Generic Scenario: Electroplating for Metal Treatment

Background

Electroplating is a diverse industry. Many plating specialty chemical suppliers and many plating shops produce and use a variety of plating solutions. Currently, there are no data available on the size of the market and the market growth rates. This information is being compiled by the Metal Finishing Suppliers Association and will be available in 1994. The major metals plated include nickel, chromium, zinc, and copper. Many other metals are plated, including cadmium, gold, silver, indium, iron, lead, tin, and rhodium.

Commercial electroplating baths are almost always aqueous-based. Exceptions are plating of aluminum from an organic electrolyte and plating of refractory-type metals (e.g. tantalum, niobium, zirconium, and tungsten) from fused electrolytes. These exceptions are plated by a few specialists. The makeup of a plating bath consists of compounds that perform one or more of the following functions:

1. Provides the source of the metal being plated
2. Keeps the metal in solution by complexing the metal
3. Makes the solution conductive
4. Stabilizes the solution from unwanted reactions
5. Acts as a buffer to maintain the desired pH
6. Deposits a modifier (i.e., brightener, leveler, smoother, and inhibitor)
7. Dissolves anodes
8. Serves as a solution/bath modifier (i.e., wetting agent, foam blanket).

Process

All of these compounds do not have to be in the plating bath for the bath to function or for the desired deposit to be applied [1]. The metal can be deposited by applying an electric current through the solution and depositing the metal on the cathode or by chemical reaction to deposit the metal, hence the name *electroless*. A process similar to electroplating is anodizing in which the metal surface being finished is the anode. During anodizing, the metal surface is converted to a beneficial oxide form.

The size of an electroplating bath varies from 10 gallons to several thousand gallons. The concentration of chemicals varies depending on the bath. Other than water, the largest constituent is the metal salt followed by the conductive material and complexers. These compounds range from amounts measured in ppm for brighteners to 20% for metal salts. The rest of the chemical compounds are at low levels (ppm levels). Because many of the baths operate at elevated temperatures, the additives are nonvolatile so they stay in the plating solution. Baths are equipped with exhaust ventilating systems to collect and discharge vapors from the bath. The additives either get used or break down during operation. On average, a bath lasts about 1 year. Some electroless baths are changed weekly, compared to other electroplating baths that last many years.

Exposure/Wastes

Regardless of the electroplating process, the routes of exposure to the worker are as follows:

1. Inhalation
2. Ingestion
3. Dermal.

The times that the worker could be exposed during normal operations are:

1. Initial bath makeup
2. Bath operation
3. Bath maintenance
4. Bath disposal/replacement.

Each of these exposure baths is described in the following paragraphs.

New and replacement baths are made up manually. The chemicals (compounds) are provided in bags, bottles, cans, etc., in liquid or solid form. The chemicals are measured into the tank either before or after water has been added to the bath. Proprietary and vendor-provided chemicals typically are premixed in the required ratios, so that the operator need only measure out the quantity of compound required for the volume of bath and add water. Operators wear the required protective equipment to reduce exposure (i.e., rubber gloves, safety glasses or face shield, rubber apron, and respirator for dusts). The total time spent to add chemicals would be about 15 minutes for small baths. For larger baths, pumps or other equipment would be used to save time and to reduce worker exposure. The longest time would be the addition of water to the bath.

During bath operation, the worker adds and removes the items being plated by hand or is assisted by a hoist. Splashing and/or drips would cause worker contact with the solution. While the worker is next to or near the tank, any vapors not picked up by the ventilation system could be inhaled. The time to add and remove a part or rack of parts from a bath would range from 1 to 2 minutes. The duration of an item in a bath is dependent on the metal thickness required and the plating rate. The worker could be at the bath from several times an hour to once a shift. If air agitation is used or if gases are evolved during plating, as in chromium plating, small particles of the plating solution could become atomized and become airborne, adding to worker exposure if ventilation is not adequate [2]. Automated lines would eliminate worker exposure during plating operations.

Bath maintenance includes solution and equipment maintenance. Solution maintenance would involve taking solution samples for analysis and adding chemicals to maintain the required concentrations. Some baths are analyzed every couple of hours, whereas others are analyzed once a week. Mechanical maintenance would include replacement of filter elements and electrodes. Maintenance would average about once a week. The exposure would depend on the frequency of solution maintenance and the number of elements and solutions requiring replacement.

