12.20 Electroplating

This section addresses the electroplating industry. However, emphasis is placed on chromium electroplating and chromic acid anodizing because the majority of emissions data and other information available were for this area of the electroplating industry. Detailed information on the process operations, emissions, and controls associated with other types of electroplating will be added to this section as it becomes available. The six-digit Source Classification Code (SCC) for electroplating is 3-09-010.

12.20.1 Process Description[1-4]

Electroplating is the process of applying a metallic coating to an article by passing an electric current through an electrolyte in contact with the article, thereby forming a surface having properties or dimensions different from those of the article. Essentially any electrically conductive surface can be electroplated. Special techniques, such as coating with metallic-loaded paints or silver-reduced spray, can be used to make nonconductive surfaces, such as plastic, electrically conductive for electroplating. The metals and alloy substrates electroplated on a commercial scale are cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, platinum group metals, silver, tin, zinc, brass, bronze, many gold alloys, lead-tin, nickel-iron, nickel-cobalt, nickel-phosphorus, tin-nickel, tin-zinc, zinc-nickel, zinc-cobalt, and zinc-iron. Electroplated materials are generally used for a specific property or function, although there may be some overlap, e. g., a material may be electroplated for decorative use as well as for corrosion resistance.

The essential components of an electroplating process are an electrode to be plated (the cathode or substrate), a second electrode to complete the circuit (the anode), an electrolyte containing the metal ions to be deposited, and a direct current power source. The electrodes are immersed in the electrolyte with the anode connected to the positive leg of the power supply and the cathode to the negative leg. As the current is increased from zero, a point is reached where metal plating begins to occur on the cathode. The plating tank is either made of or lined with totally inert materials to protect the tank. Anodes can be either soluble or insoluble, with most electroplating baths using one or the other type. The majority of power supplies are solid-state silicon rectifiers, which may have a variety of modifications, such as stepless controls, constant current, and constant voltage. Plate thickness is dependent on the cathode efficiency of a particular plating solution, the current density, and the amount of plating time. The following section describes the electroplating process. Following the description of chromium plating, information is provided on process parameters for other types of electroplating.

12.20.1.1 Chromium Electroplating -

Chromium plating and anodizing operations include hard chromium electroplating of metals, decorative chromium electroplating of metals, decorative chromium electroplating of plastics, chromic acid anodizing, and trivalent chromium plating. Each of these categories of the chromium electroplating industry is described below.

Hard Chromium Electroplating -

In hard plating, a relatively thick layer of chromium is deposited directly on the base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance, or to build up surfaces that have been eroded by use. Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware.

Figure 12.20-1 presents a process flow diagram for hard chromium electroplating. The process consists of pretreatment, alkaline cleaning, acid dipping, chromic acid anodizing, and chromium electroplating. The pretreatment step may include polishing, grinding, and degreasing. Degreasing consists of either dipping the part in organic solvents, such as trichloroethylene or perchloroethylene, or using the vapors from organic solvents to remove surface grease. Alkaline cleaning is used to dislodge surface soil with inorganic cleaning solutions, such as sodium carbonate, sodium phosphate, or sodium hydroxide. Acid dipping, which is optional, is used to remove tarnish or oxide films formed in the alkaline cleaning step and to neutralize the alkaline film. Acid dip solutions typically contain 10 to 30 percent hydrochloric or sulfuric acid. Chromic acid anodic treatment, which also is optional, cleans the metal surface and enhances the adhesion of chromium in the electroplating step. The final step in the process is the electroplating operation itself.

The plating tanks typically are equipped with some type of heat exchanger. Mechanical agitators or compressed air supplied through pipes on the tank bottom provide uniformity of bath temperature and composition. Chromium electroplating requires constant control of the plating bath temperature, current density, plating time, and bath composition.

Hexavalent chromium plating baths are the most widely used baths to deposit chromium on metal. Hexavalent chromium baths are composed of chromic acid, sulfuric acid, and water. The chromic acid is the source of the hexavalent chromium that reacts and deposits on the metal and is emitted to the atmosphere. The sulfuric acid in the bath catalyzes the chromium deposition reactions.

The evolution of hydrogen gas from chemical reactions at the cathode consumes 80 to 90 percent of the power supplied to the plating bath, leaving the remaining 10 to 20 percent for the deposition reaction. When the hydrogen gas evolves, it causes misting at the surface of the plating bath, which results in the loss of chromic acid to the atmosphere.

Decorative Chromium Electroplating -

Decorative chromium electroplating is applied to metals and plastics. In decorative plating of metals, the base material generally is plated with layers of copper and nickel followed by a relatively thin layer of chromium to provide a bright surface with wear and tarnish resistance. Decorative plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing fixtures.

Figure 12.20-2 presents a process flow diagram for decorative chromium electroplating. The process consists of pretreatment, alkaline cleaning, and acid dipping, which were described previously, followed by strike plating of copper, copper electroplating, nickel electroplating, and chromium electroplating. The copper strike plating step consists of applying a thin layer of copper in a copper cyanide solution to enhance the conductive properties of the base metal. Following the copper strike plate, the substrate is acid dipped again, and then electroplated with an undercoat of copper to improve corrosion resistance and cover defects. Either a copper cyanide or acid copper solution is used in this step. The substrate then is plated with nickel in two layers (semibright nickel and bright nickel) to further improve corrosion resistance and activate the surface metal for chromium electroplating.

