WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

M. Sundaravadivel
Graduate School of the Environment, Macquarie University, Sydney, Australia

S. Vigneswaran
Faculty of Engineering, University of Technology Sydney, Australia.

C. Visvanathan
Environmental Engineering Program, Asian Institute of Technology, Bangkok, Thailand

Keywords: Bioaccumulation, Case hardening, Diffusion coating, Drag-out, Electrochemical conversion, Hazardous waste, Metal finishing ,Rinsing

Contents

Summary

Metal finishing operations are carried out by most of the industries engaged in forming and finishing metal products. The wastes from metal finishing industries include cleaning acids, sludge containing toxic heavy metals, solvents and oils, and spent chromate and cyanide solutions, which are classified as hazardous substances. Treatment of hazardous wastes is not only tedious, but also involves huge costs. Alternately, waste minimization approach that involves adoption of technological and management options to reduce or avoid generation of wastes leads to both environmental as well as economic benefits. Introduction of waste minimization practices in metal finishing industries can result in reduction of total quantities of hazardous wastes generated by the industry as a whole. The economic viability of applicable waste minimization techniques depend on factors such as cost of water, cost of disposal, value of materials recovered. Case studies illustrated in this paper clearly establish that in most cases, waste minimization practices, apart from being environment friendly, are economically profitable.

1. Introduction

In the era of industrial growth and economic development, the concept of waste minimization stems from the need to "produce better while polluting less" in order to avoid environmental damages that may affect quality of life in short and medium terms, and threaten the survival of living beings on the planet, in longer terms. The basic goal of waste minimization is to eliminate formation of byproducts which are discarded as wastes and harm the environment. Waste minimization techniques in industrial production processes aim to avoid production inefficiencies, which results in excessive waste generation. Waste minimization assumes more significance when the wastes generated in an industry are "hazardous" in nature, because treatment of hazardous wastes is tedious, as they are not readily amenable to treatment, and involve huge costs. Moreover, improper disposal of hazardous wastes may cause irreparable environmental damages in shorter terms.

Hazardous wastes in an industry can be generated directly as a by-product, and also as a result of treatment of wastes. In case of metal finishing industries, hazardous wastes are generated in both of these ways. Hence, metal finishing industries are regarded as major generators of hazardous wastes in many industrialized nations. Waste minimization in metal finishing industries helps to reduce hazardous waste generation, and hence the cost of treatment and disposal. This article briefly reviews major metal finishing operations and characteristics of waste streams from these operations. While identifying opportunities for waste minimization, proven techniques and their practical implementation in many industries around the world are presented. Two feasibility studies, one on a metal plating unit in Thailand, and another on metal pickling units in India, conducted for assessing pollution minimization potential, are discussed.

2. Metal Finishing Operations

Metal finishing operations are carried out by most of the industries engaged in forming and finishing metallic products. Metal finishing involves alteration of the metal workpiece’s surface properties in order to increase the corrosion or abrasion resistance, alter appearance or to enhance the utility of the manufactured product. Most metal finishing operations have three basic steps, namely:

i. surface cleaning or preparation;
ii. surface treatment, that involves coating a layer of another metal, paint, plastic etc., or changing the surface properties;
iii. rinsing and drying.

Metal finishing operations can be broadly classified into three major categories as follows:

1. Chemical and electrochemical conversions.
2. Diffusion coating techniques.

3. Case-hardening techniques.

Table 1 lists various operations employed for metal finishing under each of these categories

Table 1. Categories of metal finishing operations.

2.1. Chemical and Electrochemical Conversions

Chemical and electrochemical conversions are designed to deposit a coating on a metal surface that performs a corrosion protection and/or decorative function, and in some instances for preparation for painting. These processes include phosphating, chromating, anodising, passivation and metal colouring.

Phosphating treatments provide a coating of insoluble metal phosphate crystals that adhere strongly to the base metal. The main function of the coating, due to its absorptivity, is to act as a base for the adhesion of paints, lacquers and oils to the metal surface. They also provide corrosion resistance to some extent.

Chromating is to minimize rust formation and to guarantee paint adhesion.

Anodising employs electrochemical means to develop a surface oxide film on the work-piece, thereby enhancing its corrosion resistance.

Passivation is a process by which protective coatings are formed through immersion of the work-piece in an acid solution.

2.2. Case-hardening

Case-hardening operations produce a hard surface (case) over a metal core that remains relatively soft. The case is wear resistant and durable, while the core is left soft and ductile. Case hardening methodologies include carburising, carbo-nitriding, nitriding, cyaniding, microcasing and thermal hardening.

The most widely used case hardening operation, **carburising**, involves diffusion of carbon into a steel surface at temperatures of 845° C to 955ºC, producing a hard case in the high carbon areas.

Nitriding processes diffuse nascent nitrogen into a steel surface to produce case hardening. It is normally accomplished through use of either nitrogenous gas (usually ammonia) or a liquid salt bath, typically consisting of 60% to 70% sodium salts (mainly sodium cyanide) and 30% to 40% potassium salts (mainly potassium cyanide).

Carbo-nitriding and **cyaniding** involves the diffusion of both carbon and nitrogen simultaneously into a steel surface.

Thermal hardening methods are those that generate a case through localized heat and quenching, rather than through chemicals. Very rapid heat application results in surface hardening with little heat conducted inward. Since no carbon or nitrogen is diffused into the work-piece, it is the existing carbon content of the ferrous metal that determines the hardness. The heating is accomplished through electromagnetic induction, high temperature flames or high velocity combustion product gases.

2.3. Diffusion Coating

Diffusion coating provides a layer that changes the surface properties of the work-piece to those of the metal being applied (diffused). The work-piece becomes a composite material with properties generally not achievable by either material singly. The coating functions as a durable, corrosion-resistant protective layer, while the core material provides the load-bearing functions. In this process, the coating is achieved through contact or exposing the base metal to the coating metal at elevated temperatures allowing lattice inter-diffusion of the two metals. Alternately, spraying techniques, cladding (application of mechanical techniques), vapour deposition and vacuum coating are also used.

