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Waste Minimization in Electroplating Industries: A Review

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Wastewater, spent solvent, spent process solutions, and sludge are the major waste streams generated in large volumes daily in electroplating industries. These waste streams can be significantly minimized through process modification and operational improvement. Waste minimization methods have been implemented in some of the electroplating industries. Suggestions such as practicing source reduction approaches, reduction in drag out and waste, process modification and environmental benefits, have also been adopted. In this endeavor, extensive knowledge covering various disciplines has been studied, which makes problem solving extremely easy. Moreover, available process data pertaining to waste minimization (WM) is usually imprecise, incomplete, and uncertain due to the lack of sensors, the difficulty of measurement, and process variations. In this article waste minimization techniques and its advantages on the improvement of working atmosphere and reduction in operating cost have been discussed.

Key Words: Electroplating; wastewater; recycling; recovery; waste minimization

INTRODUCTION

Electroplating is the process of applying a thin layer of metal to an object by means of electrolytic position. While the exact method may vary in detail, virtually all electroplating processes are identical. The objects to be plated are suspended (either on a rack, in a barrel, or by wire fixture) in an electrolytic solution; these objects become the cathode (negative electrode) in the electrolytic deposition process. The anode (positive electrode) is introduced and is typically a plate of the metal to be deposited. A low-voltage direct current applied to the system induces metallic ions to migrate to the cathode (the object to be plated)

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where they are deposited. Electroplating is done to either metal or plastic to provide corrosion or wear resistance, to improve the object's appearance, or to increase the object's dimension.

The reasons for continuous research and development on waste minimization and prevention technologies toward zero discharge of waste minimization are studied. Waste minimization (WM) in the manufacturing industries is one of the major tasks in the prevention of industrial pollution. Virtually all manufacturing of precious metal products involves electroplating. Industrial waste pollution control is a major issue in waste management. To comply with the specific effluent standards, industries are forced to treat their waste before discharge. This is neither a cost effective nor an environmentally friendly solution. The over 6700 electroplating plants in the United States utilize more than 100 chemicals to electroplate parts with one or a combination of more than 100 metallic coatings. This industry has been generating a huge amount of waste in the forms of wastewater, spent solvent, spent process solutions, and sludge (1). The waste streams contain numerous hazardous or toxic chemical, metal, and non-metal contaminants that are regulated by the Environmental Protection Agency (2), and must be significantly reduced in order to prevent pollution and to reduce end-of-pipe treatment costs. An electroplating process is a typical chemical process in which a number of process units are sequentially connected.

For this process, source reduction can be realized mainly through (i) process and equipment modification, (ii) process control and optimization, (iii) technology change, and (iv) material substitution and product reformation. Over the past decade, a variety of methodologies and technologies for source reduction have been developed in this industry (3, 4). According to a recent survey, however, they have not fully permeated the plants (5). In recent years, research activities increasingly focus on replacement of hexavalent chromium plating technology by different methods, e.g. deposition from trivalent chromium solutions, physical and chemical vapour deposition, and thermal spray processes (6, 7). However, in many applications, for instance in functional electroplating, electro-deposition from hexavalent chromium cannot be replaced by other technologies due to excellent layer quality, easy handling of the process bath.

Industries have traditionally treated the waste products before discharging them to the environment. Because the treatment occurs after the production of waste, this type of treatment is called "end-of-pipe" treatment, and this is being seriously questioned. The alternative solution, "waste minimization," aims at reducing the pollution problem by dealing with it during the manufacturing process itself. There are many ways by which waste minimization can be achieved, and they are discussed in the subsequent sections.

STATE-OF-THE-ART TREATMENT AND RECYCLING TECHNOLOGIES FOR CHROMIUM

Chromic acid containing waste effluents is generally treated by a combination of physicochemical methods (8–12):

- Acidification with sulphuric acid
- Chemical reduction with sulfite sulfur compounds 1 or Fe(II) salts at pH 2.5
- Sludge separation and disposal
- Neutralization with sodium hydroxide solution or milk of lime (precipitation of metal hydroxides)
- Bath maintenance: ion-exchange, ion-transfer and membrane electrolysis
- Recovery of chemicals: evaporation and ion-exchange
- Closed-loop rinsing (final or flow-rinse): ion-exchange

This wastewater treatment procedure is chemical intensive and a considerable amount of sludge is produced that has to be disposed. In addition to the government regulations due to the toxicity of the chromate, this is the reason for the effort to reduce the volume of chromate containing waste effluents. On the other hand, complete wastewater reduction, aiming at zero liquid waste on-site, and consequently, relinquishment of wastewater treatment, doesn't seem feasible for plating companies from practical or economical or from an energetic standpoint (13, 14). However, it can be favorable by sodium sulfite (Na_2SO_3), sodium hydrogen sulfite as solution (sodium bisulfite, $NaHSO_3$), sodium disulfite (sodium metabisulfite, $Na_2S_2O_5$), sodium dithionite ($Na_2S_2O_4$), and sulfur dioxide (SO_2).

