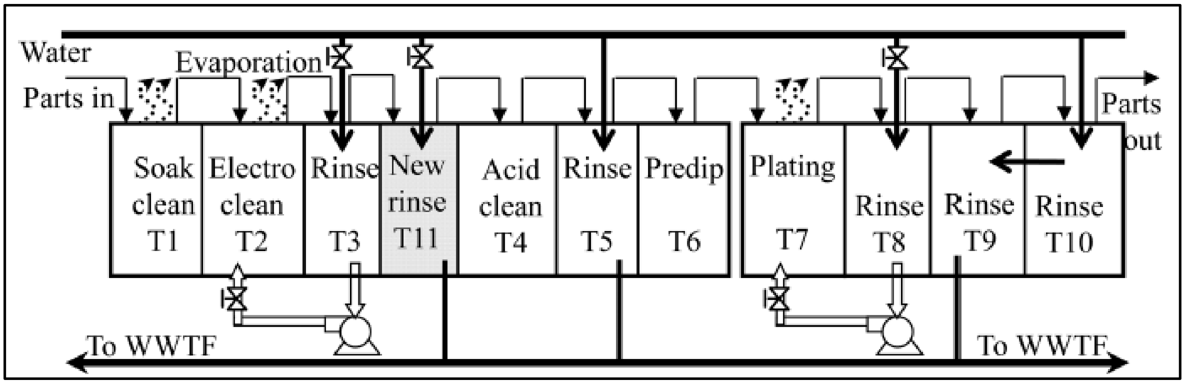
To demonstrate the effectiveness of IP3 technologies, the researchers also described a manually operated bronze cyanide plating line at a facility that implemented a near-zero chemical and metal discharge system, intended to reduce chemical consumption and water use (Xiao & Huang, 2012). Figure 4-1 presents the original configuration of the bronze cyanide plating line. Each rack of parts is first cleaned (soak cleaning and electro cleaning or de-rusting) and then rinsed. As shown in the diagram, the initial cleaning and rinsing are followed by an acid clean step, followed by another rinse before the actual copper and tin plating (Xiao & Huang, 2012).



Source: (Xiao & Huang, 2012)

Figure 4-1. Original Process at the Bronze Cyanide Plating Facility

Figure 4-2 presents a revised rinsing configuration. The facility installed a new rinse tank (Tank 11) so chemical solvents from the soak clean and electro clean steps, accumulated in Rinse Tank 3, could be recovered and reused. The tank before New Rinse Tank 11 is charged for static rinse, and New Rinse Tank 11 is for flow rinse. Rinse Tank 8 is also charged for static rinse, while Rinse Tanks 9 and 10 are countercurrent rinse tanks. Two pumps are added to the system, one to pump the solution from Rinse Tank 3 to the electrocleaning tank, and one to pump water back to the plating tank from Rinse Tank 8 (Xiao & Huang, 2012).



Source: (Xiao & Huang, 2012)

Figure 4-2. New Process at the Bronze Cyanide Plating Facility

After making these changes, the facility reduced use of the derusting chemicals (used in the electroclean and acid clean steps) by 40 percent, the soak cleaners by 100 percent, and the acid by 8 percent. Rinse water costs were reduced by 40 percent and wastewater treatment costs were reduced by 70 percent. According to the study authors, implementation of profitable pollution prevention techniques typically involve slight modifications of processes, which require little capital investment but can increase efficiency and reduce waste (Xiao & Huang, 2012).

Traditional rinsing methods include independent rinse tanks, with rinse water flowing in and out of each tank, and countercurrent rinsing, with relatively clean rinse water flowing from the second rinse tank to the more contaminated primary rinse tank. The top diagram in Figure 4-3 shows a typical rinse system with four independent rinse tanks; and the bottom diagram depicts a reduced flow rinse scheme (Fister, 2010).

The study done by the Pollution Prevention Institute (PPI) at the Rochester Institute of Technology (Fister, 2010) indicates that reactive rinsing can be used to reduce water use in rinsing processes that include both acid and alkaline rinse tanks. In a reactive rinse system, as shown in the bottom diagram of Figure 4-3, the acid from the acid rinse is sent to a preceding alkaline rinse tank where it neutralizes residual alkalinity in the water. In traditional rinsing methods, the acid contained in the rinse water is sent to be treated. Reactive rinsing allows any rinse water from the alkaline rinse that is dragged out by parts to the acid tank to now contain acid that would have otherwise been wasted (Fister, 2010). According to Fister (2010), the total water use for a rinse system with four independent rinse tanks is 12 gallons per minute (gpm) (top diagram, Figure 4-3). By incorporating reactive rinsing into a reduced flow rinsing scheme (bottom diagram, Figure 4-3), the water use is 3 gpm. This results in a savings of $5,400 per year in water costs (at a rate of $5 per 1,000 gallons for a 2,000 hours-per-year operation) (Fister, 2010).

Powder coating facilities commonly use phosphate-based cleaning and rinsing systems before painting large fabricated products. Conventional cleaning and rinsing systems are generally separate and use large amounts of water and chemicals to clean, degrease, and apply a pretreatment chemical to products (Guidetti, et al., 2009). EPA identified two alternatives to conventional phosphate-based cleaning and rinsing systems: the Cleaner Phosphoric Recycling (CPR) System and the plaforization process.

From reviewing vendor literature and a facility case study, EPA found that CPR Systems, a division of T. George Podell & Co, Inc., has developed the CPR System primarily for companies that manufacture large fabricated steel and aluminum products. The CPR System incorporates non-rinse cleaning, degreasing, and pretreatment in one-step. PhosBite 101, a combined cleaning and coating chemical, is used in the wash water to surface clean and generate a conversion coating on the metal substrate to improve paint adhesion. Water and chemicals used in the system are recycled, greatly reducing water and chemical use compared to conventional systems. The CPR system was introduced in 1989. According to CPR Systems, over 100 facilities in the United States have installed the CPR System (ERG, 2016; Tucker, 2013).

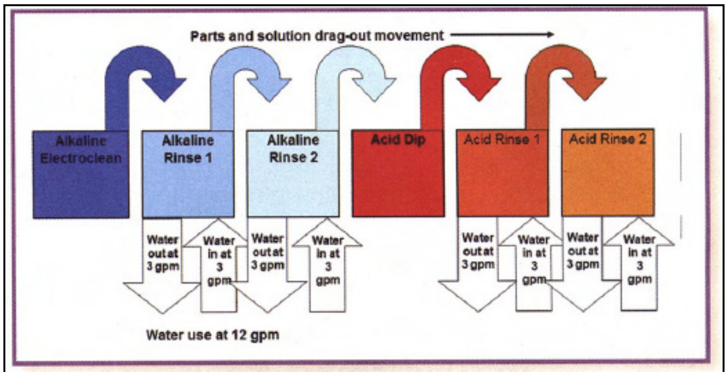


Figure 1. Rinse system with four independent rinse tanks.

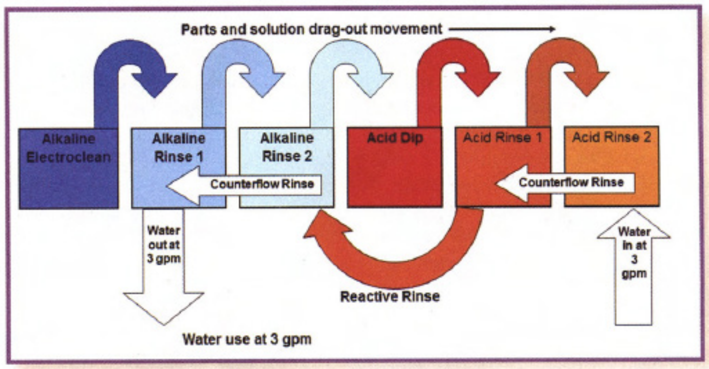


Figure 2. Maximized use of counterflow and reactive rinses.

Source: (Fister, 2010)

Figure 4-3. Potential Rinse Systems in Facility with Metal Finishing Processes

A powder coating facility in Pennsylvania installed the CPR System in 2013 to clean and pretreat large hydraulic dump trailers, while also decreasing water and chemical use. Facility contacts reported that after learning to use the new process, they were able to reduce chemical and water consumption by 70 percent, primarily through recycling (Tucker, 2013).

From reviewing industry literature, EPA identified the plaforization process, a second alternative to conventional phosphate-based cleaning and rinsing systems. The technology was first introduced in the European market by PAI-KOR S.r.l, in Italy, in the late 1960s. As of 2009, approximately 500 industrial facilities in more than 25 countries had incorporated plaforization processes. Plaforization is a one-step process with no rinse; it does not use water and creates no wastewater, sludge, or other contaminants (Guidetti, et al., 2009).

The chemistry is based on organic high-boiling-point fluids and an organic polymeric resin modified by phosphating groups. Several different processes occur almost simultaneously: organic fluids dissolve oily contaminants, solid particles are washed off and taken into the solution, the phosphating acid part of the organic resin attacks the metal surface to clean and pretreat the metal. Finally, an organic polymeric resin is applied to the part with a thickness of about one micron (Guidetti, et al., 2009).

According to the developer of plaforization, the process eliminates the need for continuous chemical analysis, dumping tanks, chemical replenishment, and sludge removal, all of which are required with conventional phosphate-based cleaning and rinsing systems (Guidetti, et al., 2009). Plaforization also allows many metals, such as steel, aluminum, and cast iron, to be treated with the same chemistry (Guidetti, et al., 2009). Figure 4-4 shows an example of a plaforization system installed for batch spraying equipment. In this system, parts are manually hung in the washer; the unit is equipped with three risers with nozzles that move during treatment to completely bathe all the part surfaces.

Source: (Guidetti, et al., 2009)

Figure 4-4. Plaforization System for Batch Spraying Equipment

4.2.2 Coating and Plating Processes

Numerous coating types are used in metal finishing, including transition metal coatings, hexavalent and trivalent chromium coatings, and graphene nanocomposite coatings. In 2008, the Strategic Environmental Research and Development Program (SERDP), an environmental research program under the Department of Defense (DoD),[14] completed a study on ultraviolet (UV)-curable, corrosion-inhibiting primers and high-performance topcoats that protect aluminum substrates, specifically for aircraft interiors. Conventional coatings used for DoD vehicles release volatile organic compounds (VOC) during application and curing. Additionally, while the equipment is in use, flaking and chipping of the coating can cause hazardous substances, such as hexavalent chromium, to enter the environment. The goal of DoD's study was to test a combination of chromate-free and VOC-free substrate preparation and coating systems to identify a coating system that eases compliance with current and anticipated environmental regulations, and at the same time makes coating application simpler and faster. Results from the study indicated that all tested coating systems provided good adhesion, fluid resistance, impact and solvent resistance, and low-temperature flexibility, making them viable alternatives to conventional coatings. These coating systems do not release VOCs during application or curing, and minimize flaking and chipping, thereby reducing hazardous materials (such as hexavalent chromium) in the environment. The process tested can be used in many industries and products,

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[14] Two environmental research programs exist under the DoD: the Strategic Environmental Research and Development Program (SERDP), and the Environmental Security Technology Certification Program (ESTCP).

including aircraft and spacecraft, ground and marine vehicles and equipment for all military branches, and industrial coatings in chemical and mechanical plants (Phely-Bobin, 2010).

A study performed at the University of Ulster investigated the corrosive response of hot rolled steel (HRS) after exposure to various pre-powder-coating surface treatments (Tepe, et al., 2008). Powder-coated HRS is used extensively in the automotive, agricultural, and appliance industries, among others. The study reviewed conventional pre-powder coating treatments, including iron and zinc phosphate, as well as newer nano-structured conversion coatings (such as zirconium-based coatings). The study reported that the nano-structured conversion coatings perform as well as or better than the conventional coatings, and can enhance the corrosion resistance of powder coated HRS. However, researchers determined that achieving the optimally effective corrosion barrier with zirconium-based nano-scaled conversion coatings requires the removal of oxide scale from the substrate before any pre-powder-coating treatments (Tepe & Gunay, 2008). Zirconium-based coatings are further discussed in Section 4.3.

According to a study on the use of ionic liquids in metal finishing practices, conventional coating and plating processes based on aqueous technologies such as cyanide or hexavalent chromium are well established in the metal finishing industry (Smith, et al., 2010).[15] However, many companies are feeling pressure to develop new coating and plating processes in order to increase process efficiency, decrease energy use and wastewater discharges, and reduce the use of toxic chemicals (Smith, et al., 2010). Due to this pressure, the New Ionic Liquid Solvent Technology to Transform Metal Finishing Products and Processes (IONMET) consortium was developed in Europe. The IONMET project consists of 33 partners, including industrial companies, trade associations, and research institutions. The overall objective of the project is to introduce breakthrough ionic liquid technology into metal finishing processes. Ionic liquids are ionic materials that are liquid below 100 degrees Celsius and have properties that make them well-suited for metal finishing, such as high solubility of metal salts, high conductivity, and unique metal ion coordination chemistry (Smith, et al., 2010).

The IONMET consortium scaled up five room temperature ionic liquid metal deposition processes:

- Electropolishing;
- Hard chromium electroplating;
- Aluminum plating;
- Immersion silver displacement; and
- Zinc-tin barrel plating.

The IONMET consortium found that in all five processes, ionic liquids could be considered drop-in replacements for existing aqueous solutions composed of strong inorganic acids and toxic reagents (i.e., all five processes are effective metal coating processes). Ionic liquids are easy to handle, inexpensive, and have low toxicity, making them attractive alternatives to conventional coating and plating solutions. The IONMET consortium stated that

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[15] Ionic liquids are salts in the liquid state, which act as powerful solvents or electrically conducting fluids.

further research is necessary, but that ionic liquids have a high potential to be incorporated into metal finishing processes (Smith, et al., 2010).

In the United States, SERDP is researching the application of ionic liquids. The DoD expects this research to illuminate key mechanisms and process variables for using ionic liquids in electroplating aluminum, specifically related to weapon systems. The project is expected to be completed in 2016 (Dai, 2014).

According to industry experts, brush plating, also known as spot plating, is an electroplating process in which a pad is used to apply aqueous coatings, such as nickel, hard chromium, silver, etc., to a substrate (Chaix, et al., 2013). Advantages of brush plating include low costs, limited need for extensive air handling or scrubbing, and portability. However, it can be messy, with drips and splatters, and is best used for small areas. An alternative to brush plating is brush electrofinishing, which features a computerized non-drip stylus. According to industry experts, brush electrofinishing can be performed in any orientation, including overhead, and it eliminates drips, splashes, and most of the fumes associated with brush plating (Chaix, et al., 2013). The brush electrofinishing technique can reduce air emissions and replace toxic materials with less toxic alternatives, while still maintaining process control (Chaix, et al., 2013).

4.2.3 Polishing

Polishing (i.e., smoothing out surface defects) is typically one of the final steps in metal finishing. According to industry literature, some polishing is traditionally done by hand, making it one of the most time-consuming and expensive steps in metal finishing (Pusavec, et al., 2014). An alternative to hand polishing is abrasive flow machining (AFM), in which the flow of a pressurized abrasive polymer medium removes excess material from part surfaces. Pusavec and Kenda (2014) researched the performance and energy efficiency of AFM, focusing on an upgrade of AFM that incorporates a movable/rotatable mandrel (AFMmm). Their study looked at a computer simulation of AFMmm in the finishing of gear injection molds and performed fatigue and performance tests. They concluded that the AFMmm finishing system uses less polishing fluid and energy compared to the traditional AFM system and hand polishing, which improves the efficiency and environmental impact of the technology (Pusavec & Kenda, 2014).

4.2.4 Summary of Process Technologies

Based on recent literature and industry discussions, there are a few reasons for which industry would consider process technology advances: 1) to improve the efficiency of the coating/finishing operation; 2) to implement pollution prevention strategies that would reduce the impact of the pollutants generated and discharged; and 3) to reduce the operating costs associated with chemical usage, wastewater treatment, and hazardous solid waste disposal.

Industry discussions have suggested that wastewater management and solid waste disposal generally play a significant role in the overall operating costs at metal finishing facilities. Recycling generated wastewater and chemicals back to the process minimize the need for the facility to replenish with a separate water source or with new chemicals. Minimizing the chemical usage can also reduce the volume of sludge generated and disposed during wastewater treatment. EPA learned that several facilities are implementing pollution prevention practices to minimize the volume of wastewater discharged, including a countercurrent rinsing system and replenishing plating baths that have evaporative losses with both untreated and treated rinsewater (ERG, 2016). To date, EPA has not found information that suggest that the primary sources of wastewater has changed. A significant portion of the wastewater generated continues to originate from rinsing and cleaning operations. Improvements to coating and plating processes have not shown to generate additional waste streams and generally aim to minimize the amount of process losses associated with the technology. Several facilities and vendors suggest that chemical recovery operations do occur at metal finishing facilities to minimize the need to treat and dispose of process losses containing valuable plating chemicals as waste (see Section 4.4 for information of technologies used for this purpose).

4.3 Alternative Chemistries

At the promulgation of the 1983 Metal Finishing ELGs, facilities covered by the ELGs operated one of six primary operations, including electroplating, electroless plating, anodizing, coating, etching and chemical milling, and printed circuit board manufacturing. Generally, these six operations produce a coating on the surface of the base materials that consist of a metal or metal oxide. See Section 2 for detailed descriptions of the traditional chemistries used in these six metal finishing operations, as well as the 40 additional unit operations regulated by the ELGs.

EPA's literature review identified papers reporting on alternatives to the traditional chemistries used in metal finishing operations, primarily alternatives to chemistries using cadmium, hexavalent chromium[16], phosphate, and cyanide. Exposure to these materials may result in adverse health and/or environmental impacts. In addition, solid waste and wastewater generated from these materials result in high costs for hazardous waste disposal. The following subsections discuss alternatives to the most common metal finishing chemistries: cadmium plating, the use of hexavalent chromium in plating, conversion coating, primers, sealers, and cleaners, phosphate conversion coatings and cleaners, and cyanide in plating baths.

4.3.1 Cadmium Plating Alternatives

Cadmium is widely used in electroplating and electroless plating operations to provide corrosion protection in applications for the aerospace, military, and aviation fields. Cadmium-plated high-strength steel is used in aircraft, spacecraft, and components of weapon systems. According to Keith Legg of Rowan Technology Group, the aerospace and military industries have successfully replaced most cadmium coatings used on nuts and bolts with a safer zinc-nickel plating alternative (K. Legg, 2012a). However, industry has not identified replacements for cadmium plating on structural materials because of the strict requirements for high corrosion resistance and a narrow margin for material fatigue (Berman, et al., 2009). According to the literature, the aerospace and military industries are considering potential cadmium alternatives

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[16] Chromium is a naturally occurring element, and primarily occurs in the environment in two valence states: trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Trivalent chromium occurs naturally, is an essential nutrient, and is much less toxic than hexavalent chromium. Hexavalent chromium and metallic chromium are most commonly produced by industrial processes.

for protective shells on electrical connectors and steel fasteners, as well as for brush plating repair solutions.[17]

Table 4-1 presents the cadmium-free alternatives reported in literature and the processes used to apply them. Aluminum deposition uses glass bead peening (GBP) (Aguero, et al., 2012), atmospheric pressure, chemical vapor deposition (APCVD) (Berman & Brooman, 2009), and the ion vapor deposition (IVD) (K. Legg, 2012a). Electroplating processes use tin-zinc alloys and zinc-nickel alloys as alternatives to cadmium, and etching electroless plating processes use nickel alloys (R. Mason, et al., 2010; Orduz, 2008)). According to one industry representative, commercially available coating systems use 20 to 30 percent zinc in tin-zinc alloys, and 5 to 15 percent nickel in zinc-nickel alloys, to provide the best performance (R. Mason, et al., 2010).