Hot dipping is a diffusion process that involves partial or complete immersion of the work-piece in a molten metal bath. Common coating materials include aluminum, lead, tin, zinc and the combinations of the above. The coating metal in a **cementation diffusion** process is applied in powdered form at high temperature (800° C to 1000° C), in a mixture with inert particles such as alumina or sand and a halide activator. The main applications of **spray diffusion** coatings are for workpieces difficult to coat by other means due to their size and shape, or that damaged by the high temperature heating. **Vapor deposition** and **vacuum coating** produce high quality, pure metallic layers, and can sometimes be used in place of plating processes. A layer of metal cladding can be bonded to the work-piece using high pressure welding or casting techniques.

3. Waste Streams of Metal Finishing Industries

The wastes from metal finishing industries include cleaning acids, sludge containing toxic heavy metals, solvents and oils, and spent chemical (chromate and cyanide) solutions, all classified as hazardous substances. Table 2 presents the origin and composition of hazardous wastes generated during various metal finishing operations.

Table 2. Origin and composition of hazardous wastes in metal finishing industries

The waste stream originates mainly from the discharge of:

- spent acid cleaning (pickling) solutions;
- spent process solutions;
- rinse waters.

Spent cleaning and plating solutions are the main source of hazardous wastes in metal finishing industries. Several types of cleaning solutions are used in chemical and electrochemical conversion processes. Cleaning solutions may be acidic or alkaline, and may contain organics. Spent plating solutions contain high concentrations of metal impurities, when discarded.

Metal finishing processes involve many rinsing steps. When a workpiece is withdrawn from a bath containing chemical solution, excess solution adheres to its surface (referred as drag-out), which if carried into the next bath, contaminates chemical solution in that bath resulting in poor quality of metal finish. In general, water is used to rinse the work-piece before transferring to the next chemical bath. Overflows from rinse tanks constitute the rinse water stream, which contains toxic chemical pollutants.

Wastes produced from spills and leaks also contribute to waste streams in metal finishing operations. Water is used to wash away floor spills, and the resulting wastewater contains all of the contaminants present in the original chemical solution. Wastewater is also generated from wet scrubbing of exhaust air.

4. Environmental Impacts of Metal Finishing Wastes

The waste streams from metal finishing industries consist of heavy metals in large concentrations. Heavy metals are considered hazardous materials. They can be nutritious or toxic to the living systems, depending on their concentrations. Some of these metallic elements are ‘essential’ to life, that is, animals and/or plants cannot live without a minimum supply of them; on the other hand, practically all metals produce undesirable, noxious or even lethal effects when supplemented in too high a concentration to a living system.

4.1. Impacts on Water Bodies

Toxic pollutants such as cyanide, cadmium, mercury, chromium and arsenic from the metal finishing industries are often discharged into lakes and rivers. The metal inputs into lakes and rivers are both in particulate and dissolved forms (complexed and free metal species). Yet, a substantial part of the metal load soon becomes associated with the sediments and suspended particulates. The sediments can release metals when the water body receives acidic precipitation, acid mining drainage or organic complexing agents. Major changes are usually observed in the estuarine mixing zone where the salinity gradient affects the sorption/complexation equilibrium of metals.

They can reach the living biosystem through biological uptake by bacteria and algae. Microbial activities can mobilize metals from sediments by destroying organic matters and forming lower molecular weight compounds with increased complexing capacity and solubility by the change of physical properties of the medium or by concentrating inorganic compounds into organo-metallic forms.

4.2. Impact on Soil

A large part of metals reaching soil surface get strongly bounded to colloidal components. In course of time, either due to decomposition of soil organic matter or due to soil acidification induced through soil internal process or due to acid depositions, appreciable amounts of metals could be mobilized, which could increase the mobile metal concentration. The mobile metal concentrations can be easily measured in soil solution, which can be simulated with the help of neutral salt solution or just deionized water.

The mobile metal concentration could pose a real danger either to growing organisms in the soil (plants, soil microorganisms) or to the ground water. Some of the changes in soil properties such as decrease in pH, change in redox potential, enhanced decomposition of organic matter, losses of fine textured particles from soil, are responsible for the mobilization of metals.

5. Opportunities for Waste Minimization

The five basic waste minimization tactics that industries can explore are:

1. Substituting and reducing raw materials/process chemicals.
2. Improving housekeeping and operating procedures.
3. On-site/in-plant recovery and reuse.
4. Innovative technological improvements.
5. Product change.

Examples of simple and proven practices that have been implemented in many metal finishing industries are discussed for each of these waste minimization tactics.

5.1. Substituting and Reducing Raw Materials/Process Chemicals

There are possibilities to minimize generation of hazardous wastes through substitution of less hazardous chemicals than the ones currently being used.

5.1.1. Non-cyanide Processes

One of the most toxic of wastes produced in metal finishing industries is cyanide. Cyanide is generally used as a solubility enhancing agent because of its chelating properties. Studies have shown that acidic copper sulfate baths or non-chelated alkaline zinc solutions are feasible substitutes to cyanide-based copper plating solutions. Cyanide-based baths have better 'throwing power', a property of the solution to evenly deposit metals over the part to be plated, even during fluctuations in current distribution. However, acid-based baths have better throwing power at micro-scale, and hence fill micro-cavities more effectively. This leads to smoother and brighter finish of the plated part. The disadvantage at macro-scale can be compensated by strategically racking the workpiece within the plating bath to achieve even distribution of current. Further, non-cyanide chemicals require more thoroughly cleaned surfaces to ensure high quality finishing, and hence require high quality degreasing techniques. There are many suppliers who can provide cost-effective, non-cyanide systems.

Substitution of cadmium-based plating solutions with other materials such as zinc, titanium dioxide and aluminum also are feasible. Replacement of highly toxic hexavalent chromium with less-toxic trivalent chromium offers important environmental advantages. Trivalent chromium uses considerably lower concentrations of chromium metal and less toxic air emissions, while hexavalent chromium produces hydrogen bubbles which entrain chromium compound and carry them out of the bath. It has been demonstrated that trivalent chromium can successfully replace hexavalent chromium for decorative chrome applications. However, trivalent chromium is not suitable for hard chrome applications.

Hard chrome plating as such can be replaced by another process in which an alloy of nickel and tungsten can be electrodeposited with fine particles of silicon carbide dispersed throughout the deposit. The alloy performs better in abrasive wear applications than chromium. The chemistry is patented in Japan in 1990, and is currently under consideration by several large manufacturing companies.

