

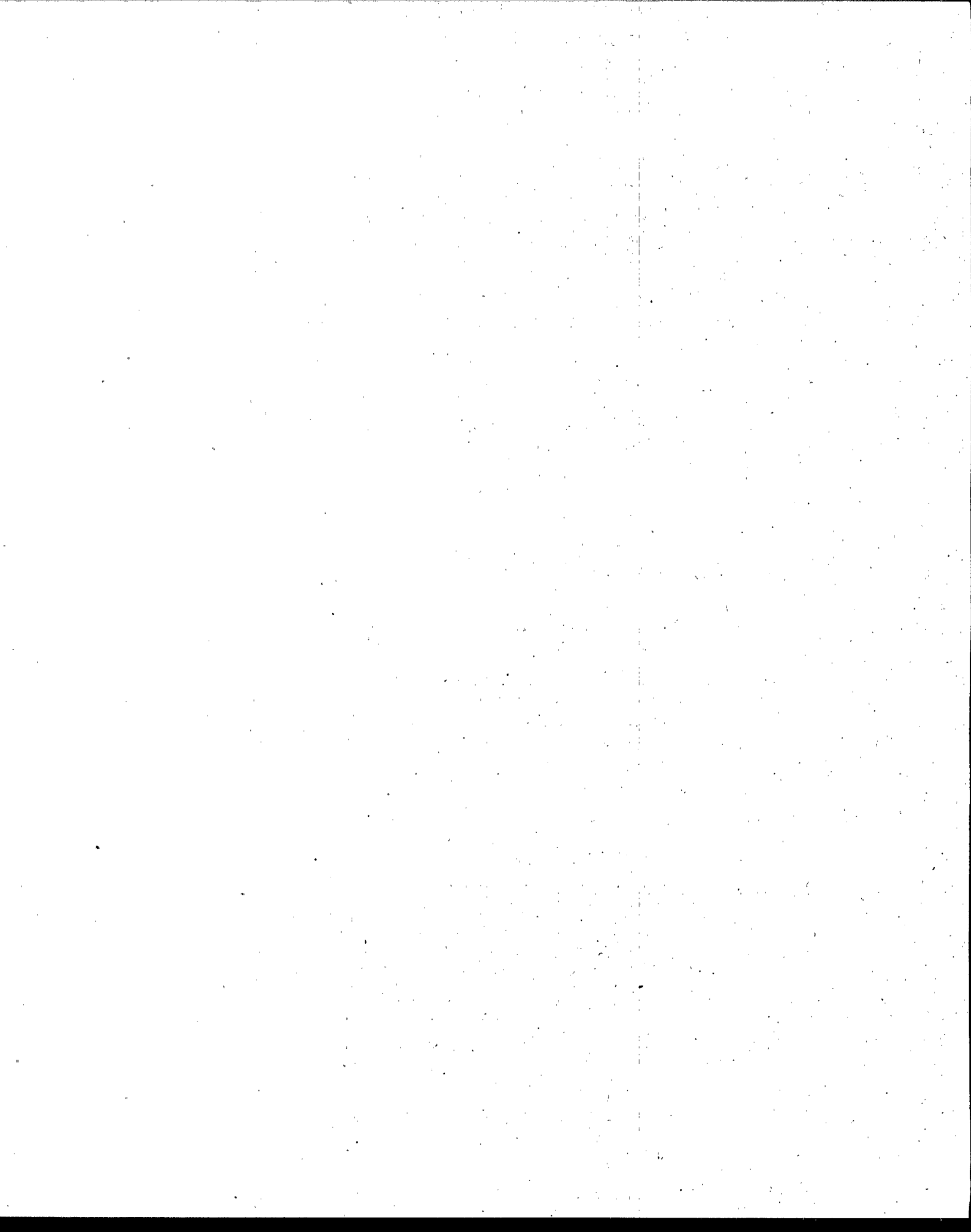


# Pollution Prevention for the Metal Finishing Industry

A Manual for  
Pollution Prevention  
Technical Assistance Providers

February 1997





# Acknowledgments

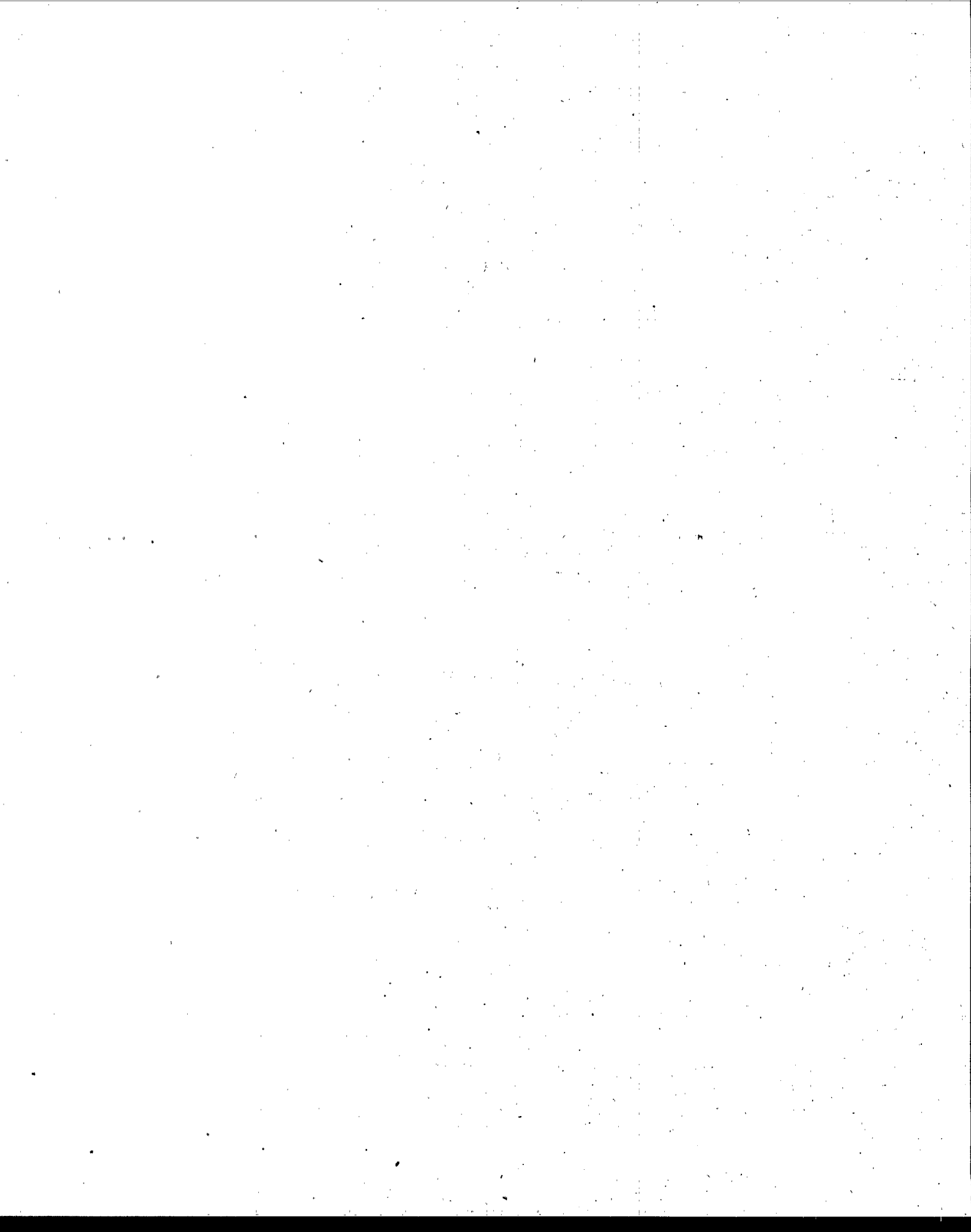
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# **Northeast Waste Management Officials' Association**

The Northeast Waste Management Officials' Association (NEWMOA) is a non-profit, nonpartisan, interstate governmental association. The membership is composed of state environmental agency directors of the hazardous waste, solid waste, waste site cleanup and pollution prevention programs in Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island, and Vermont.

