PREVENTING POLLUTION FROM ELECTROPLATING PROCESSES

Edward R. Saltzberg, Ph.D.
Senior Vice President
Viar and Company
300 N. Lee Street
Alexandria, VA 22134

ABSTRACT

The majority of metals and cyanide discharged by industry into the Nation's waterways comes from metal-finishing facilities, primarily from electroplating processes. Because of the toxicity of pollutants in metal-finishing wastes and the amounts of these discharges, the U.S. Environmental Protection Agency established national wastewater regulations for this industry. The goal of these regulations is to reduce the contaminants in metal-finishing discharges to levels that are environmentally acceptable while remaining technically feasible and affordable of the industry. However, Federal waste regulations could have a severe economic impact on facilities conducting metal-finishing. EPA has estimated that up to 20 percent of all commercial electroplating firms may close due to wastewater regulations alone. Since the conventional methods used to treat metal-finishing wastewater produce sludges that are subject to costly hazardous waste regulations, the financial impact is even larger.

Fortunately, the outlook for managing metal-finishing wastes is not as bleak as EPA expected. Recently, some electroplating firms have found that very inexpensive changes in processing and waste control methods can greatly minimize the generation of wastewater and hazardous waste. These techniques enable plating shops to avoid much of the cost of waste treatment originally estimated by the EPA. Moreover, these techniques can actually pay for themselves in a very short period of time because they save large quantities of water and process chemicals, as well as reducing sludge volumes.

These techniques rely on conservation practices -- usually low cost technology methods that are inexpensive and easy to use. The techniques depend more on a change in attitude toward production than they do on expensive hardware. The central theme of the techniques is to strictly conserve and reuse water and chemicals, and to employ waste treatment technologies only when absolutely necessary.

Waste minimization depends on common drag-out and rinse rate controls, but the techniques are slightly different, more effective, and less costly than those traditionally used in the industry.

The principal measures used in the new methods are:

- Multiple drag-outs -- a variation on single drag-out tanks;
- Reactive rinsing -- a powerful technique for reusing rinsewaters.

Rather than reducing the size of end-of-pipe treatment equipment, the new methods of plating waste controls use multiple drag-out tanks and apply reactive rinsing techniques in order to avoid the need for end-of-pipe treatment equipment altogether, resulting in very small pollution control costs. In instances where some final waste treatment is still necessary, the cost of the treatment is still far less than it would be using standard techniques.

This paper explains how to use these techniques. It describes institutional as well as technical barriers to their implementation and provides hands-on examples of how to overcome them.

INTRODUCTION

The majority of metals and cyanide discharged by industry into the Nation's waterways comes from metal-finishing facilities, primarily from electroplating processes. The U.S. Environmental Protection Agency (EPA) figures released a few years ago, show that of the 34 industries covered by EPA's toxic wastewater regulations, metal finishers contribute 57 percent of the metals released to sewers (1). The degree of risk posed by these discharges is hard to determine because it depends on site-specific factors; however, small amounts of the types of chemicals discharged by metal finishers are toxic enough to cause EPA to set stringent, safe threshold levels for these chemicals in surface waters.

Because of the toxicity of pollutants in metal-finishing wastes and the amounts of these discharges, EPA established national wastewater regulations for this industry. The goal of these regulations is to reduce the contaminants in metal-finishing discharges to levels that are environmentally acceptable while remaining technically feasible and affordable by the industry. However, federal wastewater regulations could have a severe economic impact on the metal-finishing industry. EPA has estimated that up to 20 percent of all electroplating firms may close due to wastewater regulation (2). Since the conventional methods used to treat metal-finishing wastewater produce sludges that are subject to costly hazardous waste regulations, even a larger percentage of this industry than was estimated by EPA could go out of business.