5.1.2. Pretreatment and Process Monitoring

The use of mechanical scrapping/scrubbing techniques to clean and prepare the metal prior to cleaning with chemical solutions can extend the life of bath solutions, and hence reduction in chemical requirement. Chemical requirements can also be reduced through regular monitoring of chemical concentrations. Baths should be maintained at minimum chemical concentrations to achieve necessary product quality. By experimenting and lowering levels to just above the concentrations when defects start to occur, chemical requirements can be reduced. A decrease in concentration of metal salts and other components of the plating solution directly reduces the amount of hazardous substances dragged out of the bath. Many concentration reductions have been successfully implemented. Notably, it has been found that acceptable chromium plate can be obtained from baths containing only 25 to 50 g/L of CrO_3 compared to the traditional concentration of 250 g/L. Reduction in chemicals leads to savings in terms of cost of raw materials as well as the costs associated with disposal or treatment.

5.1.3. A Case Study of Substitution of Less Toxic Chemicals

In an electrical light fixture manufacturing company in Sweden, components were fabricated from aluminum or steel sheets and coated with solvent-based paints. Thus, 200 tons of volatile organic compounds (VOCs) from solvents were generated annually with incompletely quantified amounts of hazardous paint residues. Based on a waste audit, by simply changing the use of solvent-based paints with powder paints, the company achieved major cost savings, in terms of manufacturing costs, energy (fuel) costs, and waste management costs. This is apart from elimination of health hazards to the operators who were otherwise exposed to organic solvent vapors from the paints. Table 3 compares various costs for the company before and after the change to waste minimization procedures.

Table 3. Annual painting costs before and after waste minimization

The net saving per annum, thus, was 2 504 000 SEK. The payback period for the investment made in new power paint equipment (2 300 000 SEK) was less than one year.

5.2. Improving Housekeeping and Operating Procedures

Changes in housekeeping and maintenance practices can be made rapidly with little capital investments.

Successfully implemented, these changes can increase production rates, improve product quality and improve workplace safety, apart from reduced generation of wastes. Reduced generation of waste can yield significant savings in raw material usage and waste treatment

5.2.1. Reducing drag-out

Reducing drag-out from plating baths saves bath replacement costs and reduces waste disposal costs. This can be achieved simply by following simple operation procedures. Strategies to reduce drag-out include:

- increasing drainage time;
- changing the hanging orientation on racks;
- providing ‘drag-out’ bath;
- fog sprays and air-knives;
- use of chemical agents.

The faster the workpiece is removed from the bath, the higher the drag-out will be. By reducing the speed of withdrawal of workpiece from the bath solution, the drag-out can be easily reduced. Allowing ample time to drain the solution adhered to the surface of the workpiece, especially for higher viscosity solutions, will also reduce drag-out. Usually, 30 s allows most of the drag-out to drain back to the bath. A study in America showed that a drain time of at least 10 s has been demonstrated to reduce drag-out by more than 40%, compared to the three-second average by industries.

Proper positioning of the workpiece also plays a part in reducing the drag-out. The following guidelines were found to be effective in this regard:

- orientation of surface as close to vertical as possible;
- rack with lower longer dimension of the work-piece in horizontal;
- rack with lower edge tilted slightly from the horizontal so that the run-off is from a corner rather than an entire edge.

By providing a static ‘drag-out’ bath with no running water after the plating tank for most heated plating solutions, the drag-out can be allowed to build-up in concentrations, and used to replenish the process bath, in place of fresh water.

Fog-sprays and air-knives operate by forcing some of the drag-out on work-piece back into the bath. Fog sprays provide fine water-mist to rinse the piece and return chemicals to the bath. Air knives operate in a similar way but use compressed air rather than water.

Use of wetting agents and surfactants to lower the surface tension of plating solutions can also reduce drag-out. A solution with high surface tension is retained in the crevices and surface imperfections of the workpiece upon removal from the plating bath. Only non-ionic wetting agents, which will not degrade by electrolysis in the plating bath, should be employed. The use of surfactants is sometimes limited due to their adverse effect on the quality of the plate produced.

Increased temperature lowers both the viscosity and surface tension of the bath solution, thus reducing drag-out. The resulting higher evaporation rate may also inhibit the carbon dioxide absorption rate, slowing down carbonate formation in cyanide solution. However, this technique has disadvantages such as formation of carbonate by the breakdown of cyanide at elevated temperature, higher energy costs, need for air pollution control due to higher evaporation rate, etc.

Drag-outs can be captured by use of drain boards, drip bars and drip tanks and then can be returned to the bath. These simple devices can save chemicals, reduce rinse requirements and prevent unnecessary floor washing.

5.2.2. Modifying Rinsing Method

Rinsing is done to remove residual drag-out from the parts of the workpiece and the racks. Rinse water must be sufficiently clean to reduce the concentration of these chemicals in a reasonable period of time. Most platers and surface finishers employ continuously flowing single-tank rinses to wash the drag-out. Through modification of the rinsing methods, generation of rinse water can be reduced. Also, such modifications will also lead to reuse of rinse water as make-up for evaporative losses in plating tanks and increase in efficiencies of metal recovery, by using concentration processes such as evaporation, ion-exchange and reverse osmosis.

Possible modifications of rinsing are:

1. **Counter-current rinsing.** Counter-current rinsing is one of the efficient ways of achieving waste reduction and water conservation. In counter current rinsing, the work-piece is rinsed in several tanks in series. Water flows counter to the movement of the work-piece so that clean water enters the last rinse tank from where the clean product is removed. The overflow from one tank becomes the feed for the rinsing tank preceding it. Thus, the concentration of dissolved salts decreases rapidly from the first to the last tank. Wastewater is discharged from the first tank, which intially receives the contaminated product needing to be rinsed. The rinse water flow requirement in counter-current rinsing method is drastically reduced. The reduction is of the order of 95% when compared to the conventional method of single tank rinsing and over 50% when compared to series rinsing.
2. **Spray rinsing.** Automated control of spray rinsing through nozzles has become popular for application in rinsing operations. It is well suited for flat sheets, particularly for work with holes in it. Spray rinsing is considered the most efficient way of various rinsing techniques. The impact of spray also provides an effective mechanism for removing drag-out from recessess with a large width to depth ration. Spray rinsing method reduces the water usage by 20% as compared to conventional methods. Spray rinsing is ineffective for rinsing workpieces with recesses and inaccessible surfaces. In addition, they cannot be used for small racked parts that could cause rinse water from adequately reaching the parts.
3. **Static or still or reclaim rinse.** This method of rinsing is particularly applicable for initial rinsing after metal plating. The dead rinse allows for easier recovery of the metal and lower water

usage. The rinse water often be transferred to the plating tank that precedes it. The dead rinse is followed by spray or other rinses.