Table 4-1. Process Descriptions of Cadmium-Free Alternative Coatings

Cadmium Alternative	Coating Process	Process Description	Source
Aluminum	Glass bead peening (GBP)	Parts are sand-blasted and vapor-degreased prior to coating. The coating slurry is applied by brush, immersion, or spray gun and cured using a proprietary curing process under air, followed by glass bead peening.	(Aguero, et al., 2012)
	Atmospheric pressure chemical vapor deposition (APCVD)	Parts are cleaned, subjected to a tri-isobutyl-aluminum coating in a deposition chamber, using nitrogen as the carrier gas and an induction heater to deposit aluminum at temperatures between 275 and 300 degrees Celsius. After removing from the chamber the surface may or may not be treated with a conversion coating.	(Berman & Brooman, 2009)
	Ion vapor deposition (IVD)	Parts are placed in a vacuum chamber and subjected to ionized gas (typically argon), which generates a glow discharge and acts as a cleaning process prior to coating. Pure aluminum is added to the chamber and deposited onto the surface. As the coating is formed, ions from the glow discharge attract to the aluminum and increase the coating's density.	(R. Mason, et al., 2010)
Tin-Zinc Alloy	Electroplating	Parts are electroplated in a bath of an aqueous solution containing a tin-zinc alloy composed of 20 to 30 percent zinc.	(R. Mason, et al., 2010)
Zinc-Nickel Alloy	Electroplating	Parts are electroplated in a bath of an aqueous solution containing a zinc-nickel alloy composed of 5 to 15 percent nickel.	(R. Mason, et al., 2010)
Nickel	Etching Electroless plating	Parts are soaked in an acid cleaner, and acid etched. Parts are submerged in a nitric acid solution, then a zincate ($Zn(OH)_4^{2-}$) solution, then placed in each solution once more before plating in an electroless nickel bath. Parts are rinsed between each step.	(Orduz, 2008)

When tested against a cadmium coating, the GBP aluminum coating demonstrated comparable or better performance, exhibiting higher fatigue strength and equal corrosion resistance. According to the study, the coating process produces significantly less process waste compared to electroplating, and is therefore more cost-effective (Aguero, et al., 2012). A study

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[17] Brush plating is a portable process where an electroplated or anodized coating is applied locally to a metal part, focusing only on the specific areas that require the coating.

on APCVD aluminum coatings by the Air Force Research Laboratory presented several advantages. The study found that no vacuum chamber, pumps, or ancillary control equipment are needed for coating. The process allows for higher throughput due to short processing times and provides consistent and even coating thickness across the part. However, drawbacks to APCVD aluminum coatings include susceptibility to embrittlement when exposed to hydrogen gas, unacceptable performance in handling fatigue, and less lubricity than traditional coatings, which allow parts to operate more smoothly (Berman & Brooman, 2009). The aircraft industry has used IVD aluminum for years on high-strength steels; however, the vacuum deposition method is significantly more expensive than cadmium plating (K. Legg, 2012a). An ongoing project by the Environmental Security Technology Certification Program found that high purity aluminum plating applied to high strength steel fasteners combined with an electrocoated topcoat was comparable to cadmium plating in corrosion resistance. Aluminum coating is potentially costlier than cadmium plating (Scott, 2013).

Non-aluminum alloy coatings are primarily made from tin-zinc and zinc-nickel alloys, of varying composition. A tin-zinc alloy coating, specifically tin-20 wt. percent zinc, provided efficient electrochemical protection and superior corrosion protection compared to both cadmium and zinc-nickel coatings, but also has a slightly higher friction coefficient (Dubent, et al., 2010). Zinc-nickel coating exhibited sufficient adhesion after bending, adhesion to paint, long-term corrosion resistance, and resistance to embrittlement when exposed to hydrogen gas; however, the coatings only performed marginally better when tested for environmentally induced cracking. Boeing determined that zinc-nickel plating is a commercially acceptable cadmium replacement for use on component parts made of low strength steel, stainless steel, aluminum, and copper alloys (Indumathi, et al., 2011; R. Mason, et al., 2010). A zinc coating consisting of an inorganic metal flake dip-spin coating offered high corrosion resistance with an equal or lower cost than cadmium (Scott, 2013). A zinc-nickel brush plated coating for repairing weapon systems was found to have several advantages compared to cadmium, mainly in cost savings – the plating solution is recycled and reused in a closed-loop process (Slife, 2014).

Lastly, Uyemura Corporation developed a cadmium- and lead-free electroless nickel coating system that provides a long bath life, corrosion resistance, and passed bend testing without blistering or flaking the plated aluminum sheet (Orduz, 2008).

Although the chemistries reviewed eliminate the use of cadmium coatings, some may require post-treatment conversion coatings to improve corrosion resistance and paint adhesion. For example, the APCVD process described in Table 4-1 may use a hexavalent chromium-based conversion coating (i.e., chromate conversion coating), which would also present health and environmental concerns (Berman & Brooman, 2009).

4.3.2 Hexavalent Chromium Plating, Conversion Coating, Primer, Sealer, and Cleaner Alternatives

Hexavalent chromium finishing processes provide self-healing corrosion protection and improve adhesion between the paint and metal surface. Hexavalent chromium is applied in hard chrome plating conversion coating, in primers and paint, and with anodizing processes (K. Legg, 2012b). Hexavalent chromium is hazardous to human health and the environment, and therefore, researchers are exploring and developing alternatives that would reduce human and environmental exposure to the chemical during use and disposal.

Hexavalent chromium may be present in wastewater generated by a facility and when further treated, may end up in wastewater discharged to POTWs or surface waters and wastewater sludge. Hexavalent chromium is also volatile and likely present in the air emissions surrounding open tank baths. The Office of the Secretary of Defense in 2009 issued a memorandum restricting the use of hexavalent chromium unless no cost-effective alternatives that provide satisfactory performance are available (K. Legg, 2009). These actions pushed defense and other industries to identify and adopt alternatives to hexavalent chromium. According to Paul Wynn of MacDermid, for chromium-free alternatives to be widely adopted, cooperation is required along the entire metal finishing supply chain to achieve low operating costs, high performance, and best practice techniques (Morose, 2013; Wynn, 2006).

In EPA's review, EPA identified alternatives to hexavalent chromium that replace it with a less toxic metal or that substitute a mechanical treatment step that imparts similar surface characteristics, or a combination of both. The following sections discuss hard chrome plating alternatives, chromate conversion coating alternatives, and alternatives for chromium-based primers, sealers, and cleaners.

4.3.2.1 Hard Chrome Plating Alternatives

Hard chrome plating applies a thin layer of chromium metal to a base metal by electroplating in a chromic acid solution. Hard chrome plating[18] is used to make industrial equipment and automobile parts wear- and corrosion-resistant. Since chromic acid contains hexavalent chromium, researchers are testing alternative treatments for a variety of applications. Table 4-2 presents examples of commercially available alternatives to hard chrome plating, their market applications, and descriptions of the chemistries of each method. Commercially available alternatives include thermal spraying with high velocity oxygen fuel (HVOF), which can replace hard chrome plating of parts for commercial and military aircraft, off-road vehicles, and hydraulic systems. The Air Force began implementing HVOF coatings on landing gear components in 2003. HVOF sprays provide high performance, but according to industry experts, the spray process is not as forgiving as hard chrome plating and requires more preparation, training, and process control (K. Legg, 2008; K. Legg, 2010, 2012b; Sartwell, et al., 2004).

Table 4-2. Commercially Available Hard Chrome Plating Alternatives

Alternative Methods	Typical Applications	Description of Alternative Chemistries	Sources
Thermal spray (high velocity oxygen fuel, etc.)	Aircraft landing gear, hydraulic rods, industrial rolls	Thermal spraying can be performed with a wider range of coating materials than hard chrome plating, including materials that incorporate non-hexavalent chromium. The most common materials used in thermal sprays are chrome carbide-nickel chrome (Cr_3C_2-NiCr) and tungsten carbide-cobalt (WC-Co or WC-CoCr). The chromium in these coating materials is not in hexavalent form.	(K. Legg, 2012c)

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[18] Hard chrome plating is used as a protective layer for increased corrosion resistance, while decorative chrome plating is used to provide metal parts with a bright and shiny finish.

Table 4-2. Commercially Available Hard Chrome Plating Alternatives

Alternative Methods	Typical Applications	Description of Alternative Chemistries	Sources
Electroplating and electroless plating	Aircraft engines, internals (especially electroless Ni)	The most common chromium-free electroplates are based on nickel; other available materials are based on nickel-tungsten, nickel-tungsten-boron, and nickel-tungsten-boron combined with silicon carbide. Cobalt-based electroplates are also used, including a nanocrystalline cobalt phosphorous alloy plating. Electroless nickel plating alternatives to chromium include nickel-phosphorous and nickel-boron.	(K. Legg, 2012c; Prado, et al., 2010)
Heat treating	Hydraulic rods, gears, bearings	Heat treating puts metal through cycles of high temperatures and cooling in a controlled atmosphere. Processes include nitriding, carburizing, and nitrocarburizing, which add nitrogen, carbon, and both, respectively, to the surface of the metal. The controlled heating and cooling cycles harden the surface.	(K. Legg, 2012c)
Vacuum coatings	Typically small, high value items, molds, and dies	Physical vapor deposition (PVD) vacuum coating most commonly uses titanium nitride, chromium nitride, and various diamond-like coatings. Chromium nitride contains chromium in trivalent form.	(K. Legg, 2012c)
Welding methods	Rebuild of worn or corroded items	Welding involves melting the surface of the treated material; hence, only materials that can withstand the required heating can be welded successfully. Welding replaces chromium application with a mechanical method, instead of chemical alternatives, to impart similar properties (e.g., wear resistance).	(K. Legg, 2012c)

The hard chrome plating alternatives presented in Table 4-2 have advantages and disadvantages, described below in Table 4-3.

Table 4-3. Advantages and Disadvantages of Hard Chrome Plating Alternatives

Alternative Methods	Advantages	Disadvantages	Sources
Thermal spray (high velocity oxygen fuel, etc.)	Harder and more wear resistant; can rebuild; spraying is faster than hard chrome plating.	Require more careful process control; spraying requires constant attention.	(K. Legg, 2012c)
Electroplating and electroless plating	Drop-in chrome replacement due to similar bath process; cobalt-phosphorous plating exhibited good wear and corrosion resistance in a lab-scale study; electroless nickel is a very flexible process and can apply uniform coatings to complex parts.	Generally no better than chrome; nickel electroplating baths periodically require complete replacement; alternatives may be based on alloys that are usually more complicated than elemental coatings.	(K. Legg, 2012c; Prado, et al., 2010)
Heat treats	Almost any size and shape; not a coating process and therefore cannot come off as coatings can.	Cannot be used for rebuild or for heat-sensitive materials.	(K. Legg, 2012c)
Vacuum coatings	Extremely hard and wear resistant, can be cost effective on small components.	Complex and expensive; cannot be used for rebuild; highly sensitive to contaminants.	(K. Legg, 2012c)
Welding methods	Good for thick coatings, mostly on externals, can be highly controlled and automated.	Not for heat sensitive materials, must be refinished.	(K. Legg, 2012c)

4.3.2.2 Chromate Conversion Coating Alternatives

The metal finishing industry is developing alternatives to hexavalent chromium-based conversion coatings, also referred to as chromate conversion coatings. Chromate conversion coatings are widely used in the aircraft and defense industries, on large components as well as on screws, nuts, and bolts, to provide corrosion resistance and self-healing properties (K. Legg, 2009). Several alternatives are undergoing laboratory testing and some are commercially available. Table 4-4 lists chromate conversion coating alternatives and descriptions of their performance.

Table 4-4. Chromate Conversion Coating Alternatives

Alternatives	Materials Coated	Description	Sources
Trivalent chromium coatings	Aluminum alloys and magnesium alloys	A trivalent chromium process can replace hexavalent chromium on aluminum alloys with comparable properties and costs. Tests of a trivalent chromium conversion coating applied to magnesium alloys displayed better corrosion resistance than hexavalent chromium.	(Bhatt, et al., 2009; La Scala, 2009; Manavbasi, et al., 2012; Nickerson, et al., 2012)
Silicate-based ceramic coatings	Steel screws, nuts, and bolts	Elisha Technologies researched and tested a passivation system that replaces chromium with silicates, which form a ceramic, glass-like layer on the finished parts. In a lab-scale salt spray performance test, the ceramic surface treatment combined with a zinc plate and aluminum-rich epoxy coating displayed great corrosion resistance.	(Winn, et al., 2008)
Polymer-based coatings	Aluminum alloys and magnesium alloys	NEI Corporation's NANOMYTE® PT-60 is commercially available hexavalent chromium conversion coating replacement for use on magnesium alloys. Another coating comprised of zeolites provides a universal solution and process that can coat several types of aluminum alloys.	(Bhargava, et al., 2012; Lew, et al., 2010; NEI Corporation, 2014; Yan, 2009)
Permanganate-based coatings	Zinc and zinc alloys	John Bibber with Sanchem, Inc. explored alternatives to chromium-based conversion coatings and found that permanganate-based coatings duplicate chromium's chemical and physically properties without heavy metals.	(Bibber, 2008)
Phytic acid coatings	Zinc alloys	Phytic acid is a non-toxic acid requiring no hazardous waste treatment. A phytic acid conversion coating and chromate conversion coating were applied to a zinc-cobalt alloy and tested for corrosion. According to the study, the phytic acid with a 15-minute deposition time resulted in superior corrosion resistance compared to the chromate coating.	(Bikulcius, et al., 2010)
Cerium conversion coating	Aluminum alloys	A system using a cerium conversion coating and a multifunctional UV curable coating with inorganic corrosion inhibitors resulted in aluminum alloys exhibiting good flexibility, adhesion, and fluid resistance. The coating system met most aerospace metal finishing requirements.	(O'Keefe, 2010)

According to Keith Legg of Rowan Technology Group, most industries have already adopted hexavalent chromium-free conversion coatings for aluminum, however hexavalent chromium is still used in the aerospace and defense industries due to the increased importance of high performance corrosion resistance in these industries (Eichinger, et al., 1997; K. Legg, 2011). Out of several non-chromate conversion coatings laboratory tested by the Naval Aviation

Systems Command (NAVAIR), the only coatings based on trivalent chromium were comparable to hexavalent chromium conversion coatings (Nickerson & Matzdorf, 2012). NAVAIR's trivalent chromium process requires no additional equipment or operator training when changing from hexavalent chromium processes (La Scala, 2009). During testing, NAVAIR found that process parameters, such as coating time, temperature, and chemical concentration required adjustment for each specific aluminum alloy. Due to trivalent chromium's increased dependence on process parameters, some facilities may be discouraged to change from conventional hexavalent chromium processes (Bhatt, et al., 2009). In recent discussions with metal finishing facilities, EPA learned that some facilities that conduct hexavalent chromium plating operations may have also installed trivalent chromium plating operations in response to increasing demand for safer alternatives. However, this practice is not widespread. Trivalent chromium generally presents a less durable product which can lead to product performance issues. Its use also requires higher operating costs to maintain the plating baths and equipment used, although facilities incur less costs for wastewater treatment (ERG, 2016).

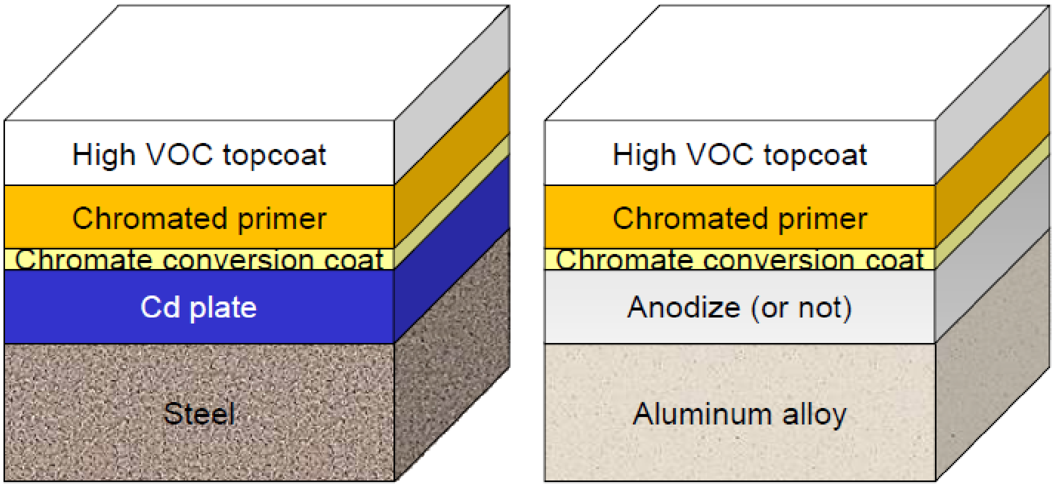
NEI Corporation developed and tested NANOMYTE® PT-60, a chromium-free, self-healing, polymer-based nanocomposite conversion coating, consisting of organic, inorganic, and/or both polymer types. According to NEI Corporation, the alternative coating applied by immersion into a bath of PT-60 solution displayed uniform distribution and consistent thickness, higher electrochemical resistance compared to chromate coatings, and excellent corrosion resistance and self-healing properties after salt-fog exposure when applied to magnesium alloy during a laboratory-scale test (Bhargava & Allen, 2012).

The University of California conducted laboratory-scale research on a zeolite coating developed to replace military chromium-based coatings. Zeolites are inexpensive, non-toxic, crystalline inorganic polymers containing silica and aluminum. Zeolite coatings were tested on hundreds of 1 by 2 inch and 3 by 6 inch metal panels and 99 percent passed corrosion resistance tests including adhesion, impact, bending, salt-fog, and UV testing. The researchers were able to develop a universal solution composition and deposition procedure that produces high quality coatings on several different aluminum alloys, which involved immersing the metal panels into the solution and then heating in a convection oven at 175 degrees Celsius for 12 to 16 hours. This results in significant cost savings because no adjustments are needed for coating different types of alloys (Lew, et al., 2010; Yan, 2009).

An experiment examining several types of conversion coatings concluded that while some coatings work well in certain areas, none of them compare against hexavalent chromium. Trivalent chromium had better heat resistance but less corrosion resistance. Permanganate-based coatings had equal corrosion resistance but was unable to regenerate (Pommiers, et al., 2014).

4.3.2.3 Alternatives for Chromium-based Primers, Sealers, and Cleaners

Most research for replacing hexavalent chromium has focused on alternatives to hard chrome plating and chromate conversion coatings; however, researchers are also exploring alternatives for chromium-based primers, sealers, and cleaning solutions. Primers provide additional adhesion between the surface and topcoat paint. Sealers are mainly used to prevent the surface from absorbing paint, but may also act as a primer. Figure 4-5 illustrates traditional steel and aluminum coating systems. As shown, traditional coating systems also use primers containing hexavalent chromium on top of a chromate conversion coating.



Source: (K. Legg, 2009)

Figure 4-5. Traditional Coating Systems

Researchers at an Air Force facility that anodizes aluminum landing gear investigated alternatives to their sodium dichromate sealer. They identified two: a commercial off-the-shelf nickel-based sealer and permanganate-based sealer. The nickel-based sealer is applied at a lower temperature than the sodium dichromate but seals at a slower rate. Researchers found that the permanganate-based sealer had exceptional corrosion resistance but exhibited less adhesion than the sodium dichromate (R. Mason, et al., 2011). In addition to the nickel- and permanganate-based sealers, the aerospace industry tested a magnesium-rich primer to replace chromate-based primers used on aluminum alloys. They found this primer was the only chromium-free alternative that provides equal or superior corrosion protection to conventional chromate systems, and does not require any pretreatment other than a good cleaning (Bierwagen, et al., 2010).

Along with sealers and primers, hexavalent chromium is a constituent of acidic cleaning solutions used to remove impurities and inorganic contaminants from metals before plating. Acid treatments are also known as pickling. Researchers tested a pickling solution consisting of phosphoric acid and sodium molybdate and found it produced a more uniform film and less corrosion when compared to a pickling bath of chromium trioxide and nitric acid (Lei, et al., 2011).

4.3.3 Phosphate Conversion Coating and Cleaning Alternatives

Phosphate conversion coatings are used to provide a good base for paints and other organic coatings, to condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and to impart corrosion resistance to the metal surface by the coating itself or by providing a suitable base for rust-preventative oils or waxes (U.S. EPA, 1979). Along with phosphate conversion coatings, phosphate cleaners may also be used in order to remove grease and other contaminants from metal substrates prior to coating (List, et al., 2012). Note that phosphate cleaners or other alkaline cleaners are also subject to the Metal Finishing ELGs (U.S. EPA, 2004).

Phosphorous is an essential nutrient for plants and animals. Increased phosphorous levels in water bodies from the discharge of phosphate-containing wastewater can impact aquatic ecosystems and lead to fish kill by lowering dissolved oxygen levels in the water (U.S. EPA, 2012b; USGS, 2015). In recent years, metal finishing companies have converted to phosphate-free processes to address strict environmental regulations on phosphorus discharges in some localities and high operating costs associated with phosphate sludge removal (List, et al., 2012).

Kaluzny (2012) noted several benefits to alternative phosphorus-free conversion coating processes, mainly in cost savings by avoiding POTW surcharges due to phosphate restrictions, eliminating onsite wastewater treatment, minimizing heat required during the surface treatment process, and significantly reducing the amount of sludge produced. They also identified several disadvantages of phosphorous-free processes, including the need for additional rinsing and cleaning between each process step (Kaluzny, 2012).

One alternative to phosphate conversion coatings is the use of ionic liquids containing ethylene glycol and choline chloride for electropolishing steel in a process that incorporates a recycling protocol for the liquid waste. Researchers found the ionic liquids were as effective as aqueous solutions using phosphoric acid mixtures. Additionally, metals are highly soluble in ionic liquids, so such liquids are suitable for electrodepositing tin, zinc, and zinc alloys. The study shows the ionic liquid surface finishes for the electropolishing process were at least as good as conventional aqueous solutions and incorporated a recycling system that allowed for full metal recovery (Abbott, et al., 2007).

Zirconium-based conversion coatings are an alternative to phosphate conversion coatings. Klingenberg and Jones (2007) tested zirconium and zirconium-vanadium coatings against iron phosphate coatings and found several benefits in the zirconium-based alternatives. The phosphate-free process involved immersing metals into a bath of the zirconium-based solution. When compared to traditional phosphate conversion coating processes, this process requires less heat, shorter contact time, and lower coating bath volume. The process also provided thinner surfaces, produced much less process waste, and exhibited better corrosion-resistance (Klingenberg, et al., 2007).