A study performed in 1994 concerning 318 plating companies in the United States (15) showed that the above technologies are not very widespread and physico-chemical treatment was preferred. However, Baral and Engelken reported in 2002 that in the United States "a number of metal finishing industries, mainly large businesses, have adopted 'greening' as the principal philosophy of business management." The authors stated that "greening is occurring slowly because of lack of personnel and capital resources, awareness, and technical competence, as well as organizational resistance, high costs of production, uncertainty about future regulatory activity, and substantial marketplace constraints." From technical point of view, some of the following characteristics might have prevented the common use of these technologies in chromium plating industry: From a process design point of view, the *three-compartment* electro-electro dialysis (EED) technology might be better for the plating industry because it can manage three different tasks simultaneously (16):

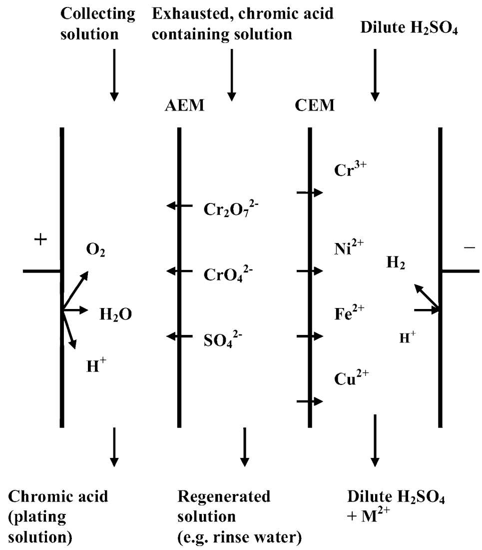


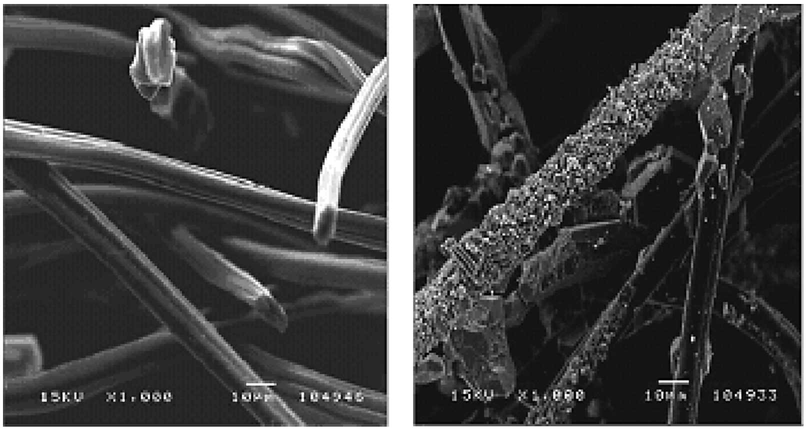
Figure 1: Principles of three compartment electro-electro dialysis for chromium recovery.

(i) removal of contaminants, (ii) chromic acid recovery, and (iii) purification of static rinse water, as shown in Figure 1.

Dalla Costa et al. (16) compared a two- and three-compartment configuration at laboratory scale and found maximum process efficiency in the three-compartment system in the absence of sulfate ions. A publication and patent of Bergman and Lourtchouk (17, 18) described a three-compartment cell for chromic acid recovery at bench-scale. The authors studied various electrode materials and compared a two- and three-compartment system using exhausted plating solution in the central compartment. They reported process limitations due to high voltage increase and current efficiencies between 12% (chromating solution) and 20% (hard chromium plating solution). Shuster et al. and Kidon et al. (19, 20) also patented a three-compartment system; however, they used a porous diaphragm to separate the anode compartment.

Three-compartment EED seems better to meet the demands of the plating industry for successful and simple chromic acid recovery. However, up to now this technology was not yet industrially applied and the literature in this field shows that the main reasons are poor anion-exchange membrane stability and process limitations by high voltage drop.

Existing publications do not prove either long-term stability of commercially anionic exchange membrane (AEM) and membrane modules or propose solutions to overcome the process limitations. This thesis aims to evaluate suitable anion-exchange membranes regarding their stability, long-term performance, and optimum process conditions and possible implementation of this technology in the industry. Besides, alternative solutions for waste minimization in chromium plating industry are evaluated. The electrochemical



(a) (b)

Figure 2: (a) SEM pictures of the carbon unused felt. (b) SEM pictures of the copper deposited on the carbon fibers.

reduction of chromate on carbon felt is an alternative method to the chemical chromate reduction and could help to reduce the amount of treatment chemicals used and the sludge produced. The combination of membranes and evaporation could be an efficient way to downsize the cost- and energy-intensive evaporation equipment. A combination of different membrane processes is studied for efficient reduction of the wastewater volume before evaporation.