4. **Combination rinsing.** In many metal finishing industries, where multiple lines are employed to carry out a variety of operations, there exists a possibility for a variety of creative rinsing combinations that can take advantage of specific process characteristics and requirements to reduce water use and minimize heavy metal pollutants in waste streams.
5. **Flow control.** Water flow control valves can be used to reduce wastewater flows to a minimum. They can usually be set to regulate the feed rate of fresh water despite variations in line pressure. The conductivity controller is the commonly used device for the control of flow during plating operations. The system has the advantage of overcoming the usual open valve practice in the plating operation, regardless of whether water is needed or not. Rinse water usage can be reduced up to 15%, when such systems are installed.

Table 4 presents theoretical rinse water flows required to maintain a 1000 to 1 concentration reduction for the most frequently used rinsing methods.

Table 4. Theoretical rinse water requirements to maintain 1000 to 1 concentration

5.2.3. Modifying Process Operations and Controls

The following modifications to plating operations and controls have been recommended to reduce hazardous waste generation:

- Use of level controls and alarms to eliminate accidental tank overfills.
- Automated process lines, where practical, to provide consistent and improved control of drag-in and drag-out and to improve the effectiveness of rinsing .
- Enclosed process lines to minimize airborne contaminants in process solution tanks and rinse tanks.
- Automated chemical monitoring and replenishment systems to significantly extend process bath life and minimize wastes. For example, electroless nickel baths have a limited life span because when they consume solution components they are self-contaminating. Automatic monitoring and chemical replenishment systems can significantly extend the life of these baths.
- Installing mist eliminators to capture and return mist lost from plating solution.

5.3. On-site/In-plant Recovery for Recycle and Reuse

Chemicals and other raw materials that join the waste streams can be recovered within the industry premises for recycle/reuse in the metal finishing process. Chemicals in rinse water can be recovered by collecting and concentrating the rinse water. Evaporation, ion exchange, reverse osmosis, ultrafiltration and electrodialysis processes have been used to concentrate chemicals from rinse water for recovery of chemicals. These processes reconcentrate plating solutions from rinse water, sometimes also producing relatively pure water that can be recycled for rinsing purposes.

The high energy consumption in evaporation process for recovery makes it cost-effective only in concentrating rinse waters that are to be returned to hot baths, such as those used in chromium plating, where high evaporation rates reduce the concentration required. Ion-exchange systems are suitable for chemical recovery applications where the rinse water is relatively dilute and where a relatively low degree of concentration is required for recycling the concentrate. Recovery of plating chemicals from acid-copper, acid-zinc, nickel, tin, cobalt, and chromium plating baths using ion exchange process have been commercially demonstrated. Reverse osmosis process is more suitable for low-volume processes. The most popular process in the metal finishing industry that is utilizing the reverse osmosis process for recovery of chemicals is nickel plating. Used cutting oil from metal workshops can be recovered through ultrafiltration for reuse. Apart from saving material cost, elimination of incineration for disposal of waste oils and associated pollution problems are the advantages of such material recovery process. Electrodialysis (ED) is a process, which uses a stack of closely spaced ion-selective membranes through which ionic materials are selectively transferred or rejected. In a plating operation, ED is typically applied to a rinse tank to separate dissolved metal and associated anions from the rinse water. Typical applications are on drag-out tanks after plating tanks for gold, silver, nickel and acid tin plating.

5.3.1. A Case Study of Raw Material Recovery

A car industry in Europe paints 70 cars in an hour (250 000 cars/year) using electrophoretic (cathodic) painting process. The total surface area painted is 4500–m^2/hr (65 m^2/car). A good rinsing after painting requires one liter of water for every square meter of surface area painted. Around 25–45% of paint consumed goes into the wastewater stream. Feasibility studies indicated that paint in wastewater can be completely recovered using ultrafiltration process. The permeating water in this process can be reused to effect water economy. The cost details of implementation of this recovery scheme were as follows:

- Capital cost of the ultrafiltration system: US$450 000.
- Operation cost (energy costs): US$25 920.
- Maintenance cost (membrane change once in three years): US$23 000/yr.
- Cost savings through recovery of paint: US$1 552 500/yr.
- Cost savings through water recovery: US$135 000/yr.

The capital cost of the ultrafiltration system has been recovered within 4 months of operation. This also has generated profit amounting to US$1.4 million/year.

5.4. Innovative technological improvements

Technological improvements aiming to achieve minimization of waste generation can be implemented through changing or developing innovative process technologies and equipment/machinery. Changing process technology is an important technique for reducing wastes in quantity and/or strength. Changes in

Minor changes to the product can greatly increase operational efficiencies leading to lesser generation of wastes. An example can be cited in the area of drag-out reduction in metal finishing industries. Drilling holes in a workpiece can eliminate pockets where solution can collect without changing its structural integrity. This can also significantly reduce draining time. Racking holes can be added and positioned to promote drainage and to protect critical metals.

Folded or lapped spot-welded seams form thin recesses that draw substantial volumes of liquid into them due to capillary forces. When exposed to heat, which expands the liquid and air volumes, or to harsh chemicals, this residual liquid bleeds out contaminating metal parts and baths. Possible solutions to this problem include:

- Elimination of lapped seams wherever possible.
- Using butt welds or reducing the number of pieces in an assembly.
- Minimizing lapped seam area by reducing its length or width.
- Minimizing the number of spot welds and creating a dimple to minimize the area of tight clearance.