Researchers found that phosphorous-free coatings that use Zirconization™ provide similar benefits. Zirconization eliminates the need for a conditioning step, which further reduces required chemicals and water use (Moore, et al., 2008). David Schmipff of DuBois Chemicals was reported to have said that in two years of testing Zirconization™ and iron phosphate coatings, “less than 5% of results favor an iron phosphate over Zirconization™ or other non-phosphate technology” (Dunham, 2012).

Atotech provides phosphorous-free cleaners and conversion coatings. According to Atotech, after a metal finishing company changed to these products, the company reduced costs by 22 percent and reduced their defect rate from 25 to 11 percent. The phosphorous-free chemistries improved the company’s process by lowering the operating temperatures of the cleaning and coating stages and eliminating the build-up of significant sludge on their spray line (List, et al., 2012).

4.3.4 Cyanide Plating Solution Alternatives

Plating operations use cyanide with copper, zinc, brass, cadmium, silver, and gold. Cyanide is also in chromate and phosphate coatings and etching operations. Cyanide is used as an additive in plating baths due to its ability to form more fine grained metal deposits and increase the bath's tolerance to impurities and contaminants. Many cyanide compounds are highly toxic and can be readily absorbed through the skin and lungs. Some compounds are highly stable, making them difficult to break down during wastewater treatment processes (U.S. EPA, 2000b). According to industry experts, replacing cyanide in metal finishing operations has become increasingly popular due to the health and environmental concerns associated with cyanide (Abdel-Hamid, et al., 2009; Lei, et al., 2010). The literature presents cyanide-free alternatives for coatings on stainless steel and magnesium alloy surfaces.

Researchers tested non-cyanide alkaline baths on stainless steel and demonstrated successful electroplating of a copper layer using an alkaline electrolyte (Abdel-Hamid & Abdel-Aal, 2009). The presence of sorbitol in the plating bath improved efficiency and helped form a dense copper layer, even in the absence of cyanide (Abdel-Hamid & Abdel-Aal, 2009).

Researchers also studied cyanide-free coating processes for magnesium alloys (Lei, et al., 2010). Magnesium alloys are widely used in the aerospace, automotive, electronic, and communication industries due to their low weight; however, their use generally requires a metal plating finish to improve corrosion resistance, and the plating solutions usually contain cyanide (Lei, et al., 2010). The study showed successful coating applications on magnesium alloys without the use of cyanide for the following metal finishes (Lei, et al., 2010):

- Electroless nickel plating
- Electrodeposited nickel
- Electroplated copper
- Electroplated copper/nickel/chromium composite layer plating

The copper/nickel/chromium composite was obtained through multi-electrodeposition. The magnesium alloys were electroplated in three bath compositions of acid copper, bright nickel, and chromium, each with different operating conditions (Lei, et al., 2010). Researchers found nickel and copper-based processes are the most viable alternatives to cyanide-containing plating solutions (Abdel-Hamid & Abdel-Aal, 2009; Lei, et al., 2010).

4.3.5 Summary of Alternative Chemistries

Another key research focus for the industry is finding and applying less toxic alternatives than those commonly used in metal finishing operations. In practice, this proves a challenge to industries that have more stringent product quality specifications that cannot be achieved by those alternatives to date. There is evidence that these alternatives have been applied commercially in the metal finishing industry for products with less stringent specifications. The alternative chemistries show that there may be emerging pollutants of interest because 1) the industry has introduced new chemicals that were not identified in metal finishing wastewater during the 1983 regulations (e.g., zirconium, platinum, tungsten) or 2) increased use of chemicals that may have been identified in the 1983 regulations may have increased presence in metal finishing wastewater (e.g., magnesium, manganese, boron). This may also be evident for other chemicals that are used in plating processes; however, EPA did not identify in literature any specific chemicals used outside of the primary plating chemicals.

Alternative chemistries may also require a change to commonly used metal finishing operations. In recent literature, many of the alternative chemistries that have been commercially applied use different operations than the typical plating operations, such as thermal spray and vapor deposition applications. As a result of changes to plating chemistries, new finishing operations may require EPA to further evaluate them in the context of the existing six primary metal finishing operations that subject facilities to the Metal Finishing ELGs.

4.4 Wastewater Treatment Technologies

As part of its preliminary study, EPA reviewed literature describing recent technological advances in removing metals from wastewaters (e.g., metal finishing wastewater). This section first presents the heavy metals removal technologies that EPA evaluated while promulgating the 1983 Metal Finishing ELGs, and then compares them with the performance of treatment technologies that EPA identified in its recent literature search.

4.4.1 Technologies Evaluated for the 1983 Metal Finishing ELGs

Metal finishing operations generate wastewater primarily from rinsing the surfaces of metals (often several times) during cleaning and preparation, and again after coating or plating is completed. Other sources of metal finishing wastewater include spills, spent process fluids, wash or quench water from auxiliary operations, and water from air pollution control devices. The wastewater may include inorganic wastes (primarily heavy metals) and organic wastes (including cyanide, oils, and toxic organics). As such, the 1983 Metal Finishing ELGs regulate the direct and indirect discharge of metal finishing wastewater containing heavy metals, cyanide, and TTO to surface waters of the United States (see Section 2 of this report) (U.S. EPA, 1983a).

In setting the pretreatment standards and discharge limitations for metal finishing wastewater in the 1983 regulations, EPA evaluated several wastewater treatment technologies for removal of heavy metals, cyanide, and other organic waste. Table 4-5 summarizes these treatment technologies and their calculated daily maximum, monthly average, and long-term average concentrations. Ultimately, EPA selected hydroxide precipitation followed by sedimentation (regulatory option 1) as both the BPT and the BAT. Hydroxide precipitation followed by sedimentation with in-plant cadmium controls (regulatory option 3) was selected as the NSPS/PSNS technology for the ELGs. (See Section 2.3 of this report for a more detailed description of these technologies). Although the technology considered in regulatory option 2 demonstrated better treatment performance, EPA did not select this option because filtration presented a very high incremental cost to the industry (U.S. EPA, 1983a).

In identifying these regulatory options, EPA evaluated the performance of individual treatment technologies for heavy metals removal. Table C-1 in Appendix C presents additional treatment technologies that EPA identified in the 1983 regulations as being used to remove

Table 4-5. Regulatory Options Considered in the 1983 ELGs and their Daily Maximum, Monthly Average, and Long-Term Average Concentrations

Regulatory Option	Technology Description	Pollutant	Daily Maximum Concentration (mg/L)	Monthly Average Concentration (mg/L)	Long-term Average (LTA) Concentration (mg/L)[a]
1: Hydroxide precipitation followed by sedimentation (the BPT technology basis in the 1983 ELGs)	A precipitation technique to form insoluble metal hydroxides and phosphates that are removed by gravity settling techniques including sedimentation basins or circular clarifier. May require pretreatment of wastewater containing cyanide, precious metals, hexavalent chromium and oily wastes. Wastewater containing complexed metals are also segregated and treated separately using this treatment technology.	TSS	60[b]	31[b]	16.7[b]
		Cadmium	0.69	0.26	0.13
		Chromium	2.77	1.71	0.572
		Copper	3.38	2.07	0.815
		Lead	0.69	0.43	0.2
		Nickel	3.98	2.38	0.942
		Zinc	2.61	1.48	0.549
		Silver	0.43	0.24	0.096
		Cyanide	1.20	0.65	0.18
		TTO	2.13	NA	0.434
		Oil and Grease	52[b]	26[b]	12[b]
2: Hydroxide precipitation followed by sedimentation and filtration (not selected as a technology basis in the 1983 ELGs)[c]	In addition to Regulatory Option 1, a filtration device is placed after the primary solids removal to remove metal hydroxides that did not settle out via gravity settling. Filtration devices include granular bed or diatomaceous earth.	TSS	46	24	12.8
		Cadmium	0.42	0.16	0.08
		Chromium	1.55	0.95	0.32
		Copper	1.52	0.93	0.37
		Lead	0.14	0.09	0.04
		Nickel	1.94	1.16	0.46
		Zinc	1.13	0.67	0.25
3: Hydroxide precipitation followed by sedimentation with in-plant cadmium controls (the NSPS/PSNS technology basis in the 1983 ELGs)	In addition to Regulatory Option 1, in-plant controls to nearly eliminate cadmium from the wastewater. Controls can include evaporative recovery, ion exchange, and recovery rinses.	TSS	60[b]	31[b]	16.7[b]
		Cadmium	0.114	0.066	0.058
		Chromium	2.77	1.71	0.572
		Copper	3.38	2.07	0.815
		Lead	0.69	0.43	0.2
		Nickel	3.98	2.38	0.942
		Zinc	2.61	1.48	0.549
		Silver	0.43	0.24	0.096
		Cyanide	1.20	0.65	0.18
		TTO	2.13	NA	0.434
		Oil and Grease	52[b]	26[b]	12[b]

TSS – Total suspended solids; TTO – Total toxic organics; NA – Not applicable

[a] Based on Table 3.4 of the *Guidance Manual for Electroplating and Metal Finishing Pretreatment Standards*, unless otherwise noted (U.S. EPA, 1984).

[b] LTA is based on the daily variability factor of 3.59 mg/L for TSS and 4.36 mg/L for Oil and Grease (U.S. EPA, 1983a).

[c] Regulatory option 2 was based on Table 7-32 of the *Development Document for Effluent Limitations Guidelines New Source Performance Standards for the Metal Finishing Point Source Category* (U.S. EPA, 1983a).

heavy metals. The table also includes performance data for each technology used to treat metal finishing wastewater.

4.4.2 Chemical Precipitation

Chemical precipitation has been used to remove heavy metals from metal finishing wastewater for many years. In general, chemical precipitation involves the conversion of soluble heavy metals into insoluble compounds (i.e., precipitates) that are then physically separated from the water using any of several removal techniques, such as clarification, sedimentation, or membrane filtration (WEF, 2008). Precipitation techniques commonly used to remove heavy metals include hydroxide precipitation and sulfide precipitation; complex metals precipitation and electrochemical precipitation have also been used to remove heavy metals. All of these precipitation techniques were evaluated during the 1983 rulemaking. Electrochemical precipitation is further discussed in the electrochemical treatment methods section below (see Section 4.4.5).

4.4.2.1 Hydroxide Precipitation

As discussed in Section 2.3, hydroxide precipitation is widely used to treat metal finishing wastewater and is part of the technology basis for the Metal Finishing ELGs (see Table 4-1). The BPT for the Metal Finishing ELGs includes hydroxide precipitation, followed by clarification and a sludge dewatering step. BPT also includes pretreatment steps for cyanides, hexavalent chromium, and oil and grease prior to hydroxide precipitation (U.S. EPA, 1983a). Hydroxide precipitation relies on the solubility curves of targeted heavy metals and uses hydroxide compounds to manipulate this characteristic in the wastewater. Although lime (CaO) and caustic (NaOH) are common treatment chemicals, calcium hydroxide ($Ca(OH_2)$) and magnesium hydroxide ($Mg(OH_2)$) are also effective for treating metal finishing wastewater (Fu, et al., 2011; U.S. EPA, 1983a).

A disadvantage of hydroxide precipitation is that the process generates large volumes of low-density sludge that can be difficult and costly to dewater and dispose of. Optimization of single stage hydroxide precipitation for wastewater containing multiple metals may also be difficult to attain because metal hydroxides can have dissimilar solubility ranges and pH adjustment may return metals back into solution. Moreover, complexing agents (which are used in metal finishing processes) are also present in the wastewater and can inhibit hydroxide precipitation, thereby making it difficult to remove heavy metals completely (Fu & Wang, 2011; Islamoglu, et al., 2006). EPA did not identify literature indicating any advances in hydroxide precipitation treatment of metal finishing wastewater.

4.4.2.2 Sulfide Precipitation

Sulfide precipitation uses treatment chemicals such as sodium hydrogen sulfide (NaSH), sodium sulfide (Na_2S), calcium sulfide (CaS), and iron sulfide (FeS) to precipitate heavy metals from wastewater. Ferrous and ferric sulfate may also be used in this process (Huisman, et al., 2006; U.S. EPA, 1983a). Like hydroxide precipitation, sulfide precipitation relies on the solubility of metals in wastewater; however, metal sulfide precipitates have a much lower solubility, and therefore, more metal is removed over a broader pH range than metal hydroxide precipitates. This characteristic of sulfide precipitation allows metal precipitation to be more selective, particularly for divalent soluble metals, such as cadmium, copper, zinc, and lead (WEF, 2008).

During the development of the 1983 Metal Finishing ELGs, EPA identified a few facilities treating metal finishing wastewater by sulfide precipitation in conjunction with hydroxide precipitation. EPA's literature search indicates that the chemistry employed by sulfide precipitation systems remains relatively unchanged; however, the use of multi-stage precipitation, applying multiple precipitation techniques, was a relatively new approach for metal finishing wastewater treatment at the time of the 1983 regulations. This approach may be more widely used now. Sulfide precipitation combined with hydroxide precipitation can improve removal of several metals over a wide pH range (Fu & Wang, 2011; Huisman, et al., 2006).

Compared to hydroxide precipitation, sulfide precipitation generates a more dense sludge that is more amenable to thickening and dewatering for disposal. The pH of the system must also be maintained at a neutral to basic medium because sulfide precipitates in an acidic medium can generate toxic hydrogen sulfide gas (H_2S) (WEF, 2008).

4.4.2.3 Chelated Metals Precipitation

Complexing (or chelating) agents in industrial wastewater can hinder conventional precipitation techniques, such as hydroxide precipitation. Complexing agents are used in chemical processes to help maintain metals in solution, and these metals are present in the wastewater as complexed metals (or chelated metals). Commonly used complexing agents in metal finishing include phosphates, tartrates, ethylenediaminetetraacetic acid (EDTA), cyanide, and ammonia. Successful removal of complexed metals in wastewater require adjusting the pH of the wastewater to very low or very high levels. The technology basis for the 1983 regulations includes the separate treatment of wastewaters using hydroxide precipitation (lime) to drive up the pH of the system to disassociate the complexed metals and free the metal ions to allow hydroxide precipitates to form. Wastewater containing complexed metals can also be treated by adding chemicals to lower the pH of the wastewater and followed by chemical reduction and precipitation. In the acidic environment, the complexed metals disassociate and subsequently, a reducing agent added to reduce the free metal ions to an oxidation state which can then be removed using hydroxide precipitation. In this process, a suitable cation (e.g., calcium, iron) may be added to tie up the complexing agents and allow for effective precipitation of the targeted metal using hydroxide precipitation techniques (U.S. EPA, 1983a; WEF, 2008).

Another approach to treating wastewater containing complexed metals that EPA identified in the 1983 regulations uses sulfide precipitation (through addition of ferrous or ferric sulfate) to facilitate metals removal. Similar to the chemical reduction process, the approach introduces a suitable cation (i.e., iron) into the wastewater, which frees the metal ions targeted for removal (U.S. EPA, 1983a; WEF, 2008). Recent studies focus on the synthesis of precipitants that effectively remove heavy metals even in the presence of complexed metals (Fu & Wang, 2011; Li, et al., 2003). The treatment effectiveness of the precipitants in forming metal precipitates depends on the complexing agents present in the wastewater. In addition to ferrous and ferric sulfate, three other commercially available precipitants used in treating wastewater containing complexed metals are trimercaptotriazine, potassium or sodium thiocarbonate, and sodium dimethyldithiocarbamate. All three are known pesticides, but are effective at removing complexed metals from the wastewater. Experimental xanthates, thiol-based compounds, and dithiocarbamate compounds have also been studied for treating electroplating wastewater containing complexing agents (Fu & Wang, 2011; Li, et al., 2003). Some of these precipitants, particularly the pesticides, present their own environmental risks when discharged into surface waters (U.S. EPA, 2000a). Table 4-6 summarizes the effectiveness of precipitants used in chelated metals precipitation that EPA identified in recent literature. According to Li et al. (2003), the concentration of complexed metals can have an impact on the overall metal removal observed and additional adjustments to the precipitant doses would need to be considered to optimize the removal by the system. On a bench scale, several precipitants demonstrate the ability to remove heavy metals to concentrations that are lower than the LTAs for the BPT technology basis, specifically for copper.

In addition to hydroxide precipitation, EPA also identified chemical reduction and sulfide precipitation as alternative methods for treating wastewater containing complexed metals in the 1983 regulations, although chemical reduction was much less prevalent in the industry at that time. Treatment performance data at that time indicated that sulfide precipitation effectively treated wastewater containing cyanide complexes using ferrous sulfate as the precipitant (see Appendix C). EPA did not identify recent literature describing treatment performance for chemical reduction or sulfide precipitation.

4.4.3 Sorption

Recent literature shows increased research interest in sorption technologies for heavy metals removal. The most common sorption technologies studied involve adsorption and ion exchange processes. The literature reviewed to date did not identify absorption processes for heavy metal removal. This section discusses the advances in adsorption and ion exchange processes in the metal finishing industry.

4.4.3.1 Adsorption

Adsorption involves the physical or chemical binding of a substance that exists in a liquid solution (e.g., metals in wastewater) onto the surface of a solid resin or adsorbent, thereby removing the substance from the liquid solution (Kurniawan, et al., 2006; WEF, 2008). The effectiveness of adsorption (i.e., adsorptive capacity) relies on the number of binding sites available on the adsorbent and can be greatly affected by how the adsorbent is synthesized. Some adsorption processes are reversible, which allows for the recovery of metals via desorption processes. In the 1983 regulations, EPA identified several adsorption technologies as polishing steps (tertiary treatment steps) for removing organics, dissolved metals, and trace metals. These technologies included carbon adsorption, integrated adsorption, peat adsorption, and synthetic resin adsorption. However, the adsorption technologies were relatively new at the time and no metals removal data were available (U.S. EPA, 1983a). Recent studies apparently continue to evaluate adsorption as a tertiary treatment step, rather than as a primary technology for heavy metals removal (Kurniawan, et al., 2006). Adsorbents that have been identified in literature for the removal of heavy metals from wastewater include activated carbon and low-cost alternatives to activated carbon, described below.

Table 4-6. Chelated Metals Precipitation Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Precipitant	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Bench scale, batch operation	Synthetic (without complexing agents)	Sodium diethyldithiocarbamate (DDTC), Ferric sulfate (Fe2(SO4)$_{3)}$; polyacrylamide (PAM)	Copper	0.815	**0.08**	99.6	(Li, et al., 2003)
	Synthetic (with complexing agents)[c]				**0.38**	92.3	
					0.40	96.0	
					0.41	98.0	
					5.35	73.3	
					10.3	48.6	
Uncertain	Uncertain (synthetic or industrial)	Potassium ethyl xanthate	Copper	0.815	3	94.0 – 99.7	(Chang et al., 2002)[d]
Uncertain	Uncertain (synthetic or industrial)	Dipropyl dithiophosphate	Lead	0.2	1	99.5	(Xu and Zhang, 2006)[d]
			Cadmium	0.13	**0.1**	100	
			Copper	0.815	**0.5**	99.8	
			Mercury	NA	0.05	100	
Uncertain	Uncertain (synthetic or industrial)	1,3,5-hexahydrotriazinedithiocarbamate	Copper	0.815	**0.25**	99.0	(Fu et al., 2007)[d]
					0.35	99.3	
					0.4	99.6	

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] The results represent the total copper removal observed for multiple scenarios of complexed copper and total copper concentrations in the sample. Total copper removals of 73.3 and 48.6 percent present scenarios in which the complexed copper represents at least half of the total copper concentrations.

[d] As cited in (Fu & Wang, 2011).

Activated carbon is a widely used adsorbent made from carbonaceous materials such as coal, wood, lignite, peat, coconut husks, or nutshells. A majority of commercially available activated carbon is made from coal. Generally, activated carbon is an effective adsorbent because its microporosity offers a large surface area to which substances can adhere. In EPA's review of the literature, several articles noted its effectiveness in heavy metal removals (Fu & Wang, 2011; Haynes, 2014); however, there were limited quantitative results showing the treatment effectiveness of these adsorbents for heavy metals removal. Sancey et al. (2011) suggested that the high cost of activated carbon adsorption as a tertiary treatment technology makes it less desirable for heavy metals treatment. According to the Water Environment Federation, the effectiveness of activated carbon adsorption for treating inorganic compounds such as metals has not been well demonstrated (WEF, 2008).

The primary focus of many of the adsorption studies EPA reviewed was the adsorptive capacities of activated carbon derived from inexpensive alternatives to coal. These alternatives include agricultural wastes, industrial by-products, natural materials, and many other carbonaceous materials that can be converted to activated carbon and used for adsorbing polyvalent metals such as zinc, nickel, cadmium, copper, lead, mercury, and arsenic. Table 4-7 lists low-cost activated carbon alternatives that EPA identified in recent literature.

