

Citation: Schwartz S, Lorber M. 1999. Characterizing site-specific source emissions for EPA's risk assessment tool for the metal finishing industry. Pages 7-29 in, Proceedings: The AESF/EPA Conference for Environmental Excellence. Held Jan 24-27, 1999, at Lake Buena Vista, FL. Published by, AESF, 12644 Research Parkway, Orlando, FL 32826-3298.

Characterizing Site-Specific Source Emissions for EPA's Risk Assessment Tool for the Metal Finishing Industry

Stephen Schwartz¹, Matthew Lorber²

¹Versar, Inc., 6850 Versar Center, Springfield, VA, 22151; ²Office of Research and Development, EPA, Washington, DC 20460

Introduction

EPA's risk assessment tool for the metal finishing industry is described in a companion paper to this one (Lorber and coauthors. A Risk Assessment Tool for the Metal Finishing. These proceedings). The most challenging aspect to producing this risk assessment tool is characterizing indoor and outdoor emissions of contaminants from metal finishing line processes. These emissions drive indoor worker exposures and outdoor nearby resident exposures. This tool contains default source emission rates of 22 contaminants for 15 different line processes. This paper describes the line processes and generation of emission rates for these processes. The companion paper shows how these default source characterizations fit into the risk assessment tool in general.

Description of Typical Electroplating Lines

All metal plating must consist of at least two steps: (1) removing oily deposits from the surface of the substrate metal and (2) the actual "electroplating" in which a film of metal is electrochemically applied to a substrate metal (or properly pretreated plastic). Also, some metal plating, such as nickel and copper, can be accomplished electrolessly. If oily deposits are

not removed from the metal surface before plating, poor plated-metal adhesion will result in the electroplating step. Electroplating usually involves additional steps, especially in decorative chromium electroplating.

After each step in the plating process (such as the two above), one or more tap, distilled, or deionized water rinses must take place prior to the next operation. Rinsing, therefore, can be considered an additional required step. If thorough rinsing is not done between steps, chemicals from each step will be "dragged out" from one step to the next, possibly poisoning/contaminating the chemicals in the subsequent step, which would require premature replacement of those chemicals. Each step in the plating process is carried out in an appropriately sized tank. The surface area of a typical tank is probably 30 - 80 square feet (ft²), and tanks are as deep as necessary to allow insertion of the racked parts. For rinsing, there are typically one to three rinse tanks after each process step. Rinsing is a source of wastewater discharge.

Removing oily deposits (i.e., Step 1) is usually carried out in a tank containing strong hot (over 100 grams/liter [g/L] cleaner concentration, at over 150°F) alkaline cleaners (e.g., surfactants, phosphates, sodium hydroxide [caustic soda]) and/or in a solvent degreaser, in

which various hot or cold organic solvents and/or vapors from those solvents are used to dissolve and flush oils from the surface of the substrate metal. Historically, typical solvents have included 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), methylene chloride, perchloroethylene (PCE), xylene, toluene, mineral spirits, naphthas, and methyl ethyl ketone (MEK). Chlorinated solvents (e.g., TCA, TCE, PCE) are becoming rare due to the phaseout of their production as mandated by the Clean Air Act (CAA), as it relates to ozone depleting substances (ODSs). (See 40 CFR 82.)

After the deoiling/degreasing step, it is typical to use an acid cleaning/etching step prior to electrolytic and electroless plating. The acid cleaning/etching step removes metal oxides from the surface of the substrate metal and provides a more active and rougher surface to which the plated metal(s) can better adhere. Acids used for etching depend, in part, on the type of substrate metals. For steel, sulfuric and hydrochloric acids are common, typically at concentrations of up to 25% (250 g/L). For some applications and for other substrate metals, however, nitric, hydrofluoric, phosphoric, chromic, acetic, and oxalic acids, or combinations of such acids are used. Acid etching is typically accomplished at room temperature. As with the other plating process steps (except solvent degreasing), water rinse(s) is usually required after acid cleaning/etching.

Other steps are also required to manufacture a plated metal part, many of which are not wet processes. The dry processes that take place prior to the electroplating processes are typically combinations of metal forming (shaping the substrate metal by a number of mechanical processes), cutting, machining (primarily for metal castings rather than sheet metal), punching (making holes), welding, grinding, and buffing. Some of these processes are also used after electroplating. Some electroplated products will receive a protective clear coating of lacquer or other solvent-based coating after electroplating. Clear coatings are common for decorative plated metals that tarnish (e.g., copper, and brass).

In developing a set of default line processes for this risk assessment tool, we attempted to characterize some of the major line processes, and quantify the emissions of the most important contaminants (particularly those that are likely to exhibit some toxicity) from these line processes. Our efforts are obviously not exhaustive; hundreds of metals/metal alloys are electroplated. Cleaning, acid etching, plating, and rinsing practices vary significantly from shop to shop based upon: proprietary practices, the use of proprietary chemicals, the substrate being plated, and the final use of the plated product. In particular, the concentrations of chemicals for plating tanks constituents vary over wide ranges, as do bath temperatures.

Our initial source characterization includes 15 separate line processes, broadly grouped into two categories: electroplating and other electrolytic process, and nonelectrolytic processes. For electrolytic processes, we have characterized hexavalent chromium (Cr^{+6}) - both "hard" and decorative, trivalent chromium (Cr^{+3}), nickel, anodizing - both sulfuric and chromic acid, copper cyanide, acid copper, cadmium, zinc cyanide, zinc chloride, and gold. Among the non-electrolytic process, we have characterized electroless nickel, chromium conversion, and phosphate coating. The sub-processes for these lines, contaminants emitted, and key sub-process descriptors (surface area, exhaust rates, etc.) are shown in Figure 1(a) through 1(o).

Within these 15 line processes, we have estimated emissions of 22 contaminants including: hexavalent chromium, trivalent chromium, sulfuric acid, gold, cyanide, copper, cadmium, zinc, nickel, sodium hypophosphite, hydrochloric acid, nitric acid, sodium hydroxide, sodium phosphate, sodium metasilicate, hydrofluoric acid, phosphoric acid, and 5 solvent degreasers including 1,1,1-trichloroethane, perchloroethylene, methanol, methyl ethyl ketone, and toluene.

[Procedure to Develop Emission Rates for These Line Process](#)

This study uses as a basis and a starting point for all of its emission calculations the following two documents:

- *Hard Chrome Pollution Prevention Demonstration Project*, Interim Report, by the U.S. EPA Common Sense Initiative (CSI), Metal Finishing Subcommittee, (EPA, 1996);
- *Compilation of Air Pollutant Emission Factors*, from the 5th Edition of EPA's AP-42 (EPA, 1995).

The CSI report is an excellent study of total and hexavalent chromium emissions from hard chromium plating tanks in several electroplating shops. It attempts to relate operating parameters, such as current density, use and concentration of fume suppressants, use of polymer balls, and various combinations of air pollution control devices, to the concentration of total and hexavalent chromium (Cr^{+6}) emissions. Significant attention is given to sampling and analytical detail. For example, more than one technique was used for some analyses of air emissions. Also, duplicate data from different laboratories are presented. In addition, this document was jointly sponsored by EPA and industry; therefore, it is expected to be an extremely credible quantitative work on the subject. Consequently, data from this document were used as much as possible.

AP-42 contains emission factors from all industrial sectors. EPA routinely updates the emission factors as better (or additional) data become available. The document is to be used for guidance purposes only. EPA rates the data quality in AP-42 on a scale of A to E; A being excellent quality, and E being poor. With respect to the quality of the data on electroplating (Section 12.20 of AP-42), EPA rated almost all of the data D or E. AP-42 contains data on hard chromium electroplating and chromic acid anodizing, and only 1 datum on decorative chromium electroplating. For other electroplating processes, AP-42

recommends extrapolation from the hard chromium data (EPA, 1995).

The methodology used to determine mass emission rates (e.g., milligrams per day [mg/day]) of electroplating industry bath components, required the following steps:

- Determine the concentration of emissions from each process tank (e.g., milligrams per cubic meter [mg/m^3]), based on CSI data or other sources;
- Estimate the rate of ventilation of each process tank (e.g., cubic feet per minute [ft^3/min]); and
- Combine the concentration and ventilation rate data to determine the mass emission rate.

Following now are descriptions of how these procedures were followed in determining mass emission rates from the plating bath components, including electrolytic, non-electrolytic, and solvent degreasing. Detailed data pertaining to these three plating bath components are shown in Tables 1-4.