6. Profitability of Process Modifications—a Feasibility Study in Bangkok, Thailand

Traditionally, the electroplating industry is the major source of heavy metal pollution in Bangkok. According to official estimation, these industries generate approximately 500 m^3 per day of toxic effluents. While 50% of such wastewater originates from medium or large scale units, whose effluents are treated, small-scale units account for the remaining quantity, which is usually discharged directly into a nearby water course. A feasibility study was conducted to set up a demonstration project on revealing the profitability of waste minimization in small-scale electroplating units in Bangkok. A family-owned plating shop located in North Bangkok was selected for the study. The shop has 10 workers, working 8hrs a day within an area of 4m x 15m and carry out two conventional types of non-cyanide based chrome plating process.

1. Dull Ni → Bright Cu → Bright Ni → Cr
   (for parts requiring more thickness such as car bumpers)
2. Bright Ni → Cr

This shop serves different kinds of clients to plate their materials and spare parts. Most of the metal parts being electroplated are heater stands, car bumpers, exercising machine parts, motorcycle spare parts and furniture parts.

An analysis of wastewater from the shop showed a wide fluctuation in quantity and quality. In general, equipment also lead to reductions in the strength (concentration of pollutants) of waste streams.

In metal finishing industries, metal parts are cleaned by chemical degreasing agents. An innovative biological degreasing system has been developed in Sweden that avoided the use of chemicals and generation of hazardous chemical wastes.

Although waste can be minimized, they cannot be totally eliminated. Through adoption of appropriate end-of-pipe treatment technologies, waste treatment can be made effective in a manner that it will not result in hazardous wastes. A major problem of metal finishing industries, where the treatment of spent plating and rinse solutions results in the production of hazardous metal hydroxide sludge, is their disposal in both an economically and environmentally sustainable manner. Most of the heavy metals in electroplating wastewater are ultimately removed by precipitation using caustic (NaOH), after destroying chelating agents such as cyanides or ammonia through oxidation. Complexes involving these ions can be removed by adsorption to magnesium hydroxide. Magnesium hydroxide also precipitates heavy metals as hydroxide salts. Several commercial companies in Australia have indicated that the use of $MgOH_2$ results in significant cost and environmental savings. This treatment process immobilizes the toxic components of the sludge to make them stable to leaching in the long terms, have been developed.

5.4.1. A Case Study of Process Technology Improvement

In an electroplating industry in Sweden, degreasing of metal parts was carried out using chemicals such as caustic soda, phosphates, silicates and tensides at a pH range of 11-14. Thus, the wastewater produced from degreasing was alkaline containing these chemicals. A large quantity of water was used for rinsing which produced water containing ion, zinc, chrome, fats, oils and tensides. These ions were precipitated as metal hydroxides at 30 tonnes/yr. A biological degreasing system that is economical, non-polluting with low consumption of energy is developed in order to minimize hazardous waste generation during degreasing process.

In the new process, metal parts are washed in an aqueous solution of tensides and contaminants such as oil are dissolved in the washing liquids, and are degreased biologically, with the help of oil-eating microorganisms, in the degreasing tank. Oil eating bacteria are activated in the tank by feeding nutrients (tensides emulsified in oil). A separator keeps the concentration of microorganisms in the degreasing tank constant.

Due to biological degreasing, in the subsequent pickling process, the metal parts are not rinsed as the biological film blocks dissolution of iron in the pickling bath. Pickling should dissolve iron oxide scales while keeping iron losses to a minimum, which is achieved by biological degreasing. Economic benefits of biological degreasing system are summarized in Table 5.

Table 5. Economic benefits of changeover to biological degreasing process

The capital investment for the new process was US$421 700, with a payback period of 5.5 years.

5.5. Product Change

the process consumes about 3–5 m^3 per day of water, and discharges wastewater into the nearby sewer system without any treatment. Heavy metal concentrations in wastewater generated from the plating shop are presented in Table 6.

Table 6. Heavy metals concentration in wastewater

6.1. Implementation of In-plant Control Measures

The plating shop essentially generates four types of wastewater, which originates from a) chrome plating; b) Nickel plating; c) Copper plating; and d) Electrocleaning (alkaline) and acid cleaning. The waste stream from the cleaning operation mainly contains suspended solids, acid and alkali, contributing 40% of total wastewater generated at this plant. Considering its non-hazardous nature, and high volume, focus was made mainly to the first three streams of metal-bearing wastes. The control measures included the following:

1. *Wastewater segregation.* Chromium, nickel and copper-bearing wastewater were segregated and collected separately. These wastewaters were treated employing ion exchange process, and concentrated solutions (Cr, Ni, Cu) were recovered for reuse or recycling.
2. *Control of positioning and withdrawal of workpieces.* Workers were asked to orient the workpiece so that only a small surface comes into contact with liquid surface, as it leaves the plating solution. Workers were also instructed to hold the workpiece for sometime above the plating bath to reduce the volume of drag-out.
3. *Drag-out recovery.* Recovery of drag-out was made by placing plastic buckets to collect dripping plating solution as the workpieces were taken out of the tank, before rinsing. This bucket was used as a drag-out tank, and at the same time, workpieces were sprayed with a small amount of water prior to rinsing. The bucket solutions were then returned to replenish the plating bath.
4. *Effective rinsing.* The effectiveness of rinsing was improved using spray rinsing technique, and spray effluent was trapped by a drag-out bucket. Fresh water was introduced at the bottom of the tank by nozzles to provide agitation during rinsing to improve the effectiveness.
5. Water consumption monitoring was done by installing water meters to the two taps through which water is withdrawn for various processes.

6.2. Results of Implementation of In-plant Control Measures

1. *Water consumption.* Records of water consumption before and after the implementation of in-plant control measures indicated an average reduction of 18.7% in water consumption.
2. *Heavy metals concentration in wastewater*. Chromium concentration in wastewater decreased significantly after process modifications. About 73% reduction in the average Cr concentration was observed. Average reduction of concentrations of Ni and Cu were 71% and 54% respectively.

6.3. Cost Evaluation

The estimation of savings due to the reduction in quantity and pollutant concentration in wastewater is presented in Table 7 and 8.

Table 7. Savings due to wastewater reduction

Table 8. Savings due to metal concentration reduction

Total cost savings due to water and wastewater reduction is 12 117 Baht per month.