SEM pictures of the carbon felt were shown in Figure 2a and Figure 2b (15). Figure 2a shows an unused felt and Figure 2b shows a sample of the electrode used for 120 hours of operation in which the copper deposit on the fibers is obvious. The copper mainly deposits in the region near the entrance and the outlet of the electrode, in agreement with previous studies (21). The author observed that apparent current efficiencies were higher than 100%. This indicates that current-free reduction of Cr(VI) must occur by alternative reductants. In order to investigate this, it was placed two felt samples (one fresh and one used in process for 120 hours) in synthetic hexavalent chromium solution (50 ml, 16 ppm Cr(VI) prepared from chromic acid anhydride) for 50 hours, under stirring. From the Table 1 (15) observed that no hexavalent chromium was reduced with the unused felt, but the chromate was reduced almost completely with the felt having the copper deposit. This clearly shows that copper can additionally reduce the chromate.

Table 1: Current free reduction of Cr(VI) at carbon felt GFA 10 (process conditions: 50 ml of 16 ppm Cr(VI) solution).

Description	**Cr(VI) reduction**
Carbon felt unused	0
Carbon felt used in process solution for 120 hours	99%

WASTE MINIMIZATION

Waste minimization is defined as the continuous application of a systematic approach to reducing the generation of waste at the source. It entails source reduction and on-site recycling. Source reduction is achieved through changing or improving the existing processes and by introducing more efficient process control. Recycling involves the re-use or recycling of waste for the same process or another purpose.

The benefits of implementing WM include improved process efficiency; savings in manufacturing, landfill disposal, and treatment costs, as well as a reduction in the liability for environmental problems. Waste minimization does not necessarily imply a cost for the company, because the majority of WM options involve simple tasks like repairing leaks, ensuring that all taps are closed when not in use, and avoiding spillage. It is necessary to take into account all pollutant emissions into air, water, and land when implementing waste minimization. It is also important to note that transferring the pollutants from one medium to another does not constitute WM. Generators of hazardous waste can benefit greatly from implementing a waste minimization program but need to acknowledge that it is an ongoing process and therefore requires long-term commitment. The primary goal of WM is the reduction of waste but it also may result in improved production efficiency (22).

A successful WM program requires as follows:

- Commitment and support from management
- Clear objectives
- Accurate waste accounting
- Accurate Cost Accounting
- WM philosophy
- Technology transfer

Waste minimization assessments are key components of a WM program. During the assessment, the plant's process and waste streams are reviewed and assessed. Areas requiring specific attention are identified, and the appropriate WM options are developed. The technical and economic feasibility of those options is evaluated. The most feasible options are then implemented (23).

When a waste minimization program is being set up within a company, a WM team who become responsible for all WM activities for the company usually accompanies it. The number of people in the team will depend on the size of the company. In a small company a single person may be responsible. The establishment of quantifiable goals is important to a WM program. It serves

Table 2: Effluents from the electroplating industry (milligrams per liter, except for pH).

Parameter	Maximum value
pH	7–10
TSS	25
Oil and grease	10
Arsenic	0.1
Cadmium	0.1
Chromium (hexavalent)	0.1
Chromium (total)	0.5
Copper	0.5
Lead	0.2
Mercury	0.01
Nickel	0.5
Silver	0.5
Zinc	2
Total metals	10
Cyanides (free)	0.2
Fluorides	20
Trichloroethane	0.05
Trichloroethylene	0.05
Phosphorus	5

as a guide for the company and is a good measure of success. Table 2 shows the effluent from the electro-chemical plating industry.

AN INTEGRAL APPROACH TO WASTE MINIMIZATION

Pollution prevention includes a number of heuristic rules. These rules of thumb are typically based on accumulated experience from a large number of similar applications and can provide guidelines for the development of good design or retrofit options. Seven heuristic rules have been proposed (24).

1. Eliminate waste materials at their source wherever possible.
2. Rapid low-cost reduction in waste generation can often be achieved through changing set points or tightening control variations of key variables. Modifications to single equipment items can also yield significant improvements with little capital expenditures.
3. Recycle waste material within the process. If this is not possible, use off-site recycling.
4. If waste byproducts are formed reversibly within a reaction process, they should be recycled to extension.
5. Use the utility with the lowest practical temperature for all heating duties that require utilities.
6. Minimize the total number of main equipment items in the process, especially in areas that handle toxic materials. Also, minimize the total number of pipe work connections to and from equipment items.

7. Due to practical purposes, continuous processes are preferred to others because pollution prevention is generally more costly in batch operations.

These heuristic rules are useful tools and can be applied in each waste minimization program. Their use helps us to achieve the goals of the waste minimization program more easily and more efficiently.