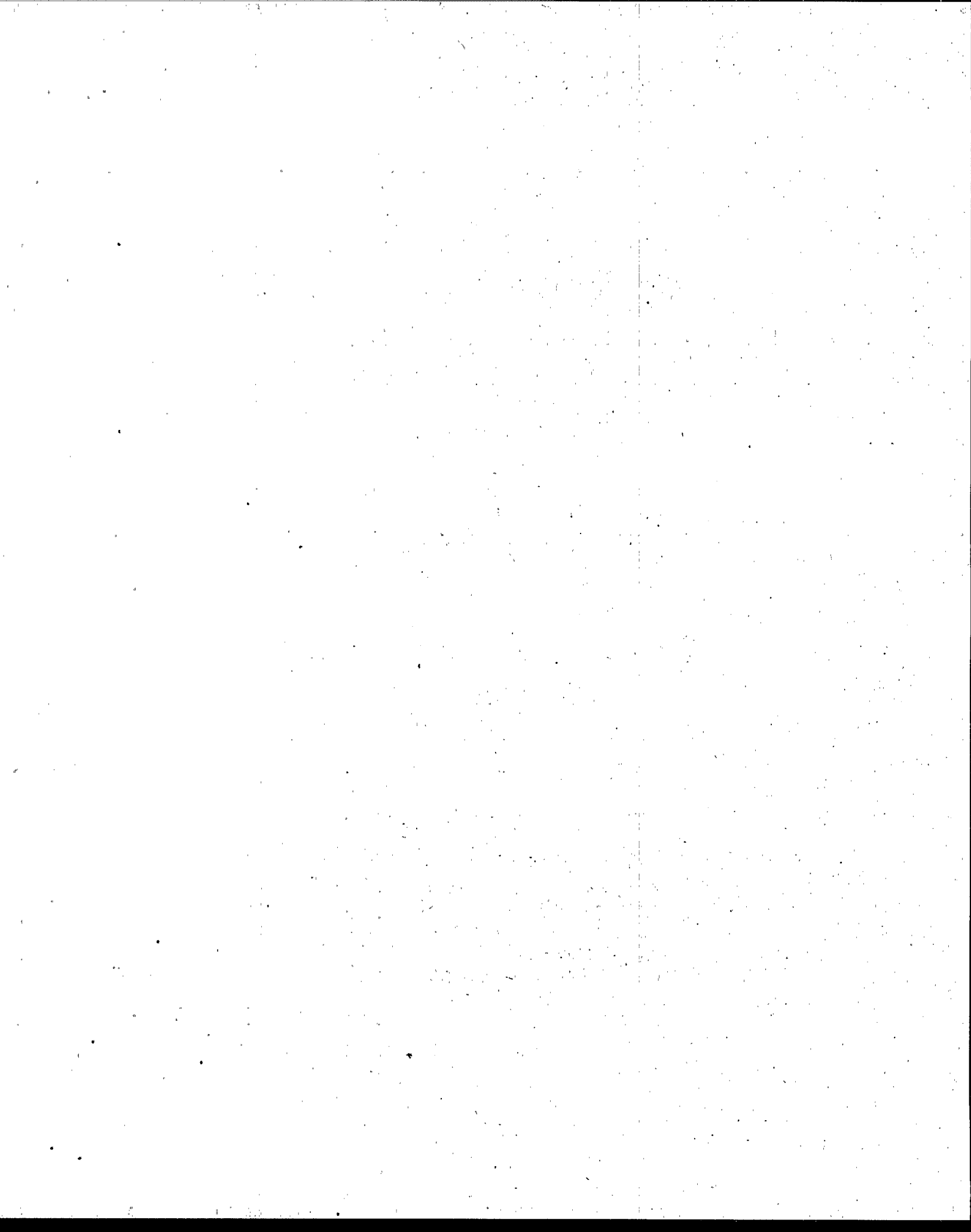
NEWMOA's mission is to help states articulate, promote and implement economically sound regional programs for the enhancement of environmental protection. The group fulfills this mission by providing a variety of support services that facilitate communication and cooperation among member states and between the states and EPA, and promote the efficient sharing of state and federal program resources.

NEWMOA was established by the governors of the New England states as an official interstate regional organization, in accordance with Section 1005 of the Resource Conservation and Recovery Act (RCRA). The organization was formally recognized by the U.S. Environmental Protection Agency (EPA) in 1986. It is funded by state membership dues and EPA grants.

NEWMOA established the Northeast States Pollution Prevention Roundtable (NE P2 Roundtable) in 1989 to enhance the capabilities of member state environmental officials to implement effective source reduction programs. The NE P2 Roundtable's program involves the following components: (1) managing a regional roundtable of state pollution prevention programs; (2) publishing a newsletter; (2) managing a clearinghouse of books, reports, case studies, fact sheets, notices of upcoming meetings and conferences, and a list of P2 experts; (3) organizing training; and (4) conducting research and publishing reports and other documents. The clearinghouse provides pollution prevention information to state and local government officials, the public, industry, and others. Funding for the NE P2 Roundtable is provided by the NEWMOA member states and the U.S. EPA. For more information contact: Terri Goldberg, NEWMOA, 129 Portland Street, 6th floor, Boston, MA 02114, (617) 367-8558 x302 (Phone); (617) 367-0449 (Fax); NEPPR@TIAC.NET (e-mail).

The views expressed in this manual do not necessarily reflect those of NEWMOA, US EPA, WMRC, or the NEWMOA member states. Mention of any company, process, or product name should not be considered an endorsement by NEWMOA, NEWMOA member states, or the US EPA.

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## Using This Manual

The Northeast Waste Management Officials' Association (NEWMOA) designed this manual to provide environmental assistance staff with a basic reference on metal finishing. The purpose of the manual is to enable assistance providers to rely on a single publication to jump start their research on pollution prevention for metal finishers with whom they are working. The manual is explicitly designed to be useful to assistance professionals with experience working with metal platers and those who have never encountered metal finishing before. The U.S. Environmental Protection Agency Pollution Prevention Division funded this manual as a model of a comprehensive packet of information on a single industry.

NEWMOA collaborates with state and local environmental assistance programs in the Northeast; these programs have requested this manual to help them provide more efficient and effective help to the numerous metal finishers in the region. Assistance providers have reported frustration with having to search databases for materials only to obtain a list of citations and case studies that they have to spend considerable time finding in order to provide information to their client companies. In addition, these officials rarely have the opportunity to check the accuracy of the information they find in databases to determine whether the material is still current. To avoid duplicating efforts and to ensure that the information platers receive is up-to-date and accurate, NEWMOA developed this manual as a model "synthesized" information packet that includes an exhaustive compilation and synthesis of existing materials on P2 for the metal finishing industry.

To compile this manual, NEWMOA reviewed over 700 books, articles, fact sheets, reports and guides on P2 for metal finishing. NEWMOA staff also sent a draft of the manual to more than 15 expert reviewers for their comments and suggestions. The result is an up-to-date compilation of information on P2 options for metal finishing. However, pollution prevention is a rapidly changing field, and all users should check with the various centers identified in Appendix B to determine whether any new information is available.

The first three chapters of the manual include a statistical characterization of the industry, overview of federal regulations for metal finishing, pointers on implementing process planning and a description of general pollution prevention options. Chapter 4 covers general issues that apply to overall facility operations. Chapters 5 through 7 address specific issues within each process line. These three chapters focus on specific processes, pollution prevention options for these processes, issues pertaining to the options and case studies highlighting the options. Chapter 8 covers alternative deposition processes that replace traditional electroplating operations. Chapter 9 provides information on integrating P2 into a facility's design. In order to reduce redundancy where topics overlap, the text refers the reader to other sections within the document. The manual also has an index to facilitate quick information retrieval. The Appendices provide a glossary and resource listing.

## Audience

NEWMOA designed this manual for individuals who are involved in providing some form of environmental technical assistance to metal finishing companies. NEWMOA believes that the information in this manual would be useful to environmental inspectors and permit writers that are involved in regulatory compliance activities at metal finishing companies. This manual could help these regulatory officials identify possible pollution prevention opportunities at the firms that they are inspecting or permitting.

NEWMOA designed this manual for assistance providers with little or no experience with metal finishing. NEWMOA suggests that these users pay particular attention to Chapters 1 through 4 to gain a basic understanding of P2 for the industry. Chapters 5 through 9 will become increasingly



useful to these users as they work with specific companies on particular issues. To facilitate searching for specific information and topics, the last section of the manual includes an index. NEWMOA expects users of this manual, who are experienced assistance providers to metal finishers, to use only those sections that pertain to their specific situations in client companies. These users may find the information in Chapters 5 through 9 to be the most useful.

As stated above, this is a model for additional manuals that NEWMOA and other regional and national organizations are developing for other industry groups. NEWMOA is interested in obtaining comments and suggestions from manual users on its content and format. Please take a moment and complete the evaluation form at the end of the document to help us with future versions of this and other manuals, or call NEWMOA at (617) 367-8558 ext. 304 and talk with us about the manual.



# 1 Overview of the Metal Finishing Industry

These days everyone doing pollution prevention assistance seems interested in helping the metal finishing industry; ever wonder why? Metal finishing, when taken as a whole, is one of the largest users of many toxic chemicals in the country. Electroplating alone is the second largest end user of nickel and nickel compounds, and the third largest end user of cadmium and cadmium compounds. Electroplating also accounts for a substantial amount of chromium use in the United States. In other words, this industry is responsible for managing large amounts of hazardous materials (Davis 1994).

Many industries use metal finishing in their manufacturing processes including automotive, electronics, aerospace, hardware, jewelry, heavy equipment, appliances, tires, and telecommunications. Figure 1 shows the percent of markets served by metal finishers in 1992.

Why is metal finishing so prevalent? Without metal finishing, products made from metals would last only a fraction of their present lifespan because of corrosion and wear. Finishing is also used to enhance electrical properties, to form and shape components, and to enhance the bonding of adhesives or organic coatings. Sometimes the finishes are used to meet consumer demand for a decorative appearance.