7. Water Reclamation from Small-scale Metal Pickling Units—a Feasibility Study in Delhi, India

Metal pickling is a process of removing scales, rusts (metal oxides) and other foreign materials from the surface of the metal by treating it with acids. In India, pickling of stainless steel plates is carried out in small scale units, which process about 50 to 100 tonnes of stainless steel per year. In the Capital Territory of Delhi, many such pickling units are located in the 70 industrial estates. They are particularly concentrated in the Wazirpur Industrial Area of Delhi, numbering around 400 in this industrial area alone. The stainless steel that is pickled in these units goes mainly for utensil manufacturing, to cater for the local and regional demand.

Pickling of stainless steel plates is carried out as a batch process in two baths. The process is pictorially presented in Figure 1.

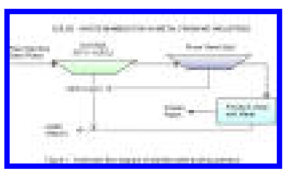

Figure 1. Schematic flow diagram of stainless steel pickling operation

The main problem of pollution from the small scale pickling units is the acidic nature of their effluent. A feasibility study carried out in four small-scale pickling units in Wazirpur Industrial Area in Delhi indicated that the pH value of the combined effluent range from 3 to 4 and acidity in the range of 1500 to 2000 mg/L of $CaCO_3$. Apart from acidity, the effluent contains the metallic impurities, which are removed during washing with water under pressure and are in the form of easily settleable solids. Wastewater is discharged into open drains without any treatment. Since the wastewater is not polluted much, except for acidity and easily settleable solids, there is a good opportunity to reclaim the effluent and recycle it. This is particularly so, as the quality of the water required in the pickling operation is not necessarily to be of high standard. Therefore, simple neutralization using lime solution, with sufficient arrangement for mixing with the effluent and settling, can easily recover most of the water. The neutralization process can be carried out in the collection drain within the unit. The extra requirement will be only a small sized settling tank where the grit and metallic impurities will be settled and removed. The overflow can be stored in a separate tank for recycling purpose. Proposed arrangements for water reclamation are shown in Figure 2.

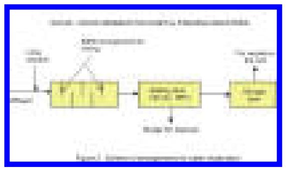

Figure 2. Scheme of arrangements for water reclamation

For an industry discharging 10 m^3/day of effluent, the daily lime requirement will be of the order of 40 kg. The lime solution can be prepared in batches of 20 kg, once during pre-lunch session and another for the post-lunch pickling operations. For the locally available limestone, the lime solution can be prepared by adding 50 L of water to every 20 kg of lime. This solution is to be kept in a well-mixed condition using a small mechanical mixer and is to be added to the drain at the rate of 200 mL per minute from a container placed above the effluent collection drain.

Care should be taken not to discharge the spent liquor from the acid bath directly to the collection drain. Instead, it should be neutralized in the batch itself by addition of lime and then disposed in the drain. For the purpose of controlling addition of lime, pH paper can be used. Also the settling tank is to be cleaned as and when required.

The cost of providing wastewater reclamation arrangement has been estimated to be Rs10 000–15 000, and the cost of lime is approximately Rs60 per day. The quantity of freshwater saved will be at least 2500 m^3 per year per industry.

Related Chapters

Click Here To View The Related Chapters

Glossary

Bioaccumulation	**:** The phenomena of accumulation of toxic substances that could not be metabolized or excreted, in the body tissues of living organisms.
Case-hardening	**:** Hardening the surface of a metal workpiece that remains relatively soft at the core.
Diffusion coating	**:** Deposition of a metallic layer over the surface that changes the surface properties of the workpiece to those of the metal deposited.
Drag-out	**:** The excess chemical solution adhering to the surface of a workpiece while immersed in chemical baths that will be washed away to waste stream or carried to subsequent chemical baths.

Electrochemical conversion : Deposition of a coat on a metal surface using electrochemical properties of the metals.

Metal finishing : Alteration of metal workpiece's surface properties in order to increase the corrosion or abrasion resistance, alter appearance, or to enhance the utility of the manufactured products.

Rinsing : Washing and cleaning of a workpiece with water to get rid of chemicals on its surface.

Bibliography

Office of Pollution Prevention (1996). Source reduction and metal recovery techniques for metal finishers, *Fact Sheet #24*, Ohio Environmental Protection Agency. [Provides simple procedures for waste minimization in metal finishing industries.]

Overcash M. R. (1986) *Techniques for industrial pollution prevention - A compendium for hazardous and non-hazardous waste minimization*, Chelsea: Lewis Publishers. [A comprehensive text on industrial waste minimization techniques.]

Pullar S., Lake M., Pagan R., and Clarke W. (1996). Minimizing liquid wastes in the metal finishing industry—a case study. *4th National Hazardous and Solid Waste Convention*, AWWA, Brisbane, Australia. [Provides a concise overview of opportunities for minimizing wastewater in metal finishing industries.]

Roulet M. (1984) *Les applications industrielles de l'ultrafiltration, Techniques Separatives sur Membranes*, Cycle ICPI, Lyon, France, October 22–26.

Thibault J. (1986) The costs and benefits of source reduction in metal finishing—Meeting hazardous waste requirements for metal finishers. *USEPA Seminar Publication EPA/625/4-87/018.*

UNEP (1995). *Cleaner Production Worldwide, Volume II*, United Nations Environment Program, New York [A compendium of application of cleaner production processes in various countries.]

Vigneswaran S., Visvanathan C., and Jegatheesan V. *Industrial waste minimization*. Environmental Management and Research Association of Malaysia, Petaling Jaya, Malaysia [This monograph presents a number of case studies on industrial waste minimization.]

Visvanathan C., Vigneswaran S., and Lien Ha N. T. (1995). Profitability of process modifications in pollution control. *AWWA Biannual conference on 'Solid and Hazardous waste management'*, Melbourne, April [Presents the details of a case study conducted to ascertain the economics of waste minimization in metal finishing industries in Thailand.]