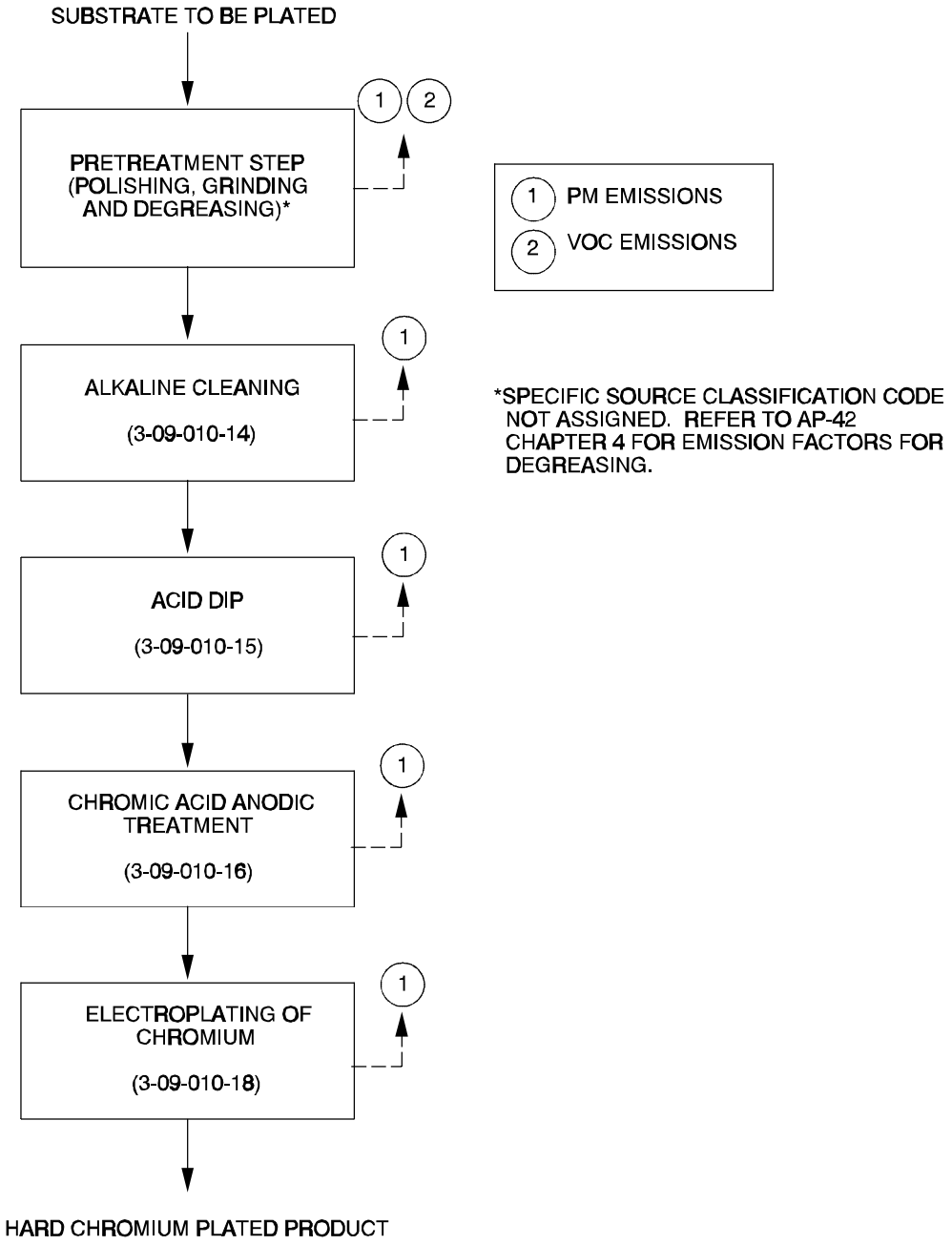

Figure 12.20-1. Flow diagram for a typical hard chromium plating process.[3]
(Source Classification Codes in parentheses.)

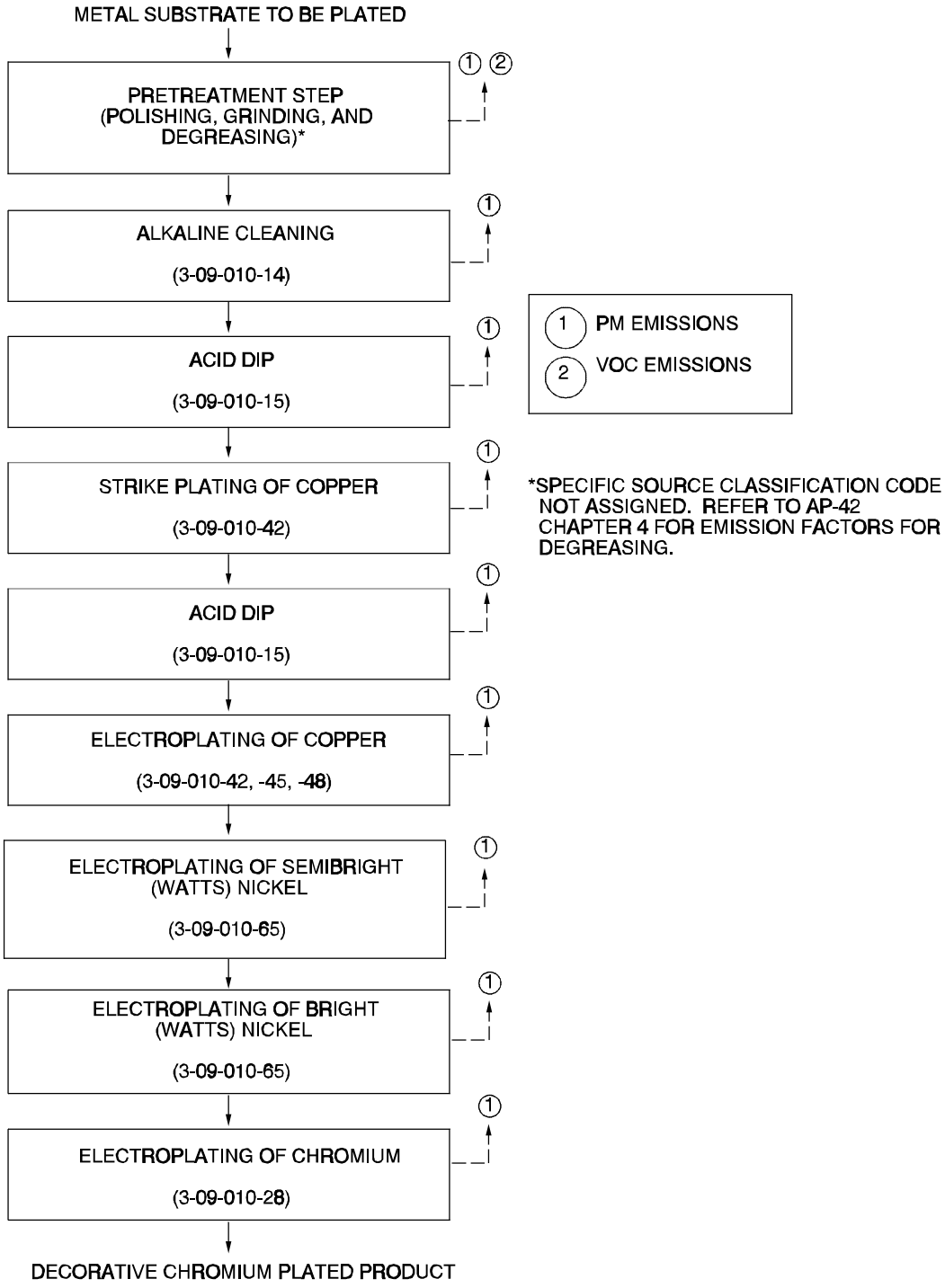

Figure 12.20-2. Flow diagram for decorative chromium plating on a metal substrate.[3] (Source Classification Codes in parentheses.)

Semibright and bright nickel plating both use Watts plating baths. The final step in the process is the electroplating operation itself.

Decorative electroplating baths operate on the same principle as that of the hard chromium plating process. However, decorative chromium plating requires shorter plating times and operates at lower current densities than does hard chromium plating. Some decorative chromium plating operations use fluoride catalysts instead of sulfuric acid because fluoride catalysts, such as fluosilicate or fluoborate, have been found to produce higher bath efficiencies.