PROCESS WASTE SOURCES

An electroplating process involves the application of thin metal through electro-deposition. In the process, work pieces are loaded in barrels or on racks and are processed in a series of process units. As illustrated in Figure 3, one

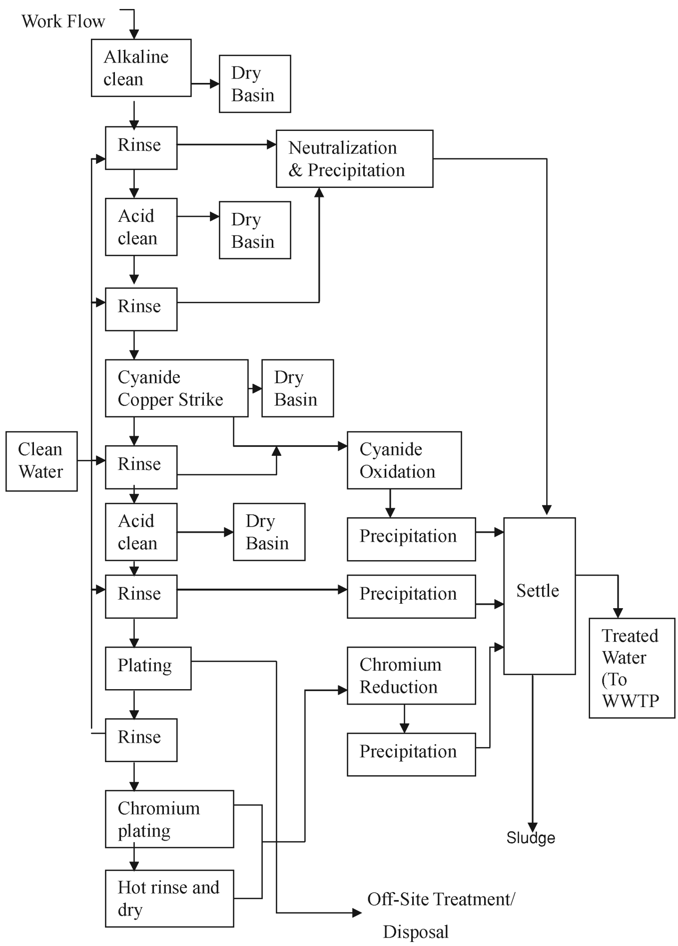


Figure 3: Typical electroplating process with waste treatment facilities.

Table 3: Major process wastes generated in the electroplating industry (25).

Waste category	Waste description	Process origin	Composition
Wastewater	Waste rinse water	Drag-out, equipment cleaning, spills	Same as the compositions in relevant process solutions and solvents
Spent solvent	Spent alkaline cleaning solution	Aqueous cleaning	NaOH, Na_2CO_3, Na_2SiO_3, Na_3PO_4, cyanide, soils, EDTA + Mg/Ca, saponified and/or emulsified grease
	Spent acid cleaning solution	Acid pickling	HCl, H_2SO_4, HNO_3, H_2CrO_4 H_3PO_4, Mg^+, oils, soils
Spent solution	Spent plating solutions	Electroplating	Same as the composition in relevant plating solutions
Treatment residue	Degrease sludge	Solvent recycling	Kerosene, naphtha, toluene, ketones, alcohols, ethers, Halogenated hydrocarbons, oils, soils, water
	Solvent recycle still bottoms	Solvent recycling	Same as above solvents. May contain HCl from solvent decomposition
	Filter sludge	Electroplating	Silica, silicides, carbides, ash, plating bath constituents
	Wastewater treatment sludge	Waste treatment	Metal hydroxide, sulfides carbonates
	Vent scrubber waste	Vent scrubbing	Similar to process solution composition
	Ion exchange Resin reagents	Demineralization of process water	Brine, HCl, NaOH

follows each process bath or two rinse units for removing the residual process solutions from the surfaces of work pieces. Thus, cross-contamination and plating quality can be improved. The plated work pieces are finally air-dried. Waste streams generated from the process can be classified into four categories: wastewater, spent solvents, spent process solutions, and sludge. Table 3 indicates the waste generated from electroplating industry (25). A major portion of the wastewater comes from the rinsing steps. Wastewater also comes from leakages, spillage, cleaning, and dumping process solutions. A plant may generate 80 to 200 m^3 of wastewater per day, which contains heavy metals, cyanide, oil, and many chemical compounds (4). Various solvents, such as soak cleaners, electro-cleaners, and acid cleaners, are widely used to remove oil, grease, soil, and other extraneous substances from metal surfaces. Thus, large quantities of spent solvents are generated. All process bath solutions have to be dumped after exceeding their useful lives due to contaminants in the baths. The contaminants contain a large quantity of metals, and some compounds are difficult to handle. The solutions can be bled into on-site waste-treatment facilities for pretreatment and recovery; otherwise, they can be encapsulated for off-site treatment and disposal. Treatment residues always occur in the form of sludge, such as degreaser sludge, filter sludge, and wastewater treatment sludge. The sludge contains more than 65% of water on average, which can be largely reduced through waste segregation, water de-ionization, and sludge dewatering.

PRACTICING SOURCE REDUCTION APPROACHES

Changes in Process

- Replace cadmium with high-quality, corrosion-resistant zinc plating. Use cyanide-free systems for zinc plating where appropriate. Where cadmium plating is necessary, use bright chloride, high-alkaline baths, or other alternatives. Note, however, that use of some alternatives to cyanide may lead to the release of heavy metals and cause problems in wastewater treatment.
- Use trivalent chrome instead of hexavalent chrome; acceptance of the change in finish needs to be promoted.
- Give preference to water-based surface-cleaning agents, where feasible, instead of organic cleaning agents, some of which are considered toxic. Regenerate acids and other process ingredients whenever feasible.