1. Electroplating and other electrolytic processes:

The concentration of metal emissions (and other components) to the atmosphere from electrolytic tanks (electroplating and anodizing) are proportional to:

- The current density applied to perform the plating operation;
- The inverse of the cathode efficiency; and
- The concentration of the chemical components in the process tank.

Cathode efficiency is the fraction of the applied electrical power that results in depositing metal on the substrate (which is the cathode). For most plated metals, the efficiency exceeds 90%. However, for hard and decorative chromium

from Cr⁺⁶ baths, it is typically less than 20%. The portion of the electrical power that does not result in metal deposition is spent on decomposition of the water in the bath into hydrogen and oxygen. Production of hydrogen and oxygen produces turbulence that contributes to atmospheric emissions.

This relationship is supported by AP-42 (EPA, 1995). Further, in order to determine emissions from other electrolytic baths, AP-42 recommends extrapolation from hard chromium plating data using these three factors. Consequently, for this risk assessment tool, the emission concentration data for hard chromium electroplating baths from the CSI report (EPA, 1996) is extrapolated to electroplating baths for other contaminants using the three factors noted above in the following relationship:

$$RC_c = \frac{(CC_c CD_c) / (CE_c)}{(CC_{Cr} CD_{Cr}) / (CE_{Cr})}$$

where RC_c is the concentration of the contaminant relative to the concentration of Cr⁺⁶ above a hard chromium plating bath, $CC_{c,Cr}$ is the concentration of the contaminant in the plating bath of interest (c) and the concentration of Cr in the hard chromium plating bath (Cr), $CD_{c,Cr}$ is the current density of the bath of interest (c) and of the chromium hard plating bath (Cr), and $CE_{c,Cr}$ is the cathode efficiency of the bath of interest (c) and of the chromium hard plating bath (Cr).

Table 1 shows the result of this extrapolation, where the key result, RC_c , is shown in the last column of this table.

This table also provides results for anodizing baths, which are electrolytic processes. Anodizing is a process in which the metal substrate (usually aluminum or magnesium) forms the anode. With application of electrical current, a protective oxide coating forms on the substrate, rather than a coating of plated metal.

Table 2 presents emissions concentration data for all electrolytic processes, based on the CSI hard chromium data (EPA, 1996). The CSI hard chromium data are presented in the second row on this table (the first row is AP-42 data, which will be discussed shortly). The CSI data include information on uncontrolled emissions, as well as emissions from a variety of combinations of emission control devices. These “devices” include suppression of emissions by including additives in the electroplating baths and by floating polymeric balls on the tank surface, as well as various “end-of-pipe” capture devices. The CSI report typically presents more than one datum point for each controlled and uncontrolled scenario. In these cases, the data were typically averaged to derive the hard chromium plating data on Table 2. AP-42 data were used for determining hard chromium plating emission values for the packed bed scrubber/mist eliminator pollution control device combination, because this combination did not exist in the CSI report.

Each entry below the hard chromium plating bath row was calculated using the RC_c calculated as described above and shown in Table 1. For example, the uncontrolled emission of nickel from a nickel plating bath is calculated as the uncontrolled chromium emission rate of 5.4 mg/m³ times the RC for nickel of 0.017 (from Table 1) to arrive at the Table 2 entry of 0.093.

For purposes of comparison to the CSI hard chromium data, the AP-42 data for hard chromium plating are presented (shaded values) in Table 2. In general, the corresponding values differ an order of magnitude or less. For uncontrolled emissions, AP-42 is about half the concentration as compared to the CSI report. For all but one controlled emission scenario, AP-42 show higher emission concentrations than CSI.

It is also noted that the concentration levels for uncontrolled emissions are used in the worker exposure algorithm for this risk assessment tool. As described in the companion

paper to this one, worker inhalation exposures are assumed to be comprised of two exposure regimes - one in which the worker is exposed some portion of his time to these uncontrolled emissions and one in which the worker is exposed only to the ambient air levels in the workplace. The user of the risk assessment tool defines the amount of time the worker is exposed to both concentrations. Further details on the exposure procedures are found in the companion paper to this one.

In order to determine the mass emissions rates (e.g., mg/day), it is necessary to combine the emissions concentration data presented in Table 2 with the process volumetric air flow rate (e.g., in ft³/min of exhaust air). To determine process volumetric flow rates, the typical surface area of a ventilated process tank (in square feet [ft²]) was multiplied by the minimum ventilation rate (in ft³/min-ft²) prescribed by the Occupational Safety and Health Administration (OSHA) (OSHA, 1998). Table 3 presents estimated OSHA ventilation categories for all electroplating process tanks, corresponding OSHA minimum ventilation rates, estimated typical process tank surface areas, and the calculated volumetric air flow rates.

OSHA ventilation categories are an alpha-numeric code that assist in determining control ventilation velocity. The alphabetical symbol relates to the hazard level of the chemical component based on toxicity (i.e., "A" being most hazardous, and "D" being least hazardous). The numeric designation relates primarily to the temperature/volatility characteristics of the material being ventilated. A liquid close to its boiling point receives a value of "1," and a liquid that is least volatile is given a rating of "4." Essentially, a material with a rating of A-1 will require the highest ventilation velocity, and a material with a rating of D-4 will require the least (or only general room ventilation). Once the ventilation category is determined, OSHA specifies the minimum ventilation rate for that category, based on the type of exhaust hood employed and the shape of the tank. For this study, it was assumed that a

lateral exhaust hood was being used on an un baffled tank that is not located adjacent to a wall and that the width to length ratio of the tank is between 0.5 and 0.99 (based on observations in numerous electroplating facilities). Other assumptions will change the required minimum ventilation rate shown in Table 3.

Once the volumetric air flow rates are calculated (last column Table 3), they are multiplied by the corresponding air emissions concentration values in Table 2, as well as by a conversion factor to make the units of measure compatible. The resulting product is the daily mass emissions from each combination of process tank and emission control device. The mass emission rates are shown on Table 4. For those electrolytic processes with an OSHA alpha-numeric rating that does not appear to require ventilation (gold plating, acid copper plating, and chloride zinc plating), mass flow rates external to the plant are not expected to be significant, unless the tanks are aerated (which is so-stated in Table 4).

As a final note, the uncontrolled emission rates shown in Table 4 are used in the algorithm to evaluate indoor air exposures, as are the uncontrolled air concentrations. As mentioned above, the worker is assumed to be exposed in part to uncontrolled air concentrations as well as the indoor ambient air away from the baths. A small portion of the uncontrolled emissions are assumed to escape into the indoor environment as fugitive emissions not captured by the exhaust hood. These emissions are assumed to mix in the indoor air using a simple box model in order to estimate the ambient indoor air concentrations. Further discussion of these procedures can be found in the companion paper to this one.

2. Nonelectrolytic processes (not including vapor degreasing):

A number of nonelectrolytic processes take place in typical electroplating shops. Ones considered in this methodology are listed in

Tables 1-4. These processes are similar to electrolytic processes, in that they are aqueous, consisting of dissolved inorganic chemicals. Emissions from nonelectrolytic tanks do not relate to current density or cathode efficiency (which are obviously irrelevant terms for these processes). Therefore, another method is necessary to determine the mass emission rates from these processes.

Specifically, it is assumed that atmospheric emissions from each nonelectrolytic tank are the result of turbulence caused by mixing the tank contents with compressed air. It is recognized that mixing may be accomplished by mechanical mixers and/or recirculating pumps, or there may be no mixing at all (other than the insertion and removal of parts). If there is no tank turbulence, it is reasonable to assume that there are no emissions (other than water vapor), because little or no volatile materials are in the electroplating process tanks. For aerated tanks that do not appear to require external ventilation by OSHA (acid etch/bright dip processes, and phosphate coating), it is assumed that the emissions from the process tanks will exit the plant as fugitive emissions.

In the electroplating industry section of AP-42 (12.20.2), EPA presents the following equation for calculating the emissions resulting from mixing process tanks with air:

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

where:

E = Emission factor in grains/cubic foot of aeration air;

σ = Surface tension of bath, in pounds force per foot (lb_f/ft);

R_b = Average bubble radius, in inches;

$a = 0.072 R_b^2 / \sigma$

This equation calculates the mass of tank liquids emitted per volume of aeration air. The calculated values are a function of the size (i.e., radius) of the bubbles being generated and the surface tension of the tank contents. The calculated emissions are sensitive to bubble size in the range of about 0.05- to 0.5-inch radius, increasing with bubble size by about 50% within that range. Emissions also increase by about 100%, with an increase in surface tension from 20 to 80 dynes per centimeter, which are the anticipated realistic extremes of surface tension based on data in the CSI report (EPA, 1996). For this risk assessment tool, it was assumed that the bubble radius is 0.05 inch in all nonelectrolytic tanks; and that the surface tension is 40 dynes per centimeter in alkaline cleaning tanks and 70 dynes per centimeter in all other nonelectrolytic tanks. Alkaline cleaning tanks contain surfactants, which lower surface tension.

