Generic Scenario: Electroplating
August 8, 1996
Prepared for the Chemical Engineering Branch by SAIC

Introduction

Electroplating is the process by which a metal coating is applied to an object immersed in an electrolytic solution by passing a current through the solution. The article to be plated is the cathode. The plating metal is the anode, and when power is applied, it is oxidized and dissolved in the solution. The ions in solution are then reduced, or plated, on the cathode. When the surface to be plated is the anode, the process is called anodizing. Electroless or autocatalytic plating, uses a chemical reducing agent to reduce a dissolved metal onto a surface without the use of an electric current. This scenario will handle these similar processes.

Any electrically conductive surface can be electroplated. The most common metals plated on these surfaces include cadmium, chromium, cobalt, copper, gold, iron, lead, nickel, silver, tin, zinc and many alloys. The various uses for electroplating include: corrosion resistance, decoration, worn parts salvage, paint base, barrier coating, and electronic circuitry.

The process begins with several pre-treatment cleaning steps including immersion and spray rinses with deionized water and alkaline or acidic solutions. The parts are then dipped into the plating bath and then rinsed by several more immersion and spray rinses with deionized and permeate water. Lastly the part is baked to cure the coating. Although electroplating includes all of the above-mentioned stages, this generic scenario is applicable only to plating followed by rinsing.

Market

The number of electroplating shops dropped from 12,000 to 7,500 between the years of 1980 and 1992 due to the difficulty of meeting waste regulations imposed upon stream effluents (KO, 1994). This reduction impacted the smaller job shops moreso than the larger electroplating shops. One indicator for gauging the market is anode sales.

Electroplating in the automobile industry is declining due to the replacement of some metal parts by plastics, but the plumbing and appliance sectors are allowing for moderate growth with the increased use of electroless and other functional plating. The printed circuit board industry adds another market for the use of electroplating, as well as off-shore drilling in Texas. (USEPA, 1984)

Use-Industrial Electroplating

Electroplating is an estimated 4.5 billion dollar industry (BOC, 1995) with applications ranging from automobiles and sporting goods to electronics and jewelry. Approximately 14.2 million ft^2 of metal are plated each year (USEPA, May 1995). The industry produces 557,000 lb/yr of priority metal pollutants along with 1.195 billion gallons of wastewater generated from the unit operations and rinse water of the process (USEPA, May 1995). Additionally, chromium was chosen in determining an average bath size based on its prevalence in industry and on its wide range of uses in both decorative and functional plating. Bath size varies significantly however,

according to several parameters including the type of bath and the size and shape of the immersed objects. The size of a bath can range from just a liter to over 100,000 liters. The automobile industry uses tanks of 250,000 liters in size (KO, 1994).

Process Description

Parts are dipped into a plating bath, which consists of the metal ions in solution (as provided by dissolved metal from the anode or metal salts/oxides), complexing agents, stabilizers to prevent hydrolysis, buffers for pH maintenance, and catalysts (USEPA, May 1995). These chemicals range from amounts measured in ppm for brighteners or other additives to 20% for metal salts. The additives are nonvolatile and tend to remain in the bath. The baths, however, are equipped with exhaust systems for any vapors that may exist above the solution. Electroplating baths are almost always aqueous-based. The dip time and bath size depend on the metal to be plated, the thickness of the desired coating, and the size and shape of the immersed object. After dipping is complete, the rinsing stages begin.

For Plating baths:

Number of use sites:

NS = PV (kg/yr)/[((gallons of bath solution/site-yr) x (3.78 l/gal) x (Concentration of PMN in bath)) + ((gallons of rinsewater produced/site-yr) x (3.78 l/gal) x (concentration of PMN in rinsewater) x (1 - waste water recovery efficiency))]

Assume 15,570 gallons of plating bath solution per site-yr (basis: 14.9 million gallons of plating bath water are generated from 957 sites per year (U.S.EPA, May, 1995))

Assume 1.233 million gallons of rinse water produced per site-yr (basis: U.S.EPA, May, 1995)

Assume concentration of PMN in rinsewater is half of that in bath (basis: the metals concentration in rinsewaters is found as high as 23,500 mg/l and as high as 43,400 mg/l in the bath itself, or about half the concentration (USEPA, May 1995))

Assume a recovery efficiency of 90% (basis: a valid recovery of plating bath solution from rinse water can recover 90% of the value lost (Durney, 1984))

Days/year Operation

Assume 250
(basis: 50,300 people perform production work in electroplating and polishing for a total of 103,900,000 hours (BOC, 1995). At 8 hr/d, there are 258 days of operation.