Overall, metal finishing alters the surface of metal products to enhance:

- ◆ Corrosion resistance
- ◆ Wear resistance
- ◆ Electrical conductivity
- ◆ Electrical resistance
- ◆ Reflectivity and appearance (e.g., brightness or color)

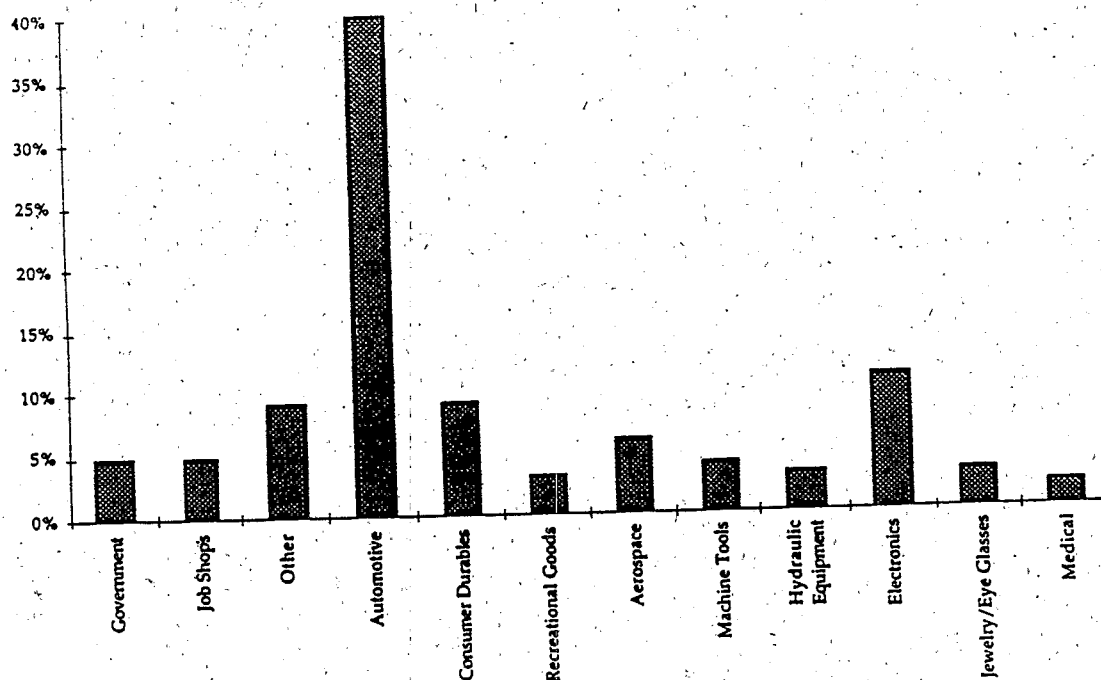


Figure 1. Markets Served by Metal Finishers—Percent of 1992 Market (EPA 1995a)

- ◆ Torque tolerance
- ◆ Solderability
- ◆ Tarnish resistance
- ◆ Chemical resistance
- ◆ Ability to bond to rubber (e.g., vulcanizing)
- ◆ Hardness

Metal finishers use a variety of materials and processes to clean, etch, and plate metallic and non-metallic surfaces to create a workpiece that has the desired surface characteristics. Electrolytic plating, electroless plating, and chemical and electrochemical conversion processes are typically used in the industry. Typical supporting processes can include degreasing, cleaning, pickling, etching, and/or polishing.

Some of the materials used in metal finishing are solvents and surfactants for cleaning, acids and bases for etching, and solutions of metal salts for plating the finish onto the substrate. Figure 2 presents an overview of the fabricated metal products manufacturing process and shows the types of emissions and wastes that are generated during production.

## Types of Shops

The electroplating, plating, polishing, anodizing, and coloring industry is classified under the Standard Industrial Classification (SIC) code 3471 and includes establishments primarily engaged in all types of metal finishing. Companies that both manufacture and finish products are classified according to products they make. Nonetheless, they are still considered part of the metal finishing industry.

Firms that rely on one customer or that conduct metal finishing as part of a larger operation are referred to as captive shops. These companies tend to have larger operations than job shops. Independent facilities, often referred to as job shops, rely on a variety of customers and coat a variety of workpieces and substrates. In general, job shops tend to be small and independently owned. Enough similarities exist between the job and captive shops that they are essentially

considered part of one industry. The job and captive shops use the same types of processes and fall within the same regulatory framework (EPA 1995a).

However, the barriers they face in deciding upon and implementing new technologies reflect the differences in their environmental performance and in the corporate capabilities of the two segments. Captive operations, which are more specialized, can focus their operations because they often work on a limited number of products and/or use a limited number of processes. Job shops, on the other hand, tend to be less focused in their operations because they can have many customers often with different requirements. In general, captive shops tend to have greater access to financial and organizational resources and, as a result, tend to be more proactive in their approach to environmental management. However, this is not always the case. The vastly different cultures in these shops greatly affects their perceived ability to implement pollution prevention (EPA 1994).

Job shops and captive shops do not ordinarily compete against each other because captive finishers seldom seek contract work. However, captive facilities might use job shops as subcontractors to perform tasks that their operations are unable to or that they choose not to do. As a nationwide trend, many manufacturers are choosing to eliminate or reduce metal finishing operations from their facilities because it is not of strategic importance for their long-term success. In some of these cases, the larger firms have shifted their plating activities to job shops (EPA 1995a).

## Types of Metal Finishing Processes

Metal finishing comprises a broad range of processes that are practiced by most industries which manufacture metal parts. Typically, manufacturers perform the finishing after a metal part has been formed. Finishing can be any operation that alters the surface of a workpiece to achieve a certain property. Common metal finishes include paint, lacquer, ceramic coatings, and other surface treatments. This manual

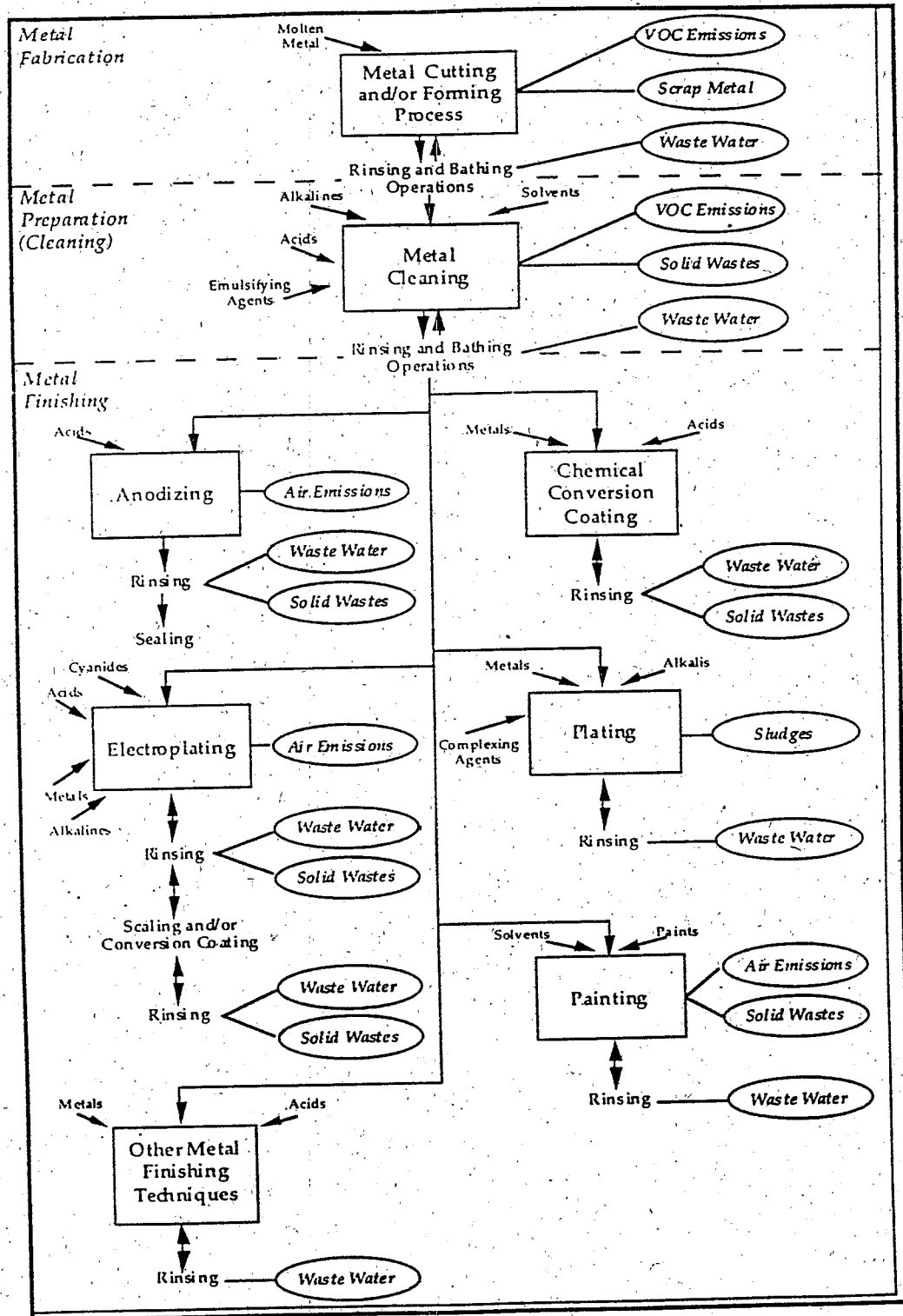


Figure 2. Overview of the Metal Fabricating Process (EPA 1995a)

mainly addresses the plating and surface treatment processes.