Table 4-7. Low-Cost Adsorbents Identified in EPA's Literature Review

Adsorbent	Source
Agricultural Byproducts and Natural Materials	
Eucalyptus bark	(Kongsuwan et al., 2009)[a]
Dried plants	(Chiban, et al., 2011)
Hulls (peanut, soybean)	(Periasamy & Namasivayam, 1995)[b]; (Marshall et al., 1999)[b]
Husks (corn, rice, almond, black gram, coffee)	(Ahmaruzzaman, et al., 2011; Ajmal, et al., 2003; Hegazi, 2013; Wong, et al., 2003) (Oliveira et al., 2008)[a]; (Saeed et al., 2005)[a]; (Hasar, 2003)[b]
Peels (orange, banana, potato)	(Ahmen-Basha, et al., 2008; Ajmal, et al., 2000) (Annadurai et al., 2002)[b]
Piths (coconut, sugar cane)	(Namasivayam, et al., 2008); (Khan et al., 2001)[c]; (Tan et al., 1993)[c]
Shells (pecan, hazelnut, almond, seed, egg)	(Jai et al., 2007)[a]; (Amudaa et al., 2009)[a]; (Bansode et al., 2003)[b]; (Demirbas¸, et al., 2002)[b]; (Kobya, 2004)[b]; (Dakiky et al., 2002)[b]
Corn cobs	(Ahmaruzzaman & Gupta, 2011)
Poultry litter	(Guo et al., 2010)[a]
Sawdust	(Agoubordea & Navia, 2009)[a]
Modified starch (flour)	(Sancey, et al., 2011)
Industrial Byproducts	
Pulp and paper byproducts	(Sthiannopkao, et al., 2009)
Fly ash	(Ahmaruzzaman & Gupta, 2011; Haynes, 2014; Hegazi, 2013)
Slag (blast furnace, iron or steel)	(Haynes, 2014)
Lignin	(Betancur et al., 2009)[a]; (Reyes et al., 2009)[a]
Lignite, diatomite, clino-pyrrhotite, kyanite	(Mohan & Chander, 2006)[a]; (Sheng et al., 2009)[a]; (Lu et al., 2006)[a]; (Ajmal, et al., 2001)

Table 4-7. Low-Cost Adsorbents Identified in EPA's Literature Review

Adsorbent	Source
Clays (Clinoptilolite, kaolinite, montmorillonite)	(Fu & Wang, 2011); (Bhattacharyya & Gupta, 2008)[a]
Zeolites, vermiculite, bentonite	(Alvarez-Ayuso, et al., 2003); (Apiratikul & Pavasant, 2008)[a]
Aragonite shells	(Kohler et al., 2007)[a]
Peat	(Liu et al., 2008)[a]
Natural Materials	
Sodium alginate (natural polymer)	(Abdel-Halima, et al., 2011)
Olive (stone, cake)	(Dakiky et al., 2002)[b]
Pine needles, cactus	(Dakiky et al., 2002)[b]
Synthetic Materials	
Activated alumina	(Bishnoi et al., 2004)[d]
Synthesized Layered Double Hydroxide (LDH)	(Lv, et al., 2013)
Silicates	(Fu & Wang, 2011)

[a] As cited in (Fu & Wang, 2011).

[b] As cited in (Kurniawan, et al., 2006).

[c] As cited in (Hegazi, 2013).

[d] As cited in (Ahmaruzzaman & Gupta, 2011).

The literature describes methods to optimize heavy metals removal by adjusting adsorbent dose and pH levels (Kurniawan, et al., 2006). Table 4-8 summarizes the optimal percent removals for heavy metals using various adsorbents and determined by using optimal adsorbent dose and operating pH ranges. Adsorption of heavy metals was not well demonstrated at the time of the 1983 regulations. Many of the alternative adsorbents demonstrate at bench scale the capability to achieve effluent concentrations equal to or lower than the LTAs for the BPT technology basis.

Another form of adsorption is biosorption (or bioadsorption), which uses inexpensive biomass adsorbents (e.g., non-living, algal, and microbial biomasses) to remove toxic heavy copper, zinc, cadmium, lead, etc. from water. These low-cost alternatives can be available in large quantities, relative to more common adsorption media, such as coal-based activated carbon (Ahluwalia, et al., 2007; Fu & Wang, 2011; Lesmana, et al., 2009). Table 4-9 summarizes the treatment effectiveness of biosorbents in heavy metals removal identified in EPA's literature review. Many of the studies are bench scale and hence, do not firmly establish applicability of the treatment to full scale operations. EPA did not identify biosorbents in the 1983 regulations; however, most of the results show final treated effluent concentrations that do not yet meet the LTAs for chromium, nickel, or zinc.

Research on nanomaterials is relatively new. None of the studies reviewed to date investigated the technology for treating metal finishing wastewater. Most of the studies focus on the adsorption capacities achieved for heavy metals, such as lead, copper, chromium, cadmium, zinc, and nickel, but few studies presented removal data. Table 4-10 lists the nanomaterials EPA identified in recent literature. Because the nanomaterials are usually present in fine or ultrafine particles, their treatment effectiveness can be improved by using structural supports, such as those incorporating natural materials, metal oxides, or manufactured polymers (Hua, et al., 2012).

Table 4-8. Low-Cost Alternatives to Coal-based Activated Carbon Treatment Identified in EPA's Literature Search – Summary of Treatment Results

Scale of Study	Type of Wastewater	Adsorbent Material	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Pilot scale, batch operation	Electroplating	Synthesized LDH	Chromium (VI)	0.572	**<0.5**	>99.9	(Lv, et al., 2013)
Bench scale, continuous operation (column)	Synthetic	Rice husk (tartartic acid treated)	Copper	0.815	**0.007 –** 32.0	46.9 – 100.0	(Wong, et al., 2003)
			Lead	0.2	**0.007 –** 35.5	49.4 – 100.0	
	Electroplating	Orange peels	Nickel (II)	0.942	1.5	89	(Ajmal, et al., 2000)
Bench scale, batch operation	Metal finishing	Lime mud (pulp and paper byproduct)	Chromium	0.572	2.16 – 4.06	89.7 – 93.7	(Sthiannopkao & Sreesai, 2009)
			Copper	0.815	**0.11 –** 3.08	95.4 – 99.8	
			Lead	0.2	**0.10 – 0.17**	93.3 – 97.1	
			Zinc	0.549	**0.059 –** 12.33	56.4 – 99.8	
	Metal finishing	Recovery boiler ash (pulp and paper)	Chromium	0.572	2.93 – 36.6	6.61 – 92.5	
			Copper	0.815	5.90 -62.24	6.85 – 91.2	
			Lead	0.2	0.327 – 1.46	22.9 – 90.8	
			Zinc	0.549	0.736 – 29.4	-0.789 – 97.6	
	Electroplating	Coconut coir pith	Chromium	0.572	2.46	80	(Namasivayam & Sureshkumar, 2008)
	Electroplating	Kyanite (commercial mineral)	Copper (II)	0.815	1.50	81.3	(Ajmal, et al., 2001)
			Zinc (II)	0.549	2.70	15.6	
			Nickel (II)	0.942	4.06	71	
			Chromium (VI)	0.572	39.7	5.5	
	Acid zinc electroplating	Synthetic zeolite	Zinc	0.549	42.5	66	(Alvarez-Ayuso, et al., 2003)
	Nickel electroplating		Nickel	0.942	7.0	86	
	Chromium electroplating		Chromium	0.572	9.0	91	
			Zinc	0.549	**0.08 –** 4.77	44.2 – 97.2	

Table 4-8. Low-Cost Alternatives to Coal-based Activated Carbon Treatment Identified in EPA's Literature Search – Summary of Treatment Results

Scale of Study	Type of Wastewater	Adsorbent Material	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
	Treated surface finishing	Modified starch (flour)	Iron	NA	0.04 – 0.66	53.5 – 95.4	(Sancey, et al., 2011)
			Copper	0.815	**0 – 0.076**	66.7 – 100	
			Lead	0.2	1.03 – 5.01	40.3 – 77.6	
			Cadmium	0.13	**0.071 –** 2.18	38.3 – 91.7	
			Nickel	0.942	87.2 - 503	41.8 – 85.9	
	Industrial	Dried plants	Cadmium	0.13	**0.004**	94.1	(Chiban, et al., 2011)
			Copper	0.815	**0.163 - 0.338**	84.1 – 92.4	
			Lead	0.2	**0.008 - 0.051**	99.2 – 99.9	
			Zinc	0.549	**0.44 -** 2.75	84.1 – 97.5	
	Synthetic	Eucalyptus bark	Chromium (VI)	0.572	2	99	(Sarin, et al., 2006)
		Rice husk	Iron	NA	0.09 – 3.71	68.6 - 99.3	(Hegazi, 2013)
			Lead	0.2	**0.15 –** 0.93	22.2 - 87.2	
			Cadmium	0.13	0.15 – 0.36	26.0 - 67.9	
			Copper	0.815	**0.1 –** 4.1	24.5 - 98.2	
		Fly ash	Iron	NA	1.56 – 6.34	46.2 - 86.8	
			Lead	0.2	0.28 – 0.92	21.79 - 76.1	
			Cadmium	0.13	0.13 – 0.36	25.2 - 73.5	
			Copper	0.815	**0.08 –** 3.40	37.4 - 98.5	
	Uncertain	Clinoptilolite	Lead (II)	0.2	466	55	(Inglezakis et al., 2007)[c]
			Nickel (II)	0.942	1.6	93.6	(Argun, 2008)[c]
			Zinc	0.549	Negligible	100	(Athanasiadis & Helmreich, 2005)[c]

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in Fu & Wang, 2011.

Table 4-9. Biosorbent Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Biosorbent Material	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Pilot scale, continuous operation (column)	Chromium plating	Dry yeast (Saccharomyces cervisiae)	Chromium (VI)	0.572	154	61.5	(Colica, et al., 2012)
Bench scale, batch operation	Electroplating	Dead fungal biomass (A. niger)	Chromium (VI)	0.572	8.65	71.2	(Kumar, et al., 2008)
		Dead fungal biomass (A. sydoni)	Chromium (VI)	0.572	10.4	65.3	
		Dead fungal biomass (P. janthinellum)	Chromium (VI)	0.572	11.2	62.6	
		Bacterial strains isolated from electroplating effluent (B. cereus)	Chromium (VI)	0.572	239	76	(Naik, et al., 2012)
		Brown seaweed (Ecklonia sp.)	Zinc	0.549	**0.1**	97.6	(Park, et al., 2006)
			Chromium (VI)	0.572	**Negligible**	100	
			Chromium (III)		1	33.3	
	Synthetic	Brown seaweed (F. vesiculosus)	Chromium (VI)	0.572	795	18.7	(Murphy, et al., 2009)
			Chromium (III)		831	NA[c]	
		Green seaweed (Ulva spp.)	Chromium (VI)	0.572	1117	14.7	
			Chromium (III)		590	NA[c]	
		Red seaweed (P. palmata)	Chromium (VI)	0.572	930	18.4	
			Chromium (III)		702	NA[c]	

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] Chromium (III) was not present in the untreated wastewater; it was generated through the reduction of chromium (VI) and subsequently biosorbed.

Table 4-10. Nanomaterials Identified in EPA's Literature Review

Nanosized ferric oxides
Goethite (α-FeOOH)
Hematite (α-Fe_2O_3)
Hydrous ferric oxide
Maghemite (γ-Fe_2O_3)
Magnetite (Fe_2O_3)
Polymer-modified (Fe_3O_4) magnetic nanoparticles

Nanosized manganese oxides
Hydrous manganese oxide
Mixed-valence manganese oxides

Nanosized aluminum oxides

Nanosized titanium oxides

Nanosized zinc oxides

Nanosized magnesium oxides

Nanosized cerium oxides

Single- or multi-walled carbon nanotubes

Source: (Fu & Wang, 2011; Ge, et al., 2012; Hua, et al., 2012).

4.4.3.2 Ion Exchange

Ion exchange technology has been used successfully in industry for removing heavy metals from wastewater, including metal finishing wastewater. It is also effective at treating wastewater containing complexed metals (WEF, 2008). Ion exchange is a process in which ions, held by electrostatic forces within charged functional groups on the surface of the ion exchange resin, are exchanged for ions of similar charge from the solution in which the resin is immersed. This is classified as a sorption process because the exchange occurs on the surface of the resin, and the exchanging ion undergoes a phase transfer from solution phase to solid phase (i.e., from wastewater to the ion exchange resin). Resin performance declines with continued use and requires regeneration to remove the impurities removed from the wastewater (U.S. EPA, 2000a). EPA identified ion exchange in the 1983 regulations for the in-process treatment of cadmium-bearing wastewaters, but the technology was not included as part of the BPT technology basis (U.S. EPA, 1983a). During the MP&M rulemaking, EPA found that ion exchange technologies were used as a polishing step to remove trace metals from electroplating wastewater (U.S. EPA, 2000a).

Ion exchange systems have been demonstrated in recovery operations at metal finishing facilities, particularly to concentrate and purify plating baths; however, they are only part of the technology basis in the 1983 ELGs for new sources to control cadmium (see Appendix C). Table 4-11 summarizes the results of ion exchange treatment for removing hexavalent chromium—the only metal identified by EPA in the recent literature on ion exchange. Treatment performance data EPA collected in 1983 from metal finishing plants operating this technology have comparable concentrations for hexavalent chromium, as well as effective removals for a number of other heavy metals including aluminum, cadmium, copper, iron, manganese, nickel, silver, tin, and zinc. Recent studies in adsorption and ion exchange technologies focus on alternative sorbents and tend to overlap because sorption processes can include surface interactions involving both adsorption and ion exchange. Many of the low-cost adsorbents identified previously in Table 4-3, such as zeolites and silicate materials, have been identified as potentially effective adsorbents as well as ion exchange resins.

Table 4-11. Ion Exchange Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Resin Material	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Bench scale, continuous operation	Electroplating	Strongly basic resin (with trimethylbenzyl ammonium)	Chromium (VI)	0.572	**Negligible**	100	(Sapari et al., 1996)[c]
	Synthetic	Strongly basic resin (with electrodialysis)	Chromium (VI)	0.572	3.67 – 4.09	98.7 – 98.8	(Ahmen-Basha, et al., 2008)
Bench scale, batch operation	Synthetic	Acidic resin (based on hydrophilic polymer)	Chromium (VI)	0.572	**0.0005**	99.5	(Kabay et al., 2003)[c]

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in (Owlad, et al., 2009).

Based on the studies, ion exchange performance is sensitive to pH, temperature, and initial metal concentrations (Ahluwalia & Goyal, 2007; Fu & Wang, 2011; Owlad, et al., 2009). In recent discussions with industry, EPA also learned that penetration of this technology for treating metal finishing wastewater has been hindered by costs related to resin regeneration and solids disposal (ERG, 2016).

4.4.4 Membrane Filtration

The 1983 Metal Finishing rulemaking identified a total of 20 membrane filtration systems used to remove solids from industrial wastewater, including metal finishing wastewater. At that time, EPA identified seven metal finishing plants using these systems, although the types of membrane filtration systems were not specified. The research at the time also showed effective treatment of wastewater containing specific complexing agents on a pilot scale. By 1996, EPA identified nearly 700 MP&M facilities that used membrane filtration systems, a subset of which likely comprised metal finishing facilities. The 1983 regulations did not identify filtration technologies as part of the technology basis (U.S. EPA, 1983a, 2000b).

Membrane filtration technologies are basically physical sieves that separate contaminants such as metals and oils from the wastewater. They are widely used as a solids removal step due to their high removal efficiency, easy operation, and minimal space requirements. As a solids removal step, this technology is preceded by a treatment technique, such as chemical precipitation, to prepare the wastewater for solids removal (Fu & Wang, 2011; U.S. EPA, 1983a). Commercially available membranes offer a variety of pore sizes to achieve the desired level of filtration, and each type of membrane can tolerate a range of operating pressures. Figure 4-6 illustrates typical membrane pore sizes and operating pressures used to filter selected contaminants.

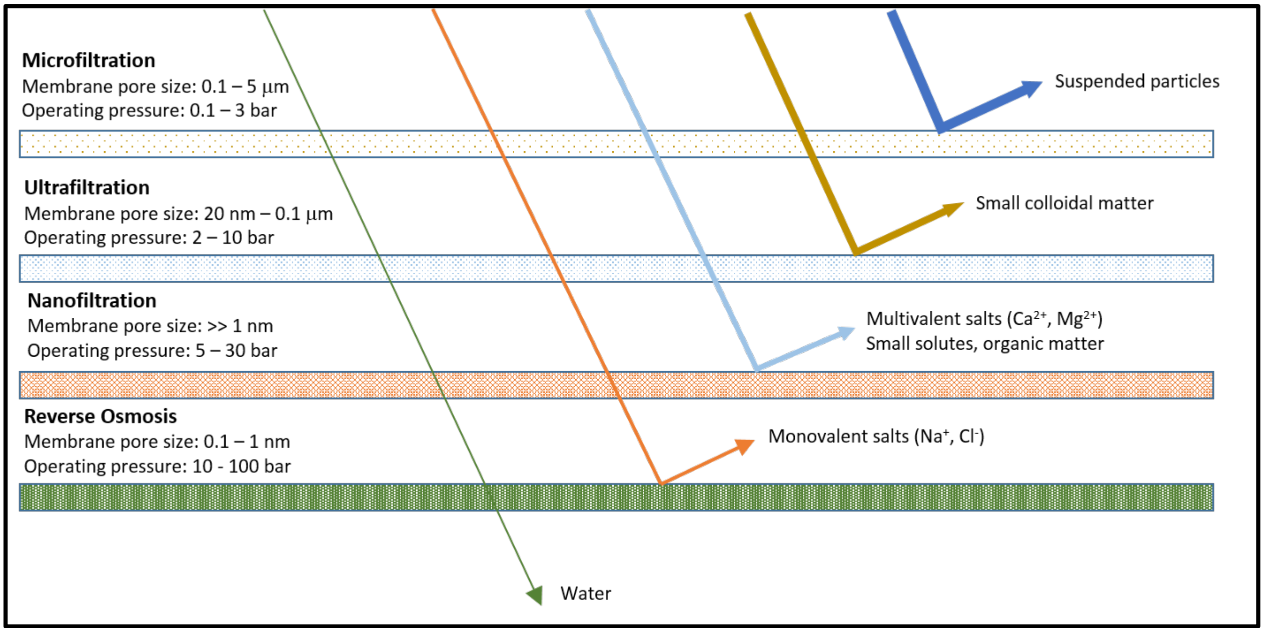


Figure 4-6. Illustration of Membrane Filtration Technologies

From the literature, EPA identified the following membrane processes used to remove metals from wastewater: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These processes differ by the pore size and the differential pressure required across the membrane for filtration to occur (Fu & Wang, 2011; U.S. EPA, 2000a).

4.4.4.1 Microfiltration

Microfiltration technologies use membranes that reject particle sizes ranging from 0.1 to 5 microns. Microfiltration is an alternative to gravity clarification after chemical precipitation and has been used to remove precipitates from metal-bearing industrial wastewater, such as metal finishing wastewater. Microfiltration membranes primarily consist of homogeneous polymer material and operate between 0.1 and 3 bar, depending on membrane pore size, to drive the separation of the contaminants across the membrane (U.S. EPA, 2000a). EPA observed use of microfiltration for solids separation following chemical precipitation at metal finishing facilities visited as part of the MP&M rulemaking development. Based on these visits, EPA determined that well-operated chemical precipitation systems followed by microfiltration removed 99.6 percent of targeted metals, compared to 96.7 percent for chemical precipitation systems followed by gravity clarification. Absent a preceding chemical precipitation step, microfiltration does not achieve high removal efficiencies of dissolved heavy metals, due to its large membrane pore size.

Similar to clarification (which is part of the BPT), microfiltration generates a concentrated, suspended-solid slurry that requires dewatering. Microfiltration is more expensive than conventional gravity clarification because it requires periodic membrane regeneration to maintain treatment effectiveness (U.S. EPA, 2000a).

4.4.4.2 Ultrafiltration

Ultrafiltration technologies reject particles ranging from 0.02 to 0.1 microns (or 20 nm to 100 nm). Ultrafiltration membranes also operate between 2 to 10 bar to drive the separation of contaminants, particularly dissolved and colloidal material, across the membrane. The pore size of the membrane does not prevent dissolved metals or some metal complexes from passing through, but has been shown to remove oil and grease (Fu & Wang, 2011; U.S. EPA, 2000a). The technology was not well demonstrated for metals removal during the 1983 Metal Finishing or the 2000 MP&M rulemakings.

Recent literature reports that micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF) use surfactants and complexing agents, respectively, to aid in the aggregation of micelles or polymers that bind with metal ions to form a macro-structure that is large enough to be rejected by ultrafiltration membranes (as illustrated in Figure 4-7 for MEUF) (Fu & Wang, 2011). In the last decade, researchers have identified several surfactants and complexing agents that form macromolecules with heavy metals (e.g., copper, chromium, nickel, cadmium), which are susceptible to this level of filtration.