Environmental Releases

Water

The electroplating industry discharges 1,195 million gallons of water per year, the majority of which, 1,180 million gallons per year, is used for the electroplating rinses (USEPA, May 1995). With 957 sites performing electroplating unit operations (USEPA, May 1995), there is, on average, 4932 gal/site-day of rinse water and 62 gal/site-day of electroplating wastewaters discharged. The bath is continuously purified at about 1 bath turnover per hour to remove metal salt impurities and organic impurities (Durney, 1984). The metal ions and additives necessary for plating are returned to the bath with the filtered bath water solution. The additives are therefore discharged with rinsewaters or spent bath disposals in the form of wastewater or sludge.

Daily water releases due to unit operations and rinses

Releases, kg/site-day = Releases from rinses/day over 250 days/yr

Daily releases from rinses, kg/site-day = (Volume of rinsewater generated/site-day) x (Conc. of PMN in rinsewater) x (1 - recovery efficiency) x (1 - wastewater treatment efficiency)

Assume 18,600 liters (4932 gallons) of wastewater generated/site-day (basis: USEPA, May 1995)

Assume a recovery efficiency of 90% (basis: a valid recovery of plating bath solution from rinse water can recover 90% of the value lost (Durney, 1984))

Assume concentration of PMN in rinsewater is half of that in bath (basis: the metals concentration in rinsewaters is found as high as 23,500 mg/l and as high as 43,400 mg/l in the bath itself, or about half the concentration (USEPA, May 1995))

Assume a raw waste water treatment efficiency of 97% for suspended solids and 50% for organic compounds (basis: The average raw waste concentration of 78 sites for total suspended solids was 600 mg/L and that for the effluent was 16 mg/L resulting in a removal of 97%. The average removal efficiency for total organic content for five samples was 45.2% using reverse osmosis (U.S.EPA, 5/1995))

Biannual water releases due to disposal of spent bath

Releases, kg/site-yr = Releases from spent bath over 2 days/yr

Yearly release, kg/site-yr = (Bath volume) x (Dumping frequency) x (PMN bath concentration) x (1 - waste water treatment efficiency)

Assume the bath volume of one site is 7500 gallons total (basis: the size and number of tanks per chromium plating facility were averaged for 17 of 66 documented sites yielding: 2500 gal/tank with 3 tanks/plant (USEPA, April 1995))

Assume Dumping frequency of six months (basis: 14.9 million gallons of wastewater from electroplating baths are generated/yr. With 957 electroplating sites and 7500 gal of bath material/site, the entire bath would be dumped twice/yr (U.S.EPA, May 1995))

Assume a raw waste water treatment efficiency of 97% for suspended solids and 50% for organic compounds (basis: The average raw waste concentration of 78 sites for total suspended solids was 600 mg/L and that for the effluent was 16 mg/L resulting in a removal of 97%. The average removal efficiency for total organic content for five samples was 45.2% using reverse osmosis (U.S.EPA, 5/1995))

Air

For vapor pressure < 0.001 torr, air releases of the baths are assumed to be negligible. (Basis: The estimated high end for releases to air of an additive at one percent concentration due to mist from chromium baths was less 10^{-6} kg/day)

For vapor pressure > 0.001 torr, see CEB models for open tank.