Fortunately, the economic outlook for cleaning up metal-finishing wastewater is not as dismal as EPA expected. Recently, some electroplating firms have found that very inexpensive changes in processing and waste control methods can greatly reduce the amount of wastewater and hazardous waste they generate. These techniques enable plating shops to avoid much of the cost of waste treatment originally estimated by EPA. Moreover, these techniques can actually pay for themselves in a very short period of time because they save large quantities of water and process chemicals. As a result, far less than 20 percent of the firms in the electroplating industry should close because of EPA's wastewater regulations.

The new methods of plating waste controls that are being used and accepted by the industry are based on what energy conservationists have been proclaiming for more than a decade: The quickest, easiest and cheapest way to save energy is to avoid using it. Likewise, *the quickest, easiest and cheapest way to keep down pollution control costs is not to pollute in the first place*. Accordingly, the new methods of pollution control for the electroplating industry rely on conservation practices -- usually low cost technology methods that are inexpensive and easy to use. The new methods depend more on a change in attitude toward production than they do on expensive hardware. The central theme of the new methods is to strictly conserve and reuse water and chemicals, and to employ wastewater treatment technologies for compliance only when absolutely necessary.

This paper explains how to use these new methods. Before examining the new methods, a brief description of electroplating is presented to provide some background to those unfamiliar with this industry.

OVERVIEW OF THE ELECTROPLATING PROCESS

Electroplating is a process for applying a thin metal coating such as zinc, copper, nickel, chromium, etc. to the surface of metal parts, which are usually made of iron, steel; brass or aluminum. The coatings serve to protect the metal from corrosion, to build up the surface thickness, or to decorate the piece. Many commonly used items are electroplated. Automobile bumpers and door handles, for example, are often chrome plated; printed circuit boards are copper plated, and watch bands and necklaces can be gold or silver plated. Industrial parts such as housings, chases and castings are usually plated.

Process Steps

Most electroplating processes can be divided into three principal work steps as shown in Fig. 1.

- **Surface Preparation**

Surface preparation involves cleaning the part before it is plated. Cleaning is usually accomplished by placing the work piece in a tank containing a solvent or alkaline solution, and then in an acid dip to remove corrosion. Both the alkaline and the acid dip are followed by rinsing in running water.

- **Plating Application**

In the second work step, a metal coating is applied from a solution containing the plating metal in dissolved form and other chemicals. The part to be plated is placed in the solution and charged with electricity to attract the dissolved metal to its surface, much like a magnet attracts iron filings. Plating is followed by rinsing with water to flush the process solution from the work piece.

- **Post-treatment**

Some plating steps are followed by post-treatment of the work pieces to color it or to add corrosion resistance. Chromate, for example, is a common post-treatment for zinc and cadmium plating. Post-treatment steps are also followed by rinsing in running water. Some electroplating processes are complete after the plating step and do not require post-treatment.

Sources of Waste

Wastes from electroplating shops originate in several ways. One source of pollution is from "drag-out," which is processing solution that clings to the work piece as it is removed from the plating bath. The amount of pollutants contributed by drag-out is a function of many factors, including the design of the racks or barrels carrying the parts to be plated, and the shape of the parts. Plating procedures and several interrelated parameters of the process solution, such as concentration of toxic chemicals, temperature, viscosity, and surface tension also affect drag-out rates.

Large volumes of rinsewater are usually needed to clean the drag-out from the work with conventional rinsing techniques. Rinsing actually serves two purposes:

1. It cleans the part, which prevents staining and other quality control problems;
2. It protects subsequent process baths from "drag-in" contamination.

Because of high flow rates used in conventional rinsing techniques, rinsewaters are contaminated with relatively dilute concentrations of process solutions. Typically, rinsewaters that follow plating solutions contain between 15 and 100 milligrams per liter (mg/l) of metal being plated (3).

Most plating shops operate several plating lines such as zinc, copper, nickel, cadmium, and chromium. The rinsewaters discharged from each line are usually combined in a common pipe or floor trench, and the concentrations of the individual metals from each process are diluted in the entire volume of the shop's wastewater, usually to less than 40 mg/l for each metal (3).