The metal finishing industry generally categorizes plating operations as electroplating and electroless plating. Surface treatments consist of chemical and electrochemical conversion, case hardening, metallic coating, and chemical coating. The following sections briefly describe the major plating and surface treatment processes in order to provide a context for the more in-depth information in the chapters that follow.

## Electroplating

Electroplating is achieved by passing an electric current through a solution containing dissolved metal ions and the metal object to be plated. The metal object serves as the cathode in an electrochemical cell, attracting ions from the solution. Ferrous and non-ferrous metal objects are plated with a variety of metals including aluminum, brass, bronze, cadmium, copper, chromium, gold, iron, lead, nickel, platinum, silver, tin, and zinc. The process is regulated by controlling a variety of parameters including voltage and amperage, temperature, residence times, and purity of bath solutions. Plating baths are almost always aqueous solutions, therefore, only those metals that can be reduced in aqueous solutions of their salts can be electrodeposited. The only major exception to this principle is aluminum, which can be plated from organic electrolytes (EPA 1995a).

Plating operations are typically batch operations in which metal objects are dipped into a series of baths containing various reagents for achieving the required surface characteristics. Operators can either carry the workpieces on racks or in barrels. Operators mount workpieces on racks that carry the part from bath to bath. Barrels rotate in the plating solution and hold smaller parts (Ford 1994).

The sequence of unit operations in an electroplating process is similar in both rack and barrel plating operations. A typical plating sequence involves various phases of cleaning, rinsing, stripping, and plating. Electroless plating uses similar steps but involves the deposition of metal

on metallic or non-metallic surfaces without the use of external electrical energy (EPA 1995a).

## Electroless Plating and Immersion Plating

Electroless plating is the chemical deposition of a metal coating onto an object using chemical reactions rather than electricity. The basic ingredients in an electroless plating solution are a source metal (usually a salt), a reducer, a complexing agent to hold the metal in solution, and various buffers and other chemicals designed to maintain bath stability and increase bath life. Copper and nickel electroless plating commonly are used for printed circuit boards (Freeman 1995).

Immersion plating is a similar process in that it uses a chemical reaction to apply the coating. However, the difference is that the reaction is caused by the metal substrate rather than by mixing two chemicals into the plating bath. This process produces a thin metal deposit by chemical displacement, commonly zinc or silver. Immersion plating baths are usually formulations of metal salts, alkalis, and complexing agents (e.g., lactic, glycolic, or malic acids salts). Electroless plating and immersion plating commonly generate more waste than other plating techniques, but individual facilities vary significantly in efficiency (Freeman 1995).

## Chemical and Electrochemical Conversion

Chemical and electrical conversion treatments deposit a protective and/or decorative coating on a metal surface. Chemical and electrochemical conversion processes include phosphating, chromating, anodizing, passivation, and metal coloring. Phosphating prepares the surface for further treatment. In some instances, this process precedes painting. Chromating uses hexavalent chromium in a certain pH range to deposit a protective film on metal surfaces. Anodizing is an immersion process in which the workpiece is placed in a solution (usually containing metal salts or acids) where a reaction occurs to form an insoluble metal oxide. The reaction continues and forms a thin, non-porous layer that provides good corrosion resistance. Sometimes this

process is used as a pretreatment for painting. Passivating also involves the immersion of the workpiece into an acid solution, usually nitric acid or nitric acid with sodium dichromate. The passivating process is used to prevent corrosion and extend the life of the product. Metal coloring involves chemically treating the workpiece to impart a decorative finish (EPA 1995a).

## Other Surface Finishing Technologies

Other commonly used finishing technologies that do not fall into the plating or chemical and electrochemical conversion processes include cladding, case hardening, dip/galvanizing, electropolishing, and vapor deposition. The following sections provide brief overviews of these different processes.

### Cladding

Cladding is a mechanical process in which the metal coating is metallurgically bonded to the workpiece surface by combining heat and pressure. An example of cladding is a quarter. The copper inside is heated and pressed between two sheets of molten nickel alloy, bonding the materials. Cladding is used to deposit a thicker coating than electroplating, and requires less preparation and emits less waste. However, equipment costs are higher than electroplating (Freeman 1995).

### Case Hardening

Case hardening is a metallurgical process that modifies the surface of a metal. The process produces a hard surface (case) over a metal core that remains relatively soft. The case is wear-resistant and durable, while the core is left strong and pliable. In case hardening, a metal is heated and molded and then the temperature is quickly dropped to quench the workpiece. An example of a material made with case hardening is the Samurai sword. The hardened surface can be easily shaped, however, the sword remains pliable. This method has low waste generation and requires a low degree of preparation. Operating difficulty and equipment cost are approximately the same as for anodizing, although case hardening imparts improved toughness and wear (Freeman 1995).

Case hardening methodologies include carburizing, nitriding, micro-casing, and hardening using localized heating and quenching operations. Carburizing, the most widely used case hardening operation, involves diffusion of carbon into a steel surface at temperatures of 845 to 955 degrees Celsius, producing a hard case coating. Nitriding processes diffuse nascent nitrogen into a steel surface to produce case hardening. Nitriding uses either a nitrogenous gas, usually ammonia, or a liquid salt bath (typically consisting of 60 to 70 percent sodium salts, mainly sodium cyanide, and 30 to 40 percent potassium salts, mainly potassium cyanide). Carbon nitriding and cyaniding involves the diffusion of both carbon and nitrogen simultaneously into a steel surface.

### Dip/Galvanized

Dip/galvanized coatings are applied primarily to iron and steel to protect the base metal from corroding. During the dipping process, the plater immerses the part in a molten bath commonly composed of zinc compounds. The metal part must be free of grease, oil, lubricants, and other surface contaminants prior to the coating process. Operating difficulty and equipment costs are low, which makes dipping an attractive coating process for most industrial applications. However, dipping does not always provide a high quality finish (Freeman 1995).

### Electropolishing

In electropolishing, the metal surface is anodically smoothed in a concentrated acid or alkaline solution. For this process, the parts are made anodic (reverse current), causing a film formation around the part that conforms to the macro-contours of the part. Because the film does not conform to the micro-roughness, the film is thinner over the micro-projections and thicker over the micro-depressions. Resistance to the current flow is lower at the micro-projections, causing a more rapid dissolution. Many different solutions are available for electropolishing depending on the substrate (Ford 1994).

### Metallic Coatings (Vapor Deposition)

Metallic coatings change the surface properties of the workpiece from those of the substrate to that of the metal being applied. This process

allows the workpiece to become a composite material with properties that generally cannot be achieved by either material alone. The coating's function is usually as a durable, corrosion-resistant protective layer, while the core material provides a load-bearing function. Common coating materials include aluminum, coated lead, tin, zinc, and combinations of these metals.

Metallic coatings often are referred to as diffusion coatings because the base metal is brought into contact with the coating metal at elevated temperatures, allowing the two materials to interlace. These systems include various metallic spraying applications, cladding (application using mechanical techniques), hot dipping, vapor deposition, and vacuum coating. The main application for spray diffusion coatings is workpieces that are difficult to coat by other means because of their size, shape, or susceptibility to damage at high temperatures. Cladding uses a layer of metal that can be bonded to the workpiece using high-pressure welding or casting techniques. In some applications, cladding can be used as an alternative to plating. Hot dipping is another diffusion process that involves partial or complete immersion of the workpiece in a molten metal bath. The facility applies the coating metal in a powdered form at high temperatures (800 to 1,100 degrees Celsius) in a mixture with inert particles such as alumina or sand, and a halide activator. Vapor deposition and vacuum coating produce high-quality pure metallic layers, and can sometimes be used in place of plating processes (EPA 1995b).