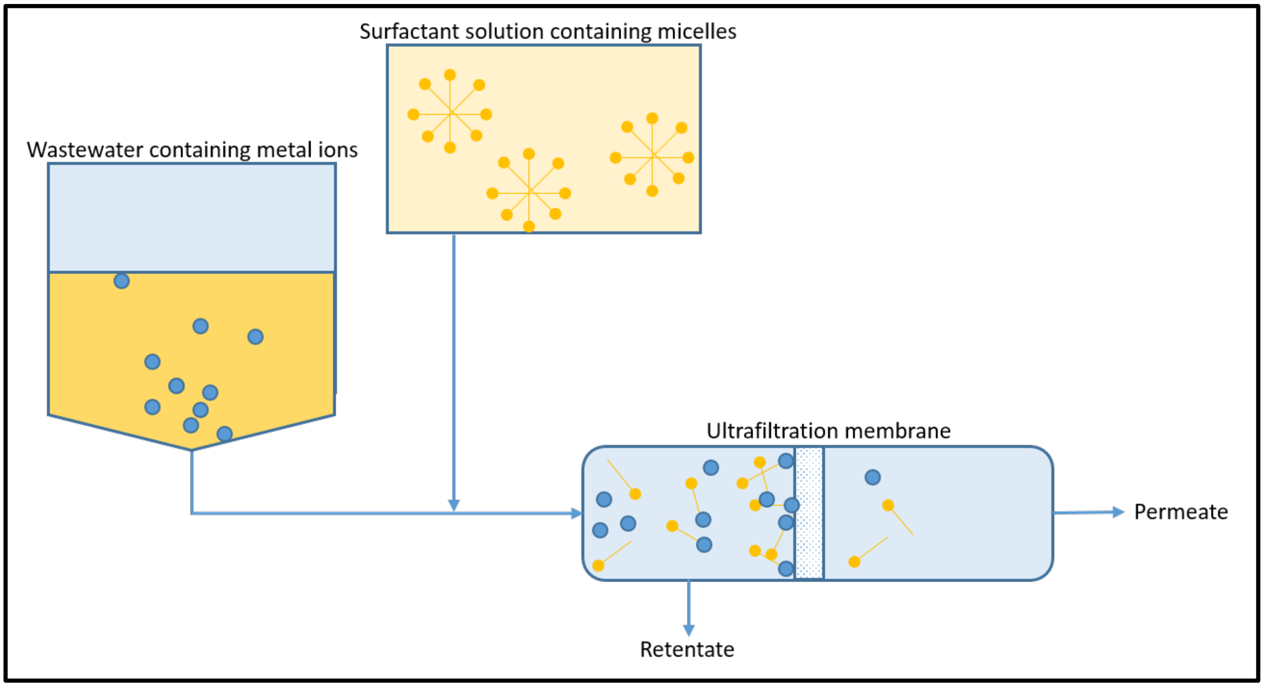


Figure 4-7. Illustration of Micellar-Enhanced Ultrafiltration

The metal removal efficiency of MEUF depends on the characteristics and concentrations of the metals and surfactants used, as well as membrane operating parameters (Fu & Wang, 2011). The effectiveness of PEUF membranes also relies on membrane operating parameters, in addition to the polymer used to selectively remove the metal, the targeted metal to polymer ratio, and the presence of other metals in solution (Bakarat, et al., 2010; Fu & Wang, 2011; Owlad, et al., 2009). Table 4-12 summarizes the treatment effectiveness of ultrafiltration membranes at optimal conditions in bench scale experiments that EPA identified in recent literature. Several MEUF and PEUF systems demonstrate at bench scale the capability to achieve effluent concentrations equal to or lower than the LTAs for the BPT technology basis.

Table 4-12. Ultrafiltration Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Ultrafiltration Membrane	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Ultrafiltration Membranes							
Bench scale, batch operation	Synthetic	Carbon	Chromium (VI)	0.572	40	96	(Pugazhenthi et al., 2005)[c]
		Nitrated carbon	Chromium (VI)	0.572	160	84	
		Aminated carbon	Chromium (VI)	0.572	120	88	
Bench scale, continuous operation	Synthetic	Polyamide thin-film	Chromium (VI)	0.572	Not reported	77	(Hafiane, 2000)[c]
MEUF and PEUF Systems							
Bench scale, continuous operation	Synthetic	Ceramic (Dodecylbenzenesulfonic acid, dodecylamine)	Lead (II)	0.2	**0.044 - 0.076**	>99	(Ferella et al., 2007)[d]
			Arsenate	NA	3.56 – 6.16	19	
		Polysulfone (Sodium dodecyl sulfate)	Cadmium (II)	0.13	1 – 4	92-98	(Huang et al., 2010)[d]
			Zinc (II)	0.549	1 – 4	92-98	
		Polyethersulfone (polyethyleneimine)	Copper (II)	0.815	3	94	(Molinari et al., 2008)[d]
			Nickel (II)	0.942	Negligible	100	
		Polyethersulfone (Carboxy methyl cellulose)	Copper (II)	0.815	**0.24**	97.6	(Bakarat & Schmidt, 2010)
			Chromium (III)	0.572	**0.05**	99.5	
			Nickel (II)	0.942	**0.09**	99.1	
		Amicon 8400	Chromium (III)	0.572	<0.9	82-100	(Korus & Loska, 2009)[d]
			Chromium (VI)	0.572	<9	82-100	
		Ceramic (Poly(acrylic acid) sodium)	Copper (II)	0.815	**0.8**	99.5	(Camarilloa et al., 2010)[d]
		Polysulfone (Poly(ammonium acrylate))	Cadmium (II)	0.13	1.12	99	(Ennigrou et al., 2009)[d]
		Polysulfone (chitosan, polyethylenimine, or pectin)	Chromium (VI)	0.572	7	30	(Aroua et al., 2007)[c]
	Ground water	Polyacrylnitrile fibre (hexadecylpyridine chloride)	Chromium (VI)	0.572	**0.02**	90	(Bohdziewicz, 2000)[c]

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in (Owlad, et al., 2009).

[d] As cited in (Fu & Wang, 2011).

In the 1983 ELGs, EPA identified ultrafiltration as an effective technology for treating oily wastes, not as a metals removal technology. These results show the potential of enhanced membrane filtration systems to treat heavy metals to concentrations lower than those established in the 1983 ELGs for cadmium, chromium, copper, lead, nickel, and zinc. A disadvantage of this technology is that surfactants and complexing agents account for a large portion of operating costs and can become less cost effective if not recovered and reused (Fu & Wang, 2011).

4.4.4.3 Nanofiltration

Nanofiltration membranes retain particle sizes greater than 0.001 microns, which approach the size of dissolved multivalent metals, such as nickel, chromium, copper, and arsenic. Similar to microfiltration and ultrafiltration, nanofiltration is a pressure driven process, with operating pressures typically ranging between 5 and 30 bar (Fu & Wang, 2011). Nanofiltration membranes are commercially available. Summarizes the information EPA identified on the treatment effectiveness of nanonfiltration membranes. Nanofiltration membranes are relatively new; EPA did not identify nanofiltration during the development of the 1983 regulations and further, did not find recent literature on the use of nanofiltration for treating metal finishing wastewater.

One disadvantage of nanofiltration membranes is that, because of the small pores, the membranes are more prone to fouling and may require frequent regeneration to remove contaminants that impact membrane performance. Frequent regeneration adds to the total operating costs of the system (Fu & Wang, 2011).

4.4.4.4 Reverse Osmosis (RO)

RO uses a semi-permeable membrane and a pressure differential to drive the wastewater across the membrane. The membrane rejects contaminants, including particulates and dissolved contaminants, from passing across the membrane (WEF, 2008). The rejection rate for specific contaminants is dependent on several operating factors. The feed rate, temperature, pH, as well as the operating pressure across the membrane, can all impact overall treatment performance (Qin, et al., 2002; WEF, 2008).

The 1983 ELGs evaluated the performance of RO units for treating oily wastes at several metal finishing facilities. During the MP&M rulemaking, EPA found that RO applications for metal recovery in cadmium, copper, nickel, and zinc plating operations rejected 99 percent of multivalent ions and 90 to 96 percent of monovalent ions. Similar to ion exchange, RO is not sensitive to the presence of chelating agents in the wastewater. The permeate stream is usually of sufficient quality to be reused as rinsewater (U.S. EPA, 2000a). As reported by Fu & Wang (2011) and summarized in Table 4-13, several studies evaluated the performance of RO under various conditions and found heavy metal removal rates up to 99.5 percent. Fu & Wang (2011) did not identify whether the treatment performance represented metal finishing wastewater; however, in a separate study by Qin et al. (2002), RO successfully removed greater than 99.8 percent nickel concentrations from nickel plating wastewater.

Table 4-13. Nanofiltration Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Nanofiltration Membrane	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Bench scale, continuous operation	Synthetic	Composite polyamide	Chromium (VI)	0.572	10	99	(Muthukrishnan & Guha, 2008)[c]
			Chromium (VI)	0.572	60	94	
		Polyamide thin-film	Nickel (II)	0.942	**0.1**	98	(Murthy & Chaudhari, 2008)[d]
			Nickel (II)	0.942	20	92	
		Commercial	Nickel	0.942	**0.05**	98.9	
			Cadmium	0.13	0.87	82.7	

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in (Owlad, et al., 2009).

[d] As cited in (Fu & Wang, 2011).

Table 4-14. RO Treatment Identified in EPA's Literature Review – Summary of Treatment Results

Scale of Study	Type of Wastewater	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)[b]	Percent Removal (%)	Source
Bench scale, continuous operation	Uncertain	Copper (II)	0.815	2.5	99.5	(Mohsen-Nia et al., 2007)[c]
		Nickel (II)	0.942	2.5	99.5	
		Copper (II)	0.815	1 – 30	70 - 95	(Zhang et al., 2009)[c]
		Arsenic (V)	NA	0.005 - 0.045	91 - 99	(Chan & Dudeney, 2008)[c]
		Arsenic (III)	NA	0.4 - 0.225	20 - 55	
		Nickel (II)	0.942	**0.31 -** 1.18	99.3	(Ipek, 2005)[c]
		Zinc (II)	0.549	0.70 - 1.87	98.9	
Bench scale, continuous operation	Nickel plating	Nickel	0.942	**<0.009**	>99.8	(Qin, et al., 2002)

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in (Fu & Wang, 2011).

The metal plating industry has a growing interest in RO for recovering and reusing rinsewater (Qin, et al., 2002). Qin, et al. (2002) evaluated RO treatment of spent rinse water for reuse as alkaline rinsewater. Their study investigated the performance of four different commercial RO membranes in treating four variations of metal plating rinsewater containing cyanide and heavy metals such as chromium, copper, zinc, lead, nickel, and iron, among other contaminants from metal plating. They observed reduced fouling when ultrafiltration preceded RO; therefore, in the treatability experiments, they pretreated nickel plating wastewater with an ultrafiltration membrane prior to RO, which resulted in greater than 99 percent removal of nickel (Qin, et al., 2002). Cséfalvay et al. (2009) and Sudilovskiy (2008) also reported greater than 95 percent copper removals, as cited in Fu & Wang (2011), using sequential RO and nanofiltration technologies.

Due to the operational costs of this technology—particularly costs of high power consumption, regenerating the membranes, and potential need for softening pretreatment—RO is not a widely applied technology in the metal plating industry (Fu & Wang, 2011).

4.4.5 Flotation

Since the 1990s, studies have investigated flotation technologies to separate heavy metal precipitates from wastewater. Common flotation technologies include dissolved air flotation (DAF), ion flotation, and precipitation flotation (Fu & Wang, 2011).

DAF relies on the physical interaction between bubbles of air introduced to the wastewater and the suspended particles in the wastewater. The interaction creates agglomerates of particles that float to the surface of the water and are skimmed off and removed (Fu & Wang, 2011; WEF, 2008). The DAF technology is well demonstrated for treating oily wastes in the metal finishing industry, and was identified as part of the technology basis for the separate treatment of oily wastes in the 1983 regulations. The review of metal finishing facilities during the MP&M rulemaking suggests that this technology is still prevalent in the industry for oily waste treatment (U.S. EPA, 1983a, 2000b). EPA did not find recent literature describing the effectiveness of DAF systems in heavy metals removal.

Ion flotation uses surfactants to make the ionic metal species in the wastewater hydrophobic, and subsequently separates the hydrophobic species from the wastewater using air bubbles. The wastes are then skimmed off the surface of the water. Several studies investigated the effectiveness of ion flotation for treating lead, copper, cadmium, silver, zinc, and trivalent chromium. Yuan et al. (2008), as cited in Fu & Wang (2011), reported use of tea saponin, sodium dodecyl sulfate, and hexadecyltrimethyl ammonium bromide as complexing agents. Tea saponin demonstrated bench scale removal of lead (II), copper (II), and cadmium (II) at 90.0, 81.1, and 71.2 percent, respectively. Also reported in Fu & Wang (2011), Polat & Erdogan (2007) indicated optimal removals of copper (II), zinc (II), chromium (III), and silver reached approximately 74 percent under acidic conditions and 90 percent under basic conditions (with the aid of secondary hydroxide precipitation in the high pH range). Fu and Wang (2011) pointed out that that study did not report treated effluent concentrations (Fu & Wang, 2011).

Precipitate flotation applies the flotation method to remove metal precipitates formed through common precipitation techniques. Air bubbles introduced into the wastewater carry the precipitates to the surface of the water, where they are skimmed off. Capponi et al. (2006), as cited in Fu and Wang (2011), conducted a bench scale study which showed 96.2 percent removal of trivalent chromium by precipitate flotation of dilute aqueous solutions. The study did not report treated effluent concentrations (Fu & Wang, 2011). EPA did not identify these technologies in the 1983 regulations or the MP&M regulations for the treatment of heavy metals.

4.4.6 Electrochemical Treatment

Electrochemical treatment involves the application of an electric potential across a cathode and anode to facilitate the recovery or precipitation of heavy metals in wastewater (Fu & Wang, 2011). As part of the 1983 ELGs, EPA identified electrochemical oxidation, reduction, and regeneration as alternative treatments for chromium and cyanide-bearing wastewaters. EPA identified several treatment methods using this electrochemical approach, including electrodialysis, electrocoagulation, electroflotation, and electrodeposition, which are further described in this section. Electrochemical treatment methods have not found application on a large industrial scale due to high initial costs and potentially high energy costs (Fu & Wang, 2011).

4.4.6.1 Electrodialysis

Electrodialysis is the process of separating metal ions across a charged membrane, typically an ion exchange membrane. The use of ion exchange membranes in this process is also referred to as electrochemical ion exchange. Electrodialysis uses an electric field as the driving force across the membrane, rather than the typical pressure driven process described for membranes above, and the literature shows effective treatment of several metals, including hexavalent chromium and lead, as well as copper and iron from copper electrowinning operations. In a pilot study, electrodialysis treated hexavalent chromium down to levels as low as 0.1 milligrams per liter, which is lower than chromium limits in the 1983 regulations (Fu & Wang, 2011; U.S. EPA, 1983a). One study observed the recovery of chromium from plating rinsewater using a combination of ion exchange and electrodialysis units, which effectively recovered nearly 99 percent of chromium on a bench scale. The treated effluent had sufficient quality to be reused in the process. The study did not describe disposal considerations for the reject stream (Ahmen-Basha, et al., 2008). Further investigations also determined that increasing voltage and temperature improved the performance of electrodialysis; however, the treatment effectiveness may be reduced with greater flow rates and concentrations (i.e., conditions that would apply to a full scale operation) (Fu & Wang, 2011).

4.4.6.2 Electrocoagulation

Electrocoagulation incorporates electric potential into conventional chemical precipitation processes to improve heavy metals removal from wastewater. The process may also be referred to as electrochemical precipitation, which involves an electrolytic cell containing steel plates (one cathode and one anode) submerged in water and between which an electric current is applied. By applying an electric potential between the cathode and anode, the charges that hold the heavy metals in solution destabilize and coagulate to form a mass, which can be easily removed. Additional chemicals are generally not required to facilitate precipitation, just the anode and cathode. The effectiveness of the process has been found to rely on the electrical potential, hydraulic retention time, and solution pH. According to Fu & Wang (2011), electrocoagulation applications have grown over the past two decades. At the promulgation of the 1983 Metal Finishing regulations, its application was evaluated for treating chromium-containing wastewater; however electrocoagulation could also be effective in removing other heavy metals from wastewater (U.S. EPA, 1983a). Table 4-15 provides a summary of available electrocoagulation treatment results that EPA identified in recent literature.

Table 4-15. Electrocoagulation Treatment Identified in EPA's Literature Review - Summary of Treatment Results

Scale of Study	Type of Wastewater	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)	Percent Removal (%)	Source
Bench scale, unknown operation	Electroplating	Chromium (VI)	0.572	**0.12**	98.5	(Owlad, et al., 2009)
				0.52	99.6	
				Not reported	77.0 – 100	
				312.9	85.1	
Uncertain	Uncertain	Manganese (II)	NA	21.8	78.2	(Shafaei et al., 2010)[c]
		Nickel (II)	0.942	**Negligible**	100	(Kabdaşli et al, 2009)[c]
		Zinc (II)	0.549	**Negligible**	100	
		Arsenic (III)	NA	<0.022	>99	(Parga et al., 2005)[c]
		Arsenic (V)	NA	<0.022	>99	
		Chromium (VI)	0.572	**Negligible**	100	(Olmez, 2009)
Bench scale, batch operation	Synthetic	Copper, Nickel, Zinc, Cadmium, Lead, Iron	0.815, 0.942, 0.549, 0.13, 0.2, NA	**0.5 -** 40	90 – 99	(Merzouk, et al., 2009)

NA – Not applicable

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] Concentrations in **bold** text indicate lower treatment results than the long-term average concentration for the BPT technology basis.

[c] As cited in (Fu & Wang, 2011).

Electrocoagulation studies involving the removal of zinc, copper, chromium, nickel, silver, lead and dichromate show effective and consistent removals across a broad concentration range (Akbal, et al., 2011; Fu & Wang, 2011; Merzouk, et al., 2009). Kabdasli et al. (2009) also investigated the treatability of complexed metals in nickel and zinc plating wastewater using electrocoagulation. In the study, both zinc and nickel were completely removed using this process (Fu & Wang, 2011; Kabdasli, et al., 2009). In Kobya et al. (2010) reported that electrocoagulation showed effective removal (greater than 99 percent) of cadmium, nickel, and cyanide at optimal conditions. Electrocoagulation may be an alternative treatment option for removing cyanide by first dissociating the metal complexes in electroplating wastewater, removing the freed cadmium and nickel ions, and generating a new metal complex with the metal ions generated by the electrodes (Kobya, et al., 2010). During an electrocoagulation process, no additional chemicals are added to the wastewater, in contrast to conventional precipitation methods. Therefore, this process generates a more compact sludge, which can significantly reduce disposal costs (Akbal & Camci, 2011).

The studies indicate that for electrocoagulation, optimization of metals removal relies on the electrode positions, electrical potential, and pH of the solution. According to Senturk (2013), iron electrodes are more effective than aluminum in treating electroplating wastewater containing zinc and cyanide; however, in a separate study, Akbal & Camci (2011) noted iron-aluminum electrode pairs to be equally efficient in electroplating wastewater containing nickel, copper, and chromium (Akbal & Camci, 2011; Senturk, 2013). Olmer (2009) noted stainless steel electrodes for use in hexavalent chromium removals in hard chrome plating rinsewater. Several studies have focused on optimization schemes for different types of wastewater characteristics and suggest that conditions for optimal removal should be identified on a case-by-case basis. EPA did not identify any full-scale application of electrocoagulation processes for metal finishing wastewater during the literature review.

4.4.6.3 Electroflotation

Similar to conventional flotation techniques, electroflotation relies on the use of air bubbles to bind with and transport metal precipitates to the surface of the water. Bubbles consisting of hydrogen and oxygen gases are generated through the electrolysis of the water on the surface of the electrodes as an electric potential is applied. These hydrogen and oxygen gases become the transport media for metal ions. Multiple studies have been reported to show potential uses in the metal finishing industry for treating iron, nickel, copper, zinc, lead, and cadmium at up to 99 percent removal efficiency (Fu & Wang, 2011). In a separate study, copper and nickel removals under optimal conditions reached 98 to 99 percent (Khelifa, et al., 2005). Table 4-16 summarizes the removals of electroflotation that EPA identified in recent literature.

Table 4-16. Electroflotation Treatment Identified in EPA's Literature Review - Summary of Treatment Results

Scale of Study	Type of Wastewater	Targeted Metal	LTA Concentration (mg/L)[a]	Final Metal Concentration (mg/L)	Percent Removal (%)	Source
Bench scale, batch operation	Synthetic	Zinc (II)	0.549	0.8	96	(Casqueira et al., 2006)[b]
		Nickel (II)	0.942	2	98-99	(Khelifa et al., 2005)[b]
		Copper (II)	0.815	1	99-99	

[a] Long-term average concentrations represent total metal concentrations for the BPT technology basis (regulatory option 1 in Table 4-1).

[b] As cited in (Fu & Wang, 2011).

4.4.6.4 Electrodeposition

Electrodeposition (or electrophoretic deposition) is a general term used for a process using an applied current across electrodes to deposit metals onto an electrode. Electrodeposition can refer to an electroplating process; however, it also covers a number of processes to recover metals from wastewater. Terms such as 'electrolytic recovery' and 'electrowinning' are also common terms for recovery processes using electrodeposition (Kirk-Othmer, 2004; U.S. EPA, 1983a). Oztekin & Yazicigil (2006) and Chang et al. (2006), as cited in Fu & Wang (2011) investigated the recovery of metals from complex wastewaters, which effectively removed up to 90 percent and nearly 96 percent, respectively, of copper from complex wastewater (Fu & Wang, 2011). A disadvantage of electrodeposition—and of other electrochemical methods discussed in this section—is the high energy requirement (resulting in high operating costs).