Source reduction in a plating plant can be realized through drag-out minimization, bath life extension, rinse water reduction, cyanide-free solution utilization, plating metal alternation, and process operational improvements (26). In evaluating these approaches, WM efficiency, cost, and productivity are the main concerns. When a barrel of parts is withdrawn from a process unit, the parts always retain some process solutions, which are called "drag-out." Usually, the drag-out can be minimized by (i) reducing the speed of withdrawal and allowing sufficient drainage time, (ii) lowering the concentrations of the process baths, (iii) using surfactants, (iv) increasing the solution temperature, (v) installing drain boards between process tanks, (vi) enlarging hole sizes on barrels, and (vii) rotating barrels above the tank or placing the work pieces in an appropriate position. Note that all these measures must be appropriately adopted: otherwise, the production rate and plating quality will be negatively affected. For instance, a long drainage time and a low bath concentration are desired for WM, but these may be detrimental to the production rate and plating quality. Keeping process bath solutions from contamination can extend the life of a bath. This requires the continuous improvement of rinse efficiency. Industrial practice suggests de-ionizing made-up water, to regenerate plating solutions by removing impurities, and to apply mechanical agitation. A properly maintained plating bath can be used for as long as 15 years without dumping, thereby greatly reducing the chemical cost and sludge volume. The quantity of sludge is usually proportional to the metal concentration in the spent rinse water. An empirical formula for estimating the sludge volume, Vs (1/1 wastewater), is as follows (27):

$$\mathrm{Vs} = 3.85 \times 10^{-4}\ \mathrm{Chm} + 5.8 \times 10^{-2} \rightarrow \qquad (1)$$

where Chm is the concentration of heavy metals in the sludge (mg/1). Here, wastewater is treated after one hour of settling (lime neutralization). Therefore, the reduction of rinse water consumption is always the first step toward sludge reduction. To do so, the design of a rinse system should be evaluated. Moreover, it is always suggested to install an automatic flow control system and to have agitation systems in all rinse tanks. Cyanide, a poisonous substance, exists in water as HCN, which is a very weak acid. Volatile HCN is highly toxic. It is highly desirable, therefore, to replace a cyanide-containing solution with a non-cyanide solution. A cyanide-zinc solution, for example, can be replaced with a non-chelated alkaline zinc solution (3). Non-cyanide cadmium baths are now available to replace a cyanide cadmium bath (28). It is possible in some instances, however, to replace cyanide cadmium plating with other materials, such as zinc, titanium dioxide (using vapor deposition), and aluminum. None of these coatings has exactly the same properties as cadmium. Hence, the replacement should be judged based on quality requirements and economic and environmental criteria. Source reduction can also be significantly enhanced by operational improvement. System optimization can always lead to the improvement of a plating operation and to the avoidance of excessive waste generation. Moreover, effective fluid control can prevent excessive rinse water consumption and hinder oil and solid build-up in the tanks. A simple waste management program can reduce unnecessary chemical losses and prevent accidental spills. Usually, the improvement of waste management is cheaper than many other methods of source reduction.

REDUCTION IN DRAG-OUT AND WASTAGE

In the electroplating industry, drag-out refers to the solution remaining on products, racks, and barrels as the products, and these suspension systems are moved from various process baths and water rinsing operations. This solution (drag-out) can flow back into the process tank, can be rinsed off, and does evaporate (29). The residual drag-out on products will show up in the next tank as drag-in. An electroplating operation is generally intolerant of the contamination of drag-out from a previous process. Thus, the general practice is to perform rinsing between processes. Because used rinse water is usually a major waste stream from electroplating facilities, it is environmentally and economically desirable to minimize rinse water. Drag out reduction will reduce the need for treatment and disposal or recovery of rinse water. A successful approach to this is to minimize the amount of drag-out remaining on the products they are removed from a process tank.

The total drag-out remaining on the product is the major factor in determining the amount of rinse water needed. If drag-out can be reduced, then the total rinse water can be reduced.

The drag-out quantity can be reduced by applying the following procedures:

1. Minimize drag-out through effective draining of bath solutions from the plated part, by, for example, making drain holes in bucket-type pieces, if necessary.
2. Allow dripping time of at least 10 to 20 seconds before rinsing.
3. Use fog spraying of parts while dripping.
4. Maintain the density, viscosity, and temperature of the baths to minimize dragout.
5. Place recovery tanks before the rinse tanks (also yielding makeup for the process tanks).
6. Monitor chemical use in plating baths and effluent treatment.
7. Increase drip time to reduce drag–out.
8. Reuse rinse water from spray rinse.
9. Improve drainage system to reduce spillages on floor.
10. Immerse heaters in baths to ensure proper heating.
11. Insulate tanks.
12. Cover hot tanks to reduce evaporation.
13. Eliminate the use of Cd plating.
14. Educate employees in waste minimization.
15. Investigate alternative arrangements of pieces on jigs to improve drainage.
16. Introduce drip trays between tanks.