Most plastics that are electroplated with chromium are formed from acrylonitrile butadiene styrene (ABS). The process for chromium electroplating of ABS plastics consists of the following steps: chromic acid/sulfuric acid etch; dilute hydrochloric acid dip; colloidal palladium activation; dilute hydrochloric acid dip; electroless nickel plating or copper plating; and chromium electroplating cycle. After each process step, the plastic is rinsed with water to prevent carry-over of solution from one bath to another. The electroplating of plastics follows the same cycle as that described for decorative chromium electroplating.

Chromic Acid Anodizing -

Chromic acid anodizing is used primarily on aircraft parts and architectural structures that are subject to high stress and corrosion. Chromic acid anodizing is used to provide an oxide layer on aluminum for corrosion protection, electrical insulation, ease of coloring, and improved dielectric strength. Figure 12.20-3 presents a flow diagram for a typical chromic acid anodizing process.

There are four primary differences between the equipment used for chromium electroplating and that used for chromic acid anodizing: chromic acid anodizing requires the rectifier to be fitted with a rheostat or other control mechanism to permit starting at about 5 V; the tank is the cathode in the electrical circuit; the aluminum substrate acts as the anode; and sidewall shields typically are used instead of a liner in the tank to minimize short circuits and to decrease the effective cathode area. Types of shield materials used are herculite glass, wire safety glass, neoprene, and vinyl chloride polymers.

Before anodizing, the aluminum must be pretreated by means of the following steps: alkaline soak, desmutting, etching, and vapor degreasing. The pretreatment steps used for a particular aluminum substrate depend upon the amount of smut and the composition of the aluminum. The aluminum substrate is rinsed between pretreatment steps to remove cleaners.

During anodizing, the voltage is applied step-wise (5 V per minute) from 0 to 40 V and maintained at 40 V for the remainder of the anodizing time. A low starting voltage (i. e., 5 V) minimizes current surge that may cause "burning" at contact points between the rack and the aluminum part. The process is effective over a wide range of voltages, temperatures, and anodizing times. All other factors being equal, high voltages tend to produce bright transparent films, and lower voltages tend to produce opaque films. Raising the bath temperature increases current density to produce thicker films in a given time period. Temperatures up to 49°C (120°F) typically are used to produce films that are to be colored by dyeing. The amount of current varies depending on the size of the aluminum parts; however, the current density typically ranges from 1,550 to 7,750 A/m^2 (144 to 720 A/ft^2).

The postanodizing steps include sealing and air drying. Sealing causes hydration of the aluminum oxide and fills the pores in the aluminum surface. As a result, the elasticity of the oxide film increases, but the hardness and wear resistance decrease. Sealing is performed by immersing

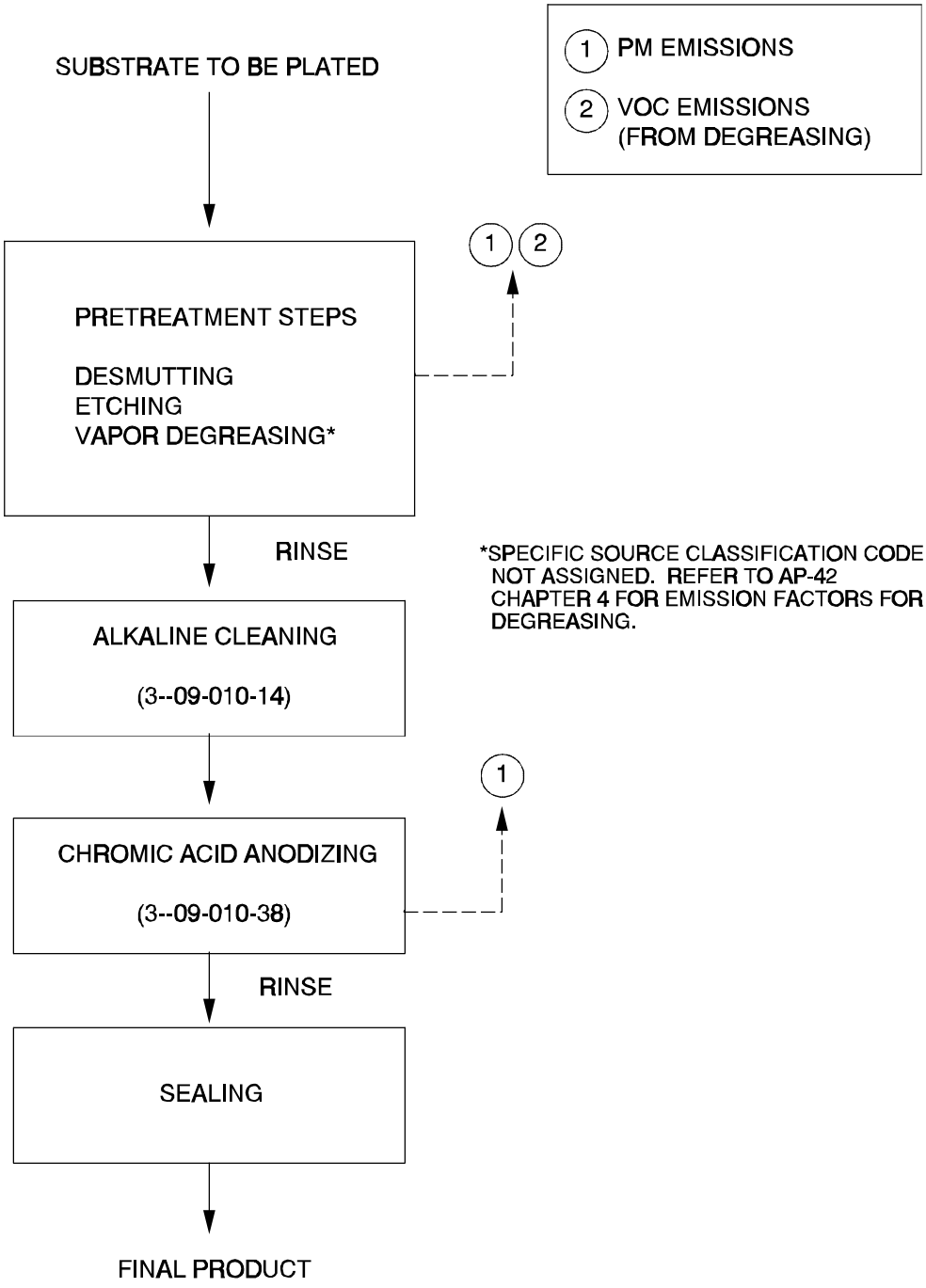

Figure 12.20-3. Flow diagram for a typical chromic acid anodizing process.[3] (Source Classification Codes in parentheses.)

aluminum in a water bath at 88° to 99°C (190° to 210°F) for a minimum of 15 minutes. Chromic acid or other chromates may be added to the solution to help improve corrosion resistance. The aluminum is allowed to air dry after it is sealed.