Bath disposal and replacement exposure would be about the same as for bath makeup.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

PMN chemicals may be used as one of the many components and additives in the electroplating bath. Specifically, PMN chemicals may be used as:

1. The metal salt
2. Conductive material and complexers
3. Additives such as buffers, deposit modifiers, and solution/bath modifiers.

Air emissions and worker exposure hazards could arise during makeup of the baths, electroplating operations, and in bath maintenance and disposal operations.

For the purposes of the environmental releases and worker exposure calculations conducted in this generic scenario, it is assumed that the PMN chemical is used as an additive to the electroplating bath. Typically, additives are present at low ppm levels in the electroplating bath. The electroplating process, discussed earlier, involves immersion of items in open electroplating baths equipped with exhaust systems for vapor removal. The items are removed from the bath following the electroplating process, and the baths themselves are periodically maintained through addition of fresh chemicals and/or replacement of bath solution. The electroplating process thus has the potential for air, liquid, and waste emissions. Worker exposure to PMN electroplating chemicals may arise from electroplating operations as well as bath makeup and maintenance operations.

Assumptions

%PMN : weight percent of PMN chemical in the electroplating solution (solution basis)
$\%PMN_S$: weight percent of PMN chemical in the electroplating solution (dry-solids basis)
D : number of days per year of operation of the electroplating facility

Environmental Releases (total lb/year at a single manufacturing facility)

Solid Wastes: Solid wastes containing the PMN chemical will arise from (1) disposal of baths following the end of their useful life and (2) cleaning and maintenance of the electroplating equipment. In addition, spent electroplating solution that is treated at a waste treatment plant will result in sludge wastes that may contain the PMN additive.

The amount of PMN chemical that would be released as solid waste from a single electroplating facility will depend on the extent to which the PMN chemical is present in the waste and the volume of waste produced annually. The release of PMN chemical as solid waste can be calculated as:

$$\%PMN_S/100 * SW * D = ?\ lb/year$$

where SW (typical range 1 ppm to 20%) is the amount of electroplating solid waste (dry-solids basis) in lb/day generated at the facility. Note that if the PMN chemical is reactive or is used up during the electroplating process or is destroyed in the waste treatment process, the content of PMN chemical in the solid waste will be much lower than in the starting solution and the solid waste emissions consequently would be reduced. We assume for solid wastes that the PMN additive can be removed as a sludge in the waste treatment facility through precipitation or other means.

Air Emissions: Air emissions of a PMN chemical additive in the electroplating solution potentially could arise from spray droplets emitted from the bath as a result of agitation and splashing from immersion of items. It is assumed here that the PMN chemical additive is nonvolatile, a reasonable assumption because many baths typically operate at elevated temperatures, and losses from volatility would be unacceptable.

The spray droplets emitted from the bath are likely to dry to form fine particulates that may then be vented by the exhaust system. Control devices may be used at exhaust vent stacks from electroplating facilities, including those pursuant to Title III of Clean Air Act Amendments of 1990 (Title III) concerning emission of hazardous air pollutants.

To estimate the extent of air emissions for a PMN chemical, the vapor pressure, solution temperature, and solution agitation are useful. If the air emissions of a current constituent of the electroplating solution or similar solution are known and a similar mechanism of emissions is suspected for the PMN additive, the potential emissions of the PMN can be estimated by analogy as:

$$\frac{VP\ PMN}{VP\ Surrogate} \quad \frac{\%\ PMN}{\%\ Surrogate} * Q_{Surrogate} = ?\ lb/year$$

where %Surrogate is the weight percent in the electroplating solution of the chemical currently used in the process, and $Q_{Surrogate}$ is its estimated annual emission. The estimate could be further adjusted by a ratio of the two vapor pressures if volatilization is the mechanism (e.g., a nickel bath operating at 140°F will evaporate 0.1 gallon water/hr/ft^2 of surface area. With air agitation, this rate is considerably higher).

Water: Liquid waste containing the PMN chemical is expected to arise from electroplating bath maintenance, rinsing, and disposal operations. In these operations, the baths may be drained periodically of spent solution and refilled with fresh liquid. The spent electroplating solution may be piped to a waste treatment facility or transferred into drums for off-site disposal. Rinse water from the electroplating facility is sent to a wastewater treatment facility. We have assumed that the electroplating solution and

rinse water treated at the waste treatment facility results in solid wastes containing the PMN. Assuming that a high percentage, >95%, of the PMN additive is removed from the aqueous electroplating solution in the waste treatment plant, there will be negligible liquid emissions of the PMN chemical. If substantial residues of the PMN chemical remain in the treated water, these wastes would have to be estimated.