17. Replace leaking tanks in barrel line.
18. Install drag out and use to top up plating bath.
19. Correct process flow in cadmium line.
20. Investigate use of counter flow rinsing.
21. Replace the use of compressed air for tank agitation.
22. Investigate the use of cyanide-free zinc.
23. Upgrade cooling water system implemented.
24. Build a roof over the front yard to protect finished articles.
25. Install new water reticulation system.
26. Upgrade floor and bund tanks.
27. Use a drag-in, drag-out system.

WASTE MINIMIZATION METHODOLOGIES

Past experiences have proven that the following measures have been successful in achieving waste minimization: improved housekeeping, changing process technology, changing product, changing input material, recycling process chemicals, and raw materials, recovering by-product/waste and reducing input to the process. The appropriate technology depends on the type of industry and its size and location.

PROCESS MODIFICATIONS

Raw Materials

Feed quality is very important in waste minimization. Working with suppliers to improve feed quality reduces waste dramatically. Even small impurities can lead to giant amounts of waste. For example, a specific feed impurity may speed up catalysts degradation, which in turn produces waste that must be separated from final products. Even if these impurities are not a compromise of your quality and are left in the product, it may increase the waste in your customer's process. Raw materials can also be evaluated for reduction or elimination.

Reactors

The transition from laboratory to industrial scale can sometimes see a drastic change in product yield if proper mixing is not employed. By using static mixers before the reactor, byproduct yield can be minimized. Constant

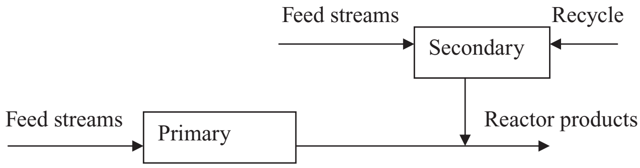


Figure 4: Reactors for different optimum conditions.

searching for better catalyst materials can also help a reactor operate at peak efficiency. Consider a separate, smaller reactor for recycle streams. Optimum conditions for recycle streams can vary from those used for fresh feeds. Figure 4 depicts a separate reactor with different optimum conditions.

Improved Housekeeping

The following steps in housekeeping can lead to significant waste minimization: (1) improve monitoring and operations of all phases of the production process, (2) schedule process in view of equipment cleaning, and (3) improve management of raw material and products inventory. Apart from that, reduction in raw material and product loss and provision of training to the employees can be effective means to improve housekeeping.

Changing Process Technology

This is an important technique for reducing waste volume and strength. Some examples are: (1) alteration in washing/cleaning procedure such as using counter current washing, recycling of used solvent, and reducing the cleaning frequency; (2) employing new methods in production line cleaning; (3) changing waste transport method; and (4) introducing biological degreasing in metal parts cleaning.

Changing Product

Changing products that can serve the purpose of those, which they substitute, can bring waste minimization as in the cases of batteries (non-rechargeable to rechargeable), spray cans (volatile chemicals to water soluble formulations), and refrigerators (chloro-fluorocarbons to ammonia or environmentally safe materials).

MANAGEMENT OF PROCESS SOLUTIONS

Table 4 shows the waste minimization options for metal plating operations. The following are some of the management process solutions (30).

- Recycle process baths after concentration and filtration. Spent bath solutions should be sent for recovery and regeneration of plating chemicals, not discharged into wastewater treatment units.

Table 4: Waste minimization options for metal plating operations (30).

Category of waste minimization option	Examples	Applications	Limitations
General waste reduction practices	Improved operating procedures • Dragout reduction • Rinsewater use reduction • Air emissions reduction	Applicable to all conventional plating operations • Should be considered standard operating practice • Cost benefit typically outweighs any necessary expenditures	Existing facilities might not be able to accommodate changes because of process configuration and/or space constraints
Alternative processes	Thermal spray coatings: • Combustions torch • Electric arc • Plasma sprays Vapor deposition: • Ion plating • Ion implantation • Sputtering and sputter ion deposition • Laser surface alloying Chemical vapor deposition	• Primarily repair operations although they are now being incorporated into original manufacturing • Primarily high-technology applications that can bear extra costs • Expected to improve product quality and durability	• Technologies in varying states of development; commercial availability might be limited in certain cases • Expense often limits applications to expensive parts (e.g., aerospace, military, and electronics) • Might require improved process controls, employee training, and automation
Process substitution	Product changes Input changes that eliminate toxic materials including: • Cyanide • Cadmium • Chromium	Applicable to most conventional plating operations Captive shops/manufacturers might be able to explore product changes	Job shops have little control over input decisions Product changes might need to be evaluated in terms of customer preference Product specifications might eliminate consideration of some process substitutes

(Continued on next page)