The output of the AP-42 emission equations, as noted above, is in mass of bath chemical contents per a unit volume of aeration air. To calculate mass emission rate (i.e., for a unit of time), the volume of aeration air used must be known. For the purposes of this study, it was assumed that the volume of aeration air was 10 ft³ per min/ft² of tank surface area. The typical tank surface areas are shown in Table 3.

Further, because the output of the AP-42 equations is in mass of total bath chemical contents, *including water*, it is necessary to adjust the output for the fraction of tank contents that represents the constituents of concern. This was accomplished using the gram/liter bath concentrations shown in the third column of Table 1 (American Electroplater's Society, undated; Noyes, 1985). Specifically, the values in the 3rd column of Table 1 were converted to the mass of constituent per mass of tank contents, assuming that a liter of tank contents weighs 1000 grams (which is probably a slight underestimate of the weight of a liter of tank contents).

After consideration of the items discussed above, the mass emission rate for

uncontrolled emissions for nonelectrolytic process tanks was calculated and included in the uncontrolled emission column, Column 3, of Table 4. To calculate the controlled emission rates using the air pollution control methods listed on the top of Table 4, the uncontrolled rates for nonelectrolytic tanks were multiplied by the ratio of the controlled emission rates for hard chromium electroplating to uncontrolled emission rates for hard chromium electroplating.

3. Solvent Vapor Degreasing:

Solvent degreasing is the only nonaqueous process considered in this risk assessment tool. Before parts can be surface coated (e.g., plated, anodized, chromium converted, phosphatized, or painted), all residual oils/greases must be removed or the coatings will not form and/or adhere. Two degreasing methods are routinely employed: solvent degreasing and alkaline cleaning. They are frequently employed in series, or sometimes only alkaline cleaning is used. Alkaline cleaning is an aqueous-based process, and is discussed in the non-electrolytic process section above.

For high production shops, solvent degreasing usually means vapor degreasing. In vapor degreasing, relatively cold parts are immersed in the warm vapors above boiling organic solvents. Historically, these solvents have been chlorinated solvents, such as 1,1,1-trichloroethane. The vapors condense on the parts, dissolving any petroleum residues; the condensation then drips back into the bulk organic liquid. When the parts are removed from the degreaser, they are warm, and the solvent evaporates rapidly, leaving a dry part, ready for the next process step. Almost all modern vapor degreasers incorporate cold water and/or refrigerant coils near the top edges of the tank, so that the rising vapor blanket will condense on these surfaces and drip back into the bulk solvent, thus minimizing the emission of solvent vapors.

For this study, uncontrolled emissions are assumed to be from vapor degreasers with cooling coils and to contain 1,1,1-trichloroethane (TCA). TCA, like many other chlorinated organic compounds, have been phased out of production under EPA's regulations 40 CFR 82, Protection of Stratospheric Ozone. Consequently, it seems unlikely that TCA should be prevalent at electroplating shops. Nevertheless, the 1996 EPA Toxic Release Inventory (TRI) database, which is submitted by industry, suggests that a large portion of volatile organic chemical emissions is from TCA. The physical data for TCA show that it has a specific gravity of 1.34, which is why Table 1 shows the bath concentration at 1,340 grams per liter (Noyes, 1991). It also has a vapor pressure of 60 millimeters of mercury (mmHg) at 45°F (the assumed temperature of the condensation coils), which would correspond to an equilibrium concentration of 4.65×10^5 mg/m³ (i.e., if there was zero ventilation). Its molecular weight is 133 gm/mole (Noyes, 1991).

The mass emission value shown in Table 4 is based on AP-42 (Section 4.6.2: EPA, 1995) rather than on nonventilated equilibrium TCA concentrations. AP-42 gives an emission factor rating of "C" to its estimate of 0.15 pounds of emissions/hour-square foot (EPA, 1995). Multiplying this value by the estimated typical tank size shown in Table 3 (and making the necessary conversion for units of measure), the mass emissions rate shown in Table 4 is anticipated to be 6.5×10^7 mg/day. This emission rate corresponds to a ventilation system inlet concentration of 177 mg/m³ (the uncontrolled emission concentration shown in Table 2) at the 9,000 ft³/min ventilation flow rate shown in Table 3.

Table 4 also shows uncontrolled emissions from four other solvents. The atmospheric emissions from these solvent operations will be related to the TCA emission rate by the ratio of their vapor pressures at the temperature of use (i.e., room temperature for the other solvents) and their molecular weights (mw). These solvents, their vapor pressures and

molecular weights are:

Solvent	Vapor Pressure, mm Hg	Molecular Weight, g/mole
Toluene	21	92
Tetrachloro-ethylene (perchloro-ethylene or PCE)	14	166
Methanol	96	32
Methyl ethyl ketone (MEK)	78	72

Another approach for estimating emission rates for degreasing solvents is to insert the amount of solvent purchased (per unit time) less the amount of spent solvent disposed of as solid waste or recycled to others. This net amount is the volume that was volatilized to the atmosphere (unless solvent vapors are captured in activated carbon that is recycled off site or are destroyed by fume incineration).

Next Steps

The procedures and quantities presented in this paper will be reviewed, and changes will likely be made, prior to finalization of the risk assessment tool. Also, information is being gathered for similar information on liquid and solid waste emissions from metal finishing facilities.

References

1. American Electroplaters' Society, Inc. (1969a) *Cyanide Copper Plating*.

2. American Electroplaters' Society, Inc. (1969b) *Sulfuric Acid Anodizing of Aluminum and Its Alloys*.

3. American Electroplaters' Society, Inc. (1970a) *Bright Acid Sulfate Copper Plating*.

4. American Electroplaters' Society, Inc. (1970b)

Chromate Conversion Coatings.

5. American Electroplaters' Society, Inc. (1972a) *Decorative Chromium Plating*.

6. American Electroplaters' Society, Inc. (1972b) *Electroless Plating of Metals*.

7. American Electroplaters' Society, Inc. (1973a) *Chromic Acid Anodizing of Aluminum*.

8. American Electroplaters' Society, Inc. (1973b) *Practical Nickel Plating*.

9. American Electroplaters' Society, Inc. (1974) *Theory and Practice of Phosphating*.

10. American Electroplaters' Society, Inc. (1975a) *Gold Plating*.

11. American Electroplaters' Society, Inc. (1975b) *Hard Chromium Plating*.

12. American Electroplaters' Society, Inc. (Undated) *Zinc and Cadmium Plating*.

13. Dupont Industrial Chemicals Publications (1973) *Decorative Chromium Plating, Bulletin No. 50*.

14. Dupont Industrial Chemicals Publications (1975) *Industrial (Hard) Chromium Plating, Bulletin No. 60*.

15. Dupont Industrial Chemicals Publications (1976) *Cyanide Zinc Plating, Bulletin No. 36*.

16. Dupont Industrial Chemicals Publications (Undated) *Cyanide Copper Plating, Bulletin No. 41*.

17. Electroplating Engineering Handbook. (1984) 4th Ed. Van Nostrand Reinhold Co.

18. Modern Electroplating. (1974) 3rd Ed. Wiley-Interscience Publication.

19. National Metal Finishing Resource Center. The Plating Retirement Plan. Internet:

<http://www.nmfrc.org/pdf/pf0396a.htm>, undated.

20. J. Electroplaters and Surface Finishers Soc. (Mar, 1994) *Plating and Surface Finishing*.

21. J. Electroplaters and Surface Finishers Soc. (April 1990) Variables in the Anodizing Process, *Plating and Surface Finishing*.

22. National Metal Finishing Resource Center. (Undated) *Plating Difficult Substrates with Electroless Nickel*, Internet:

<http://www.nmfrc.org/pdf/pf0196a.htm>, undated.