Biographical Sketches

M. Sundaravadivel is an Environmental Engineer with the Central Pollution Control Board, Ministry of Environment and Forests, Government of India. He has been working in the field of industrial pollution control since 1989, particularly in the area of waste minimization and cleaner production in agro-based industries and small-scale metal finishing industries. He has also been an engineering consultant for planning, design and development of wastewater collection and treatment systems for a few large cities of India. Currently, he is engaged in research on technology, economic and policy aspects of liquid and solid waste management in small and medium towns of developing countries in the Graduate School of the Environment, Macquarie University, Sydney, Australia.

S. Vigneswaran is currently a Professor and Head of Environmental Engineering Group in Faculty of Engineering, University of Technology, Sydney, Australia. He has been working on water and wastewater research since 1976. He has published over 175 technical papers and authored two books (both through CRC press, USA). He has established research links with the leading laboratories in France, Korea, Thailand and the USA. Also, he has been involved in number of consulting activities in this field in Australia, Indonesia, France, Korea and Thailand through various national and international agencies. Presently, Dr. Vigneswaran is coordinating the university key research strengths on "water and waste management in small communities", one of the six key research centers funded by the university on a competitive basis. His research in solid liquid separation processes in water and wastewater treatment namely filtration, adsorption is recognized internationally and widely referred.

C. Visvanathan, is an Associate Professor of the Environmental Engineering Program, School of Environment, Resources and Development, Asian Institute of Technology. He has a Ph.D. (Chemical/Environmental Engineering) from Institute National Polytechnique, Toulouse, France. His main areas of research interests include: Solid–liquid separation technologies for water and wastewater treatment, waste auditing and cleaner production and solid waste disposal and management. Dr. Visvanathan has published more than 50 international journal and conference papers. His professional experiences include: Project Engineer, Asia Division, International Training Center for Water Resources Management, Sophia Antipolis, France, and short term consultant to UNEP Industry and Environment Office, Paris, France.

To cite this chapter
M.Sundaravadivel,S.Vigneswaran,C.Visvanathan, (2004), WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES, in *Wastewater Recycle,Reuse,and Reclamation*, [Ed. Saravanamuthu (Vigi) Vigneswaran], in *Encyclopedia of Life Support Systems (EOLSS)*, Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net] [Retrieved July 13, 2006]

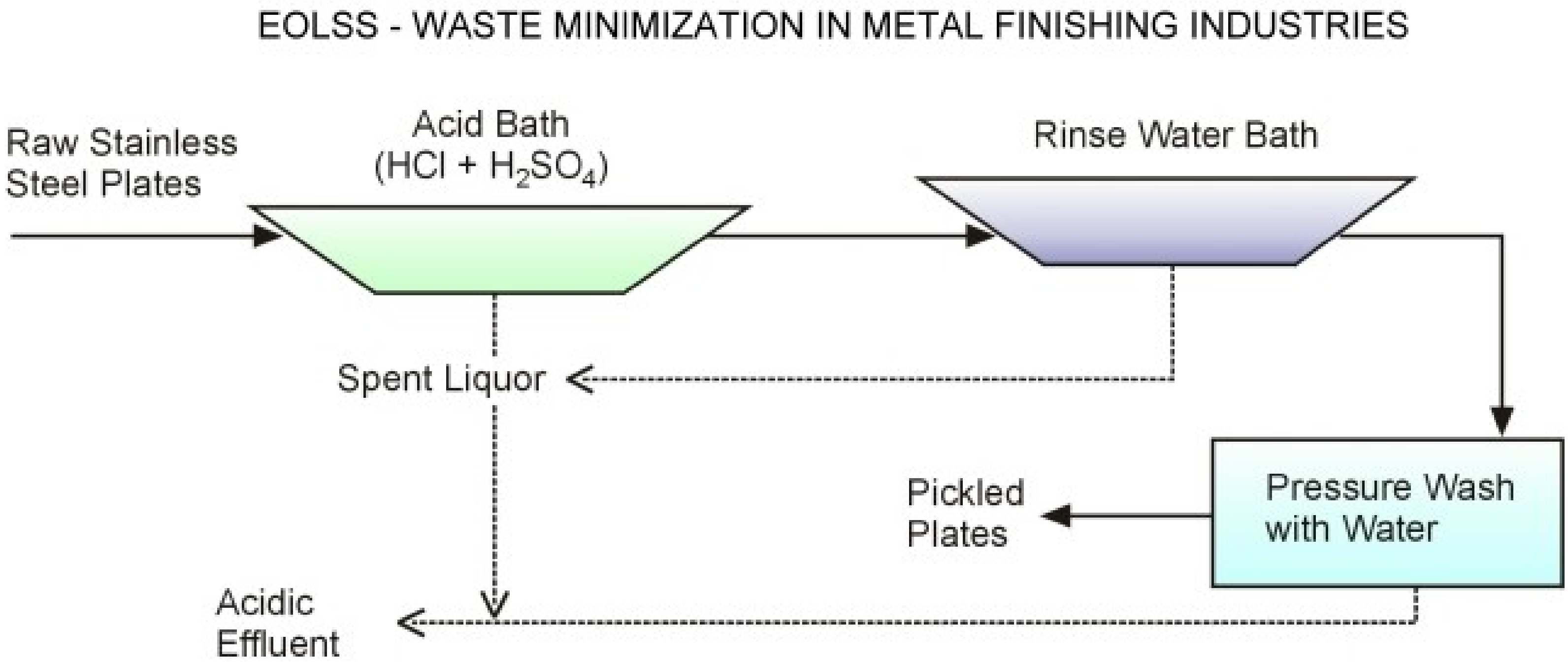

Figure 1. Schematic flow diagram of stainless steel pickling operation.