4.4.7 Biological Treatment

The literature suggests that biological treatment of metal-bearing wastewater is an expanding area of research. EPA identified a few biological treatment systems during the 1983 rulemaking; however, biological treatment was not part of the technology basis for the 1983 Metal Finishing ELGs.

Researchers have evaluated the use of biological processes to reduce hexavalent chromium (Cr (VI)) to trivalent chromium (Cr (III)) in industrial electroplating wastewater prior to conventional chemical precipitation. A pilot study conducted on the ChromeBac™ biological system in Malaysia showed successful reduction of Cr (VI) down to less than 0.05 milligrams per liter (or greater than 99.8 percent removal). Total chromium was reduced to 0.7 mg/L (or 98.6 percent removal) (Ahmad, et al., 2010). Chromium removal (as Cr (III)) was completed using conventional chemical precipitation.

Sulfide precipitation processes have used sulfate-reducing bacteria (SRB) to generate sulfide on-site. The SRB oxidizes simple organic compounds and reduces sulfates under anaerobic conditions to form biogenic hydrogen sulfide. Hydrogen sulfide is subsequently used to precipitate metals. The process was tested on zinc-bearing wastewater (containing 400 mg/L of Zn) and proved effective at completely removing soluble zinc as well as sulfate and total organic compounds (TOC) (Fu & Wang, 2011). According to Huisman et al. (2006), Paques BV, a Netherlands company, is operating full-scale Sulfateq® technology using SRB for wastewater treatment. They have implemented nearly 500 industrial installations for several industries. The technology reliably removes sulfate, nitrate, heavy metals, selenium, and fluoride from metal and mining industry wastewater. Another Pacques BV technology, the Pacques Thioteq process, was also developed to aid in the on-site generation of biogenic hydrogen sulfide when wastewater characteristics inhibit its production (Huisman, et al., 2006). EPA did not identify application of these technologies in metal finishing wastewater.

In another study, Park et al. (2005) evaluated the use of iron-oxidizing bacteria to reduce iron levels from electroplating wastewater. The researchers used a biological treatment step to remove iron from the wastewater without removing other heavy metals such as zinc or nickel. After biological pretreatment, wastewater was treated by sodium hydroxide precipitation to generate sludge with high concentrations of zinc or nickel. The iron-removal pretreatment reduced the volume of the hydroxide sludge generated, allowing for more economical recovery of higher value metals (Park, et al., 2005).

4.4.8 Summary of Wastewater Treatment Technologies

Thus far, EPA's literature review on wastewater treatment has primarily focused on articles from academic journals, which identified numerous wastewater treatment technologies for removing heavy metals; however, many are not new technologies or new applications for metal finishing wastewater treatment. In fact, EPA identified many of these technologies during the development of the 1983 Metal Finishing ELGs (as summarized in Table 4-5 and in Appendix C). Although these technologies effectively removed metals from wastewater at sampled metal finishing facilities, many were relatively new applications for the industry and likely cost more than the treatment technologies that industry used at the time. In particular, EPA had considered granular bed and diatomaceous earth filtration, or similar media filtration technologies, as part of regulatory option 2 (see Table 4-5); however, EPA ultimately did not select these alternatives because they were not economically feasible at the time.

There were additional technologies that EPA also considered in the 1983 ELGs, specifically for treating oily wastes and toxic organics, which are now finding application in heavy metals removal. These included sorption, advanced membrane filtration, flotation, and electrochemical methods. Advances in heavy metals removal have also included research into better-performing or more cost-effective chemical additives or materials. Based on the number of articles EPA identified, sorption and membrane filtration seem to be the focus of recent research for heavy metals removal. The articles present bench-scale results that suggest promising advances in treating heavy metals; however, EPA has not determined whether any of these promising technologies have been implemented at full-scale within the metal finishing industry.

From discussions with pretreatment coordinators and with industry representatives, EPA learned that most metal finishing facilities continue to use conventional chemical precipitation technologies, although some facilities have added a polishing step such as membrane filtration or sorption technologies. EPA also learned that advances in wastewater treatment technologies in the industry have been slow, and most likely inhibited by the costs of installing and operating more advanced technologies. However, EPA has not fully evaluated the extent to which the metal finishing industry is applying technologies beyond the BPT technology basis (ERG, 2016; U.S. EPA, 2015a).

4.5 Applicability and Other Regulatory Considerations

EPA expects that in the 32 years that have passed since the promulgation of the Metal Finishing ELGs, metal finishing process technologies and chemistries have evolved and advanced wastewater treatment technologies have become available for metal finishing wastewater treatment. EPA has often received requests for official EPA determinations on the applicability of the ELGs to specific operations or to provide clarification on metal finishing operations described in the rule. Additionally, stakeholders have also urged EPA to consider other regulations that may also have a bearing on the industry. This section outlines the key considerations that have been identified thus far in the Metal Finishing Preliminary Study.

4.5.1 Rule Implementation

Pretreatment coordinators noted that POTWs are still implementing 40 CFR Part 413 (Electroplating) pretreatment standards for some metal finishing facilities. Most metal finishing facilities should be covered by 40 CFR Part 433 pretreatment standards, and not 40 CFR Part 413 standards. The scope of facilities still regulated under 40 CFR Part 413 is technically limited to job shops and IPCB manufacturers that were considered existing sources at the time of the promulgation of the 1983 Metal Finishing ELGs. In a public comment on EPA's 2014 Effluent Guidelines Program Plan, the Association of Clean Water Administrators (ACWA) urged EPA to consider merging the facilities still operating under 40 CFR Part 413 regulations into the Metal Finishing ELGs (U.S. EPA, 2015c).

Unlike wastewater regulations for other metal-related industries (e.g., aluminum forming, iron and steel), which include production-based limits, the Metal Finishing ELGs are concentration-based which can make them easier to apply in wastewater permits. Due to potential overlap of Metal Finishing regulations with other metal related regulations that make take precedence, pretreatment coordinators suspect that there is confusion on when Metal Finishing ELGs versus other metals related ELGs may apply at POTWs.

4.5.2 Applicability of ELGs to New or Modified Metal Finishing Operations

EPA and regional pretreatment coordinators have received questions from stakeholders on a number of topics related to the 46 metal finishing operations that are listed in the 1983 Metal Finishing ELGs. In particular, stakeholders asked for clarification on:

- Whether a newly designed metal finishing operation would fall under the six primary metal finishing operations that would subject them to the Metal Finishing ELGs (e.g., revivation, zirconization, citric acid passivation);
- Whether modifications to the metal finishing operation over time (e.g., increasing the number of finishing lines, expanding plant operations, changing plating process) would subject them to new source standards (NSPS and PSNS) under 40 CFR Part 433 (instead of BAT and PSES or 40 CFR Part 413 electroplating standards);
- Whether newer manufacturing industries (e.g., solar panel manufacturing, cell phone manufacturing) that were not considered during development of the 1983 rule would be subject to the Metal Finishing ELGs.
- How to define current industry practices to determine whether they are subject to the Metal Finishing ELGs. For example,
  - Clarification of the distinction between "cleaning" and "etching" operations.
  - Use of phosphoric acid, chromic acid, or citric acid in "cleaning" versus "conversion coating" or "etching" operations.
  - Use of brighteners during "acid cleaning" vs "bright dipping" operations where "bright dipping" is mentioned as an example "etching" core process in the Technical Development Document (TDD) and "cleaning" is not a core process.
  - Clarification on whether facilities performing "powder coating" are subject to the Metal Finishing ELGs.

Regional pretreatment coordinators have fielded questions from industry on a case-by-case basis related to these topics. When necessary, EPA plans to develop policy memoranda to address questions on the applicability of the Metal Finishing ELGs.

4.5.3 Considerations for Other Regulations

Based on discussions with stakeholders and EPA's review of the literature, EPA identified the following regulations that may impact the characteristics of wastewater generated from metal finishing operations or inhibit the implementation of advanced wastewater treatment technologies for the industry.

4.5.3.1 National Emission Standards for Hazardous Air Pollutants (NESHAPs), Office of Air and Radiation (OAR)

EPA identified the following air regulations that have been promulgated since the 1983 Metal Finishing ELGs. These regulations can impact the overall characteristics of process wastewater generated from metal finishing operations.

- NESHAP for Chromium Emissions from Hard and Decorative Chromium (40 CFR Part 63, Subpart N), 1995 and 2012. EPA promulgated the original NESHAP in 1995 affecting all facilities using chromium electroplating tanks. In 2012, EPA amended the rule to tighten emission standards for chromium electroplating and anodizing operations, which included revised emission limits and a ban on the use of perfluorooctane sulfonate (PFOS)-based fume suppressants in air pollution control devices. Based on discussions ith some metal finishing facilities, EPA learned that wastewater generated from emission control devices used to control chromium emissions can be commingled with metal finishing wastewater prior to wastewater treatment.
- NESHAP for Plating and Polishing Operations (40 CFR Part 63, Subpart WWWWWW), 2008. EPA published the NESHAP in 2008 requiring use of generally available control technology (GACT) standards at facilities with plating, polishing or thermal spray processes that contain **cadmium, nickel, lead, manganese and/or chromium (excluding chromium electroplating and anodizing operations).** The rule does not establish emission limits for these operations. Facilities have several compliance alternatives including use of wetting agents/fume suppressants (WAFS), air pollution control devices or tank covers. Platers also need to implement management practices that reduce the generation of airborne chemicals. These modifications may introduce pollutants to metal finishing wastewater that are not commonly used in metal finishing operations.
- NESHAP for Metal Fabrication and Finishing Area Source (40 CFR Part 63, Subpart XXXXXX), 2008. In 2008, EPA promulgated requirements to reduce air pollution of compounds of metals such as cadmium, chromium, lead, manganese and nickel from nine metal fabrication and finishing source categories. This rule applies to facilities primarily engaged in these nine source categories and covers the following operations: dry abrasive blasting, dry grinding and dry polishing

with machines, dry machining, spray painting, and welding. The NESHAP may require the use of wet emission control devices for some operations, which may introduce pollutants that impact metal finishing wastewater characteristics.

4.5.3.2 Resource Conservation and Recovery Act (RCRA) Hazardous Waste Regulations, Office of Resource Conservation and Recovery (ORCR)

Based on discussions with wastewater treatment technology vendors, EPA also learned that hazardous waste regulations can inhibit the advancement of wastewater treatment technologies for the industry. Specifically, vendors noted the difficulty of applying more advanced technologies such as ion exchange or RO due to the costs to the facilities for offsite resin or membrane reclamation and/or disposal. As defined under RCRA, the resins and membranes may be classified as hazardous waste (most commonly under F006 – wastewater treatment sludges from electroplating operations). Technologies such as ion exchange and RO can treat wastewaters to a quality that can be reused in the process, which can significantly reduce the amount of wastewater discharged; however, the added cost of managing the hazardous wastes generated by these technologies may have rendered them economically infeasible for many of metal finishing facilities (particularly, job shops). On January 13, 2015, EPA published in the Federal Register (FR) a revised definition of solid waste (80 FR 1694). EPA recently revised the definition of solid waste in 2015 with the objective of encouraging reclamation of hazardous secondary materials without increasing risk to human health and the environment from discarded hazardous secondary material. This new definition may pave a way for the advancement of wastewater treatment and reuse for the metal finishing industry.

4.5.3.3 European Union (EU) End of Life Vehicle (ELV) and Restriction of Hazardous Substances (RoHS) Directives

The EU issued the End of Life Vehicles Directive in 2000 to address the issue of the recycling and/or disposal of automobiles at the end of their useful lives to limit waste containing lead, mercury, cadmium, and hexavalent chromium. The directive bans lead, mercury, and cadmium and limits hexavalent chromium to 2.0 grams per vehicle for the purpose of corrosion protection only. Similarly, in 2006, the EU also issued the RoHS Directive banning lead, mercury, cadmium, and hexavalent chromium, as well as two additional flame retardants, from electronic products, thereby reducing the amount of these substances disposed at the end of their useful lives. Based on discussions with the metal finishing industry, these directives may impact the metal finishes used in the U.S. on products that are then sold abroad.

5. NEXT STEPS

As discussed in Section 1 of this report, EPA plans to gather sufficient information to answer the following key questions for the study:

- How is the current metal finishing industry different from the industry as regulated by the Metal Finishing ELGs?
  - What is the current distribution of captive facilities and job shops within the industry?
  - Which types of facilities are conducting metal finishing operations?
- Since the promulgation of the Metal Finishing ELGs, what process technology changes have been implemented and how have the primary sources of wastewater changed?
- Since the promulgation of the Metal Finishing ELGs, what chemical formulation changes have been implemented and how have these changes affected the characteristics of the raw wastewater, i.e., pollutants, concentrations, flow rates/volume?
- What are the best available technologies for pollution prevention and wastewater treatment and to what levels do they reduce pollutants of concern?
  - What are the concentrations and loadings of pollutants currently being discharged (i.e., baseline concentrations)?
  - Which pollutant discharges require additional control?
  - How will industry discharges change if facilities implement these best available technologies and practices?
- What challenges do metal finishing facilities face in applying the Metal Finishing ELGs?

EPA plans to continue gathering and analyzing information relevant to these questions over the next year, after which it will determine whether additional data collection efforts are needed and how to proceed with updating the 1983 Metal Finishing ELGs. The information that EPA has compiled to date identifies the key topics for further investigation, as described in the subsections below.

5.1 Review Pollutant Discharge and Release Data

EPA plans to review existing industry discharge data to further evaluate and characterize both direct and indirect metal finishing wastewater discharges. EPA will evaluate discharge monitoring report (DMR) and Toxics Release Inventory (TRI) data to identify metal finishing facilities with wastewater discharges, the location of facilities reporting to DMR and TRI, the pollutants being generated and discharged, and their respective prevalence, magnitude, and relative toxicity in wastewaters that are not currently regulated by the Metal Finishing ELGs.

5.2 Evaluate Changes to Industry Profile

Currently, EPA does not have a complete understanding of how the industry profile has changed since the promulgation of the 1983 regulations. Particularly, EPA is seeking to understand any changes in metal finishing operations and markets, in wastewater treatment and discharge practices, and in the number, size, and types of facilities generating and discharging wastewater. To date, EPA's review of the industry suggests that there have been changes in the industry since 1983 that would affect wastewater characteristics and discharges from metal finishing facilities. However, EPA cannot yet adequately define the extent of those changes or their impacts.

EPA will evaluate options for developing a current profile of metal finishing facilities. These options may include using a marketing database, reviewing more recent data collected during the MP&M regulatory development, reviewing TRI and DMR data, and identifying other data collection efforts that may have been conducted by other EPA offices, such as the Office of Air and Radiation (OAR) and the Office of Resource Conservation and Recovery (ORCR), which may have already compiled these types of information. EPA will also collaborate with EPA regional offices, state and local agencies, and POTW control authorities to obtain POTW pretreatment reports, which identify categorical industrial users (CIUs) in the POTW's catchment area.

5.3 Review Literature from Conferences and Other Industry Sources

EPA has conducted an extensive literature review of metal finishing process technologies, alternative chemistries, and wastewater treatment using industry keywords on several research collections and search engines.[19] In addition, EPA collected and will review literature on wastewater treatment from the 2015 WEFTEC and 2015 IWC. EPA does not plan to conduct another extensive literature search on technical papers and reports, studies, peer-reviewed journal articles, and industry publications on metal finishing operations and wastewater management; however, EPA will review literature that it identifies from other EPA activities and industry sources described in this section.

5.4 Continue Discussions with Industry Experts on Key Topics

EPA will continue conversations with federal and regional pretreatment coordinators. These personnel often have on-site experience at POTWs that receive metal finishing wastewater. Such discussions will help EPA identify and explore issues with the implementation of the Metal Finishing ELGs, and to understand the effects of these issues on POTW operations. EPA held meetings with the ACWA and several pretreatment coordinators in November 2015 to gather different perspectives on the metal finishing category (U.S. EPA, 2015d). EPA also plans to initiate discussions with other organizations, such as NACWA and NASF, to understand their perspective on the implementation of the 1983 regulations.

EPA will also continue to reach out to personnel from metal finishing facilities and wastewater treatment technology vendors to: 1) obtain information that will help answer key

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[19] EPA used specific industry keywords for the metal finishing category, listed in Appendix B.

study questions, 2) identify potential candidate facilities for future EPA site visits, 3) gain industry perspective on the 1983 Metal Finishing ELGs, and 4) generally assess the technical and economic feasibility of implementing more advanced wastewater treatment technologies and waste minimization practices at metal finishing facilities. EPA will identify additional facilities to contact, based on discussion with these industry experts, and based on its review of available annual pretreatment reports or other sources listing metal finishing facilities that indirectly discharge wastewater.

5.5 Conduct Site Visits to Metal Finishing Facilities

EPA will visit metal finishing facilities to observe operations and wastewater management practices first-hand. EPA will seek to visit facilities representing a range of operational approaches, including facilities that are:

- Operating new or modified finishing processes.
- Using alternative chemicals in metal finishing operations.
- Using pollution prevention practices to maximize the reuse and minimize the generation and/or discharge of pollutants in wastewater.
- Operating advanced wastewater treatment technologies (aside from conventional hydroxide precipitation and clarification).

During these visits, EPA may request data on wastewater treatment effectiveness, general process design, typical operating conditions, market demands, and other topics. EPA may also request information on the wastewater treatment technologies and treatment chemicals used on site.

5.6 Investigate the Impacts of Other Regulations on the Industry

EPA will further investigate how other EPA regulations may be affecting the metal finishing industry. Possible examples of such regulations include NESHAPs (described in Section 4.5), RCRA hazardous waste disposal regulations, and other EPA efforts. As part of this investigation, EPA will collaborate with other EPA offices and analyze information regarding regulatory impacts that the Agency has already collected from the industry.

6. QUALITY ASSURANCE

In gathering information to support EPA's preliminary study of the Metal Finishing Category. EPA evaluated and documented the usefulness and quality of the data collected to date in accordance with the criteria specified in *The Environmental Engineering Support for Clean Water Regulations Programmatic Quality Assurance Project Plan* (PQAPP) (ERG, 2013). EPA's review of the data sources for this interim study also followed the quality assurance procedures specified in the PQAPP, with the addition of specific criteria discussed in Section 6.3, below. This section provides detailed information on the data sources used and data quality evaluation performed.

6.1 Project Objectives

As discussed in Section 1 one of EPA's primary objectives for the preliminary study of the Metal Finishing Category is to assess the current state of the industry to better understand how metal finishing operations, wastewater characteristics, and wastewater treatment technologies have changed since EPA promulgated the 1983 ELGs. This assessment will help EPA to determine whether additional data collection efforts are needed and how best to address the 1983 Metal Finishing ELGs. Specifically, the study seeks to answer the key questions listed in Section 1 and reiterated in Section 5 of this report.

6.2 Data Sources

To date, EPA has used the following types of data sources to support its preliminary study of the Metal Finishing Category:

- Conference proceedings, peer-reviewed journals, other academic literature.
- Interviews with industry personnel, vendors, trade association representatives, and pretreatment coordinators.
- Existing government publications and supporting information.

6.3 Data Quality Objectives and Criteria

As described in the PQAPP, EPA ensures that the data collection, processing, and analyses performed for the preliminary study will meet the data quality objectives of objectivity, integrity, and utility, as described below:

- *Objectivity*. The information must be accurate, reliable, and unbiased, and the manner in which the information is presented must be accurate, clear, complete, and unbiased.
- *Integrity*. The information may not be compromised through corruption or falsification, either by accident, or by unauthorized access or revision.
- *Utility*. The information must be useful for the intended users.

The sources of the data used will also be made transparent. As the study progresses and EPA analyzes the data, EPA will also provide information on the various assumptions, analytical methods, and statistical procedures applied throughout the study. EPA prioritized the review of the data sources described in Section 6.2 to address the key study questions listed in Section 1 of this report. The criteria that EPA will use to evaluate the quality of literature are accuracy, reliability, and representativeness, as described in Section 4.3.1 and in Table 4-2 of the PQAPP (ERG, 2013), and summarized below:

Accuracy. EPA assumed that the underlying data and information contained in state and federal reports, peer-reviewed journal articles, and industry publications are accurate. Although industry publications are not usually peer-reviewed, this resource provides useful information for understanding metal finishing processes and wastes generated.

Relevance. Selected articles must describe process operations, pollutants, or wastestreams that are representative of the metal finishing industry. Articles that most closely provide answers to the key questions listed in Section 1 are the most relevant.

Reliability. EPA considered the following factors when evaluating reliability of the data sources used to support the study: (1) data sources that have been generated by governmental agencies or are otherwise subject to peer review and assessment are considered to be the most reliable and useful for understanding industry process operations, quantitatively characterizing wastewater discharges, and demonstrating treatment system performance; (2) data sources from entities with established knowledge in the topic area (e.g. studies conducted by industry experts, academic researchers, data generated by an industrial facility using documented and approved methods) are also considered to be reliable and useful for understanding industry process operations, quantitatively characterizing wastewater discharges, demonstrating treatment system performance, and understanding applicability of the regulations; and (3) data sources that use unknown collection and data review procedures are less reliable, but may be generally useful for qualitative understanding of industry process operations and waste streams. In general, EPA evaluated reliability based on the degree to which sources met the following criteria:

- Scientific work is clearly written, so that all assumptions and methodologies can be identified.
- Variability and uncertainty (quantitative and qualitative) in the information or in the procedures, measures, methods, or models are evaluated and characterized.
- Assumptions and methodologies are consistently applied throughout the analysis as reported in the source.