23. Noyes Data Corp. (1991) *Industrial Solvents Handbook*, 4th Ed..

24. Noyes Publications. (1985) *Electroplating Wastewater Pollution Control Technology*.

25. OSHA Regulations, 29 CFR 1910.94(d), Subpart G, Occupational Health & Environmental Control.

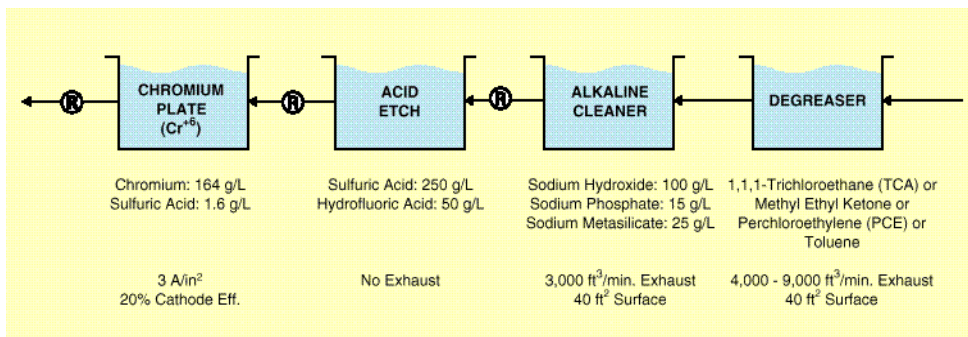
26. OSHA Regulations, 29 CFR 1910.94(d)(2)(v)&(vii), Subpart G, Occupational Health & Environmental Control.

27. OSHA Regulations, 29 CFR 1910.94(d)(4)(i), (ii), and (iii)(a)(2), Subpart G, Occupational Health & Environmental Control.

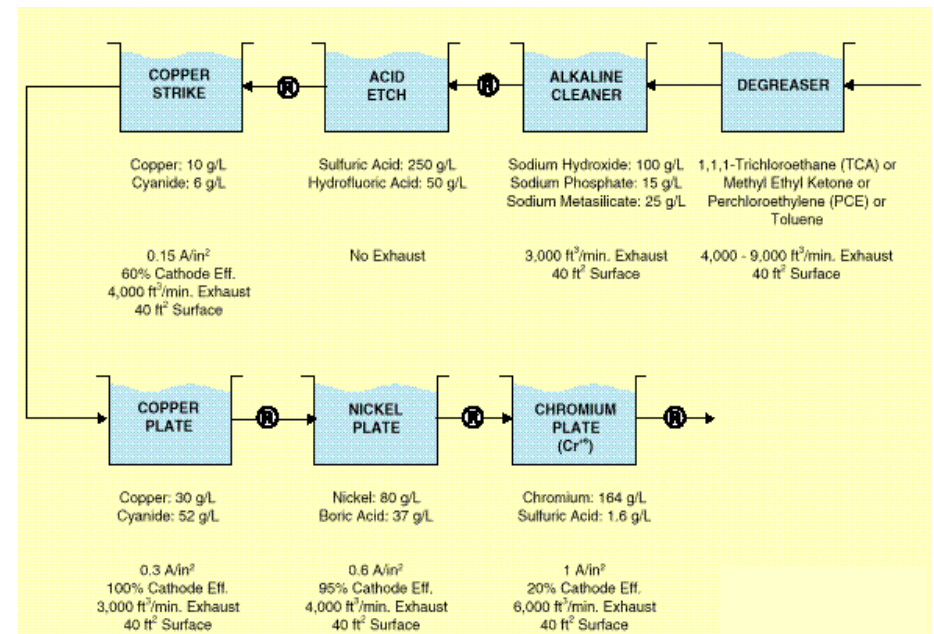
28. Products Finishing (Dec 1995) *Job Plater Keeps EN Plating Quality High*.

29. U.S. Environmental Protection Agency. (1996, Nov. 27) *Hard chrome pollution prevention demonstration project*, interim report. U.S. EPA Common Sense Initiative (CSI), Metal Finishing Subcommittee.

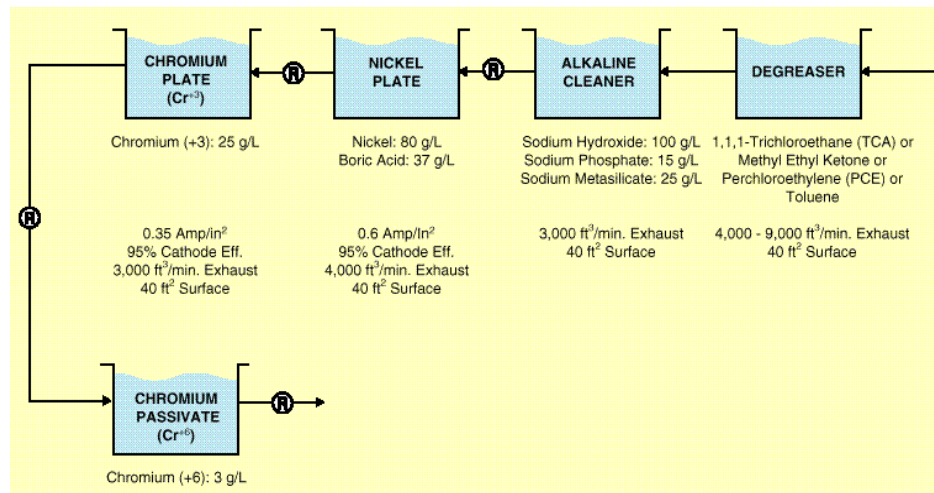
30. U.S. Environmental Protection Agency. (1995, January) *Compilation of air pollutant emission factors*. AP-42, 5th Ed.