EOLSS - WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

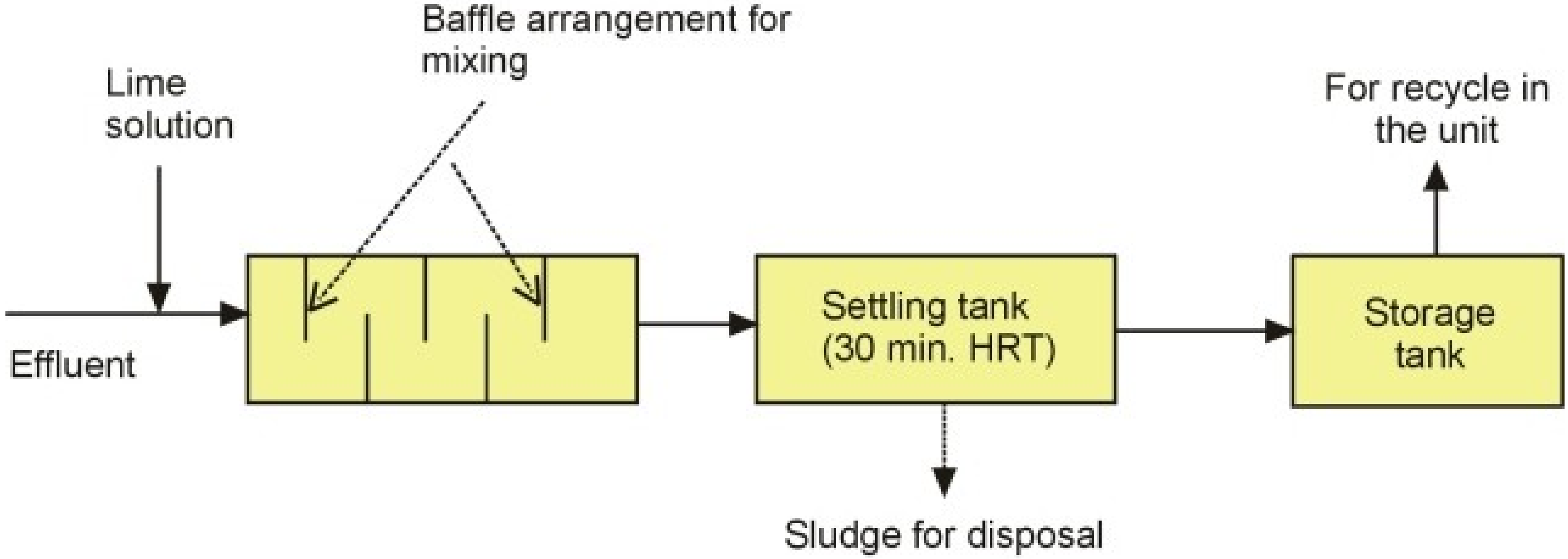

Figure 2. Scheme of arrangements for water reclamation

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Chemical/ electrochemical conversions	Diffusion coating operations	Case-hardening operations
• Phosphating • Chromating • Anodising • Passivation • Metal coloring • Electroplating	• Lattice diffusion • Spraying • Cladding • Vapour deposition • Vacuum coating • Hot dipping	• Carburising • Carbo-nitriding • Nitriding • Micro-casing • Thermal hardening

Table 1. Categories of metal finishing operations.

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Waste description	Process origin	Composition
1. Spent process solutions	Anodising, electroplating, galvanising, pickling, powder coating	Acids, bases, heavy metals, solvents and oil, caustic solutions, spent chromate and cyanide solutions
2. Filter sludge	Electroplating and chemical conversions	Silica, silicides, plating batch constituents, carbides, metal fines
3. Quench oils	Case hardening	Oils, metal fines, combustion products
4. Spent salt bath	Carburising, nitriding, cyaniding	Sodium cyanide and cyanate, potassium cyanide and cyanate
5. Effluent treatment sludge	Effluent treatment for heavy metal precipitation	Metal hydroxides, sulphides, carbonates

Table 2. Origin and composition of hazardous wastes in metal finishing industries

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Item	Before raw material substitution	After raw material substitution
Solvent based paint	1,993,200	Nil
Power paint	684,000	1,644,000
Paint thinner	135,500	Nil
Painting equipment cleaning	88,200	Nil
Labor	1,200,000	500,000
Energy	204,000	Nil
Waste management	254,400	Nil

Note: All costs are in Swedish Krona (SEK)
Source: Vigneswaran S. et al. (1998). *Industrial Waste Minimization*, Environmental Management and Research Association of Malaysia, Petaling Jaya, Malaysia

Table 3. Annual painting costs before and after waste minimization

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Type of rinse	Single	Series	Counter current
Number of rinse	1	2–3	2–3
Required flow (m^3/hr)	36	2.2–1.3	1.1–0.4

Source: Vigneswaran S et al. (1998). *Industrial Waste Minimization*, Environmental Management & Research Association of Malaysia, Petaling Jaya, Malaysia

Table 4. Theoretical rinse water requirements to maintain 1000 to 1 concentration.

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Details	Before	After	Savings in US$/yr (1990)
Sludge generation, t/yr	30	10	
Water usage, m^3/yr	8000	800	10,800
Feed stock (H_2SO_4) use (%)	20	8	6700
Savings in:			
Degreasing chemicals			7800
Inhibitor in pickling bath			10,100
Energy			7100
Shutdown of services like sulfate handling, degreasing bath etc.			37,800
Total saving			80,300

Source: Vigneswaran S., et al. (1998). *Industrial Waste Minimization*, Environmental Management & Research Association of Malaysia, Petaling Jaya, Malaysia

Table 5. Economic benefits of changeover to biological degreasing process

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Concentration	Minimum	Maximum	Quantity (m^3/day)
Cu^{2+}, mg/L	74	1000	0.2–1.3
Cr^{6+}, mg/L	50	2340	0.9–3.0
Ni^{2+}, mg/L	10	2482	0.9–3.0

Table 6. Heavy metals concentration in wastewater

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Item	Quantity reduced	Cost/ unit (Thai Baht)	Savings per month (Thai Bhat)
Water consumption	15.6 m^3	9	140.40
Reduction in wastewater requiring treatment	15.4 m^3	206	3172.00

Table 7. Savings due to wastewater reduction

EOLSS-WASTE MINIMIZATION IN METAL FINISHING INDUSTRIES

Heavy metal	Equivalent reduction per month	Cost/ kg (Thai Bhat)	Savings/month (Thai Bhat)
Cr^{6+}	476.7 g of CrO_3	950	906
Ni^{2+}	2260 g of $NiSO_4 . 7H_2O$	3360	7594
Cu^{2+}	547.8 g of $CaSO_4 . 5H_2O$	550	302

Note: Cost are based on pure chemicals of laboratory grade.

Table 8. Savings due to metal concentration reduction