Another source of contamination from electroplating shops is used or spent process solution. Platers routinely discard spent cleaners, acids, and bright dips. Although these solution are not usually made up of metals, it is not uncommon to find cyanide and heavy metals in concentrations of several thousands milligrams per liter in these solutions. This contamination is caused by drag-in from previous process cycles and from metals leached or dissolved from the work by the process chemicals. Plating solutions and other process chemicals containing high metal concentrations are rarely discarded.

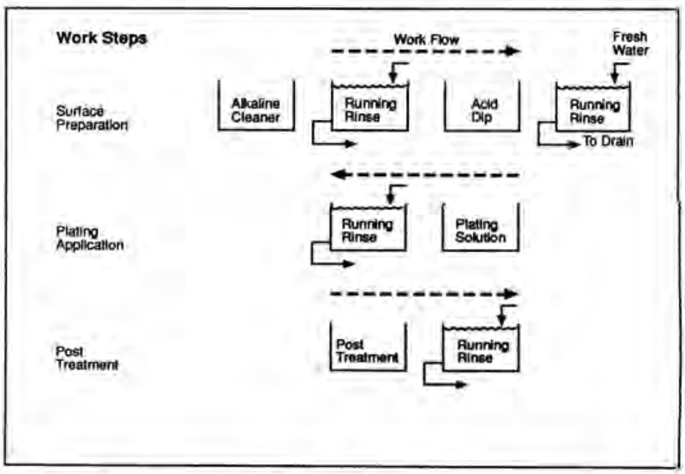

Fig. 1. Overview of the electroplating process.

Instead, they are decontaminated or rejuvenated in place so they are not usually a hazardous waste problem.

Accidental spills, leaks, and floor drips of process solutions also can contribute to effluent contamination. Additional pollution sources include sludges from the bottoms of plating baths generated during chemical purifications, backwash from plating tank filters systems, and stripping solutions.

DRAG-OUT MINIMIZATION USING MULTIPLE DRAG-OUT TANKS

Minimizing the amount of plating solution that is dragged from work pieces upon their removal from the process tank reduces the amount of contamination in the rinse tanks. A single drag-out tank, installed immediately following the plating process, will capture some of the contamination. Two or more drag-out tanks will capture most of it.

The multiple drag-out technique is similar to counterflow rinsing -- a common water conservation method -- because it uses several rinse tanks in series. The difference is that, instead of a single drag-out tank and two or more running rinses, the multiple drag-out method uses several drag-out tanks and a single running rinse, as Fig. 2 illustrates. Most of the drag-out is captured in the first tank, leaving the second tank less contaminated than the first. As a result , the concentration of pollution in the discharge from the running rinse tank is lower than it would be if only one drag-out tank is used. More drag-out tanks lower the discharge concentration even further. As a rule of thumb, each drag-out tank reduces the discharge concentration by 50 percent. Accordingly, two drag-outs are twice as effective as one, and three drag-outs are four times as effective as one.

The concentration of pollutants in the running rinse tank does not remain constant. As pollution builds up in the drag-out tanks, it also increases in the running rinse tank. However, the more drag-out tanks used, the slower the buildup of contaminants in the running rinse. This is the principle behind multiple drag-out tanks and a key feature of the new methods of plating waste control. Using two or more drag-out tanks, the concentration of pollutants in the discharge from the running rinse tank can be held below effluent limits for extended periods of time.

Recycle Drag-Out Solution to the Plating Bath

The best alternative for managing drag-out solution is to return it to the process bath from which it came. Total recycle eliminates the drag-out from being a hazardous waste problem and conserves process chemicals. Returning drag-out directly to the process is possible if the process bath is hot and there is sufficient evaporation to make room for the amount of solution dragged out each day. For example, nickel and chromium plating are both operated at or above 327.59 K (130°F) and drag-out solution can be returned to these processes.