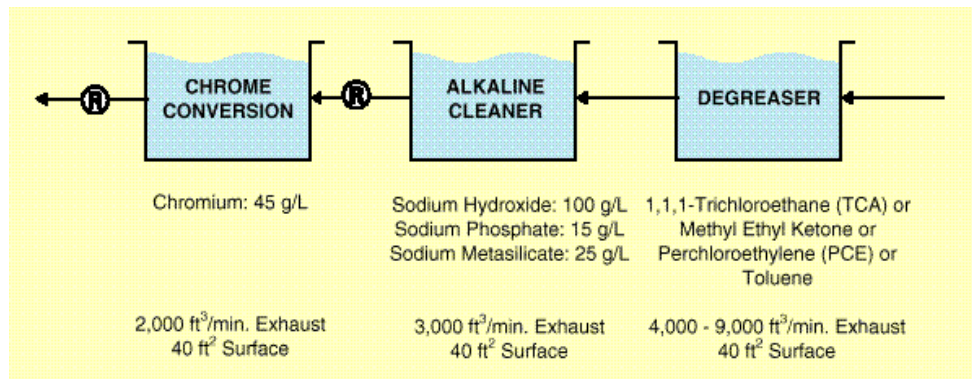
(a) Hard chromium plating




(b) Decorative chromium plating



(c) Trivalent chromium plating

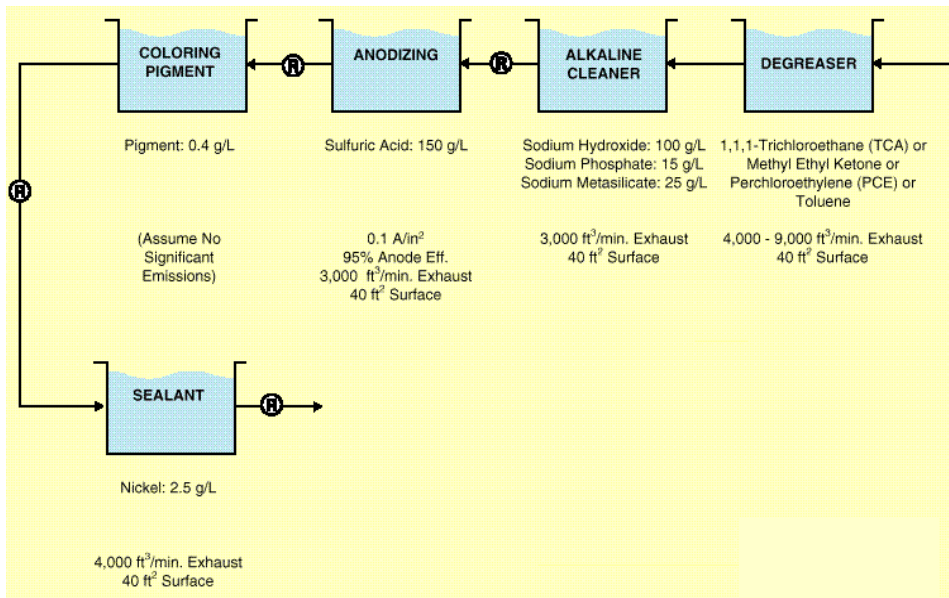


(d) Chromate conversion coating

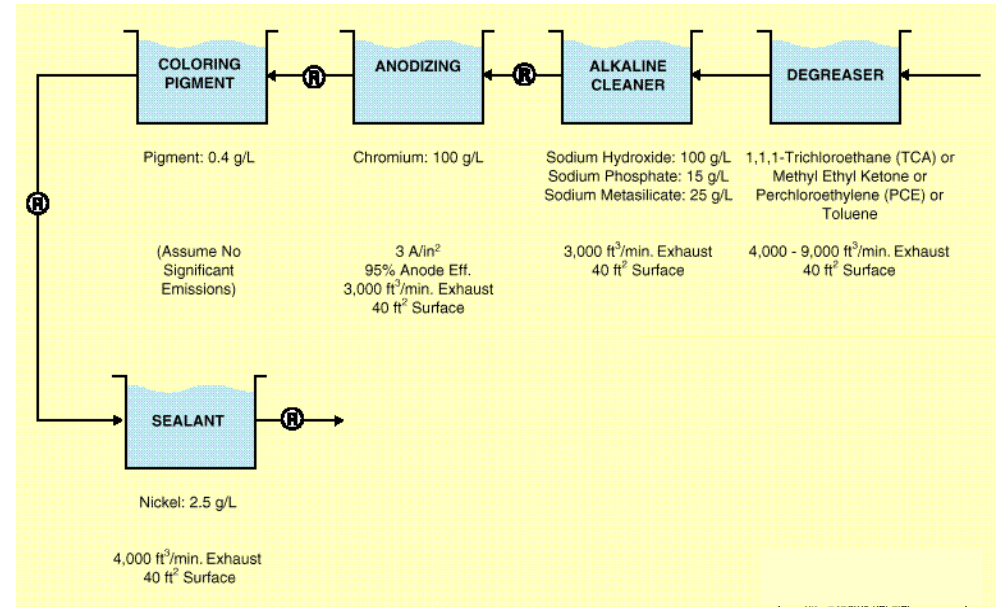
 = Rinse
 g/L = grams per liter
 A/in² = Ampere per square inch
 ft² = square foot
 ft³/min. = cubic feet per minute

Key for Figure 1

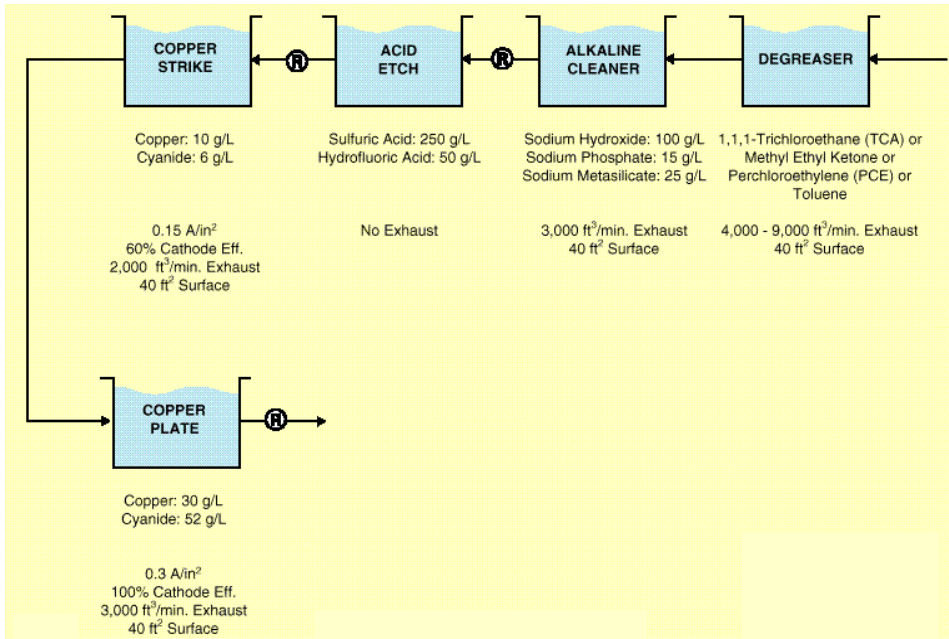
Figure 1. Default metal finishing plating lines



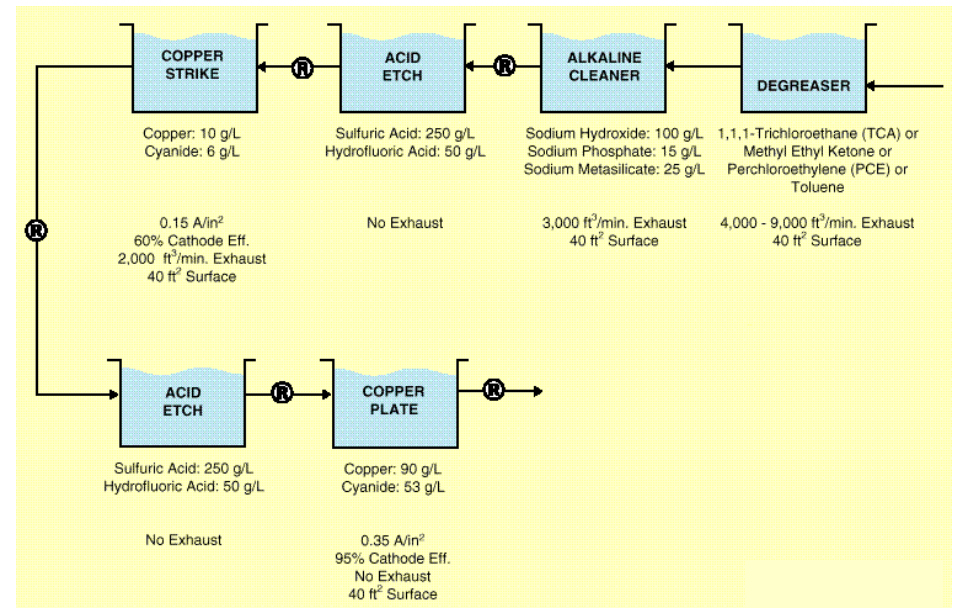
(e) Anodizing - sulfuric acid



(f) Anodizing - chromic acid

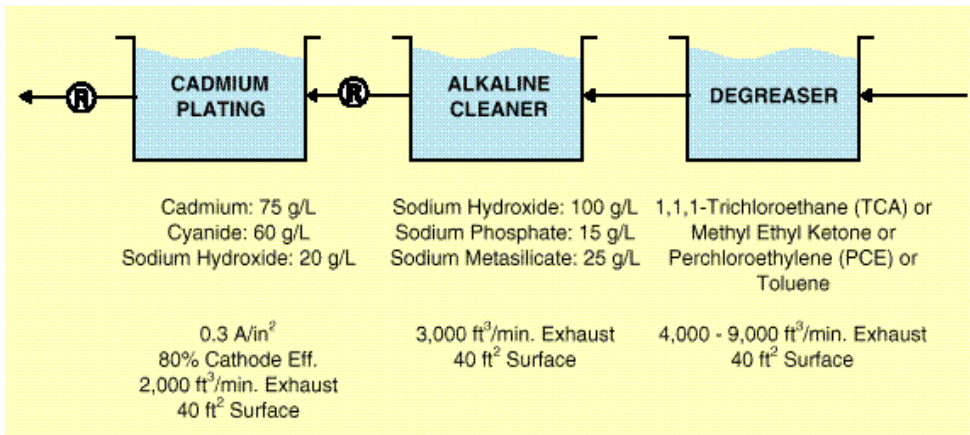


Copper plating (cyanide)