Table 4: *(Continued)*

Category of waste minimization option	Examples	Applications	Limitations
Process solution maintenance	Conventional maintenance methods Advanced maintenance methods: Micro-filtration Ion exchange Acid sorption Ion transfer Membrane electrolysis Process monitoring and control	Conventional methods applicable to all plating operations	Advanced methods might require significant changes in process design, operation, and chemistry Application limited for some plating process/technology combinations (e.g., micro-filtration should not be used for copper or aluminum)
Chemical recovery technologies	• Evaporation • Ion exchange • Electro-winning • Electro-dialysis • Reverse osmosis	Requires significant engineering, planning, and characterization of process chemistry	Costs are highly variable for advances methods
Off-site metals recovery	• Filtration • Ion exchange • Electro-winning • Electro-dialysis • Reverse osmosis	Metal-bearing wastewater treatment sludge Spent solvents	Waste materials must be acceptable to recyclers

- Recycle rinse waters (after filtration).
- Regularly analyze and regenerate process solutions to maximize useful life.
- Clean racks between baths to minimize contamination.
- Cover degreasing baths containing chlorinated solvents when not in operation to reduce losses. Spent solvents should be sent to solvent recyclers and the residue from solvent recovery properly managed (e.g., blended with fuel and burned in a combustion unit with proper controls for toxic metals).

Waste Minimization: Air Emissions

The air emissions are associated with the use of electrolytic baths operated at high temperatures with the application of an electric direct current. These operating conditions result in the release of caustic emissions, acid emissions, and chromium mist. In the hard chromium plating bath the release of H_2 and O_2 occurs from the electrochemical reaction. A wet scrubber controls the chromium emissions and recycling the scrubber blow down to the bath in appropriate quantity and concentration.

The metallic, abrasive, and ceramic powder emissions are collected by suction and filtration generating solid wastes. The minimization of the air emissions to be adopted is related to the optimum bath temperature control and the preventive maintenance of the suction and filtration unit or scrubber.

Waste Minimization: Liquids

The main sources of water pollution are: (i) the water-in-oil emulsions used as metal working fluid, which are lost by spilling, drag-out with pieces, and as waste stream; (ii) the exhausted bath solutions discharged periodically when they lose their effectiveness due to the chemical depletion or contamination; and (iii) the rinse water, to clean the drag-out from the pieces after removal from process baths.

The minimization option includes the continuous control of the bath conditions and on-site regeneration of Cr^{3+} oxidation and physico-chemical treatment of the impurities in order to increase the life of the bath. The alternative of the rinse wastewater minimization is the optimization of the rinsing stage by installation of flow meters, determination of the minimum required rinse water quantities for each piece, and improvement of rinsing efficiency by application of spray rinsing however an on-site physicochemical treatment.

Waste Minimization: Solids

The solid wastes are classified as non-hazardous wastes, and their management is the land-filling with municipal wastes. The minimization alternatives are based on the optimization of the usefulness raw materials, on-site reuse, and separate collection to off-site reuse. The ceramic and metallic sludge from rectification may be hazardous due to the emulsion content a loss of emulsion with metal particles can be reduced by the optimization of fluid dosage rate and spray direction and coverage of the metal piece. The wastes are wiping cloths, plastic, and varnish contaminated with cleaning agents and chromium; for this reason they are classified as hazardous wastes and minimization is focused to the cleaning of the chemicals before off-site management. The bottom bath sludge is hazardous due to the high concentrations in Cr^{3+} , Cr^{6+} , Fe^{3+} , SO_4^{2-} , and metallic impurities (31). Following these techniques, the minimization of sludge amounts and the increase of the baths service lifetime can be reached.

ENVIRONMENTAL BENEFITS

Environmental benefits could be gained if metal finishers, and those who work with metal finishers could access new information on a tool to improve environmental performance (32).

The five environmental costs of greatest significance to electroplating facilities are wastewater treatment (and its many individual cost components), hazardous waste disposal, sewerage, plating chemistry loss, and other process solution loss. The major cost categories analyzed are:

1. Materials: Plating materials, addition agents, water, solvent/other cleaners, acids, fillers, miscellaneous chemicals
2. Waste management: Wastewater treatment, storage, handling/disposal, insurance
3. Utilities: Energy (electricity), energy (steam/natural gas), sewerage, process air
4. Direct labor
5. Indirect labor
6. Regulatory compliance: Substance driven costs, regulatory response driven costs
7. Incremental revenues

The implementation of these waste minimization options has led to a number of environmental benefits (33). These include:

- Elimination of cyanide
- 10 to 15% reduction in metals to drain
- 10 to 15% reduction in chemicals to drain and reduced water consumption

ECONOMICAL EVALUATION

The saving of costs would be obtained by lower costs for the bath chemical and water and by lower costs for wastewater treatment and sludge disposal. Due to rather high variation in chromium plating operation (e.g., quantity of drag out, number of baths and rinses, management of waste effluents) savings of costs should be separately determined for each plating company. However, here we estimated the operation costs of this new technology involving the cost for electrolysis, pumping, consumption of H_2SO_4, membrane replacement, and personnel (maintenance).