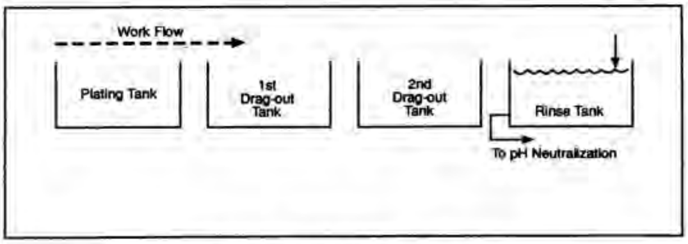

Fig. 2. Multiple drag-out.

Returning drag-out solution to the plating bath is a technique that should not be used indiscriminately because it can impact plating quality. For example, copper pyrophosphate plating is a heated process but contaminants build up in the bath because of chemical reactions that occur in the process solution.

There are many plating processes on the market, and one cannot generalize about the application of drag-out recovery to all the processes. However, in general, the technique can be used after most heated plating baths. The manufacturer of the individual process chemicals will usually advise platers on the application of drag-out recover to their processes.

Unfortunately, many plating baths are operated at room temperature, and there is little evaporation from them. Accordingly, drag-out cannot be recycled directly to these processes. In instances in which drag-out cannot be recycled directly, high technology recovery techniques such as reverse osmosis and evaporation have been used in plating shops to concentrate the drag-out into volumes small enough to be returned to cold process baths. However, there are two primary drawbacks to these techniques:

- They are very expensive;
- These techniques not only concentrate the excess solution in the drag-out tank, but they also concentrate the impurities in the drag-out.

When the concentrate is returned to the process, the concentrated impurities can contaminate the plating solution and impair the quality of the plating. The concentrate can be purified using ion exchange to selectively remove impurities, but this drives up the already high cost of recovery. In general, the following methods of handling drag-out solutions which cannot be returned to the plating bath are more cost effective than high technology controls.

Treatment in Place

When the drag-out solution cannot be returned to the plating tank, the next best alternative is treatment in place. A process called integrated treatment was developed several years ago by Lancy Laboratories, Zelienpole, Pennsylvania. It was primarily designed to complete in-process the first step in the two-step treatment of chromium and cyanide. The second step would be carried out in the end-of-pipe treatment system.

Electrolytic recovery of metals from the drag-out tank has become cost-effective in the last few years. This technique works best on zinc, cadmium, copper, silver, gold and tin processes. It is not effective on chromium and nickel.

Batch Treatment on Site

If the drag-out solution cannot be returned to the process tank or treated entirely in place, it has to be chemically treated, usually in a batch treatment system. In these cases, the drag-out solution can be handled like other spent electroplating process baths.

In addition to drag-out solutions, spent baths from plating shops include cleaners, acids, and post-treatment solutions. (Platers rarely discard plating solution.) Spent baths can be treated on-site in the firm's own bath treatment system or shipped off-site to a private waste treater. Central processing facilities that recover metals may be able to refine drag-out solutions and certain other spent plating baths.

WATER CONSERVATION THROUGH REACTIVE RINSING

Reactive rinsing is a technique to reuse or recycle rinsewater one or more times before it is discharged. This technique takes advantage of the chemical reactivity of used rinsewater. Not only can a firm's water consumption be greatly reduced by recycling, but rinsing efficiency can actually be increased by this method, thus improving plating quality.

Counterflow rinsing is the standard technique platers use to reduce flow rates. However, rinse tanks are expensive and require space for installation, while electroplating shops usually have trouble raising capital and are often located in tight quarters. Reactive rinsing is a very effective alternative to counterflow rinsing without the cost or logistical constraints. Reactive rinsing does not require additional rinse tanks, so it is less expensive than counterflow rinsing. It also does not use any additional space, so it has wider application than counterflow rinsing.