Trivalent Chromium Plating -

Trivalent chromium electroplating baths have been developed primarily to replace decorative hexavalent chromium plating baths. Development of a trivalent bath has proven to be difficult because trivalent chromium solvates in water to form complex stable ions that do not readily release chromium. Currently, there are two types of trivalent chromium processes on the market: single-cell and double-cell. The major differences in the two processes are that the double-cell process solution contains minimal-to-no chlorides, whereas the single-cell process solution contains a high concentration of chlorides. In addition, the double-cell process utilizes lead anodes that are placed in anode boxes that contain a dilute sulfuric acid solution and are lined with a permeable membrane, whereas the single-cell process utilizes carbon or graphite anodes that are placed in direct contact with the plating solution. Details on these processes are not available because the trivalent chromium baths currently on the market are proprietary.

The advantages of the trivalent chromium processes over the hexavalent chromium process are fewer environmental concerns due to the lower toxicity of trivalent chromium, higher productivity, and lower operating costs. In the trivalent chromium process, hexavalent chromium is a plating bath contaminant. Therefore, the bath does not contain any appreciable amount of hexavalent chromium. The total chromium concentration of trivalent chromium solutions is approximately one-fifth that of hexavalent chromium solutions. As a result of the chemistry of the trivalent chromium electrolyte, misting does not occur during plating as it does during hexavalent chromium plating. Use of trivalent chromium also reduces waste disposal problems and costs.

The disadvantages of the trivalent chromium process are that the process is more sensitive to contamination than the hexavalent chromium process, and the trivalent chromium process cannot plate the full range of plate thicknesses that the hexavalent chromium process can. Because it is sensitive to contamination, the trivalent chromium process requires more thorough rinsing and tighter laboratory control than does the hexavalent chromium process. Trivalent chromium baths can plate thicknesses ranging up to 0.13 to 25 µm (0.005 to 1.0 mils) and, therefore, cannot be used for most hard chromium plating applications. The hexavalent chromium process can plate thicknesses up to 762 µm (30 mils).

12.20.1.2 Electroplating-Other Metals -

Brass Electroplating -

Brass, which is an alloy of copper and uzinc, is the most widely used alloy electroplate. Brass plating primarily is used for decorative applications, but it is also used for engineering applications such as for plating steel wire cord for steel-belted radial tires. Although all of the alloys of copper and zinc can be plated, the brass alloy most often used includes 70 to 80 percent copper, with the balance zinc. Typical brass plating baths include 34 g/L (4.2 oz/gal) of copper cyanide and 10 g/L (1.3 oz/gal) of zinc cyanide. Other bath constituents include sodium cyanide, soda ash, and ammonia.

Cadmium Electroplating -

Cadmium plating generally is performed in alkaline cyanide baths that are prepared by dissolving cadmium oxide in a sodium cyanide solution. However, because of the hazards associated with cyanide use, noncyanide cadmium plating solutions are being used more widely. The primary noncyanide plating solutions are neutral sulfate, acid fluoborate, and acid sulfate. The cadmium

concentration in plating baths ranges from 3.7 to 94 g/L (0.5 to 12.6 oz/gal) depending on the type of solution. Current densities range from 22 to 970 A/m^2 (2 to 90 A/ft^2).

Copper Electroplating -

Copper cyanide plating is widely used in many plating operations as a strike. However, its use for thick deposits is decreasing. For copper cyanide plating, cuprous cyanide must be complexed with either potassium or sodium to form soluble copper compounds in aqueous solutions. Copper cyanide plating baths typically contain 30 g/L (4.0 oz/gal) of copper cyanide and either 59 g/L (7.8 oz/gal) of potassium cyanide or 48 g/L (6.4 oz/gal) of sodium cyanide. Current densities range from 54 to 430 A/m^2 (5 to 40 A/ft^2). Cathode efficiencies range from 30 to 60 percent.

Other types of baths used in copper plating include copper pyrophosphate and copper sulfate baths. Copper pyrophosphate plating, which is used for plating on plastics and printed circuits, requires more control and maintenance of the plating baths than copper cyanide plating does. However, copper pyrophosphate solutions are relatively nontoxic. Copper pyrophosphate plating baths typically contain 53 to 84 g/L (7.0 to 11.2 oz/gal) of copper pyrophosphate and 200 to 350 g/L (27 to 47 oz/gal) of potassium pyrophosphate. Current densities range from 110 to 860 A/m^2 (10 to 80 A/ft^2).

Copper sulfate baths, which are more economical to prepare and operate than copper pyrophosphate baths, are used for plating printed circuits, electronics, rotogravure, and plastics, and for electroforming and decorative uses. In this type of bath copper and sulfate and sulfuric acid form the ionized species in solution. Copper sulphate plating baths typically contain 195 to 248 g/L (26 to 33 oz/gal) of copper sulphate and 11 to 75 g/L (1.5 to 10 oz/gal) of sulfuric acid. Current densities range from 215 to 1,080 A/m^2 (20 to 100 A/ft^2).

Gold Electroplating -

Gold and gold alloy plating are used in a wide variety of applications. Gold plating solutions can be classified in five general groups: alkaline gold cyanide, for gold and gold alloy plating; neutral cyanide gold, for high purity gold plating; acid gold cyanide, for bright hard gold and gold alloy plating; noncyanide (generally sulfite), for gold and gold plating; and miscellaneous. Alkaline gold cyanide plating baths contain 8 to 20 g/L (1.1 to 2.7 oz/gal) of potassium gold cyanide and 15 to 100 g/L (2.0 to 13.4 oz/gal) of potassium cyanide. Current densities range from 11 to 86 A/m^2 (1.0 to 8 A/ft^2) and cathode efficiencies range from 90 to 100 percent.

Neutral gold cyanide plating baths contain 8 to 30 g/L (1.1 to 4.0 oz/gal) of potassium gold cyanide. Current densities range from 11 to 4,300 A/m^2 (1.0 to 400 A/ft^2), and cathode efficiencies range from 90 to 98 percent.

Acid gold cyanide plating baths contain 8 to 16 g/L (1.1 to 2.1 oz/gal) of potassium gold cyanide. Current densities range from 11 to 4,300 A/m^2 (1.0 to 400 A/ft^2), and cathode efficiencies range from 30 to 40 percent.

Indium Electroplating -

In general, indium is electroplated using three types of plating baths: cyanide, sulfamate, and fluoborate. Indium is the only trivalent metal that can be electrodeposited readily from a cyanide solution. Cyanide baths are used in applications that require very high throwing power and adhesion. Indium cyanide plating baths typically contain 33 g/L (4.0 oz/gal) of indium metal and 96 g/L (12.8 oz/gal) of total cyanide. Current densities range from 162 to 216 A/m^2 (15 to 20 A/ft^2), and cathode efficiencies range from 50 to 75 percent.

Indium sulfamate baths are very stable, relatively easy to control, and characterized by a high cathode efficiency that remains relatively high (90 percent). The plating baths typically contain 105 g/L (14 oz/gal) of indium sulfamate and 26 g/L (3.5 oz/gal) of sulfamic acid. Current densities range from 108 to 1,080 A/m^2 (10 to 100 A/ft^2).