Representativeness. EPA evaluated whether selected data sources described process operations, pollutants, or waste streams that are representative of the metal finishing industry. For the purposes of this study, EPA expanded upon the general criteria set forth in the PQAPP by establishing data quality acceptance criteria related to the geographic scope and age of the data (described below):

- *Geographic Scope*. Data sources must describe the wastewater characteristics for the metal finishing industry in the United States. EPA also collected additional information from the data sources to describe the generation of the data, such as the source of the wastewater, sample collection procedures, analytical methods, units, and relevant data qualifiers to further evaluate its quantitative use in future analyses. EPA included some international data sources that were relevant for their descriptions of other potential wastewater treatment technologies or chemical processes used in metal finishing.

- *Age*. EPA prioritized data sources published in 2000 or later, as they reflect more recent industry changes. However, information published prior to 2000 (e.g., 1983 Metal Finishing Technical Development Document, supporting documentation for the MP&M rulemaking) can provide useful qualitative information regarding the status of the industry then and the nature of any changes in the years following promulgation. In addition, EPA notes the year of the data source referenced in the preliminary study to clearly document the time period.

Table 6-1 summarizes the data quality criteria discussed above.

Table 6-1. Data Quality Criteria Summary

Data Quality Criterion	Description
Accuracy	Underlying data in state and federal reports, peer-reviewed journal articles, and industry publications are accurate.
Reliability	Clearly written, assumptions and methodologies identified.
	Variability and uncertainty in the information are evaluated and characterized.
	Assumptions and methodologies are consistently applied.
Representativeness	Process operations, pollutants, or waste streams that are representative of the metal finishing industry are described.
	Wastewater characteristics of the U.S. metal finishing industry are described. Data sources addressing industry outside of the United States were also included for descriptions of potential wastewater treatment technologies or chemical processes.
	Data sources published in 2000 or later are prioritized; data sources prior to 2000 were used qualitatively.

6.4 Data Quality Evaluation

This section describes the data sources in detail and how they met the evaluation criteria listed in Section 6.3. Table 6-2, at the end of this section, summarizes the data sources and acceptance criteria evaluated. EPA recognizes data sets contain different levels of information and limitations, therefore, EPA evaluates each type of data set and will apply appropriate acceptance criteria based on the purpose of each analysis. Table 6-2 presents the applied acceptance criteria EPA used to evaluate data for the Preliminary Study.

6.4.1 Conference Proceedings, Peer-Reviewed Journal Articles, Other Academic Literature

EPA reviewed selected conference proceedings,[20] peer-reviewed journal articles, and other academic literature in support of its preliminary study of the Metal Finishing Category. EPA used a list of key words (see Appendix B) to identify peer-reviewed journal articles and

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[20] For the preliminary study, EPA focused its literature review on peer-reviewed journal articles and other academic literature, but not on conference proceedings. EPA intends to review conference proceedings and collect additional industry data.

other academic literature. EPA collected over 130 documents from the literature search, recorded them on a quality evaluation tracking spreadsheet, and documented how each data source met (or did not meet) the quality criteria described in Section 6.3 (ERG, 2015). EPA applied the data quality criteria established in the *Environmental Engineering Support for Clean Water Regulations PQAPP* (ERG, 2013) and determined that the data and information obtained from conference proceedings, peer-reviewed journals, and other academic literature were sufficiently accurate, reliable, and relevant for characterizing metal finishing process operations, chemistries, wastewater, and treatment technology performance.

6.4.2 Data and Information Obtained from Industry, Vendors, and Trade Associations

EPA obtained information from direct email or telephone communications with industry personnel, wastewater treatment technology vendors, and trade association representatives to support its preliminary study of the Metal Finishing Category. This included contacting specific facilities, vendors, and trade associations to gather information regarding facility-specific process operations and waste streams. EPA also obtained information from the web sites of metal finishing facilities, vendors, and trade associations. Web site information included descriptions of process operations and company profiles, including, for example, the types of products and services performed. EPA applied the criteria established in the *Environmental Engineering Support for Clean Water Regulations PQAPP* (ERG, 2013) and determined this information was sufficiently accurate, reliable, and representative of the facilities of interest for use in characterizing industry sector trends and qualitative understanding of process operations and treatment technologies used.

6.4.3 Existing Government Publications and Supporting Information

EPA obtained information from government publications and supporting documents, specifically documents supporting the Metal Finishing ELGs and the MP&M proposed rulemaking. During the MP&M proposed rulemaking, EPA evaluated facilities covered under the Metal Finishing ELGs in the 1980's and 1990's. EPA applied the criteria established in the *Environmental Engineering Support for Clean Water Regulations PQAPP* (ERG, 2013) and determined this information was sufficiently accurate and reliable for characterizing metal finishing process operations, chemistries, wastewater characteristics, and wastewater treatment technologies. However, due to the age of the data, EPA determined that the information may not be representative of current industry practices, and only used the information qualitatively to establish a timeline for changes within the industry.

Table 6-2. Data Acceptance Criteria for the Preliminary Study of the Metal Finishing Category

Type of Data	Data Not Usable	Data Usable to Profile Operations and Wastewater Treatment Technologies	Data Usable to Characterize In-Process Waste Streams	Data Usable to Demonstrate Wastewater Treatment Performance/Efficiency
Conference Proceedings, Peer-Reviewed Journal Articles, Other Academic Literature	Article/paper not peer-reviewed or otherwise deemed sufficient for limited purposes such as identifying incidental and qualitative data.	Current and relevant to the specific facilities/industry operations of interest.	Waste stream identified and analytes, units, analytical methods, and detection limits identified. Geographic scope is within the United States.	(1) Represents full-scale system operated at applicable metal finishing facility. (2) Influent and effluent data show that treatment system is well designed and operated. (3) Detailed description of the treatment system and operating conditions. (4) Analytes identified; units, analytical methods and detection limits included.
Data and Information Obtained from Industry, Vendors, and Trade Associations (e.g., direct email or telephone communications with industry, wastewater treatment technology vendors, and trade associations)	(1) The plant has since changed operations (e.g., installed a new treatment system) since the data were collected. (2) Data collected during upset conditions. (3) Represents a process that is not of interest (e.g., sanitary wastewater).	Process operations clearly described.	Waste stream identified and analytes, units, analytical methods, and detection limits identified.	(1) Represent full-scale system operated at applicable metal finishing facility. (2) Influent and effluent data or percent removal identified and show that treatment system is well designed and operated. (3) Detailed description of the treatment system and operating conditions. (4) Analytes identified; units, analytical methods and detection limits included.
Government Publications and Supporting Information (e.g., documents supporting the Metal Finishing ELGs, data collected during the MP&M Rulemaking, DMR and TRI databases, other governmental agency databases/lists)	(1) Data collected by an unknown method or units undefined. (2) Data collected during upset conditions. (3) Represents a process that is not of interest (e.g., sanitary wastewater).	Process operations clearly described.	Waste stream identified and analytes, units, analytical methods, and detection limits identified.	(1) Represents full-scale system operated at applicable metal finishing facility. (2) Influent and effluent data show that treatment system is well designed and operated. (3) Detailed description of the treatment system and operating conditions. (4) Analytes identified; units, analytical methods and detection limits included.

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Appendix A
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Electroplating is the production of a thin surface coating of one metal upon another by electrodeposition. This surface coating is applied to provide corrosion protection, wear or erosion resistance, anti-frictional characteristics, or for decorative purposes. The electroplating of common metals includes the processes in which ferrous or nonferrous basis material is electroplated with copper, nickel, chromium, brass, bronze, zinc, tin, lead, cadmium, iron, aluminum or combinations thereof. Precious metals electroplating includes the processes in which a ferrous or nonferrous basis material is plated with gold, silver, palladium, platinum, rhodium, indium, ruthenium, iridium, osmium, or combinations thereof.

In electroplating, metal ions in either acid, alkaline, or neutral solutions are reduced on cathodic surfaces. The cathodic surfaces are the workpieces being plated. The metal ions in solution are usually replenished by the dissolution of metal from anodes or small pieces contained in inert wire or metal baskets. Replenishment with metal salts is also practiced, especially for chromium plating. In this case, an inert material must be selected for the anodes. Hundreds of different electroplating solutions have been adopted commercially but only two or three types are utilized widely for a particular metal or alloy. For example, cyanide solutions are popular for copper, zinc, brass, cadmium, silver, and gold. However, non-cyanide alkaline solutions containing pyrophosphate have come into use recently for zinc and copper. Zinc, copper, tin and nickel are plated with acid sulfate solutions, especially for plating relatively simple shapes. Cadmium and zinc are sometimes electroplated from neutral or slightly acidic chloride solutions. The most common methods of plating are in barrels, on racks, and continuously from a spool or coil.

Electroless Plating is a chemical reduction process which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of metal without the use of external electrical energy. It has found widespread use in industry due to several unique advantages over conventional electroplating. Electroless plating provides a uniform plating thickness on all areas of the part regardless of the configuration or geometry of the part. An electroless plate on a properly prepared surface is dense and virtually non-porous. Copper and nickel electroless plating are the most common. The basic ingredients in an electroless plating solution are:

1. A source of metal, usually a salt.
2. A reducer to reduce the metal to its base state.
3. A complexing agent to hold the metal in solution (so the metal will not plate out indiscriminately).
4. Various buffers and other chemicals designed to maintain bath stability and increase bath life.

Electroless plating is autocatalytic, i.e., catalysis is promoted from one of the products of a chemical reaction. The chemistry of electroless plating is best exemplified by examining electroless nickel plating. The source of nickel is a salt, such as nickel chloride or nickel sulfate, and the reducer is sodium hypophosphite. The most commonly used complexing agents are citric and glycolic acid. Hypophosphite anions in the presence of water are dehydrogenated by the solid catalytic surface provided by nickel to form acid orthophosphite anions. Active hydrogen atoms are bonded on the catalyst forming a hydride. Nickel ions are reduced to metallic nickel by the active hydrogen atoms, which are in turn oxidized to hydrogen ions. Simultaneously, a portion of the hypophosphite anions are reduced by the active hydrogen and adsorbed on the catalytic surface, producing elemental phosphorus, water and hydroxyl ions. Elemental phosphorus is bonded to or dissolved in the nickel making the reaction irreversible. At the same time hypophosphite anions are catalytically oxidized to acid orthophosphite anions, evolving gaseous hydrogen. The basic plating reactions proceed as follows:

The nickel salt is ionized in water
$NiS0_4 = Ni^{+2} + SO_4^{-2}$
There is then a reduction-oxidation reaction with nickel and sodium hypophosphite.
$Ni^{+2} + SO_4^{-2} + 2NaH_2PO_2 + 2\ H_20 = Ni + 2NaH_2PO_3 + H_2 + H_2SO_4$
The sodium hypophosphite also reacts in the following manner:
$2NaH_2PO_2 + H_2 = 2P + 2NaOH + 2H_2O$

As can be seen in the equations above, both nickel and phosphorus are produced, and the actual metal deposited is a nickel-phosphorus alloy. The phosphorus content can be varied to produce different characteristics in the nickel plate.

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When electroless plating is done on a plastic basis material, catalyst application and acceleration steps are necessary as surface preparation operations. These steps are considered part of the electroless plating unit operation.

Immersion plating is a chemical plating process in which a thin metal deposit is obtained by chemical displacement of the basis metal. Unlike electroless plating, it is not an autocatalytic process. In immersion plating, a metal will displace from solution any other metal that is below it in the electromotive series of elements.

The lower (more noble) metal will be deposited from solution while the more active metal (higher in the series) will be dissolved. A common example of immersion plating is the deposition of copper on steel from an acid copper solution. Because of the similarity of the wastes generated and the materials involved, immersion plating is considered part of the electroless plating unit operation.

Anodizing is an electrolytic oxidation process which converts the surface of the metal to an insoluble oxide. These oxide coatings provide corrosion protection, decorative surfaces, a base for painting and other coating processes, and special electrical and mechanical properties. Aluminum is the most frequently anodized material, while some magnesium and limited amounts of zinc and titanium are also treated.

Although most anodizing involves immersion of racked parts in tanks, continuous anodizing is done on large coils of aluminum in a manner similar to continuous electroplating. For aluminum parts, the formation of the oxide occurs when the parts are made anodic in dilute sulfuric acid or dilute chromic acid solutions. The oxide layer begins formation at the extreme outer surface, and as the reaction proceeds, the oxide grows into the metal. The last formed oxide, known as the boundary layer, is located at the interface between the base metal and the oxide. The boundary is extremely thin and nonporous. The sulfuric acid process is typically used for all parts fabricated from aluminum alloys except for parts subject to stress or containing recesses in which the sulfuric acid solution may be retained and attack the aluminum. Chromic acid anodic coatings are more protective than sulfuric acid coatings and have a relatively thick boundary layer. For these reasons, a chromic acid bath is used if a complete rinsing of the part cannot be achieved.

Coating – This manufacturing operation includes chromating, phosphating, metal coloring, and passivating. These coatings are applied to previously deposited metal or basis material for increased corrosion protection, lubricity, and preparation of the surface for additional coatings or formulation of a special surface appearance. In chromating, a portion of the base metal is converted to one of the components of the protective film formed by the coating solution. This occurs by reaction with aqueous solutions containing hexavalent chromium and active organic or inorganic compounds. Chromate coatings are most frequently applied to zinc, cadmium, aluminum, magnesium, copper, brass, bronze, and silver. Most of the coatings are applied by chemical immersion, although a spray or brush treatment can be used. Changes in the solutions can impart a wide range of colors to the coatings from colorless to iridescent yellow, brass, brown, and olive drab. Additional coloring of the coatings can be achieved by dipping the parts in organic dye baths to produce red, green, blue, and other colors.

Phosphate coatings are used to provide a good base for paints and other organic coatings, to condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and to impart corrosion resistance to the metal surface by the coating itself or by providing a suitable base for rust-preventative oils or waxes. Phosphate conversion coatings are formed by the immersion of iron, steel, or zinc plated steel in a dilute solution of phosphoric acid plus other reagents. The method of applying the phosphate coating is dependent upon the size and shape of the part to be coated. Small parts are coated in barrels immersed in the phosphating solution. Large parts, such as steel sheet and strip, are spray coated or continuously passed through the phosphating solution. Supplemental oil or wax coatings are usually applied after phosphating unless the part is to be painted.

Metal coloring by chemical conversion methods produces a large group of decorative finishes. This operation covers only chemical methods of coloring in which the metal surface is converted into an oxide or similar metallic compound. The most common colored finishes are used on copper, steel, zinc, and cadmium.

Application of the color to the cleaned basis metal involves only a brief immersion in a dilute aqueous solution. The colored films produced on the metal surface are extremely thin and delicate. Consequently, they lack

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resistance to handling and the atmosphere. A clear lacquer is often used to protect the colored metal surface. A large quantity of copper and brass is colored to yield a wide variety of shades and colors. Shades of black, brown, gray, green and patina can be obtained on copper and brass by use of appropriate coloring solutions. The most widely-used colors for ferrous metals are based on oxides which yield black, brown, or blue colors. A number of colors can be developed on zinc depending on the length of immersion in the coloring solution. Yellow, bronze, dark green, black and brown colors can be produced on cadmium. Silver, tin, and aluminum are also colored commercially. Silver is given a gray color by immersion in a polysulfide solution such as ammonium polysulfide. Tin can be darkened to produce an antique finish of pewter by immersion in a solution of nitric acid and copper sulfate.

Passivation refers to forming a protective film on metals, particularly stainless steel and copper, by immersion in an acid solution. Stainless steel is passivated to dissolve any imbedded iron particles and to form a thin oxide film on the surface of the metal. Typical solutions for passivating stainless steel include nitric acid and nitric acid with sodium dichromate. Copper is passivated with a solution of ammonium sulfate and copper sulfate forming a blue-green patina on the surface of the metal.

Etching and Chemical Milling - These processes are used to produce specific design configurations and tolerances or surface appearances on parts (or metal-clad plastic in the case of printed circuit boards)-by controlled dissolution with chemical reagents or etchants. Included in this classification are chemical milling, chemical etching, and bright dipping. Chemical etching is the same process as chemical milling except the rates and depths of metal removal are usually much greater in chemical milling. Typical solutions for chemical milling and etching include ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride, hydrochloric acid, and combinations of these reagents. Bright dipping is a specialized form of etching and is used to remove oxide and tarnish from ferrous and nonferrous materials and is frequently performed just prior to anodizing. Bright dipping can produce a range of surface appearances from bright clean to brilliant, depending on the surface smoothness desired for the finished part. Bright dipping solutions usually involve mixtures of sulfuric, chromic, phosphoric, nitric, or hydrochloric acids. This unit operation also includes the stripping of metallic coatings.

Printed Circuit Board Manufacturing involves the formation of a circuit pattern of conductive metal (usually copper) on nonconductive board materials such as plastic or glass. There are five basic steps involved in the manufacture of printed circuit boards: cleaning and surface preparation, catalyst and electroless plating, pattern printing and masking, electroplating, and etching.

After the initial cutting, drilling and sanding of the boards, the board surface is prepared for plating electroless copper. This surface preparation involves an etchback (removal of built-up plastic around holes) and an acid and alkaline cleaning to remove grime, oils, and fingerprints. The board is then etched and rinsed. Following etching, the catalyst is applied and rinsing operations following catalyst application. The entire board is then electroless copper plated and rinsed.

Following electroless copper plating, a plating resist is applied in non-circuit areas. Following application of a resist, a series of electroplates are applied. First the circuit is copper plated. A solder electroplate is applied next followed by a rinse. For copper removal in non-circuit areas, an etch step is next. After the etch operation, a variety of tab plating processes can be utilized depending on the board design requirements. These include nickel electroplating, gold electroplating, rhodium electroplating, and tin immersion plating. There are presently three main production methods for printed circuit boards: additive, semi-additive, and subtractive. The additive method uses pre-sensitized, unclad material as the starting board; the semi-additive method uses unclad, unsensitized material as the starting board; and the subtractive method begins with copper clad, unsensitized material.

Cleaning involves the removal of oil, grease, and dirt from the surface of the basis material using water, with or without a detergent or other dispersing agent. Alkaline cleaning (both electrolytic and non-electrolytic) and acid cleaning are both included.

Alkaline cleaning is used to remove oily dirt or solid soils from workpieces. The detergent nature of the cleaning solution provides most of the cleaning action; agitation of the solution and movement of the workpiece are secondary. There are three types of alkaline cleaners: soak, spray, and electrolytic. Soak cleaners are used on

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easily removed soil; they are less efficient than spray or electrolytic cleaners. Spray cleaners combine the detergent properties of the solution with the impact force of the spray, which mechanically loosens the soil. The most effective conventional alkaline cleaning method is electrolytic cleaning. The strong agitation of the solution by gas evolution, and oxidation-reduction reactions that occur during electrolysis produce the cleanest surface of the three methods. Also, certain dirt particles become electrically charged and are repelled from the surface.

Direct current (cathodic) cleaning uses the workpiece as the cathode; reverse current (anodic) cleaning uses the workpiece as the anode. In periodic reverse current cleaning, the current is periodically reversed from direct current to reverse current. Periodic reverse cleaning gives improved smut removal, accelerated cleaning, and a more active surface for any subsequent surface finishing operation.

Acid cleaning employs a combination of a wetting agent or detergent with a solution of an inorganic (mineral) acid, organic acid, or an acid salt to remove oil, dirt, or oxide from metal surfaces. Depending on the acid concentration, acid cleaning may be referred to as pickling, acid dipping, descaling, or desmutting. The solution may or may not be heated and can be an immersion or spray operation. Agitation is normally required with soaking, and spray is usually used with complex shapes. An acid dip operation may also follow alkaline cleaning prior to plating. Phosphoric acid mixtures are also commonly used to remove oils and light rust while leaving a phosphate coating that provides a paint base or temporary resistance to rusting. Strong acid solutions are used to remove rust and scale prior to surface finishing.

Machining removes stock from a workpiece by forcing a cutting tool through the workpiece and removing a chip of basis material. Machining operations such as turning, milling, drilling, boring, tapping, planing, broaching, sawing and cutoff, shaving, threading, reaming, shaping, slotting, bobbing, filing, and chamfering are included in this definition.

Grinding removes stock from a workpiece with abrasive grains held by a rigid or semirigid binder. The grinding tool is usually in the form of a disk (the basic shape of grinding wheels), but may also be in the form of a cylinder, ring, cup, stick, strip, or belt. The most commonly used abrasives are aluminum oxide, silicon carbide, and diamond. The processes included in this unit operation are sanding (or cleaning to remove rough edges or excess material), surface finishing, and separating (as in cut-off or slicing operations).

Polishing is an abrading operation used to remove or smooth out surface defects (scratches, pits, tool marks, etc.) that adversely affect the appearance or function of a part. Polishing is usually performed with either a belt or wheel to which an abrasive, such as aluminum oxide or silicon carbide, is bonded. Both wheels and belts are flexible and will conform to irregular or rounded areas where necessary. The operation usually referred to as buffing is included in the polishing operation.