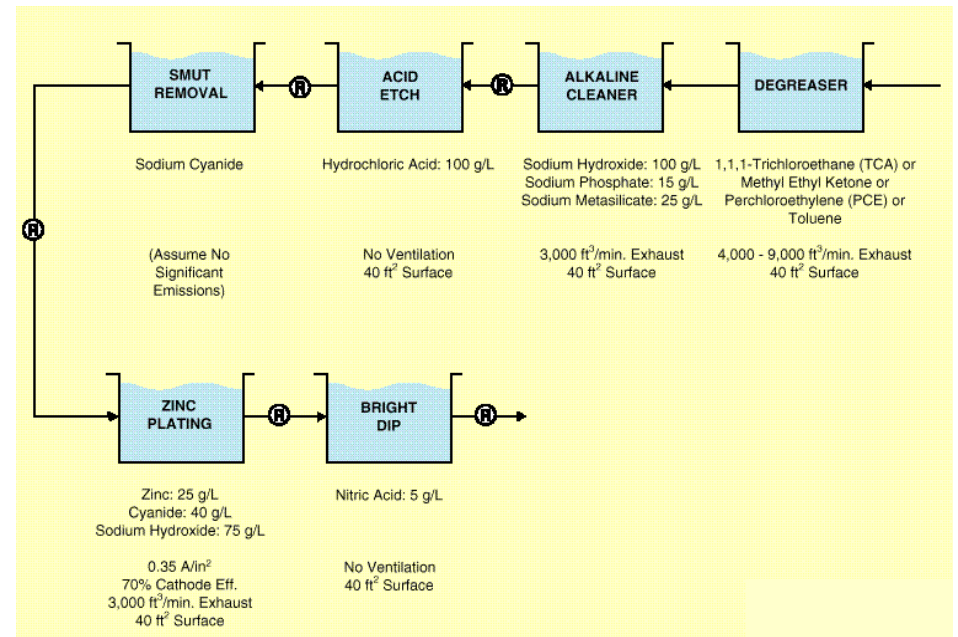


(g) Copper plating (acid)

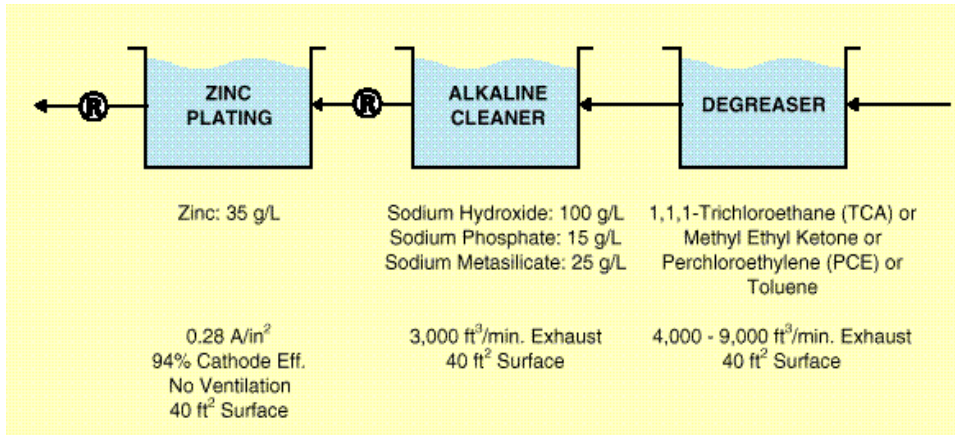
Figure 1 (cont'd)



(i) Cadmium plating

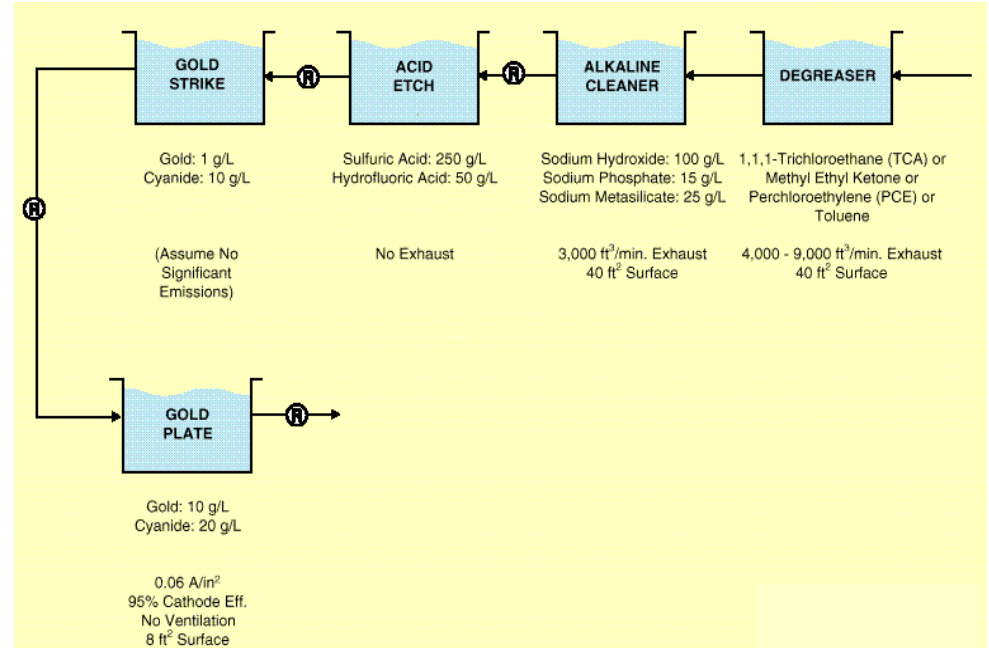


(j) Zinc plating (cyanide)

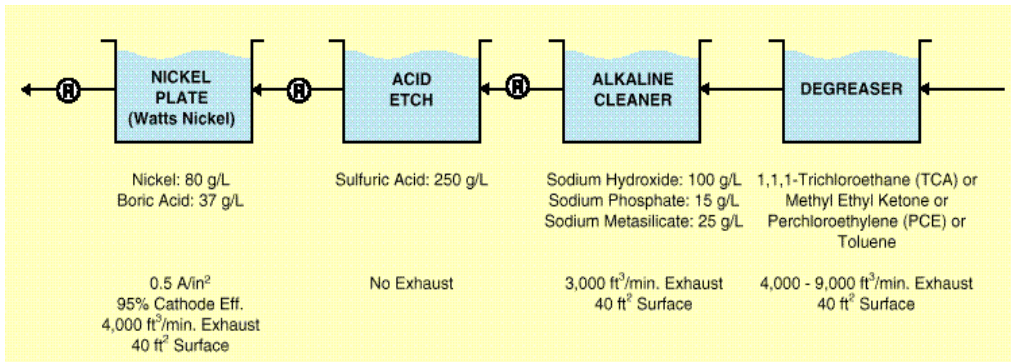


(k) Zinc plating (chloride)

Figure 1. (cont'd)

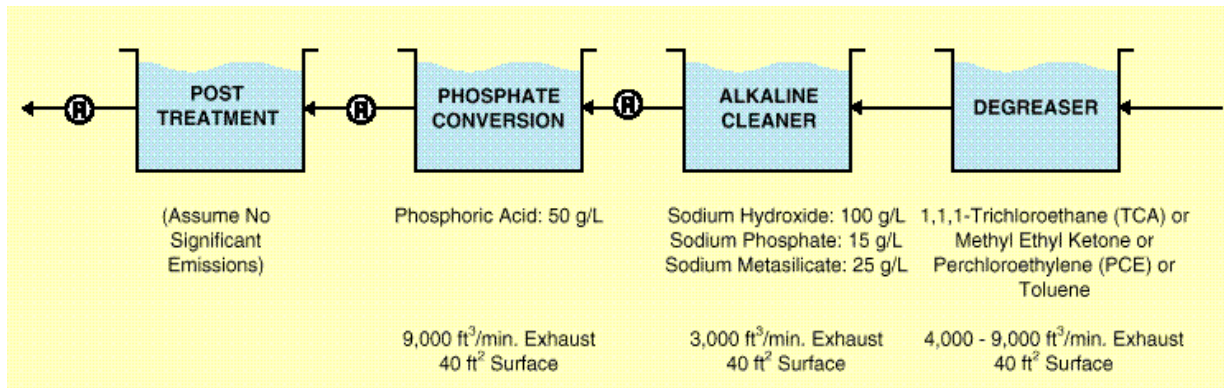
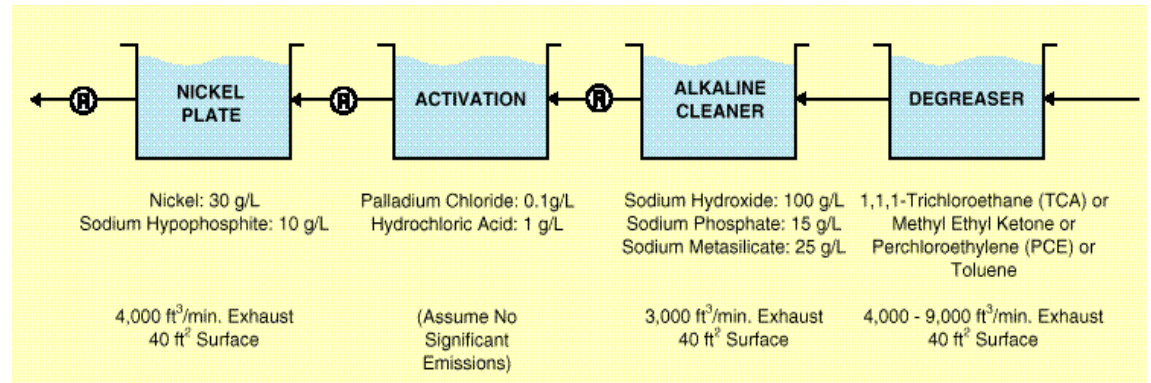


(l) Gold plating



(m) Nickel plating

(n) Electroless nickel plating



(o) Phosphate coating

Figure 1. (cont'd)

Table 1. Relative Atmospheric Emissions Concentration from Various Surface Coating Operations in the Electroplating Industry.