Landfill/Incineration

Yearly discharge to sludge = Sludge losses due to disposal of spent bath + Sludge losses due to rinsewater disposal:

Yearly release, kg/site-yr = (waste water treatment filter efficiency)[(Volume of bath) x (Dumping frequency) x (PMN bath concentration) + (Volume of rinse water) x (1 - rinse water recovery efficiency) x (Conc. of PMN in rinsewater)]

Assume a waste water treatment efficiency of 97% for suspended solids and 50% for organic compounds (basis: The average raw waste concentration of 78 sites for total susended solids was 600 mg/L and that for the effluent was 16 mg/L or a removal of 97%. The average removal efficiency for total organic content for five samples was 45.2% using reverse osmosis (U.S.EPA, 5/1995))

Assume 1.233 million gallons of wastewater generated/site-yr (basis: USEPA, May 1995)

Assume a recovery efficiency of 90% (basis: a valid recovery of plating bath solution from rinse water can recover 90% of the value lost (Durney, 1984))

Assume concentration of PMN in rinsewater is half of that in bath (basis: the metals concentration in rinsewaters is found as high as 23,500 mg/l and as high as 43,400 mg/l in the bath itself, or about half the concentration (USEPA, May 1995))

Occupational Exposure

Electroplating personnel may be classified as line operators, lead persons, maintenance, or laboratory technicians. The amount of exposure depends on the job description. Operators and lead persons walk the line, operate the controls, load and unload plated objects, and repair minor malfunctions. The exposure time for maintenance crews varies with the frequency of system malfunctions. Laboratory technicians perform one quality control assessment per day and are responsible for chemically recharging the tanks once or twice per week. (HETA 81-439-1256)

Days/year Operation:

Assume 250

(50,300 production workers work in electroplating and polishing for a total of 103,900,000 hours (BOC, 1995). At 8 hr/d, there are 258 days of operation.)

Hours/site-day:

Assume 8

Number of workers/site

20 workers/site

Assume number of workers/site for electroplating and polishing sites is similar to number of workers/site at electroplating sites alone

(basis: 65,400 total employees in electroplating and polishing at 3,296 total establishments yielding 19.8 employees/site (BOC,1995))

Inhalation Exposure:

Inhalation exposure is a result of evolved hydrogen and oxygen gas rising from the submerged part, the anode, or the cathode, and dragging bath solution with it into the air.

For PMN exposure during electroplating,
Potential dose rate (mg/d), $I = C_m bh$

Where:
I = Daily inhalation exposure, mg/day
C_m = Airborne concentration of PMN, mg/m^3
b = Inhalation rate, m^3/hr
h = Duration, hr/day

Assume inhalation rate of 1.25 m^3/hr (basis: typical worker breathing volume (CEB, 1991))

Assume 8 hr duration (BOC, 1995)

To obtain C_m
Assume for mist, the airborne concentration of PMN can be expressed as:

$$C_{m,PMN} = C_{m,k}\, Y_{PMN}/Y_k \text{ (basis: CEB, 1991)}$$

Where: $C_{m,PMN}$ = Estimated airborne concentration of the PMN chemical, mg/m^3
$C_{m,k}$ = Measured airborne concentration of the known chemical
Y_{PMN} = Weight fraction of PMN chemical in mixture
Y_k = Weight fraction of known chemical in mixture

Assume airborne concentration to be the maximum allowed OSHA limit (see Chart B for airborne limits for constituents typically found in metal plating baths). For default value, choose the OSHA value for chromium of 0.5 mg/m^3.
Typical values for metal concentrations in electroplating baths can also be found in Chart B. For a default value, use the chromium bath weight fraction of 0.25.

For volatile PMN's (vapor pressure > 0.001 torr) use the CEB models for an open tank.

Dermal exposure:

To estimate dermal exposure to the PMN during sampling of baths or the measurement and addition of bath replenishment chemicals, the dermal contact model presented in the CEB manual should be used with the following assumptions for incidental 2-hand contact (CEB, 1991):

$$D = SQC$$

Where: D = Dermal Exposure (mg/day)
S = Surface area of contact (cm^2) = 1300
Q = Quantity typically remaining on the skin (mg/cm^2) = 1-3
C = PMN concentration in bath

Uncertainties/Data Gaps

Data for releases tend to be available for metals only. Most PMN's however, are additives and therefore the filter efficiencies and volatilities will vary. Filter efficiencies were determined for broad classes such as "total suspended solids" or "total toxic organics" and it was assumed that relative concentrations of constituents in all streams and in the mist would be constant.