Indium fluoborate plating baths typically contain 236 g/L (31.5 oz/gal) of indium fluoborate and 22 to 30 g/L (2.9 to 4.0 oz/gal) of boric acid. Current densities range from 540 to 1,080 A/m^2 (50 to 100 A/ft^2), and cathode efficiencies range from 40 to 75 percent.

Nickel Electroplating -

Nickel plating is used for decorative, engineering, and electroforming purposes. Decorative nickel plating differs from other types of nickel plating in that the solutions contain organic agents, such as benzene disulfonic acids, benzene trisulfonic acid, naphthalene trisulfonic acid, benzene sulfonamide, formaldehyde, coumarin, ethylene cyanohydrin, and butynediol. Nickel plating for engineering applications uses solutions that deposit pure nickel. In nickel plating baths, the total nickel content ranges from 60 to 84 g/L (8 to 11.2 oz/gal), and boric acid concentrations range from 30 to 37.5 g/L (4 to 5 oz/gal). Current densities range from 540 to 600 A/m^2 (50 to 60 A/ft^2), and cathode efficiencies range from 93 to 97 percent.

Palladium and Palladium-Nickel Electroplating -

Palladium plating solutions are categorized as ammoniacal, chelated, or acid. Ammoniacal palladium plating baths contain 10 to 15 g/L (1.3 to 2.0 oz/gal) of palladium ammonium nitrate or palladium ammonium chloride, and current densities range from 1 to 25 A/m^2 (0.093 to 2.3 A/ft^2). Palladium acid plating baths contain 50 g/L (6.7 oz/gal) of palladium chloride, and current densities range from 1 to 10 A/m^2 (0.093 to 0.93 A/ft^2).

Palladium alloys readily with other metals, the most important of which is nickel. Palladium nickel electroplating baths contain 3 g/L (6.7 oz/gal) of palladium metal and 3 g/L (6.7 oz/gal) of nickel metal.

Platinum Electroplating -

Solutions used for platinum plating are similar to those used for palladium plating. Plating baths contain 5.0 to 20 g/L (0.68 oz/gal) of either dinitroplatinite sulfate or chloroplatinic acid, and current densities range from 1 to 20 A/m^2 (0.093 to 1.86 A/ft^2).

Rhodium Electroplating -

Rhodium plating traditionally has been used as decorative plating in jewelry and silverware. However, the use of rhodium plating for electronics and other industrial applications has been increasing in recent years. For decorative plating, rhodium baths contain 1.3 to 2.0 g/L (0.17 to 0.27 oz/gal) of rhodium phosphate or rhodium sulfate concentrate and 25 to 80 ml/L (3.0 to 11 oz/gal) of phosphoric or sulfuric acid. Current densities typically range from 20 to 100 A/m^2 (1.86 to 9.3 $A\text{-}ft^2$). For industrial and electronic applications, rhodium plating baths contain approximately 5.0 g/L (0.67 oz/gal) of rhodium metal as sulfate concentrate and 25 to 50 ml/L (3.0 to 7.0 oz/gal) of sulfuric acid. Current densities typically range from 10 to 30 A/m^2 (0.93 to 2.79 $A\text{-}ft^2$), and cathode efficiency ranges from 70 to 90 percent with agitation or 50 to 60 percent without agitation.

Ruthenium Electroplating -

Electroplated ruthenium is a very good electrical conductor and produces a very hard deposit. Typical plating baths contain approximately 5.3 g/L (0.71 oz/gal) of ruthenium as sulfamate or nitrosyl

sulfamate and 8.0 g/L (1.1 oz/gal) of sulfamic acid. Current densities typically range from 108 to 320 A/m^2 (10 to 30 A-ft^2), and cathode efficiency is typically about 20 percent.

Silver Electroplating -

Silver plating traditionally has been performed using a cyanide-based plating solution. Although some noncyanide solutions have been developed, due to various shortcomings, cyanide solutions still are commonly used. Typical plating baths contain 5.0 to 40 g/L (0.67 to 5.3 oz/gal) of silver as potassium silver cyanide and 12 to 120 g/L (1.6 to 16 oz/gal) of potassium cyanide. Current densities typically range from 11 to 430 A/m^2 (1 to 40 A-ft^2).

Tin-Lead, Lead, and Tin Electroplating -

Fluoborate and fluoboric acid can be used to plate all percentages of tin and lead. Alloys of tin and lead are most commonly used for plating in the proportions of 60 percent tin and 40 percent lead. Tin-lead plating baths typically contain 52 to 60 g/L (7.0 to 8.0 oz/gal) of stannous tin, 23 to 30 g/L (3.0 to 4.0 oz/gal) of lead, 98 to 150 g/L (13 to 20 oz/gal) of fluoboric acid, and 23 to 38 g/L (3.0 to 5.0 oz/gal) of boric acid. Current densities typically range from 270 to 380 A/m^2 (25 to 35 A-ft^2).

Lead fluoborate plating baths typically contain 340 to 410 g/L (45 to 55 oz/gal) of lead fluoborate, 195 to 240 g/L (26 to 32 oz/gal) of lead, 15 to 30 g/L (2.0 to 4.0 oz/gal) of fluoboric acid, and 23 to 38 g/L (3.0 to 5.0 oz/gal) of boric acid. Current densities typically range from 215 to 750 A/m^2 (20 to 70 A-ft^2).

Tin plating generally is performed using one of three types of plating solutions (stannous fluoborate, stannous sulfate, or sodium or potassium stannate) or by the halogen tin process. Stannous fluoborate plating baths include 75 to 110 g/L (10 to 15 oz/gal) of stannous fluoborate, 30 to 45 g/L (4.0 to 6.0 oz/gal) of tin, 190 to 260 g/L (25 to 35 oz/gal) of fluoboric acid, and 23 to 38 g/L (3.0 to 5.0 oz/gal) of boric acid. Current densities typically range from 215 to 270 A/m^2 (20 to 25 A-ft^2), and cathode efficiencies are greater than 95 percent.

Stannous sulfate plating baths include 15 to 45 g/L (2.0 to 6.0 oz/gal) of stannous sulfate, 7.5 to 22.5 g/L (1.0 to 3.0 oz/gal) of stannous tin, and 135 to 210 g/L (18 to 28 oz/gal) of sulfuric acid. Current densities typically range from 10 to 270 A/m^2 (1 to 25 A-ft^2), and cathode efficiencies are greater than 95 percent.

Sodium/potassium stannate plating baths include 90 to 180 g/L (12 to 24 oz/gal) of sodium stannate or 100 to 200 g/L (13 to 27 oz/gal) of potassium stannate and 40 to 80 g/L (5.3 to 11 oz/gal) of tin metal. Current densities typically range from 10 to 1,080 A/m^2 (1 to 100 A-ft^2).

Tin-Nickel Electroplating -

Tin-nickel alloy plating is used in light engineering and electronic applications and is used as an alternative to decorative chromium plating. Tin-nickel fluoride plating baths contain 49 g/L (6.5 oz/gal) of stannous chloride anhydrous, 300 g/L (40 oz/gal) of nickel chloride, and 56 g/L (7.5 oz/gal) of ammonium bifluoride. Current densities are typically about 270 A/m^2 (25 A-ft^2).