WASTE MINIMIZATION STRATEGY

A WM strategy is formulated taking into consideration of the following aspects:

1. Baseline data generation
2. Analysis of all parameters of process operation
3. Identification of waste generation areas
4. Material balance preparation
5. Cost estimation
6. Formulation and application of waste minimization measures
7. Monitoring and analysis

In Waste Minimization Assessment (WMA) meetings, waste minimization measures were usually formulated under two broad categories:

1. Supportive services
   Good house keeping; Use of instruments for carrying out measurements; Training of manpower; Exchange of views and information; Promotion of scientific and technological temperament; Proper inventory management, etc.
2. Technological Services
   It is focused to help hazardous and solid waste generators to reduce environmental health risks by eliminating and reducing hazardous waste generation and releases by adopting suitable technologies for processing. It suggests incorporating environmental considerations into the design and redesign of products, processes, and technical and management systems to the electroplaters.

GUIDANCE ON WM OPTIONS AND TECHNICAL SOLUTIONS FOR IMPROVING PROCESS OPERATIONS

Various WM measures have been adopted such as establishing a proper measuring system, inventory maintenance, use of hangers, and tools to avoid spillage, covering of acid tub, fixing of a corrosion resistance tray, adopting a monitoring methodology to assess the quality and quantity of electroplated components, use of impurity filtration device, use of gloves and masks by workers, lime treatment for spent acid, and installing proper drainage system. Further washing operations are improved and a flow meter installed to assess the exact quantity of water consumed. The spent water is reused in subsequent washing. A proper drainage system is followed to avoid water logging and stagnation. Regarding cleaning components using kerosene, a suitable filter is used to separate rust and a big rectangular tub is used to avoid oil spillage.

As advised, good quality of salt is bought from a reputed manufacturer. The preparation of salt solution is done as per standardized norms to prepare nickel and chrome plating baths by using good quality water (distilled water). The wash tank is placed adjacent to nickel and chrome vat, and overhead hangers are used to avoid spillage. The nickel vat and chrome vat are covered to avoid evaporation losses and to check mixing of impurities. Reusing dragout reduces further nickel loss. In order to increase work efficiency the workers are advised to use masks, gloves, and shoes. The effluent treatment plant (ETP) is operated regularly and efficiently.

In order to improve efficiency of electrical systems new ones made by reputed manufacturer replace rewound motors. Electricity consumption is also thus being regulated.

WASTE MINIMIZATION AND IN PLANT ABATEMENT TECHNIQUES FOR ELECTROPLATERS

Realizing that end of pipe wastewater treatment is not always within the ability and capacity of the small and tiny sector, Central Pollution Control Board (CPCB) and Pollution Control Boards (PCB'S) are focusing on abatement techniques as a means of eliminating hazardous wastes from the stream by waste management and cleaner production technologies. These methods are well within the capacity of every electroplater and within the ability of every trained worker.

For reduction/removal of heavy metals, precipitation is employed through the addition of lime or caustic. This is done under certain pH conditions when the solubility of metal is minimum. For example, solubility of zinc is minimum when pH is around 10–11. Initially due to acidic rinsing/washing, etc., the pH of raw waste goes down to less than 6 or so. Hence, during treatment for precipitation of zinc into zinc hydroxide, the pH has got to be raised up to 10 or

11. Similar is the case of chromium, its solubility is less when pH is around 7.5–8. The pH has got to be controlled by addition of lime, which is to be added for precipitation. Copper has got minimum solubility at pH 9–10. Chromium is present in its hexavalent form and it is first reduced to trivalent form at pH less than 4 and then precipitated with lime. Sodium meta-bisulphite is used as reducing agent. Thus, it is seen that lime plays a very important role in chemical treatment of waste generated in electroplating units.

Silver, nickel, and copper plating wastes contain cyanide in the form of silver cyanide, nickel cyanide, and copper cyanide. Cyanide limits the removal of metals by precipitation. Hence, cyanide has to be removed first by alkaline chlorination by additions of sodium hypo-chlorite. Thereafter, these metals are removed/reduced by precipitation.

Various companies have performed a description of the waste minimization alternatives, which works in batch mode with big pieces. Minimization options have been suggested and adopted by the various electroplating industries. The process flow sheet of the unit operations and the main emissions are also been studied (34, 35).

CONCLUSIONS

It can be clearly seen that there have been many demonstrative, environmental improvements to the metal finishing industry. The bad image has been cleaned up to a great degree. The attack on cyanide, hexavalent chromium, cadmium, leads, and chlorinated solvents are being reduced by the application of waste minimization techniques.

Other benefits of waste minimization being realized are as follows:

1. Environment friendly industrial system with minimum pollution load.
2. Awareness of good house keeping measures is adopted.
3. Conservation of raw material and energy has been minimized and increases the financial strength of the company.
4. Skilled, trained, and stable labor with a good work spirit has been developed.
5. A reputation for quality products with customer demand is being established.
6. Co-operative and friendly relations among other companies are established.
7. A systematic, disciplined financial management system to keep account records, inventory of raw materials, and processed goods have been developed.

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