When the metal salt impurities and organic impurities are removed from the bath by the continuous purification filter, some types of organic wetting and brightening agents may be removed to some degree. Without information on a given PMN, it is impossible to predict the releases of PMN from the continuous filtration system without more information on its solubility

in water. For this reason, it is assumed that releases of PMN occur only from spent bath disposal and from rinsewater.

References

(BOC, 1995) 1992 Census of Manufactures, Industry Series, Screw Machine Products, Fasteners and Washers; Metal Forgings and Stampings; and Metal Services, U.S. Department of Commerce, Economics and Statistics Administration, Bureau of Census, 1995.

(CEB, 1991) U.S.EPA, Office of Toxic Substances, Chemical Engineering Branch Manual for the Preparation of Engineering Assessments, Submitted by IT Environmental Programs, Inc., February 28, 1991.

(Durney, 1984) Durney, Lawrence. Electroplating Engineering Handbook, 4th ed, Van Nostrand Reinhold Co., New York,1984.

(EC, 1981) Electronic Chemicals: United States, Western Europe, and Japan, Vol 2, 1981, United States.

(KO, 1994) Kirk-Othmer Encyclopedia of Chemical Technology vol 9, fourth ed.1994.

(NIOSH, 1984) U.S. Department of Health and Human Services: Public Health Service, Centers for Disease Control, and National Institute for Occupational Safety and Health; Division of Physical Sciences and Engineering, Niosh Technical Report, Control Technology Assessment: Metal Plating and Cleaning Operations; Cincinnati, Ohio, December, 1984.

(PRC, 1988) PRC, Environmental Management, Inc., Waste Audit Study: Metal Finishing Industry, May 1988.

(SRI, 1992) Stanford Research Institute International Chemical Economics Handbook; Metal Plating, Activated Carbon Consumed, September, 1992.

(SRI, 1993) SRI International Chemical Economics Handbook; Metal Plating, Chromic Acid Consumed, September, 1993.

(SRI, July 1994) SRI International Chemical Economics Handbook; Metal Plating, Nickel Consumed, July, 1994.

(SRI, Nov. 1994) SRI International Chemical Economics Handbook; Metal Plating, Cadmium Consumed, November, 1994.

(SRI, 1995) SRI International Chemical Economics Handbook; Metal Plating, Hypophosphite Consumed for Electroless Nickel Plating, May, 1995.

(Schrantz, 1986) Schrantz, Joe. "New E-Coat 'Hoist' Paint Line Job Shop" Industrial Finishing. October, 1986.

(SRER,1995) Standard Review Engineering Report, Submitted by LeaRonal, Inc., Revised Draft Report, January 31, 1995.

(USEPA, 1983) U.S.EPA, Office of Toxic Substances, ETD, Industrial Process Profiles to support PMN Review: Metal Treatment Chemicals, contract No. 68-01-6065, Submitted by Walk, Haydel, and Associates, Inc., 1983.

(USEPA, June 1983) U.S.EPA, Office of Water, Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards: Metal Finishing; Final, June 1983.

(USEPA, 1984) Plating Bath Additives, R. Rakutis, C. Hughes, SRI International, contract 68-02-4055, Sept 28, 1984.

(USEPA, 4/1995) U.S.EPA, Office of Air, AP-42, Section 12.20, Electroplating, Draft Report, April, 1995.

(USEPA, 5/1995) U.S.EPA, Office of Water, Effluent Limitations Guidelines,Pretreatment Standards, and New Source Performance Standards: Metal Products and Machinery; Proposed Rule, May, 1995.

(USEPA, 7/1995) U.S.EPA, Office of Solid Waste, Waste Minimization Approaches to Metal Plating; Submitted by Science Applications International Corporation, July 1995.