Type of Plating-Related Process Operation	Contaminant of Concern	Concentration of Contaminant in Bath** (gm/lit.)	Typical Current Density** (amp/sq.in.)	Cathode Efficiency** (%)	Concentration of Emissions Relative to Chromium Emiss. from Hard Chromium Plating Tanks (no units)
I. ELECTROLYTIC PROCESSES					
Hard Chromium Plating Bath	Chromium (+6)	164	3	20	1.0e+00
	Sulfuric Acid	1.6	3	20	9.8e-03
Decorative Chromium Plat. Bath	Chromium (+6)	164	1	20	3.3e-01
	Sulfuric Acid	1.6	1	20	3.3e-03
Trivalent Chromium Plating Bath	Chromium (+3)	25	0.35	95	3.7e-03
Nickel Plating Bath	Nickel	80	0.5	95	1.7e-02
Anodizing, Sulfuric Acid	Sulfuric Acid	150	0.1	95	6.4e-03
Anodizing, Chromic Acid	Chromic Acid	100	3	95	1.3e-01
Gold Plating Bath	Gold	10	0.06	95	2.6e-04
	Cyanide (CN)	20	0.06	95	5.1e-04
Copper Strike Bath	Copper	10	0.15	60	1.0e-03
	Cyanide (CN)	6	0.15	60	6.1e-04
Copper (Cyanide) Plating Bath	Copper	30	0.3	100	3.7e-03
	Cyanide (CN)	52	0.3	100	6.3e-03
Copper (Acid) Plating Bath	Copper	90	0.35	95	1.3e-02
	Sulfuric Acid	53	0.35	95	7.9e-03
Cadmium Plating Bath	Cadmium	75	0.3	80	1.1e-02
	Cyanide (CN)	60	0.3	80	9.2e-03
Zinc (Cyanide) Plating Bath	Zinc	25	0.35	70	5.1e-03
	Cyanide (CN)	40	0.35	70	8.1e-03
Zinc (Chloride) Plating Bath	Zinc	35	0.28	94	4.2e-03
II. NON-ELECTROLYTIC PROCESSES					
Hexavalent Chromium Passivation	Chromium (+6)	3	n/a	n/a	n/a
Anodizing Sealer	Nickel	2.5	n/a	n/a	n/a
Nickel Plating Bath (Electroless)	Nickel	30	n/a	n/a	n/a
	Sod. Hypophosph.	10	n/a	n/a	n/a
Acid Etch (for Zinc Plating)	Hydrochloric Acid	100	n/a	n/a	n/a
Bright Dip (for Zinc Plating)	Nitric Acid	5	n/a	n/a	n/a
Alkaline Cleaning Bath (typical)	Sod. Hydroxide	100	n/a	n/a	n/a
	Sod. Phosphate	15	n/a	n/a	n/a
	Sod. Metasilicate	25	n/a	n/a	n/a
Acid Etch/Desmut Bath (typical)	Sulfuric Acid	250	n/a	n/a	n/a
	Hydrofluoric Acid	50	n/a	n/a	n/a
Phosphate Coating Bath	Phosphoric Acid	50	n/a	n/a	n/a
Chromate Conversion Bath	Chromium (+6)	45	n/a	n/a	n/a
III. SOLVENT DEGREASER					
	1,1,1-Trichloroethane	1,340	n/a	n/a	n/a
	Perchloroethylene	1,620	n/a	n/a	n/a
	Methanol	790	n/a	n/a	n/a
	Methyl Ethyl Ketone	810	n/a	n/a	n/a
	Toluene	870	n/a	n/a	n/a

** References 1-9

Table 3. Ventilation rates, tank surface areas, and volumetric flow rates for various surface coating operations in the electroplating industry.

Type of Plating Operation	Contaminant of Concern	Estimated OSHA Ventilation Category (40CFR1910.94 (d)(2)(v)&(vii))	Minimum Ventilation Rate (cu.ft./min-sq.ft) (40CFR1910.94(d)(4) (i),(ii), & (iii)(a)(2))	Estimated Tank Surface Area (sq.ft.)	Calculated Volumetric Flow Rates (cu.ft./min.)
I. ELECTROLYTIC PROCESSES					
Hard Chromium Plating Bath	Chromium (+6)	A-1	340	20	6,800
	Sulfuric Acid	B-1	225	20	4,500
Decorative Chromium Plat. Bath	Chromium (+6)	A-1	340	40	13,600
	Sulfuric Acid	B-1	225	40	9,000
Trivalent Chromium Plating Bath	Chromium (+3)	B-3	170	40	6,800
Nickel Plating Bath	Nickel	B-2	225	40	9,000
Anodizing, Sulfuric Acid	Sulfuric Acid	B-3	170	40	6,800
Anodizing, Chromic Acid	Chromic Acid	A-3	170	40	6,800
Gold Plating Bath	Gold	D-4	0	8	0
	Cyanide (CN)	C-4	0	8	0
Copper Strike Bath	Copper	D-3	0	40	0
	Cyanide (CN)	C-3	110	40	4,400
Copper (Cyanide) Plating Bath	Copper	D-2	110	40	4,400
	Cyanide (CN)	C-2	170	40	6,800
Copper (Acid) Plating Bath	Copper	D-4	0	40	0
	Sulfuric Acid	B-4	0	40	0
Cadmium Plating Bath	Cadmium	D-3	0	40	0
	Cyanide (CN)	C-3	110	40	4,400
Zinc (Cyanide) Plating Bath	Zinc	B-3	170	40	6,800
	Cyanide (CN)	C-3	110	40	4,400
II. NON-ELECTROLYTIC PROCESSES					
Hexavalent Chromium Passivation	Chromium (+6)	A-3	225	40	9,000
Anodizing Sealer	Nickel	B-1	225	40	9,000
Nickel Plating Bath (Electroless)	Nickel	B-2	225	40	9,000
	Sod. Hypophosphite	D-4	0	40	0
Acid Etch (for Zinc Plating)	Hydrochloric Acid	C-4	0	40	0
Bright Dip (for Zinc Plating)	Nitric Acid	C-4	0	40	0
Zinc (Chloride) Plating Bath	Zinc	B-4	0	40	0
Alkaline Cleaning Bath (typical)	Sod. Hydroxide	C-2	170	40	6,800
	Sod. Phosphate	D-2	110	40	4,400
	Sod. Metasilicate	D-2	110	40	4,400
Acid Etch/Desmut Bath (typical)	Sulfuric Acid	B-4	0	40	0
	Hydrofluoric Acid	C-4	0	40	0
Phosphate Coating Bath	Phosphoric Acid	B-2	225	40	9,000
Chromate Conversion Bath	Chromium (+6)	A-4	110	40	4,400
III. SOLVENT DEGREASER					
	1,1,1-Trichloroethane	C-1	225	40	9,000
	Perchloroethylene	B-2	225	40	9,000
	Methanol	C-3	110	40	4,400
	Methyl Ethyl Ketone	C-3	110	40	4,400
	Toluene	C-3	110	40	4,400

Table 4. Daily Mass emission levels external to the plant with various control devices for various surface coating operations in the electroplating industry (mg/day).