## The Finishing Process

In general, objects to be finished undergo three stages of processing, each of which involves moving the workpiece through a series of baths

containing chemicals designed to complete certain steps in the process. The following list illustrates each of the three basic finishing stages and the steps typically associated with them:

- ◆ **Surface preparation:** Platers clean the surface of the workpiece to remove greases, soils, oxides, and other materials in preparation for application of the surface treatment. The operator typically uses detergents, solvents, caustics, and other media first in this stage and then rinses the workpiece. Next, an acid dip is used to remove oxides from the workpiece, which is then rinsed. The part is now ready to have the treatment applied. Figure 3 shows the steps in the process of preparing a metal part/product for electroplating.
- ◆ **Surface treatment:** This stage involves the actual modification of the workpiece surface including plating. The actual finishing process includes a series of baths and rinses to achieve the desired finish. For example, a common three-step plating system is copper-nickel-chrome. The copper is plated first to improve the adhesion of the nickel to the steel substrate and the final layer, chrome, provides additional corrosion and tarnish protection. Following the application of each of the plate layers, workpieces are rinsed to remove the process solution. The final step in the process is drying. This step can consist of simple air drying or a more complex system such as forced air evaporation or spin dry. Figure 4 presents an overview of the metal finishing process.
- ◆ **Post treatment:** The workpiece, having been plated, is rinsed and further finishing operations can follow. These processes are

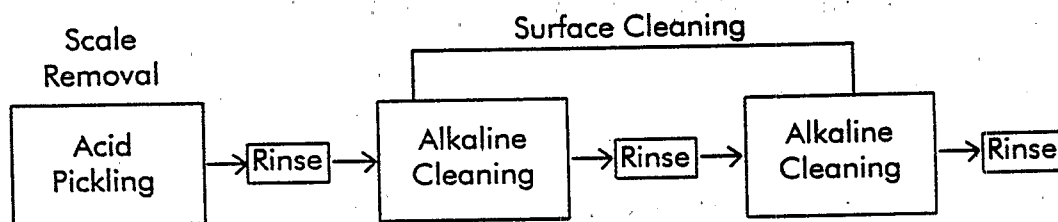


Figure 3. Process for Surface Preparation for Electroplating (EPA 1995a)



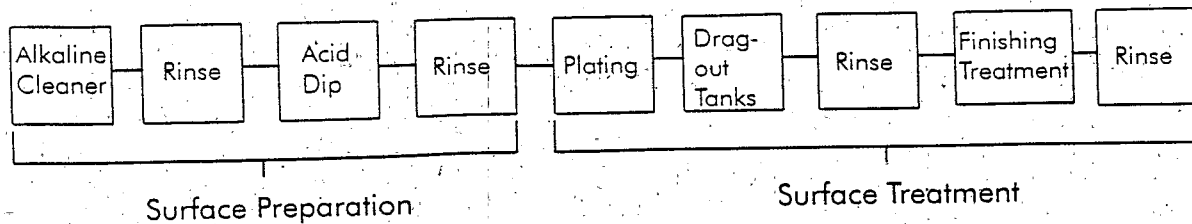


Figure 4. Overview of the Metal Finishing Process (EPA 1994)

used to enhance the appearance or add to the properties of the workpiece. A common example of a post-treatment process is heat treating to relieve hydrogen embrittlement or stress. Chromate conversion is another post-treatment process that often follows zinc or cadmium plating to increase corrosion resistance (EPA 1995b).

In each of these stages, opportunities for pollution prevention exist. Chapters 5-8 provide information on specific techniques/technologies. For an overview of pollution prevention opportunities, refer to Figure 5 and Table 1 on the following pages. The two figures provide an overview of the different pollution prevention techniques/technologies that metal finishers can use and their place on the waste management hierarchy. Table 1 presents more detailed information on specific waste reduction techniques and an overview of the applications and limitations of each. The information provided in this table is consistent with the United States Environmental Protection Agency's (EPA) environmental protection hierarchy and their definition of pollution prevention.

EPA defines pollution prevention as any practice which reduces the amount of any hazardous substance, pollutant, or contaminant entering the wastestream or otherwise released to the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and reduces the hazards to public health and the environment. Pollution prevention practices can include changes in the design, inputs, production, and delivery of a product including:

- ◆ Raw material substitution: Switching raw materials to use less hazardous materials

- ◆ Process modification: Changing the production process to improve efficiency and reduce the use of toxic substances
- ◆ Equipment upgrade: Installing more efficient equipment to reduce raw material consumption and produce less waste
- ◆ Product redesign: Reducing certain raw materials in products and packaging or improving manufacturability

What we call pollution prevention often can be called something else in another profession. For instance:

- ◆ Accountants call it loss control
- ◆ Process engineers call it an efficient process
- ◆ Managers call it total quality management
- ◆ People unaccustomed to long definitions call it common sense

Many waste minimization options, including process recovery and reuse as well as improved operating procedures, represent significant opportunities for waste reduction with relatively low investment costs. Similarly, such options as product replacement can represent the ultimate pollution prevention solution, however, the implementation of these options is largely driven by consumer preference and not favored by the industry (EPA 1995b).

Often, technical assistance providers can have greater success in getting companies to implement pollution prevention if they understand the nature of the industry. The following sections

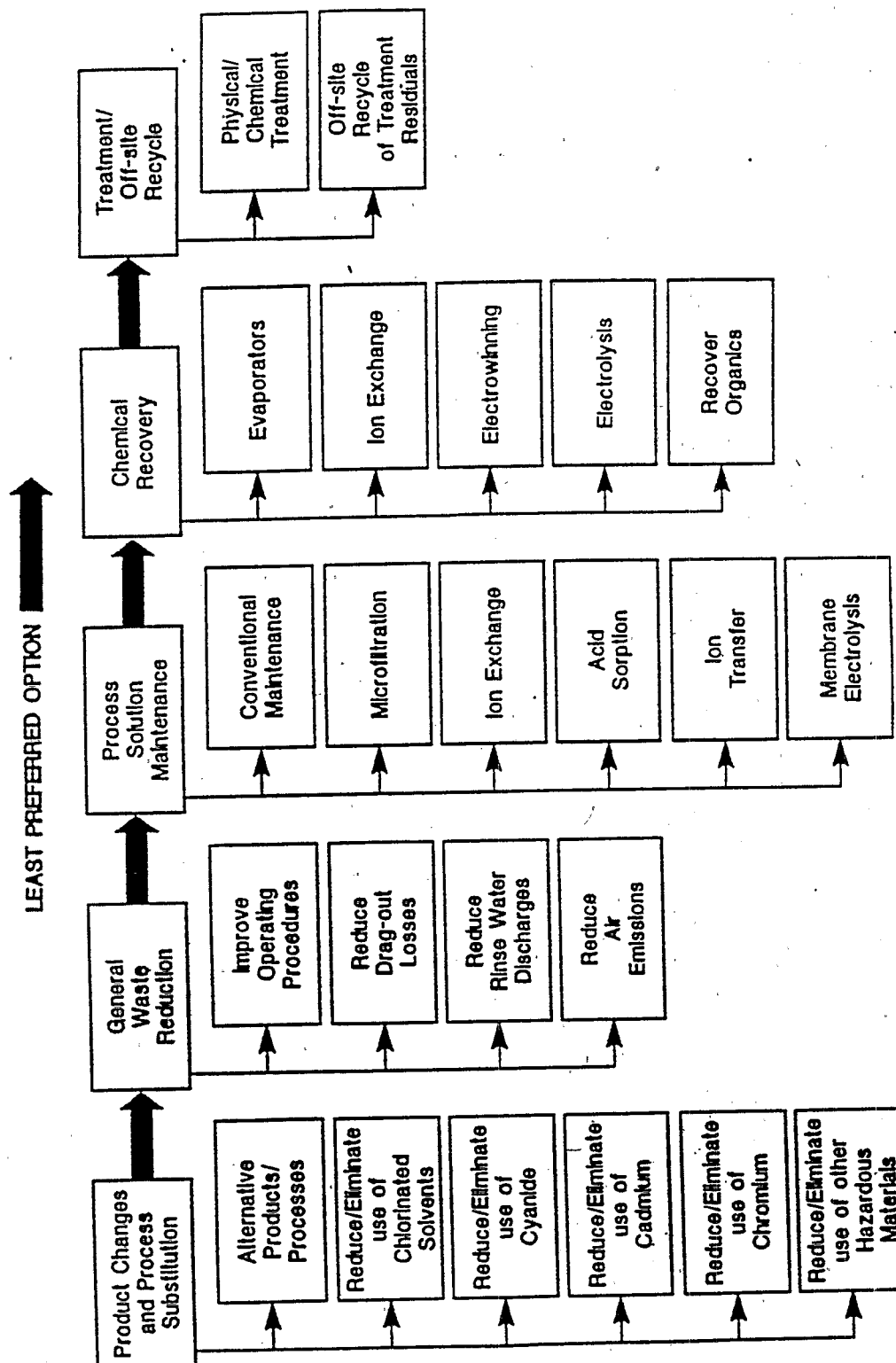


Figure 5. Waste Minimization/Pollution Prevention Methods and Technologies (EPA 1995b)

Table 1. Waste Minimization Options for Metal Plating Operations (EPA 1995b)