Chart B, Metal Concentrations

Metal	Bath type	Bath Conc.s[1], g/L	Conc.above bath, mg/m^3
Brass	Yellow, regular	CuCN: 32 $Zn(CN)_2$: 10 NaCN: 50 Na_2CO_3: 7.5 $NaHCO_3$: 10 NaOH:-- NH_4OH:2.5-5mL/L	
	Yellow, high speed	CuCN: 75 $Zn(CN)_2$: 5 NaCN: 125 Na_2CO_3: -- $NaHCO_3$: --- NaOH: 45 NH_4OH:	
	White	CuCN: 10 $Zn(CN)_2$: 60 NaCN: 100 Na_2CO_3: 40 $NaHCO_3$: --- NaOH: 38 NH_4OH: --	
Bronze	Typical	CuCN: 29-35 Cu metal: 20-25 $Na_2SnO_3.3H_2O$: 35-38 Sn metal:14-17 NaCN: 54-64 NaOH: 7.5-10	
	Speculum	CuCN: 11 Cu metal: 8 $Na_2SnO_3.3H_2O$: 90 Sn metal: 40 NaCN: 27 NaOH: 16	

Cd	Cyanide bath	Cd metal: 20-30 NaCN: 90-150 Na_2CO_3: 30-60 H_2SO_4:-- NH_4BF_4:-- NaOH:10-20	NIOSH: 0.04 (NIOSH, 1984)
	Acid sulfate	Cd metal: 15-30 NaCN: --- Na_2CO_3: --- H_2SO_4:45-90 NH_4BF^4:-- NaOH: --	
	Fluoro-borate	Cd metal:75-150 NaCN: -- Na_2CO_3: -- H_2SO_4:-- NH_4BF^4:60-120 NaOH:--	
Cr, typical	Conventional	CrO_3: 240-260 SO^{2-}_4: 2.4-2.6 SiF^{2-}_6: -- CrO3:SO^{2-}_4 ratio: 90-110:1	OSHA: 0.5 HETA-87-353-1899 5/88
		CrO_3: 150-180 SO^{2-}_4: 0.9-1.0 SiF^{2-}_6: 0.5-0.6 CrO_3:SO^{2-}_4 ratio:170-180:1	
Cu, cyanide	CN, strike	Cu metal: 15-22 CuCN: 21-31 KCN: 31-70 KOH: 3-18 Rochelle salts: 10-20 Na_2CO_3: 10-15	OSHA: 0.5 (HETA-87-353-1899, 5/88)
	Rochelle	Cu metal: 22-36 CuCN: 31-51 KCN: 55-89 KOH: 12-18 Rochelle salts: 15-25 Na_2CO_3: 30-45	

	High speed	Cu metal: 56-71 CuCN: 79-100 KCN: 130-165 KOH: 20-25 Rochelle salts: 15-25 Na_2CO_3: 35-55	
Cu, acid	Sulfate, average range	Cu metal: 38-64 $CuSO_4.5H_2O$: 150-250 H_2SO_4: 30-75 Cl^-:0.20-0.12 $Cu(BF_4)_2$:-- HBF_4: -- H_3BO_3: --	
	Fluoroborate, range	Cu metal:60-120 $CuSO_4.5H_2O$:-- H_2SO_4: -- Cl^-:-- $Cu(BF_4)_2$: 225-450 HBF_4: 15-30 H_3BO_3: 15-30	
Cu, Pyro-phosphate	Typical	Cu metal: 19-30 $Cu_2P_2O_7.3H_2O$: 53-84 $K_4P_2O_7.3H_2O$: 235-405 NH_4OH: 3.75-11 KNO_3:3.0-6.0 P_2O_7:Cu ratio: 7.0-7.5:1	
Au	Alkaline	Au metal: 2-12 $KAu(CN)_2$:3-18 KCN: 15-48 K_2CO_3: 0-45 K_2HPO_4: 0-45 KOH: 1-30	
	Neutral	Au metal: 4-16 $KAu(CN)_2$:6-24 KCN: -- K_2CO_3: -- K_2HPO_4: 0-90 KOH: --	