Worker Exposure

Worker exposure to the PMN chemical in the electroplating solution potentially could occur from various operations within the electroplating process. These include operations for:

1. Filling the baths with the PMN chemical additive
2. Loading and unloading of items into the baths and being in the vicinity of the baths to oversee the electroplating process
3. Maintenance and disposal of the immersion tank liquid.

The extent of worker exposure to the PMN chemical in these process steps would depend on the nature of the various chemical additives and parts-handling processes, and the proximity of the workers to the baths. Accurate quantification of the various routes for potential worker exposure is difficult with the limited information currently available. For the purpose of this generic scenario, the various potential routes of worker exposure are discussed qualitatively.

Inhalation (mg/day): Inhalation of the PMN chemical is expected to be a significant route of worker exposure to the PMN chemical. The extent of human exposure will depend on the efficiency of the exhaust system in preventing workplace air concentrations of the PMN chemical. Determining the extent of inhalation exposure will require measurement of the typical air concentrations of the PMN chemical in the work environment. If data on the air concentrations of the PMN chemical are not available, concentrations of suitable surrogate chemicals used in current electroplating solutions could be utilized. If the mechanism of air emissions for the known chemical is similar to that suspected for the PMN chemical, i.e., spray droplet generation from agitation and immersion operations, and if both chemicals are mixed using similar process steps, then measurements of the air concentrations of the surrogate chemical could be utilized to estimate potential exposure to the PMN chemical.

Assuming that the work involved in the various electroplating process operations is medium-duty work in terms of the level of physical activity required, an inhalation rate of 1.25 m^3/hr can be assumed (CEB, 1991). Further, assuming that H is the fraction of the hours in a process day during which electroplating-related operations are conducted, then inhalation exposure of a worker during an operating day to PMN chemical in the electroplating solution is (following CEB, 1991):

$$C\ (mg/m^3) * \frac{\%PMN}{\%Surrogate} * 1.25\ (m^3/hr) * H = ??\ (mg/day)$$

where C is the concentration of the surrogate chemical measured in the workplace air, and %Surrogate is the weight percent in the electroplating solution of the surrogate chemical. C typically would range from 0.01 to 50 mg/m^3, the percent surrogate would range from 0.0001 to 5%, and H would range from 0.05 to 0.12. Note that these estimates of inhalation exposure would be reduced significantly if normal bath exhaust systems were in operation.

Dermal Exposure (mg/day): Dermal exposure can arise from operations involving transfers of the electroplating solution, addition of the PMN chemical additive to the baths, and mechanical contact with the items during immersion and removal from the baths. Automated handling of items would reduce the amount of physical contact, and dermal exposure from such operations would be minimal.

Dermal exposure from the PMN chemical may be calculated using typical factors for dermal exposure from the types of routine contact operations involved [3]. The operations responsible for the majority of the dermal exposure would be the transfer and mixing of chemicals to prepare the electroplating solution.

If routine contact with the electroplating solution (and PMN chemical) occurs in these operations with a frequency, FT (number/day), then the dermal exposure is:

(1,300-3,900) mg/m^3 * FT * %PMN/100 = ?? mg/day

Note that these estimates of the extent of dermal exposure would be mitigated if normal operating procedures in the electroplating facility were to involve the use of dermal protective gear, such as gloves. Because electroplating solution constituents may be skin irritants, it is likely that skin protective gear will be used at most electroplating facilities.

Disposal Concerns

The containers used to transport the PMN chemical to the facility are assumed to be recycled, cleaned to remove contamination, and appropriately landfilled or incinerated. All liquid and water wastes are assumed to be reused, reprocessed or air dried, and then disposed of as solid wastes. Solid wastes containing the PMN chemical are assumed to be disposed of using appropriate mechanisms.

Note that release of the PMN chemical to the environment also may occur as a result of the retention of PMN on the electroplated items. Rinsing of items following electroplating may remove the majority of the surface-coated PMN additive; however, the surface-bonded and some fraction of surface-coated PMN additive may not be removed by rinsing. The implications of this release route may need to be addressed for the PMN chemical.

References

[1] Lowenheim, Frederick A., *Electroplating; Fundamentals of Surface Finishing*, McGraw-Hill, Inc., 1978.

[2] Durney, Lawrence J., *Electroplating Engineering Handbook*, 4th ed., Van Nostrand Reinhold Company, 1984.

[3] CEB, 1991. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessments*, Volume 1, Contract No. 68-D8-0112, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, February 1991.