<b>Category of Waste Minimization Option</b>	<b>Examples</b>	<b>Applications</b>	<b>Limitations</b>
<b>General Waste Reduction Practices</b>	<p>Improved operating procedures</p> <p>Dragout reduction</p> <p>Rinsewater use reduction</p> <p>Air emissions reduction</p>	<p>Applicable to all conventional plating operations</p> <p>Should be considered standard operating practice</p> <p>Cost benefit typically outweighs any necessary expenditures</p>	<p>Existing facilities might not be able to accommodate changes because of process configuration and/or space constraints</p>
<b>Alternative Processes</b>	<p>Thermal spray coatings:</p> <ul style="list-style-type: none"> <li>◆ Combustion torch</li> <li>◆ Electric arc</li> <li>◆ Plasma sprays</li> </ul> <p>Vapor deposition:</p> <ul style="list-style-type: none"> <li>◆ Ion plating</li> <li>◆ Ion implantation</li> <li>◆ Sputtering and sputterion deposition</li> <li>◆ Laser surface alloying</li> </ul> <p>Chemical vapor deposition</p>	<p>Primarily repair operations although they are now being incorporated into original manufacturing</p> <p>Primarily high-technology applications that can bear extra costs</p> <p>Expected to improve product quality and durability</p>	<p>Technologies in varying states of development; commercial availability might be limited in certain cases</p> <p>Expense often limits applications to expensive parts (e.g., aerospace, military, and electronics)</p> <p>Might require improved process controls, employee training, and automation</p>
<b>Process Substitution</b>	<p>Product changes</p> <p>Input changes that eliminate toxic materials including:</p> <ul style="list-style-type: none"> <li>◆ Cyanide</li> <li>◆ Cadmium</li> <li>◆ Chromium</li> </ul>	<p>Applicable to most conventional plating operations</p> <p>Captive shops/manufacturers might be able to explore product changes</p>	<p>Job shops have little control over input decisions</p> <p>Product changes might need to be evaluated in terms of customer preference</p> <p>Product specifications might eliminate consideration of some process substitutes</p>

Table 1. Continued

<b>Category of Waste Minimization Option</b>	<b>Examples</b>	<b>Applications</b>	<b>Limitations</b>
<b>Process Solution Maintenance</b>	<p>Conventional maintenance methods</p> <p>Advanced maintenance methods:</p> <ul style="list-style-type: none"> <li>◆ Microfiltration</li> <li>◆ Ion exchange</li> <li>◆ Acid sorption</li> <li>◆ Ion transfer</li> <li>◆ Membrane electrolysis</li> <li>◆ Process monitoring and control</li> </ul>	Conventional methods applicable to all plating operations	<p>Advanced methods might require significant changes in process design, operation, and chemistry</p> <p>Application limited for some plating process/technology combinations (e.g., microfiltration should not be used for copper or aluminum)</p>
<b>Chemical Recovery Technologies</b>	<p>Evaporation</p> <p>Ion exchange</p> <p>Electrowinning</p> <p>Electrodialysis</p> <p>Reverse osmosis</p>	Requires significant engineering, planning, and characterization of process chemistry	Costs are highly variable for advanced methods
<b>Off-Site Metals Recovery</b>	<p>Filtration</p> <p>Ion exchange</p> <p>Electrowinning</p> <p>Electrodialysis</p> <p>Reverse osmosis</p>	<p>Metal-bearing wastewater treatment sludge</p> <p>Spent solvents</p>	Waste materials must be acceptable to recyclers

provide background on metal finishing, demographics, characterization, and motivations to assist in gaining that understanding.

## Metal Finishing Demographics

There are an estimated 3,500 independently owned metal finishing shops, mostly small operations with limited capital and personnel (EPA 1994). A typical job shop is a small single establishment that employs 15 to 20 people, receives their workpieces from an outside source, and generates \$800,000 to \$1 million in annual gross revenues. Between 1982 and 1987, the number of smaller shops declined, while the number of larger metal finishers increased. This development appears to signal a trend toward smaller shops closing down and medium and larger shops incrementally increasing in number (EPA 1995a). Overall, however, there has been a sharp decline in the number of job shops in the United States. Moreover, there are an estimated 10,000 captive finishing operations in the United States that are not listed under SIC 3471.

Although geographically diverse, the metal finishing industry is concentrated in what are usually considered the heavily industrialized regions of the United States: the Northeast, Midwest, and California. This geographic concentration has occurred in part because small plating facilities locate near their customer base to be cost effective (EPA 1995a).

## Characterization of the Metal Finishing Industry

In describing the industry, EPA sometimes groups metal finishers into four categories or tiers with regard to their environmental performance. These groups each face different drivers and barriers in their environmental performance. The list below characterizes these categories and their most significant challenges. These challenges can affect a company's decision-making process. Understanding the various types of firms can help technical assistance providers determine the most effective way for different platers to implement pollution prevention.

- ◆ Tier 1: EPA characterizes Tier 1 companies as environmentally proactive firms that are actively pursuing and investing in strategic environmental management projects. These firms are in compliance with environmental regulations and are actively pursuing and investing capital in continuous improvement projects that go beyond compliance.
- ◆ Tier 2A: These are firms that EPA characterizes as consistently in compliance, but do not or cannot look for opportunities to improve environmental performance beyond that level.
- ◆ Tier 2B: EPA characterizes these firms as those that would like to be in compliance but are not able to do so.
- ◆ Tier 3: EPA characterizes Tier 3 metal finishing firms as companies that are older and want to close operations, but stay in operation because they fear the liability and legal consequences of shutting down.
- ◆ Tier 4: EPA characterizes Tier 4 metal finishing shops as shops that are out of compliance or "outlaw" firms that are not substantial competitors but pull down the reputation of the industry; they have little or no interest in complying with environmental regulations (EPA 1994).

Some metal finishers (Tier 3 and some Tier 4 firms) might have a perverse incentive to operate, even in the face of disappearing profits, because of the potentially high environmental cleanup costs associated with shutting down and liquidating. These facilities, although operational, are not making any additional capital investments to improve environmental performance. Because they lack internal capital and cannot secure external financing to fund cleanups, these firms continue to perform poorly and represent a significant barrier to entry for more efficient firms that might have higher short-term costs (EPA 1994).

## Motivations for Implementing Pollution Prevention

Assistance providers can use a number of pollution prevention motivators in discussions with company personnel. Using the information provided in the previous section, combined with the proper motivators, can help assistance providers develop successful strategies to sell pollution prevention to the facility management. Drivers for metal finishers seem to depend on the tier in which they are classified. The following list contains the drivers for different tiers:

- ◆ Tier 1: Top firms are driven by recognition and pride in industry performance. They see the economic payoffs of strategic environmental investments and contend that flexibility in compliance would promote innovative approaches and increase their willingness to help other firms.
- ◆ Tier 2: Regulatory compliance is a strong driver for this large middle tier. Barriers to proactive performance include a lack of capital and information, a lack of positive reinforcement, and an uneven enforcement playing field. Some job shops in this tier depend on suppliers for ingredients and process recipes that restrict their willingness and/or ability to undertake environmental improvement activities.
- ◆ Tier 3: These are generally older, outdated shops that have a strong fear of liability and little ability to improve because they lack capital, information, and skills to do so. Some of these firms might want to go out of business but, because of environmental and financial liability concerns, they remain open. The firms in Tiers 1 and 2 might have an incentive to help close down these firms rather than to help raise them to a higher tier.
- ◆ Tier 4: These firms flagrantly disregard compliance requirements and have no incentive to improve their operations because they gain no competitive advantage. They

do not fear enforcement because they are difficult to track down. They operate without permits and do not report discharges. They profit by having a lower cost structure that undercuts the higher tier firms.

The barriers that generally apply to some or all of the tiers are:

- ◆ Regulatory compliance and/or enforcement actions: Many job shops lack the personnel and capital resources to move beyond compliance. Liability concerns are a barrier to obtaining loans for capital improvements.
- ◆ Development of safer products: Metal finishers, while possessing much understanding of the processes they use, rely heavily on chemical suppliers to optimize existing processes and to investigate new solutions. In some cases, suppliers might be reluctant to suggest environmentally proactive processes or product changes because these could mean lower product sales in the short term.
- ◆ Uncertainty about future regulatory activity: Inconsistency in existing regulatory requirements/enforcement actions at the federal, state, and local level creates, at least, uncertainty and, at worst, competitive imbalances throughout the industry. This climate generates distrust of EPA and state programs and can inhibit meaningful communication.
- ◆ Military and customer specifications: Some customers, especially those in the military, continue to require the use, at least indirectly, of environmentally harmful products and processes even when safer substitutes or processes are available.
- ◆ Lack of awareness of changes in product/process technology: Lower-tier firms often lack any incentive to change because existing liabilities can continue to overwhelm their ability to pay for remediation (Haveman 1995).