Type of Plating Operation	Contaminant of Concern	Uncontrolled Emissions	Polymer Balls	Fume Suppressants (@<28 dyne/cm)	Fume Suppressants + Polymer Balls	Packed Bed Scrubber	Packed Bed Scrubber + Fume Suppress. + Polymer Balls	Chevron Mist Eliminator	Series Dual Chevron Mist Eliminator	Mesh Pad Mist Eliminator	Packed Bed Scrubber + Mist Eliminator	Composite Mesh Pad Mist Eliminator	Composite Mesh Pad + Fume Suppressant	Chevron Mist Eliminat. + Fume Suppressant
I. ELECTROLYTIC PROCESSES														
Hard Chromium Plating Bath	Chromium (+6)	1.5e+06	6.4e+04	5.3e+03	1.7e+03	1.1e+04	6.1e+02	3.1e+04	1.4e+03	6.7e+03	2.0e+01	2.7e+03	1.7e+02	9.2e+02
	Sulfuric Acid	1.5e+04	6.2e+02	5.1e+01	1.7e+01	1.0e+02	6.0e+00	3.0e+02	1.3e+01	6.5e+01	2.0e-01	2.6e+01	1.6e+00	8.9e+00
Decorative Chromium Plating Bath	Chromium (+6)	1.0e+06	4.3e+04	3.5e+03	1.1e+03	7.0e+03	4.1e+02	2.0e+04	9.1e+02	4.4e+03	1.4e+01	1.8e+03	1.1e+02	6.1e+02
	Sulfuric Acid	9.8e+03	4.2e+02	3.4e+01	1.1e+01	6.9e+01	4.0e+00	2.0e+02	8.8e+00	4.3e+01	1.3e-01	1.7e+01	1.1e+00	6.0e+00
Trivalent Chromium Plating Bath	Chromium (+3)	5.6e+03	2.4e+02	2.0e+01	6.4e+00	4.0e+01	2.3e+00	1.1e+02	5.1e+00	2.5e+01	7.6e-02	1.0e+01	6.2e-01	3.4e+00
Nickel Plating Bath	Nickel	3.4e+04	1.4e+03	1.2e+02	3.9e+01	2.4e+02	1.4e+01	6.9e+02	3.1e+01	1.5e+02	4.6e-01	6.0e+01	3.8e+00	2.1e+01
Anodizing, Sulfuric Acid	Sulfuric Acid	9.6e+03	4.1e+02	3.4e+01	1.1e+01	6.8e+01	3.9e+00	2.0e+02	8.7e+00	4.3e+01	1.3e-01	1.7e+01	1.1e+00	5.9e+00
Anodizing, Chromic Acid	Chromic Acid	1.9e+05	8.2e+03	6.8e+02	2.2e+02	1.4e+03	7.8e+01	3.9e+03	1.7e+02	8.6e+02	2.6e+00	3.4e+02	2.1e+01	1.2e+02
Gold Plating Bath	Gold	No significant emissions from Gold Plating, unless aerated and externally ventilated.												
	Cyanide (CN)													
Copper Strike Bath	Copper	9.9e+02	4.2e+01	3.5e+00	1.1e+00	6.9e+00	4.0e-01	2.0e+01	8.9e-01	4.4e+00	1.3e-02	1.8e+00	1.1e-01	6.0e-01
	Cyanide (CN)	5.9e+02	2.5e+01	2.1e+00	6.8e-01	4.2e+00	2.4e-01	1.2e+01	5.4e-01	2.6e+00	8.0e-03	1.1e+00	6.6e-02	3.6e-01
Copper (Cyanide) Plating Bath	Copper	5.5e+03	2.3e+02	1.9e+01	6.3e+00	3.9e+01	2.2e+00	1.1e+02	5.0e+00	2.4e+01	7.4e-02	9.8e+00	6.1e-01	3.4e+00
	Cyanide (CN)	9.5e+03	4.0e+02	3.3e+01	1.1e+01	6.7e+01	3.9e+00	1.9e+02	8.6e+00	4.2e+01	1.3e-01	1.7e+01	1.1e+00	5.8e+00
Copper (Acid) Plating Bath	Copper	No significant emissions from Acid Copper Plating unless aerated and externally ventilated.												
	Sulfuric Acid													
Cadmium Plating Bath	Cadmium	1.1e+04	4.7e+02	3.9e+01	1.3e+01	7.8e+01	4.5e+00	2.3e+02	1.0e+01	4.9e+01	1.5e-01	2.0e+01	1.2e+00	6.8e+00
	Cyanide (CN)	8.9e+03	3.8e+02	3.1e+01	1.0e+01	6.2e+01	3.6e+00	1.8e+02	8.1e+00	3.9e+01	1.2e-01	1.6e+01	9.9e-01	5.4e+00
Zinc (Cyanide) Plating Bath	Zinc	7.6e+03	3.2e+02	2.7e+01	8.7e+00	5.4e+01	3.1e+00	1.6e+02	6.9e+00	3.4e+01	1.0e-01	1.4e+01	8.5e-01	4.7e+00
	Cyanide (CN)	1.2e+04	5.2e+02	4.3e+01	1.4e+01	8.6e+01	5.0e+00	2.5e+02	1.1e+01	5.4e+01	1.6e-01	2.2e+01	1.4e+00	7.4e+00
II. NON-ELECTROLYTIC PROCESSES														
Hexavalent Chromium Passivation	Chromium (+6)	4.1e+03	1.8e+02	1.4e+01	4.7e+00	2.9e+01	1.7e+00	8.4e+01	3.7e+00	1.8e+01	5.6e-02	7.3e+00	4.6e-01	2.5e+00
Anodizing Sealer	Nickel	3.4e+03	1.5e+02	1.2e+01	3.9e+00	2.4e+01	1.4e+00	7.0e+01	3.1e+00	1.5e+01	4.6e-02	6.1e+00	3.8e-01	2.1e+00
Nickel Plating Bath (Electroless)	Nickel	4.1e+04	1.8e+03	1.4e+02	4.7e+01	2.9e+02	1.7e+01	8.4e+02	3.7e+01	1.8e+02	5.6e-01	7.3e+01	4.6e+00	2.5e+01
	Sod. Hypophosphite	1.4e+04	5.8e+02	4.8e+01	1.6e+01	9.6e+01	5.6e+00	2.8e+02	1.2e+01	6.1e+01	1.9e-01	2.4e+01	1.5e+00	8.4e+00
Acid Etch (for Zinc Plating)	Hydrochloric Acid	1.4e+05	5.8e+03	4.8e+02	1.6e+02	9.6e+02	5.6e+01	2.8e+03	1.2e+02	6.1e+02	1.9e+00	2.4e+02	1.5e+01	8.4e+01
Bright Dip (for Zinc Plating)	Nitric Acid	6.9e+03	2.9e+02	2.4e+01	7.9e+00	4.8e+01	2.8e+00	1.4e+02	6.2e+00	3.0e+01	9.3e-02	1.2e+01	7.6e-01	4.2e+00
Zinc (Chloride) Plating Bath	Zinc	No significant emissions from Zinc Chloride Plating unless aerated and externally ventilated.												
Alkaline Cleaning Bath (typical)	Sod. Hydroxide	1.1e+05	4.5e+03	3.7e+02	1.2e+02	7.5e+02	4.3e+01	2.2e+03	9.7e+01	4.7e+02	1.4e+00	1.9e+02	1.2e+01	6.5e+01
	Sod. Phosphate	1.6e+04	6.8e+02	5.6e+01	1.8e+01	1.1e+02	6.5e+00	3.3e+02	1.5e+01	7.1e+01	2.2e-01	2.8e+01	1.8e+00	9.8e+00
	Sod. Metasilicate	2.7e+04	1.1e+03	9.4e+01	3.1e+01	1.9e+02	1.1e+01	5.4e+02	2.4e+01	1.2e+02	3.6e-01	4.7e+01	3.0e+00	1.6e+01
Acid Etch/Desmut Bath (typical)	Sulfuric Acid	3.4e+05	1.5e+04	1.2e+03	3.9e+02	2.4e+03	1.4e+02	7.0e+03	3.1e+02	1.5e+03	4.6e+00	6.1e+02	3.8e+01	2.1e+02
	Hydrofluoric Acid	6.9e+04	2.9e+03	2.4e+02	7.9e+01	4.8e+02	2.8e+01	1.4e+03	6.2e+01	3.0e+02	9.3e-01	1.2e+02	7.6e+00	4.2e+01
Phosphate Coating Bath	Phosphoric Acid	6.9e+04	2.9e+03	2.4e+02	7.9e+01	4.8e+02	2.8e+01	1.4e+03	6.2e+01	3.0e+02	9.3e-01	1.2e+02	7.6e+00	4.2e+01
Chromate Conversion Bath	Chromium (+6)	6.2e+04	2.6e+03	2.2e+02	7.1e+01	4.3e+02	2.5e+01	1.3e+03	5.6e+01	2.7e+02	8.3e-01	1.1e+02	6.9e+00	3.8e+01