Tin-nickel pyrophosphate plating baths contain 28 g/L (3.2 oz/gal) of stannous chloride, 31 g/L (4.2 oz/gal) of nickel chloride, and 190 g/L (26 oz/gal) of potassium pyrophosphate. Current densities range from 52 to 150 A/m^2 (4.8 to 14 A-ft^2).

Zinc Electroplating -

The most widely used zinc plating solutions are categorized as acid chloride, alkaline noncyanide, and cyanide. The most widely used zinc alloys for electroplating are zinc-nickel, zinc-cobalt, and zinc-iron. Zinc plating baths contain 15 to 38 g/L (2.0 to 5.0 oz/gal) of acid chloride zinc, 6.0 to 23 g/L (0.80 to 3.0 oz/gal) of alkaline noncyanide zinc, or 7.5 to 34 g/L (1.0 to 4.5 oz/gal) of cyanide zinc.

Acid zinc-nickel plating baths contain 120 to 130 g/L (16 to 17 oz/gal) of zinc chloride and 110 to 130 g/L (15 to 17 oz/gal) of nickel chloride. Alkaline zinc-nickel plating baths contain 8.0 g/L (1.1 oz/gal) of zinc metal and 1.6 g/L (0.21 oz/gal) of nickel metal. Current densities range from 5.0 to 40 A/m^2 (0.46 to 3.7 $A\text{-}ft^2$) and 20 to 100 A/m^2 (1.9 to 9.3 A/ft^2) for acid and alkaline baths, respectively.

Acid zinc-cobalt plating baths contain 30 g/L (4.0 oz/gal) of zinc metal and 1.9 to 3.8 g/L (0.25 to 0.51 oz/gal) of cobalt metal. Alkaline zinc-cobalt plating baths contain 6.0 to 9.0 g/L (0.80 to 1.2 oz/gal) of zinc metal and 0.030 to 0.050 g/L (0.0040 to 0.0067 oz/gal) of cobalt metal. Current densities range from 1.0 to 500 A/m^2 (0.093 to 46 $A\text{-}ft^2$) and 20 to 40 A/m^2 (1.9 to 3.7 A/ft^2) for acid and alkaline baths, respectively.

Acid zinc-iron plating baths contain 200 to 300 g/L (27 to 40 oz/gal) of ferric sulfate and 200 to 300 g/L (27 to 40 oz/gal) of zinc sulfate. Alkaline zinc-iron plating baths contain 20 to 25 g/L (2.7 to 3.3 oz/gal) of zinc metal and 0.25 to 0.50 g/L (0.033 to 0.067 oz/gal) of iron metal. Current densities range from 15 to 30 A/m^2 (1.4 to 2.8 $A\text{-}ft^2$).

12.20.2 Emissions and Controls[2-3,43-44]

Plating operations generate mists due to the evolution of hydrogen and oxygen gas. The gases are formed in the process tanks on the surface of the submerged part or on anodes or cathodes. As these gas bubbles rise to the surface, they escape into the air and may carry considerable liquid with them in the form of a fine mist. The rate of gassing is a function of the chemical or electrochemical activity in the tank and increases with the amount of work in the tank, the strength and temperature of the solution, and the current densities in the plating tanks. Air sparging also can result in emissions from the bursting of air bubbles at the surface of the plating tank liquid.

Emissions are also generated from surface preparation steps, such as alkaline cleaning, acid dipping, and vapor degreasing. These emissions are in the form of alkaline and acid mists and solvent vapors. The extent of acid misting from the plating processes depends mainly on the efficiency of the plating bath and the degree of air sparging or mechanical agitation. For many metals, plating baths have high cathode efficiencies so that the generation of mist is minimal. However, the cathode efficiency of chromium plating baths is very low (10 to 20 percent), and a substantial quantity of chromic acid mist is generated. The following paragraphs describe the methods used to control emissions from chromium electroplating. These methods generally apply to other types of plating operations as well.

Emissions of chromic acid mist from the electrodeposition of chromium from chromic acid plating baths occur because of the inefficiency of the hexavalent chromium plating process. Only about 10 to 20 percent of the current applied actually is used to deposit chromium on the item plated; the remaining 80 to 90 percent of the current applied is consumed by the evolution of hydrogen gas at the cathode with the resultant liberation of gas bubbles. Additional bubbles are formed at the anode

due to the evolution of oxygen. As the bubbles burst at the surface of the plating solution, a fine mist of chromic acid droplets is formed.

The principal techniques used to control emissions of chromic acid mist from decorative and hard chromium plating and chromic acid anodizing operations include add-on control devices and chemical fume suppressants. The control devices most frequently used are mist eliminators and wet scrubbers that are operated at relatively low pressure drops. Because of the corrosive properties of chromic acid, control devices typically are made of polyvinyl chloride (PVC) or fiberglass.

Chemical fume suppressants are added to decorative chromium plating and chromic acid anodizing baths to reduce chromic acid mist. Although chemical agents alone are effective control techniques, many plants use them in conjunction with an add-on control device.

Chevron-blade and mesh-pad mist eliminators are the types of mist eliminators most frequently used to control chromic acid mist. The most important mechanism by which mist eliminators remove chromic acid droplets from gas streams is the inertial impaction of droplets onto a stationary set of blades or a mesh pad. Mist eliminators typically are operated as dry units that are periodically washed down with water to clean the impaction media.

The wet scrubbers typically used to control emissions of chromic acid mist from chromium plating, and chromic acid anodizing operations are single and double packed-bed scrubbers. Other scrubber types used less frequently include fan-separator packed-bed and centrifugal-flow scrubbers. Scrubbers remove chromic acid droplets from the gas stream by humidifying the gas stream to increase the mass of the droplet particles, which are then removed by impingement on a packed bed. Once-through water or recirculated water typically is used as the scrubbing liquid because chromic acid is highly soluble in water.

Chemical fume suppressants are surface-active compounds that are added directly to chromium plating and chromic acid anodizing baths to reduce or control misting. Fume suppressants are classified as temporary or as permanent. Temporary fume suppressants are depleted mainly by the decomposition of the fume suppressant and dragout of the plating solution, and permanent fume suppressant are depleted mainly by dragout of the plating solution. Fume suppressants include wetting agents that reduce misting by lowering the surface tension of the plating or anodizing bath, foam blankets that entrap chromic acid mist at the surface of the plating solution, or combinations of both a wetting agent and foam blanket. Polypropylene balls, which float on the surface of the plating baths, also are used as a fume suppressant in chromium plating tanks.

National emission standards to regulate chromium emissions from new and existing hard and decorative chromium electroplating and chromium anodizing tanks at major and area sources were promulgated on January 25, 1995 (60 FR 4948). The regulation requires limits on the concentration of chromium emitted to the atmosphere (or alternative limits on the surface tension of the bath for decorative chromium electroplating and anodizing tanks) and specifies work practice standards, initial performance testing, ongoing compliance monitoring, recordkeeping, and reporting requirements.