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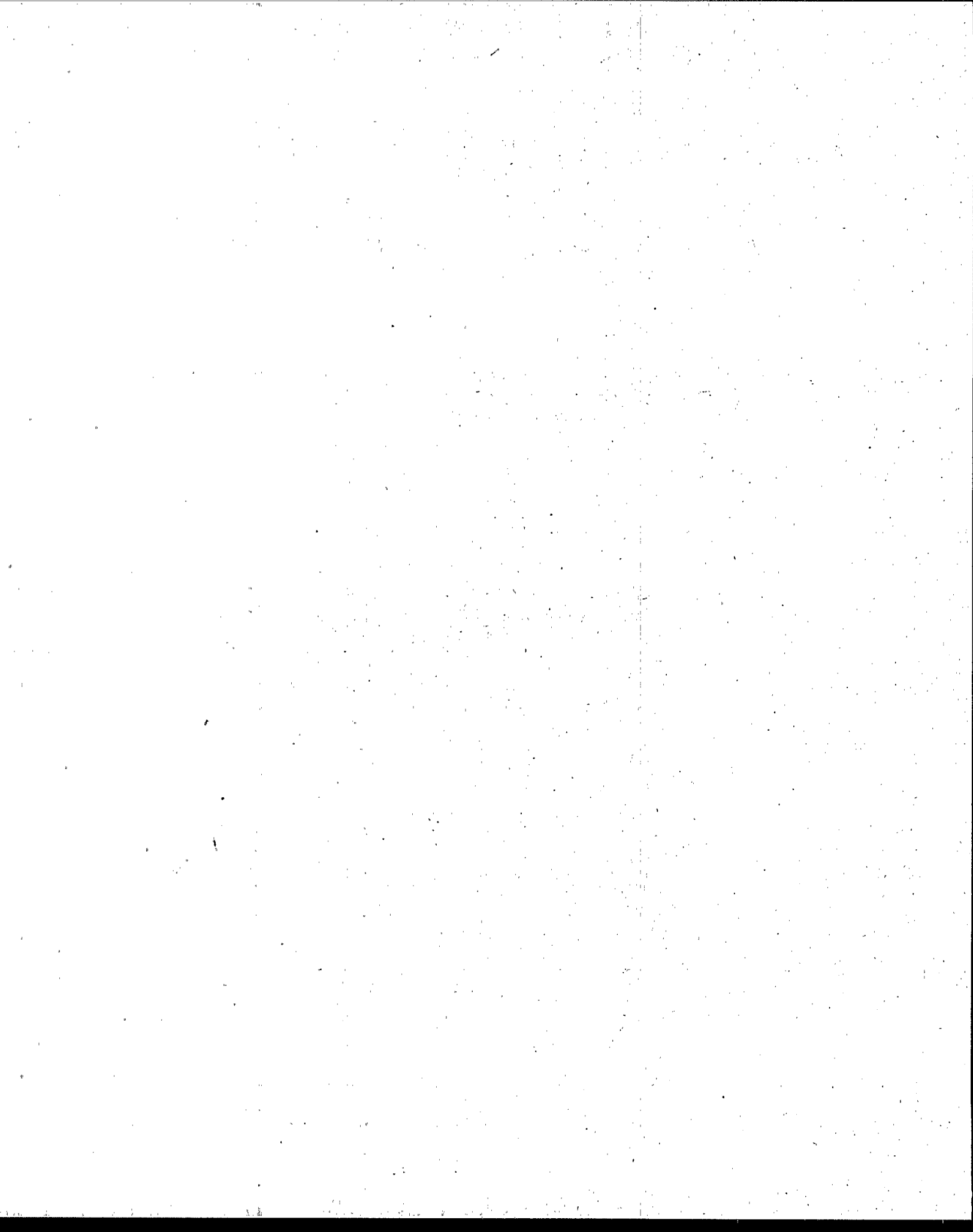
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# 2 Regulatory Overview

To varying degrees, all metal finishing processes tend to have pollution problems and to generate hazardous and solid wastes. Unlike other manufacturing operations, the vast majority of chemicals that platers use end up as waste. Of particular concern are those processes that use highly toxic or carcinogenic ingredients that are difficult to destroy or stabilize. Some of these processes are:

- ◆ Cadmium plating
- ◆ Cyanide-based plating including zinc, cadmium, copper, brass, bronze, and silver plating
- ◆ Chromium plating and conversion coatings using hexavalent chromium compounds
- ◆ Lead and lead-tin plating

## Common Wastes from Metal Finishing Operations

The metal finishing process often produces undesirable byproducts or wastes including air emissions, wastewater, and hazardous and solid wastes. These wastes predominately result from organic halogenated solvents, ketones, aromatic hydrocarbons, and acids used during the surface preparation stage of the process and from metals (primarily present in the form of dissolved salts in the plating baths) used during the surface treatment stage. Cyanide, used in many plating baths, is also a pollutant of concern. This chapter provides an overview of wastes generated from the various processes found in a metal finishing facility. Table 2 provides a summary of these pollutants and their sources.

### Wastewater

The rinsing process is the primary source of waste generated in metal finishing operations. Rinsing removes plating solutions or cleaners from the workpiece. Rinsewaters often contain

low concentrations of process chemicals carried by the workpiece into the rinse (also known as dragout).

Sources of wastewater that are typically treated on site include:

- ◆ Cleaning rinsewater
- ◆ Plating rinsewater
- ◆ Tumbling and burnishing rinsewater
- ◆ Exhaust scrubber solution

Wastewater that is typically regulated but not treated includes:

- ◆ Non-contact cooling water
- ◆ Steam condensate
- ◆ Boiler blowdown
- ◆ Stormwater

To meet air emission regulations, vapors and mists, which are emitted from process baths, are controlled by exhaust systems equipped with mist collection and scrubbing systems. This treatment process generally produces a metal hydroxide sludge that must be managed as a hazardous material. Once treated, wastewaters are discharged to a sewer authority or to a body of water (EPA 1995b).

### Solid and Hazardous Waste

Metal finishers periodically discharge process baths when they lose their effectiveness because of chemical depletion or contamination. Accidental discharges of these chemicals also can occur (e.g., when a tank is overfilled). These concentrated wastes are either treated on site or hauled to an off-site treatment or recovery facility. In general, the sources of hazardous and solid wastes at a plating shop include:

- ◆ Spent plating baths
- ◆ Spent etchants and cleaners

Table 2. Process Inputs and Pollution Generated (EPA 1995b)

Process	Material Input	Air Emission	Process Wastewater	Solid Waste
<b>Surface Preparation</b>				
<b>Solvent Degreasing and Emulsion Alkaline and Acid Cleaning</b>	Solvents Emulsifying agents Alkalis Acids	Solvents (associated with solvent degreasing and emulsion cleaning only) Caustic mists	Solvent Alkaline Acid wastes	Ignitable Wastes Solvent wastes Still bottoms
<b>Surface Finishing</b>				
<b>Anodizing</b>	Acids	Metal ion-bearing mists Acid mists	Acid wastes	Spent solutions Wastewater treatment sludges Base metals
<b>Chemical Conversion Coatings</b>	Dilute metals Dilute acids	Metal ion-bearing mists Acid mists	Metal salts Acid Base wastes	Spent solutions Wastewater treatment sludges Base metals
<b>Electroplating</b>	Acid/alkaline solutions Heavy metal-bearing solutions Cyanide-bearing solutions	Metal ion-bearing mists Acid mists	Acid/alkaline Cyanide Metal wastes	Metal Reactive wastes
<b>Plating</b>	Metals (e.g., salts) Complexing agents Alkalis	Metal ion-bearing mists	Cyanide Metal wastes	Cyanide Metal wastes
<b>Other Metal Finishing Techniques (including polishing, hot dip coating, and etching)</b>		Metal fumes Acid fumes Particulates	Metal Acid wastes	Polishing sludges Hot dip tank dross Etching sludges Scrubber residues

- ◆ Strip and pickle baths
- ◆ Exhaust scrubber solutions
- ◆ Industrial wastewater treatment sludge, which can contain materials such as cadmium, copper, chromium, nickel, tin, and zinc
- ◆ Miscellaneous solid wastes such as absorbants, filters, empty containers, aisle grates, and abrasive blasting residue
- ◆ Solvents used for degreasing

Spills, if they occur, can contribute significantly to the volume of waste. Samples of plating chemicals, which are provided by vendors but not intended for manufacturing use, also can contribute to the amount of waste that a metal finisher generates. Outdated chemicals are another example of wastes that platers and others typically do not attribute to the production process. These samples and obsolete or expired materials often accumulate and can violate waste storage requirements. These wastes eventually must be returned to the supplier or disposed of appropriately (EPA 1995b).

## Air Emissions

There are several air emission sources at a metal finishing facility. Those of greatest environmental concern are chrome plating and anodizing processes that use hexavalent chromium and solvents from vapor degreasing. Chromium emissions frequently are controlled by wet scrubbers. The discharge of these systems is sent to wastewater treatment and combined with other wastewaters for processing.

Solvents evaporate substantially during degreasing operations. Contaminated liquid solvents are recovered either by distillation (on site or off site) or sent for disposal (incineration). Most shops do not have controls for organics. However, some larger plants use carbon adsorption units to remove hydrocarbons (EPA 1995b).

Metal finishing results in a variety of hazardous compounds that are released to the land, air, and water. As a result, facilities are required to comply with numerous regulations. Regulations for metal finishers are promulgated at the federal, state, and local level. The requirements are complex and can vary, not only from state to state, but also from municipality to municipality.