Barrel Finishing or tumbling is a controlled method of processing parts to remove burrs, scale, flash, and oxides to improve surface finish. Widely used as a finishing operation for many parts, it obtains a uniformity of surface finish not possible by hand finishing. For large quantities of small parts it is generally the most economical method of cleaning and surface conditioning. Parts to be finished are placed in a rotating barrel or vibrating unit with an abrasive medium, water, or oil, and usually some chemical compound to assist in the operation. As the barrel rotates slowly, the upper layer of the work is given a sliding movement toward the lower side of the barrel, causing the abrading or polishing action. The same results may also be accomplished in a vibrating unit, in which the entire contents of the container are in constant motion.

Burnishing is the process of finish sizing or smooth finishing a workpiece (previously machined or ground) by displacement, rather than removal, of minute surface irregularities. It is accomplished with a smooth point or line-contact and fixed or rotating tools.

Impact Deformation is the process of applying an impact force to a workpiece such that the workpiece is permanently deformed or shaped. Impact deformation operations include shot peening, peening, forging, high energy forming, heading, and stamping.

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Pressure Deformation is the process of applying force (at a slower rate than an impact force) to permanently deform or shape a workpiece. Pressure deformation includes operations such as rolling, drawing, bending, embossing, coining, swaging, sizing, extruding, squeezing, spinning, seaming, staking, piercing, necking, reducing, forming, crimping, coiling, twisting, winding, flaring, or weaving.

Shearing is the process of severing or cutting a workpiece by forcing a sharp edge or opposed sharp edges into the workpiece, stressing the material to the point of shear failure and separation.

Heat Treating is the modification of the physical properties of a workpiece through the application of controlled heating and cooling cycles. Such operations as tempering, carburizing, cyaniding, nitriding, annealing, normalizing, austenizing, quenching, austempering, siliconizing, martempering, and malleabilizing are included in this definition.

Thermal Cutting comprises cutting, slotting, or piercing a workpiece with an oxyacetylene oxygen lance or electric arc cutting tool.

Welding refers to joining two or more pieces of material by applying heat, pressure, or both, with or without filler material, to produce a localized union through fusion or recrystallization across the interface. Included are gas welding, resistance welding, arc welding, cold welding, electron beam welding, and laser beam welding.

Brazing joins metals by filling a thin (capillary thickness) layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term brazing is used when the temperature exceeds 425°C (800°F).

Soldering is the process of joining metals by filling a thin (capillary thickness) layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term soldering is used when the temperature range falls below 425°C (800°F).

Flame Spraying is the application of a metallic coating to a workpiece using finely powdered fragments of wire, together with suitable fluxes, projected through a cone of flame onto the workpiece.

Sand Blasting removes stock, including surface films, from a workpiece by the use of abrasive grains pneumatically impinged against the workpiece. The abrasive grains used include sand, metal shot, slag, silica, pumice, or natural materials such as walnut shells.

Abrasive Jet Machining is a mechanical process for cutting hard brittle materials. It is similar to sand blasting, but uses much finer abrasives carried at high velocities (500-3,000 fps) by a liquid or gas stream. Uses include frosting glass, removing metal oxides, deburring, and drilling and cutting thin sections of metal.

Electrical Discharge Machining is a process which can remove metal with good dimensional control from any metal. It cannot be used for machining glass, ceramics, or other nonconducting materials. The machining action is caused by the formation of an electrical spark between an electrode, shaped to the required contour, and the workpiece. Since the cutting tool has no contact with the workpiece, it can be made from a soft, easily worked material such as brass. The tool works in conjunction with a fluid such as mineral oil or kerosene, which is fed to the work under pressure. The function of this coolant is to serve as a dielectric, to wash away particles of eroded metal from the workpiece or tool, and to maintain a uniform resistance to flow of current.

Electrical discharge machining is also known as spark machining or electronic erosion. The operation was developed primarily for machining carbides, hard nonferrous alloys, and other hard-to-machine materials.

Electrochemical Machining is a process based on the same principles used in electroplating except the workpiece is the anode and the tool is the cathode. Electrolyte is pumped between the electrodes and a potential applied with the result that metal is rapidly removed.

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In this process, electrode accuracy is important since the surface finish of the electrode tool will be reproduced in the surface of the workpiece. While copper is frequently used as the electrode, brass, graphite, and copper-tungsten are also used. The tool must be an electrical conductor, easy to machine, corrosion resistant, and able to conduct the quantity of current needed. Although there is no standard electrolyte, sodium chloride is more generally used than others.
Electron Beam Machining is a thermoelectric process. In electron beam machining, heat is generated by high velocity electrons impinging on part of the workpiece. At the point where the energy of the electrons is focused, it is transformed into sufficient thermal energy to vaporize the material locally. The process is generally carried out in a vacuum. While the metal-removal rate of electron beam machining is approximately 0.01 milligrams per second, the tool is accurate and is especially adapted for micro-machining. There is no heat affected zone or pressure on the workpiece and extremely close tolerances can be maintained. The process results in X-ray emission which requires that the work area be shielded to absorb radiation. At present the process is used for drilling holes as small as 0.0508 mm (0.002 in.) in any known material, cutting slots, shaping small parts, and machining sapphire jewel bearings.
Laser Beam Machining uses a highly focused monochromatic collimated beam of light is to remove material from a workpiece at the point of impingement. Laser beam machining is a thermoelectric process, and material removal is largely accomplished by evaporation, although some material is removed in the liquid state at high velocity. Since the metal removal rate is very small, they are used for such jobs as drilling microscopic holes in carbides or diamond wire drawing dies, and for removing metal in the balancing of high-speed rotating machinery. Lasers can vaporize any known material. They have small heat-affected zones and work easily with nonmetallic hard materials.
Plasma Arc Machining is the process of material removal or shaping of a workpiece by a high velocity jet of high temperature ionized gas. A gas (nitrogen, argon, or hydrogen) is passed through an electric arc causing it to become ionized and raised to temperatures in excess of 16,649°C (30,000°F). The relatively narrow plasma jet melts and displaces the workpiece material in its path. Because plasma machining does not depend on a chemical reaction between the gas and the work material and because plasma temperatures are extremely high, the process can be used on almost any metal, including those that are resistant to oxygen-fuel gas cutting. The method is of commercial importance mainly for profile cutting of stainless steel and aluminum alloys.
Ultrasonic Machining is a mechanical process designed to effectively machine hard, brittle materials. It removes material by the use of abrasive grains which are carried in a liquid between the tool and the work and which bombard the work surface at high velocity. This action gradually chips away minute particles of material in a pattern controlled by the tool shape and contour. A transducer causes an attached tool to oscillate linearly at a frequency of 20,000 to 30,000 times per second at an amplitude of 0.0254 to 0.127 mm (0.001 to 0.005 in.). The tool motion is produced by being part of a sound wave energy transmission line which causes the tool material to change its normal length by contraction and expansion. The tool holder is threaded to the transducer and oscillates linearly at ultrasonic frequencies, thus driving the grit particles into the workpiece. The cutting particles, boron carbide and similar materials, are of a 280-mesh size or finer, depending upon the accuracy and the finish desired. Operations that can be performed include drilling, tapping, coining, and the making of openings in all types of dies. Ultrasonic machining is used principally on materials such as carbides, tool steels, ceramics, glass, gem stones, and synthetic crystals.
Sintering is the process of forming a mechanical part from a powdered metal by fusing the particles together under pressure and heat. The temperature is maintained below the melting point of the basis metal.
Laminating is adhesive bonding of layers of metal, plastic, or wood to form a part.
Hot Dip Coating is defined by coating a metallic workpiece with another metal by immersion in a molten bath to provide a protective film. Galvanizing (hot dip zinc) is the most common hot dip coating.

Appendix A:
Descriptions of the 46 Unit Operations in the Metal Finishing Industry

Sputtering covers a metallic or nonmetallic workpiece with thin films of metal. The surface to be coated is bombarded with positive ions in a gas discharge tube, which is evacuated to a low pressure.

Vapor Plating is the decomposition of a metal or compound upon a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting point of either the deposit or the basis material.

Thermal Infusion applies a fused zinc, cadmium, or other metal coating to a ferrous workpiece by imbuing the surface of the workpiece with metal powder or dust in the presence of heat.

Salt Bath Descaling is the process of removing surface oxides or scale from a workpiece by immersion of the workpiece in a molten salt bath or a hot salt solution. Molten salt baths are used in a salt bath—water quench—acid dip sequence to clean hard-to-remove oxides from stainless steels and other corrosion-resistant alloys. The work is immersed in the molten salt (temperatures range from 400 to 540 degrees C), quenched with water, and then dipped in acid. Oxidizing, reducing, and electrolytic baths are available, and the particular type needed depends on the oxide to be removed.

Solvent Degreasing removes oils and grease from the surfaces of a workpiece by the use of organic solvents, such as aliphatic petroleums (e.g., kerosene, naptha), aromatics (e.g., benzene, toluene), oxygenated hydrocarbons (e.g., ketones, alcohol, ether), halogenated hydrocarbons (e.g., 1,1,1-trichloroethane, trichloroethylene, methylene chloride), and combinations of these classes of solvents. Solvent cleaning can be accomplished by either the liquid or vapor phase of these solvents. Solvent vapor degreasing is normally quicker than solvent liquid degreasing. However, ultrasonic vibration is sometimes used with liquid solvent so as to decrease the immersion time required with complex shapes. Solvent cleaning is often used as a precleaning operation, e.g., prior to the alkaline cleaning that precedes plating, as a final cleaning of precision parts, or as a surface preparation for some painting operations.

Emulsion cleaning is a type of solvent degreasing that uses common organic solvents (e.g., kerosene, mineral oil, glycols, and benzene) dispersed in an aqueous medium with the aid of an emulsifying agent. Depending on the solvent used, cleaning is done at temperatures from room temperature to 82°C (180°F). This operation uses less chemical than solvent degreasing because a lower solvent concentration is employed. The process is used for rapid superficial cleaning and is usually performed as emulsion spray cleaning.

Paint Stripping is the removal of an organic coating from a workpiece. The stripping of such coatings is usually performed with caustic, acid, solvent, or molten salt.

Painting refers to the application of an organic coating to a workpiece. The application of coatings such as paint, varnish, lacquer, shellac, and plastics by spraying, dipping, brushing, roll coating, lithographing, and wiping are included. Spray painting is by far the most common and can be used with nearly all varieties of paint. The paint can be sprayed manually or automatically, hot or cold, and it may be atomized with or without compressed air to force the paint through an orifice. Other processes included under this unit operation are printing, silk screening, and stenciling.

Electrostatic Painting is the application of electrostatically charged paint particles to an oppositely charged workpiece followed by thermal fusing of the paint particles to form a cohesive paint film. Usually the paint is applied in spray form and may be applied manually or automatically, hot or cold, and with or without compressed air atomization. Both waterborne and solvent-borne coatings can be sprayed electrostatically.

Electropainting is the process of coating a workpiece by making it either anodic or cathodic in a bath that is generally an aqueous emulsion of the coating material. The electrodeposition bath contains stabilized resin, dispersed pigment, surfactants, and sometimes organic solvents in water. Electropainting is used primarily for primer coats because it gives a fairly thick, highly uniform, corrosion resistant coating in relatively little time.

Vacuum Metalizing coats a workpiece with metal by flash heating metal vapor in a high-vacuum chamber containing the workpiece. The vapor condenses on all exposed surfaces.

Appendix A:

Descriptions of the 46 Unit Operations in the Metal Finishing Industry

Assembly is the fitting together of previously manufactured parts or components into a complete machine, unit of a machine, or structure.
Calibration is the application of thermal, electrical, or mechanical energy to set or establish reference points for a component or complete assembly.
Testing is the application of thermal, electrical, or mechanical energy to determine the suitability or functionality of a component or complete assembly.
Mechanical Plating is the process of depositing metal coatings on a workpiece using a tumbling barrel, metal powder, and usually glass beads for the impaction media. The operation is subject to the same cleaning and rinsing operations that are applied before and after the electroplating operation.

Source: U.S. EPA, 1983a

Appendix B
Keyword Search Terms for the Metal Finishing Industry

Appendix B: Keyword Search Terms for the Metal Finishing Industry

Master Terms

Metal Finishing
Industrial Wastewater
Industrial Wastewater Treatment
Metals Removal

General Terms

Case study
Effluent
Elimination
Green
Pilot (scale)
Full/Field (scale)
Improvement
Influent
Nano
Percent (%)
Performance
Pollution Prevention
Recovery/recycle
Reduce/Reduction
Removal
Rinse Water
Replacement

6 Primary Metal Finishing Operations

- Electroplating
- Electroless Plating
- Anodizing
- Coating
  - Chromating
  - Phosphating
  - Coloring
- Chemical Etching and Milling
- Printed Circuit Board Manufacture

Pollutants

Cadmium
Chromium
Hexavalent Chromium
Phosphate
Trivalent Chromium
Cyanide

Process Operations
Aluminum Coating
Bright Dipping
Brighteners
Cadmium Free Technologies
Cell Phone Screen Manufacturing
Chemical Etching and Milling
Dry Technologies
Hexavalent Chromium Free Technologies
New Wastewater Treatment Technologies
Nickel Fluorocarbon
Phosphate free technologies
Phosphoric Acid
Powder Coating
Reuse
Replacement for Phosphating
Solar Panel Manufacturing
Transition Metal Coatings
Transportation equipment cleaning
Zero Liquid Discharge
Zinc-Nickel Alloy Coating
Zirconization

Appendix C
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Appendix C:
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
Sulfide precipitation	A precipitation technique using hydrogen sulfide or soluble sulfide salts to precipitate metal sulfides. May also use ferrous or ferric sulfates to precipitate metals, specifically for complex wastewater. Full-scale application in metal finishing.	Inorganics Removal; Complex Metals Removal	Aluminum anodizing wastewater	Aluminum Chromium (VI) Chromium	0.112 Non-detect Non-detect	97.3 100 100
			Metal finishing wastewater	Chromium (VI) Chromium Iron Zinc	<0.01 <0.04 0.1 <0.07	>99.9 >99.9 80.8 >99.8
			Metal finishing wastewater	Chromium (VI) Chromium Copper Zinc	<0.005 <0.005 0.003 0.009	>99.9 >99.9 89.7 85
			Industrial wastewater	Chromium (VI) Chromium, total Iron Nickel Zinc	<0.02 <0.1 0.6 <0.1 <0.1	>9.1 >95.8 99.4 >85.3 >99.7
			Metal finishing wastewater (cyanide bearing)	Cyanide, total	0.024	99.2
High pH precipitation	Precipitation technique operating at high pH levels for complex wastewater treatment. Full-scale application in metal finishing.	Complex Metals Removal	No data available			
Chemical reduction	Precipitation technique operating at low pH levels for complex wastewater	Inorganics Removal; Complex Metals Removal	No data available			

Appendix C:
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
	treatment. Addition of reducing agent to reduce metals oxidation state to allow precipitation at high pH. Commonly used for hexavalent chromium reduction. Full-scale application in metal finishing for chromium reduction.					
Electrochemical Chromium Reduction	Selective reduction of hexavalent chromium by applying an electric current across iron electrodes to free ferrous ions that further react with chromate in solution to form chromic and ferrous hydroxides. Also effective with zinc. Full-scale application in metal finishing.	Inorganics Removal	Metal finishing wastewater	Chromium (VI) Zinc	0.05 0.1	99.5 96.7
Oxidation by Chlorination	Addition of chlorine in an alkaline environment to convert cyanide into carbon dioxide and nitrogen.	Inorganics Removal; Complex Metals Removal	Metal finishing wastewater	Cyanide	Non-detect	>99
Oxidation by Ozonation	The generation of ozone via an electrical discharge process that is dissolved in the wastewater to convert cyanide compounds into cyanates that are subsequently decomposed by other methods. Full-scale application in metal finishing.	Inorganics Removal	Cyanide bearing wastewater	Cyanide, total Cyanide, amenable	0.083 0.082	91.6 91.7
Oxidation by Ozonation with UV Radiation	In addition to oxidation by ozone, simultaneous application of ultraviolet light. Commonly used to treat complex cyanide salts.	Inorganics Removal; Complex Metals Removal	No data available.			

Appendix C:
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
	Full-scale application in metal finishing.					
Oxidation by Hydrogen Peroxide	Addition of peroxides to convert cyanides to cyanates. Applicable to cyanide-bearing wastewater containing zinc or cadmium. Full-scale application in metal finishing for cyanide destruction and metal recovery.	Inorganics Removal; Metal/Chemical Recovery	No data available.			
Electrochemical Cyanide Oxidation	Conversion of cyanides to cyanates by applying an electric current across iron electrodes to generate ions that further react with cyanide via ozonation and direct oxidation. No full-scale application for metal finishing in 1983.	Inorganics Removal	No data available.			
Flotation	Solids removal process using air bubbles to carry suspended solids to the surface where they are skimmed off and disposed. Commonly used to treat wastewaters with suspended solids near the specific gravity of 1.0, which make gravity settling difficult. Also used for oily waste treatment. Full-scale application in oily waste removal. Bench scale studies in heavy metals removal.	Inorganics Removal	No data available.			
Membrane Filtration	Solids removal process by recirculating wastewater through a tubular membrane	Complex Metals Removal; Polishing	Metal finishing wastewater	Chromium (VI)	0.008 0.038	98.9 99.8

Appendix C:
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
	filter to enhance removal of heavy metals. May also be used to treat complex wastewater. Full-scale application in metal finishing.			Chromium Copper Iron Lead Nickel Zinc TSS	0.13 0.28 0.01 0.18 0.05 4.05	98.5 99.3 97.5 99.8 98.4 69.2
Diatomaceous Earth Filtration	Solids separation device to further enhance suspended solids removal. Equipment includes multiple leaf screens coated with diatomaceous earth, filter housing, and pumps. Full-scale application in metal finishing.	Polishing	Unclarified chemical precipitation effluent (metal finishing)	TSS Cadmium Chromium Copper Lead Nickel Tin Zinc	35.6 0.01 0.19 1.39 0.06 0.20 0.08 1.68	94.2 59.1 97.4 94.4 70.9 87.1 87.1 89.0
Peat Adsorption	Solids removal through chemical bonding between naturally occurring functional groups in peat moss and transition metals and polar organic molecules in wastewater. Pilot scale studies in metal finishing. Full-scale application in textile, newsprint, and metal reclamation industries.	Polishing	Industrial wastewater	Antimony Chromium (VI) Copper Cyanide Lead Mercury Nickel Silver Zinc	0.9 <0.04 0.24 0.7 0.025 0.02 0.07 0.05 0.25	64.0 >99.9 99.9 98.1 99.9 >98.0 97.2 >95.0 83.3
Insoluble Starch Xanthate	Ion exchange resin material that can treat wastewater in a batch or continuous process or as a filter precoat. Full-scale application in metal finishing.	Polishing; Metal/Chemical Recovery	Treated metal finishing effluent	All metals	0.02	98.0
			Metal finishing rinse water	Copper Iron Lead Nickel	0.26 0.13 0.27 273.5	3.9 31.6 5.4 0.9

Appendix C:
Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
				Tin	0.75	25.0
				Zinc	0.063	16.4
Electrolytic Recovery	Selective reduction of a metal by applying an electric current across electrodes and allowing a plating process to occur to recover the metal. Full-scale application in metal finishing.	Metal/Chemical Recovery	Photographic processing wastewater	Silver	21	95.6
Evaporation	Concentration process where water evaporates from solution and increases concentration of solute in remaining solution. May also involve a condensation process. Full-scale application in metal finishing.	Metal/Chemical Recovery; In-plant Controls	No data available			
Ion Exchange	Exchange of ionic contaminants in wastewater with ions of the resin. Commonly used to recover process chemicals and metals from rinsewater to allow reuse. Many metal finishers use the technology to concentrate and purify plating baths. Full-scale application in metal finishing.	Metal/Chemical Recovery; In-plant Controls	Electroplating rinse water	Aluminum Cadmium Chromium (III) Chromium (VI) Copper Cyanide Iron Manganese Nickel Silver Tin Zinc	0.2 0.00 0.01 0.01 0.09 0.04 0.01 0.00 0.00 0.00 0.00 0.4	96.4 100 99.7 99.9 98.0 99.6 99.9 100 100 100 100 97.3
			Printed circuit board	Copper Cyanide	0.1 0.09	99.8 97.4

Appendix C:

Wastewater Treatment Technologies Evaluated for Metals Removal in the 1983 Metal Finishing ELGs

Treatment Technology	Technology Description	Main Treatment Purpose	Type of Wastewater	Pollutant	Average Effluent Concentration (mg/L)	Average Percent Removal (%)
			manufacturing rinse water	Gold	0.1	95.7
				Lead	0.01	99.4
				Nickel	0.01	99.4
				Silver	0.01	99.9
				Sulfate	2	99.0
				Tin	0.1	90.9
			Metal finishing rinse water	Chromium	0.03	76.9
				Copper	0.16	99.8
				Nickel	0.003	89.6
			Photographic processing wastewater	Silver	0.093	90.3