Table 12.20-1 presents the emission factors for chromium electroplating. The emission factors are based on total energy input and are presented in units of grains per ampere-hour (grains/A-hr). For controlled emissions from chromium electroplating operations, each of the add-on control devices used in the industry generally achieves a narrow range of outlet concentrations of chromium, regardless of the level of energy input. For this reason, total energy input may not be an appropriate basis for establishing emission factors for this industry. Therefore, the factors for chromium electroplating tanks

in Table 12.20-1 are presented both as concentrations and in units of total energy input. Emission rates for controlled emissions should be estimated using the concentration factors and typical exhaust flow rates for the particular type of exhaust system in question. The factors for controlled emissions based on total energy input should only be used in the absence of site-specific information.

Table 12.20-2 presents emission factors for chromic acid anodizing. The emission factors are presented in units of grains per hour per square foot (grains/hr-ft^2) of tank surface area. Table 12.20-3 presents particle size distributions for hard chromium electroplating. Table 12.20-4 presents emission factors for the plating of metals other than chromium.

Emissions from plating operations other than chromium electroplating can be estimated using the emission factors and operating parameters for chromium electroplating. Equation 1 below provides an estimate of uncontrolled emissions from nonchromium plating tanks.

$$EF_m = 3.3 \times 10^{-7} \times (EE_m/e_m) \times C_m \times D_m \qquad (1)$$

where:

EF_m = emission factor for metal "m", grains/dscf;
EE_m = electrochemical equivalent for metal "m", A-hr/mil-ft^2;
e_m = cathode efficiency for metal "m", percent;
C_m = bath concentration for metal "m", oz/gal; and
D_m = current density for metal "m", A/ft^2.

Equation 2 below provides an estimate of controlled emissions from nonchromium plating tanks.

$$EF_m = 0.028 \times EF_{Cr} \times C_m \qquad (2)$$

where EF_m and C_m are as defined above, and
EF_{Cr} = emission factor for controlled hard chromium electroplating emissions, grains/dscf.

Equations 1 and 2 estimate emissions from the formation of gas as a result of the electrical energy applied to the plating tank; the equations do not account for additional emissions that result from air sparging or mechanical agitation of the tank solution. To estimate uncontrolled emissions due to air sparging, the following equation should be used:

$$E_1 = 100\ k_1 R_b^2 \left[\frac{(1 - 2a + 9a^2)^{0.5} + (a - 1)}{(1 + 3a) - (1 - 2a + 9a^2)^{0.5}} \right]^{0.5} \qquad (3)$$

$$a = \frac{6.45\ R_b^2}{k_2},\ k_1 = \frac{56.7\ \sigma}{c_s^2},\ k_2 = \frac{1.79 \times 10^5\ \sigma}{(\rho_1 - \rho_g)\ g}$$

where:

E_1 = emission factor, grains/bubble;
R_b = average bubble radius, in.;
σ = surface tension of bath, pounds force per foot (lb_f/ft);
c_s = speed of sound, ft/sec;
ρ_1 = density of liquid, lb/ft^3;
ρ_g = density of gas (air), lb/ft^3; and
g = acceleration due to gravity, ft/sec^2.

Substituting typical values for constants c_s (1,140 ft/sec), g (32.2 ft/sec^2), and assuming values for ρ_l of 62.4 lb/ft^3 and for ρ_g of 0.0763 lb/ft^3, Equation 3 can be reduced to the following equation:

$$E_2 = \frac{1.9\ \sigma}{R_b} \left[\frac{(1 - 2a + 9a^2)^{0.5} + (a - 1)}{(1 + 3a) - (1 - 2a + 9a^2)^{0.5}} \right]^{0.5} \qquad (4)$$

where:

$$a = \frac{0.072\ R_b^2}{\sigma}$$

E_2 = emission factor in grains/ft^3 of aeration air; and
the other variables are as defined previously.

Equations 3 and 4 also can be used to estimate emissions from electroless plating operations. It should be noted that Equations 1 thorough 4 have not been validated using multiple emission tests and should be used cautiously. Furthermore, the emission factors that are calculated in units of concentration may not be applicable to plating lines in which there are multiple tanks that introduce varying amounts of dilution air to a common control device. Finally, Equation 1 does not take into account the emissions reductions achieved by using fume suppressants. If a fume suppressant is used, the corresponding emission factor for hard chromium plating with fume suppressant control should be used with Equation 2 to estimate emissions. Alternately, Equation 1 can be used and the resulting emissions can be reduced using an assumed control efficiency for hard or decorative chromium electroplating, depending upon which type of plating operation is more similar to the type of plating conducted. The control efficiencies for chemical fume suppressants are 78 percent for hard chromium electroplating controlled and 99.5 percent for decorative chromium plating. Based on the requirements for the chromium electroplating national emission standard, emissions from decorative chromium plating baths with chemical fume suppressants are considered to be controlled if the resulting surface tension is no more than 45 dynes per centimeter (dynes/cm) (3.1×10^{-3} pound-force per foot [lb_f/ft]).

Emissions chromium electroplating operations are regulated under the 40 CFR part 63, subpart N, National Emission Standards for Chromium Emissions From Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks. These standards, which were promulgated on January 25, 1995 (60 FR 4963), limit emissions of total chromium to 0.03 milligrams per dry standard cubic meter (mg/dscm) (1.3×10^{-5} grains/dscf) from plating tanks at small, hard chromium electroplating facilities; and to 0.015 mg/dscm (6.6×10^{-6} grains/dscf) from all other hard chromium plating tanks. Small, hard chromium plating facilities are defined in the rule as those which have a maximum cumulative rectifier capacity of less than 60 million amp-hr/yr. Total chromium emissions from decorative chromium plating tanks and chromic acid anodizing tanks are limited to 0.01 mg/dscm (4.4×10^{-6} grains/dscf), unless a fume suppressant is used and the bath surface tension is maintained at no more than 45 dynes/cm (3.1×10^{-3} lb_f/ft).