	Acid	Au metal: 2-16 $KAu(CN)_2$: 3-24 KCN: -- K_2CO_3: -- K_2HPO_4: 0-100 KOH: --	
	Strike	Au metal: 0.5-2 $KAu(CN)_2$:0.75-3 KCN: 15-90 K_2CO_3: -- K_2HPO_4: 15-45 KOH: --	
Ni	Watts	Ni metal: 82 $NiSO_4.6H_2O$: 300 $NiCl_2.6H_2O$: 60 $Ni(SO_3NH_2)_2.4H_2O$: -- H_3BO_3: 35-45	OSHA: 1.0 NIOSH:0.015 (HETA-81-439-1256; 1/83)
	Watts high chloride	Ni metal: 77 $NiSO_4.6H_2O$: 135 $NiCl_2.6H_2O$: 190 $Ni(SO_3NH_2)_2.4H_2O$: -- H_3BO_3: 35-45	
	Sulfamate	Ni metal: 75 $NiSO_4.6H_2O$: -- $NiCl_2.6H_2O$: -- $Ni(SO_3NH_2)_2.4H_2O$: 410 H_3BO_3: 35-45	
Ag	Decorative	AgCN: 30-35 KCN:50-78 K_2CO_3: 15 KNO_3:-- KOH:--	OSHA: 0.01 (HHE-78-53-510 7/78)
	Industrial	AgCN: 45-50 KCN: 65-72 K_2CO_3: 45-50 KNO_3: 40-80 KOH: 40-60	

	Strike	AgCN: 1.5-5.0 KCN:75-90 K_2CO_3: -- KNO_3:-- KOH:--	
Zn-Co	Acidic	Zn: 25 Co: 4 Ni: -- Fe: -- chloride: 135 boric acid: 25 NaOH: --	
	Alkaline	Zn: 8 Co: 0.04 Ni: -- Fe: -- chloride: -- boric acid: -- NaOH: 90	
Zn-Ni	Acidic	Zn: 30 Co: -- Ni: 25 Fe: -- chloride: 240 boric acid: -- NaOH: --	
	Alkaline	Zn: 8 Co: -- Ni: 1.6 Fe: -- chloride: -- boric acid: -- NaOH: 130	
Zn-Fe	Alkaline only	Zn: 8 Co: -- Ni: -- Fe: 0.05 chloride: -- boric acid: -- NaOH: 90	T.L.V.: 1.0 (Durney, 1984)

1 Unless otherwise noted, bath concentrations were taken from KO, 1994

Chemical Exposure in Metalplating:

Industry	Chemical	Activity	Exposure	OSHA standard	Reference
Industry Steel & Wire Co.	Chemical Chromate	Activity Normal Plating	Exp 0.035mg/m^3	OSHA standard	Reference HHE 73-111- 125, 3/74
Electro-metals	Chromium	Electro-plating	0.04-0.20 mg/m^3	0.5 mg/m^3	HHE 80-156-747, 10/80
Sporting goods	Chromium	Anodizing	0.01 mg/m^3	0.5 mg/m^3	HHE 79-23-603, 7/79
Chrome Plating	Chromium VI	Electro-plating	0.003-0.006 mg/m^3	0.1 mg/m^3	HHE 81-085-889, 6/81
Chrome Plating	Chromium (Total)	Electro-plating	0.009-0.81 mg/m^3	0.5 mg/m^3	HHE 81-085-889, 6/81
Steel & Wire Co.	Cyanide	Normal plating	0.08 mg/m^3		HHE 73-111-125, 3/74
Auto-motive	Fluoride	Plating Dep't	0.072 mg/m^3		HETA-81-439-1256,1/81
Steel & Wire Co.	HCl	Normal plating	0.007 mg/m^3		HHE 73-111-125, 3/74
Sporting goods	Naptha	Painting& Cleaning	7-100 mg/m^3	400 mg/m^3	HHE 79-23-603, 7/79
Auto-motive	Nickel	Electro-plating	0.005-0.008 mg/m^3	1.00 mg/m^3 (NIOSH:0.015)	HETA 81-439-1256, 1/83

Electro-plating	Nickel	Electro-plating	Acute exposure: 0.5 to 2.5 g		Sundermanet. al., 1988
Electro-plating	Nickel cmpds	Electro-plating	Urine: 0.7-50 mu g/l hands: 1.9-547 mu g face: 1.0 -86 mu g		Bavazzanoet. al., 1994
Electro-plating	Silver	Weighing& Preparing bath	0.04 mg/m^3	<0.002 (2 room samples) & 0.01 mg/m^3 close to bath	HHE-78-53-510, 7/78
Chrome plating	Sulfuric Acid	Electro-plating	0.010-0.015 mg/m^3	1 mg/m^3	HHE 81-085-889, 6/81

R16