Intraprocess Reactive Rinsing

A typical nickel plating line is diagrammed in Fig. 3. It is usually composed of three process steps:

- An alkaline cleaning tank;
- An acid dip tank;
- A nickel plating tank

Each process step is followed by a running rinse tank, and each rinse tank has a separate freshwater feed line. The rinse tanks run at about .15 m^3/min, and the nickel plating line in Fig. 3 uses a total of .45 m^3/min (or 12 gallons per minute). That is a lot of water. In a single 8-hour production day, this line alone accounts for 235 m^3 of water. An 8 by 12 meter backyard swimming pool would be filled in about 6 production days. Other types of plating lines have more than three rinse tanks, so they could use even more water than a nickel process. Plating shops employing standard rinsing methods uses tens of thousands of gallons of water each day.

Using Reactive Rinsing to Save Water

The parts to be plated "drag-in" to the nickel tank whatever is in the previous rinse tank. If that rinse tank is fed with freshwater, the drag-in will be comprised primarily of a dilute acid solution, which will reduce both the nickel concentration in the process and, to a certain extent, the acidity of the bath. (Nickel solutions are bath slightly acidic.) Instead of using freshwater, the acid rinse tank could be fed with the discharge from the nickel rinse tank. Since the nickel rinse tank contains dilute process solution, it will feed the acid rinse tank with slightly acidic water containing nickel salts and other process additives. Accordingly, the drag-in from the acid rinse tank will partially replenish process chemicals in the nickel tank. This is an example of reactive. rinsing. Nickel rinsewater does not harm the rinsing step after the acid bath, and it helps to conserve chemicals in the nickel plating tank and the freshwater feed line to the acid rinse tank can be turned off to save .15 m^3/min. This reactive rinsing application reduces water use and saves process chemicals without harming the rinse step. Some reactive rinsing applications actually aid rinsing and, therefore, improve plating quality.

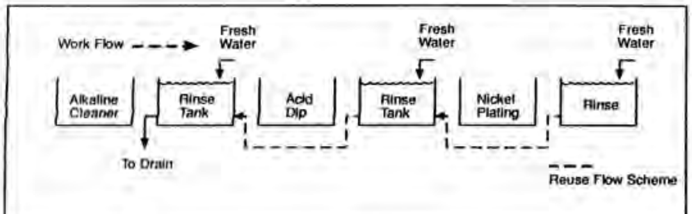

Fig. 3. Intraprocess reaction rinsing.

Improving Rinsing Efficiency Through Reactive Rinsing

A good example of how this technique can be used to improve rinsing efficiency is also illustrated in Fig. 3. Cleaner solutions are alkaline -- soapy and, therefore, difficult to rinse. Imaging trying to rinse off dishwashing detergent form dinner plates in cold water. It doesn't work very well because the detergent clings to the plates. In a kitchen, hot water is used to rinse dishes, but hot water is too expensive to use in plating cleaning lines because so mush costly energy is needed to heat the water. Therefore, platers rinse cleaning solutions in cold water tanks and depend on the subsequent acid solutions to neutralize any cleaners still clinging to work. However, cleaner solutions are neutralizing agents and they reduce the useful life of the acid baths. Clearly, this is not a very efficient rinsing system.

Acids are expensive, and their useful life should be prolonged, not reduced. Moreover, spent acid solutions are a costly waste management problem, which is a second compelling reason to lengthen the time of service of acid baths. The answer to this problem is almost obvious -- use the acid rinse tank discharge to feed the cleaner rinse tank. If this is done, then neutralization of the drag-out from the cleaning process will occur in the cleaner rinse tank and not in the acid process tank. The parts get very well rinsed, and the life of the acid solution is prolonged. In this case, another .15 m^3/min of water is saved because the fresh feed to the cleaner rinse tank can be turned off.

SUMMARY

Simple housekeeping techniques to minimize waste generation are often as effective and less expensive than "high tech" alternatives. For electroplating processes, capturing contamination before rinsing work in running water, and reusing rinse waters can sometimes eliminate the need for end-of-pipe wastewater treatment. Moreover, facilities using these techniques are in an enhanced position to recover or recycle process wastes.

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