Table 12.20-1. EMISSION FACTORS FOR CHROMIUM ELECTROPLATING[a]

Process	Chromium Compounds[b]		EMISSION FACTOR RATING	Total PM[c]		EMISSION FACTOR RATING
	grains/A-hr	grains/dscf		grains/A-hr	grains/dscf	
Hard chromium electroplating[d] (SCC 3-09-010-18)	0.12	NA	B	0.25	NA	C
-- with moisture extractor[e]	NA	0.00014	D	NA	0.00028	E
-- with polypropylene balls[f]	NA	0.00042	D	NA	0.00088	E
-- with fume suppressant[g]	NA	0.00016	D	NA	0.00034	E
-- with fume suppressant and polypropylene balls[h]	NA	3.0×10^{-5}	D	NA	6.3×10^{-5}	E
-- with packed-bed scrubber[j]	NA	2.1×10^{-5}	D	NA	4.4×10^{-5}	E
-- with packed-bed scrubber, fume suppressant, and polypropylene balls[k]	NA	2.6×10^{-6}	D	NA	5.5×10^{-6}	E
-- with chevron-blade mist eliminator[m]	NA	8.8×10^{-5}	D	NA	0.00018	E
-- with mesh-pad mist eliminator[n]	NA	1.2×10^{-5}	D	NA	2.6×10^{-5}	E
-- with packed-bed scrubber and mesh-pad eliminator[p]	NA	3.2×10^{-8}	E	NA	6.7×10^{-8}	E
-- with composite mesh-pad mist eliminator[q]	NA	3.8×10^{-6}	D	NA	8.0×10^{-6}	E
Decorative chromium electroplating[r] (SCC 3-09-010-28)	0.033	NA	D	0.069	NA	E
-- with fume suppressant[s]	NA	1.2×10^{-6}	D	NA	2.5×10^{-6}	E

[a] For chromium electroplating tanks only. Factors represent uncontrolled emissions unless otherwise noted. Emission factors based on total energy input in units of grains per ampere-hour (grains/A-hr) and based on concentrations in units of grains per dry standard cubic foot (grains/dscf). To convert from grains/A-hr to mg/A-hr multiply by 64.8. To convert grains/dscf to mg/dscm, multiply by 2,290. To convert grains/A-hr to grains/dscf, multiply by 0.01. To convert grains/dscf to grains/A-hr multiply by 100. Note that there is considerable uncertainty in these latter two conversion factors because of differences in tank geometry, ventilation, and control device performance. For controlled emissions, factors based on concentration should be used whenever possible. SCC = Source Classification Code. NA = units not applicable.

[b] Comprised almost completely of hexavalent chromium.

[c] Total PM includes filterable and condensible PM. However, condensible PM is likely to be negligible. All PM from chromium electroplating sources is likely to be emitted as PM-10. Factors estimated based on assumption that PM consists entirely of chromic acid mist.

[d] References 5-13,15,17-18,23-25,28,34.

[e] References 8,14.

[f] Reference 10.

[g] Reference 15.

[h] References 18,23-25.

[j] References 11-13,18,32,34-35.

[k] References 18, 40-42.

[m] References 5-7.

[n] References 8-10,21,28.

[p] Reference 37.

[q] References 11-13.

[r] References 19-20,25-26.

[s] References 20, 25-26.

Table 12.20-2. EMISSION FACTORS FOR CHROMIC ACID ANODIZING[a]

Process	Chromium Compounds,[b] grains/hr-ft^2	EMISSION FACTOR RATING	Total PM,[c] grains/hr-ft^2	EMISSION FACTOR RATING
Chromic acid anodizing[d] (SCC 3-09-010-38)	2.0	D	4.2	E
-- with polypropylene balls[e]	1.7	D	3.6	E
-- with fume suppressant[f]	0.064	D	0.13	E
-- with fume suppressant and polypropylene balls[g]	0.025	D	0.053	E
-- with packed-bed scrubber[h]	0.0096	D	0.020	E
-- with packed-bed scrubber and fume suppressant[d]	0.00075	D	0.0016	E
-- with mesh-pad mist eliminator[k]	0.0051	E	0.011	E
-- with packed-bed scrubber and mesh pad mist eliminator[m]	0.00054	D	0.0011	E
-- with wet scrubber, moisture extractor, and high efficiency particulate air filter[n]	0.00048	D	0.0010	E

[a] For chromium electroplating tanks only. Factors represent uncontrolled emissions unless otherwise noted. Factors are in units of grains per hour per square foot (grains/hr-ft^2) of tank surface area. SCC = Source Classification Code. To convert from grains/hr-ft^2 to mg/hr-m^2, multiply by 0.70.
[b] Comprised almost completely of hexavalent chromium.
[c] Total PM includes filterable and condensible PM. However, condensible PM is likely to be negligible. All PM from chromium electroplating sources is likely to be emitted as PM-10. Factors estimated based on assumption that PM consists entirely of chromic acid mist.
[d] References 27,29-30,33,42.
[e] Reference 30.
[f] References 27,29-30.
[g] References 27,30.
[h] References 33,39.
[j] Reference 36.
[k] Reference 21.
[m] Reference 37.
[n] Reference 42.

Table 12.20-3. SUMMARY OF PARTICLE SIZE DISTRIBUTIONS FOR CHROMIUM ELECTROPLATING[a]

Uncontrolled			Controlled[b]		
	Cumulative Percent Less Than			Cumulative Percent Less Than	
Diameter, µm	Total PM[c]	Chromium Compounds[d]	Diameter, µm	Total PM[c]	Chromium Compounds[d]
<0.5	0	0	<0.49	0	0
0.5	9.1	6.9	0.49	18.5	20.4
2.4	48.3	67.7	2.35	94.7	97.5
8.0	59.3	82.6	7.9	100	99.2

[a] Reference 6. Based on C-rated emission data for hard chromium electroplating tanks. Source Classification Code 3-09-010-18.
[b] Controlled with chevron-blade mist eliminators.
[c] Total PM consists of filterable and condensible PM. However, condensible PM is likely to be negligible.
[d] Comprised almost completely of hexavalent chromium.

Table 12.20-4. EMISSION FACTORS FOR ELECTROPLATING--OTHER METALS[a]
EMISSION FACTOR RATING: E

Source	Pollutant	Emission Factor		Ref.
		grains/A-hr	grains/dscf	
Copper cyanide electroplating tank with mesh-pad mist eliminator (SCC 3-09-010-42)	Cyanide	NA	2.7×10^{-6}	21
Copper sulfate electroplating tank with wet scrubber (SCC 3-09-010-45)	Copper	NA	8.1×10^{-5}	31
Cadmium cyanide electroplating tank (SCC 3-09-010-52)	Cadmium	0.040	NA	31
-- with mesh-pad mist eliminator	Cyanide	NA	0.00010	21
-- with mesh-pad mist eliminator	Cadmium	NA	1.4×10^{-7}	21
-- with packed-bed scrubber	Cyanide	NA	5.9×10^{-5}	22
-- with packed-bed scrubber	Cadmium	NA	1.7×10^{-6}	22, 31
-- with packed-bed scrubber	Ammonia	NA	4.2×10^{-5}	22
Nickel electroplating tank (SCC 3-09-010-68)	Nickel	0.63	NA	31
-- with wet scrubber	Nickel	NA	6.7×10^{-6}	31

[a] Factors represent uncontrolled emissions unless noted. All emission factors in units of grains per ampere-hour (grains/A-hr) and as concentrations in units of grains per dry standard cubic foot (grains/dscf). To convert from grains/A-hr to mg/A-hr multiply by 64.8. To convert grains/dscf to mg/dscm, multiply by 2,290. To convert grains/A-hr to grains/dscf, multiply by 0.01. To convert grains/dscf to grains/A-hr multiply by 100. Note that there is considerable uncertainty in these latter two conversion factors because of differences in tank geometry, ventilation, and control device performance. SCC = Source Classification Code. NA = units not applicable.

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