## Overview of Federal Regulations Affecting Metal Finishing

The metal finishing industry has made extensive progress in improving operations in recent years as environmental regulations regarding discharges have become more stringent. However, in the future, platers will need to meet new standards that require further reductions in the amount and types of wastes that they discharge. Increased costs for materials and discharges will continue to cut profit margins and force businesses to search for new ways to reduce these costs.

The metal finishing industry is regulated under numerous federal, state, and local environmental statutes. Three major federal laws regulate releases and transfers from the metal finishing industry: the Clean Air Act as amended in 1990 (CAAA), the Clean Water Act (CWA), and the

Resource Conservation and Recovery Act (RCRA). Also, the emissions reporting requirements under EPA's Toxics Release Inventory (TRI) cover many of the chemicals used in metal finishing. Table 3 presents an overview of the federal regulations affecting the metal finishing industry.

Environmental assistance providers should consult with state and local regulatory authorities to identify specific requirements that might be more stringent than those promulgated under federal law. A myriad of state and local laws pertain to metal finishers, and helping them to understand all of these regulations can be an important aspect of providing assistance. This manual does not provide specific information on state and local regulations because of the lack of consistency across state and local programs.

## Clean Air Act

With the enactment of the Clean Air Act Amendments, air emissions have become a greater concern for metal finishers. Any metal finishing operation with processes that could emit Hazardous Air Pollutants (HAPs) or volatile organic compounds (VOCs), as defined in the CAAA, could be required to obtain an operating permit and/or comply with other regulatory requirements for those processes. Regulations covering the use of halogenated solvents, a common material in most metal finishing operations, will directly affect most companies. Facilities that have processes which emit airborne metals, particularly chromium, are also going to be subject to increasing requirements (Haveman 1995).

## Hazardous Air Pollutants

The Clean Air Act Amendments of 1990 established a list of 189 hazardous air pollutants. Of the 56 SIC 3471 substances reported in the TRI database for 1990, 33 are included on the list of HAPs. Under the CAAA, Congress required EPA to identify major and area source categories associated with the emissions of one or more listed HAPs. To date, EPA has identified 174 categories. Congress also required EPA to promulgate emissions standards for listed source categories within 10 years of the enactment of the CAAA (November 15, 2000). These stan-

dards are called the National Emission Standards for Hazardous Air Pollutants (NESHAPs).

The standards will require regulated metal finishers to apply Maximum Achievable Control Technology (MACT) to all new sources of HAPs, while existing sources could be in compliance using less strict control measures. The MACT determination process is quite complicated. Put simply, it is the lowest emission rate or highest level of control demonstrated on average by the top performing companies (top 12 percent) in the source category. MACT determination is subject to negotiation among industry, environmental groups, and EPA (Haveman 1995). State environmental agencies will determine exactly which businesses are subject to the permit requirement as part of their State Implementation Plans (SIPs).

Currently, EPA is finalizing three NESHAPs (Chromium Electroplating, Solvent Degreasing, and Steel Pickling) that will directly affect the metal finishing industry (EPA 1995a). A summary of these three NESHAPs follows.

#### **NESHAP: Chromium Electroplating**

These standards limit the air emissions of chromium compounds in an effort to protect public health. The promulgated regulation will be a MACT performance standard that will set limits on chromium and chromium compounds emissions based upon concentrations (e.g., mg of chromium/m<sup>3</sup> of air).

The chromium electroplating process emits a chromic acid mist in the form of hexavalent chromium (Cr+6) and small amounts of trivalent chromium (Cr+3). Human health studies suggest that acute, intermediate, and chronic exposure to hexavalent chromium results in various adverse effects. EPA has developed a NESHAP for chromium emissions for hard and decorative chromium electroplating and chromium anodizing tanks. There is not one standard emission limit. The proposed emission standards differ according to the sources (e.g., old sources of chromium emissions will have different standards than new ones). EPA argues that these proposed performance standards allow facilities a degree of flexibility because they recognize a

difference in facilities and allow facilities to choose any technology that meets the emission standards established by the MACT (EPA 1995a).

#### **NESHAP: Organic Solvent Degreasing**

EPA also has promulgated a NESHAP for the halogenated solvent degreasing/cleaning source category that will directly affect the metal finishing industry. EPA has designed this standard to reduce halogenated solvent emissions based on MACT. The standard will apply to new and existing organic halogenated solvent cleaners (degreasers) that use any of the HAPs listed in the CAAA. Specifically, EPA is targeting vapor degreasers that use the following HAPs: methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and chloroform (EPA 1995a).

This NESHAP sets two standards. Facilities can meet these standards in a variety of ways. The MACT-based equipment and work practice compliance standard requires a facility to use a designated type of pollution prevention technology along with proper operating procedures. Existing operations that use a performance-based standard can continue to do so if they can achieve the same level of control as the equipment and work practice compliance standard (EPA 1995a).

#### **NESHAP: Steel Pickling, HCL**

EPA has identified steel pickling processes that use hydrochloric acid (HCL) and HCL regeneration processes as potentially significant sources of HCL and chlorine emissions. Hydrochloric acid and chlorine are among the pollutants listed as HAPs in Section 112 of the CAAA. EPA has drafted a presumptive MACT standard for these processes, which is currently under review. This standard is slated for promulgation by November 15, 1997, however, it might be delayed (EPA 1995a).

#### **Volatile Organic Compounds**

In effort to control smog, the CAAA required EPA to develop standards on the following substances:

- ◆ Inhalable particulates (PM-10)

- ◆ Nitrogen oxides (NO<sub>x</sub>)
- ◆ Ozone
- ◆ Sulfur oxides (SO<sub>x</sub>)
- ◆ Lead
- ◆ Carbon monoxide

The standard of interest to metal finishers is ozone. Ground level ozone results from the reaction of VOCs with nitrogen oxides. Many of the substances used in solvent cleaning and degreasing, as well as stripping, are VOCs. The extent to which a small source of VOCs will be regulated depends upon the air quality in the region in which the source is located. Basically, if a source is located in an "attainment" area (in compliance with the National Ambient Air Quality Standards (NAAQS)), it will be required to obtain a permit if its potential to emit is greater than 100 tons of VOCs per year. Special provisions for attainment areas have been made for sources located in the Northeast and Mid-Atlantic states. Facilities located in an attainment area will be subject to a permit if they have the potential to emit 50 tons of VOCs per year (Haveman 1995).

For those facilities located in non-attainment areas, the regulatory thresholds are much lower. How much lower depends on the degree of non-compliance with the NAAQs in that region. EPA classifies non-attainment areas into five types: marginal, moderate, serious, severe, and extreme. As air problems increase, the likelihood that a small source of VOCs will be required to obtain a permit will increase.

## Clean Water Act

The Clean Water Act regulates the amount of chemicals/toxics released via direct and indirect wastewater/effluent discharges. EPA has promulgated effluent guidelines and standards for different industries under the CWA provisions. These standards usually set concentration-based limits for the discharge of a given chemical. EPA defines two types of discharges: direct and indirect. Both types have different requirements.

## Direct Dischargers

A facility that is discharging directly into a body of water is regulated under the National Pollution Discharge Elimination System (NPDES) and must apply for a NPDES permit. The permit specifies what type of pollutants can be discharged and includes a schedule for compliance, reporting, and monitoring. The NPDES regulation limits the amount of metals, cyanides, and total toxic organics that a facility can discharge. These limitations remain the same whether the facility is discharging to a body of water or to a treatment facility (Haveman 1995).

## Indirect Dischargers

Most metal finishing facilities discharge their wastewater to publicly-owned treatment works (POTWs). These indirect dischargers must adhere to specified pretreatment standards because the POTWs are designed to deal mainly with domestic sewage, not industrial discharges. Often, specific state or local water regulations require more stringent treatment or pretreatment requirements than those in the federal effluent guidelines because of local water quality issues (Haveman 1995). All facilities discharging to a POTW are governed by the General Pretreatment Standards. These standards state that discharges must have a pH greater than 5.0 and cannot:

- ◆ Create fire or explosion
- ◆ Obstruct the flow of wastewater through the system
- ◆ Interfere with sewage plant operations
- ◆ Contain excessive heat
- ◆ Contain excessive petroleum, mineral, or non-biodegradable oils

In addition, two CWA regulations affect the metal finishing industry: the Effluent Guidelines and Standards for Metal Finishing (40 CFR Part 433) and the Effluent Guidelines and Standards for Electroplating (40 CFR Part 413) (Haveman 1995). Companies regulated by the electroplating standards before the metal finishing standards were promulgated become subject to the more stringent metal finishing standards when they make modifications to their facility's

Table 3. Overview of Federal Regulations Affecting the Metal Finishing Industry (EPA 1995a)

Program	Application to Metal Finishing	Implications
<b>Clean Air Act</b>	<p>EPA required to regulate 189 air toxics. Also has authority to require pollution prevention measures (installation of control equipment, process changes, substitution of materials, changes in work practices, and operator certification training). Industries addressed include metal finishers.</p> <p>Requires phase-out of the production of chloro-fluorocarbons (CFCs) and several other ozone-depleting chemicals. Imposes controls on CFC-containing products.</p> <p>New sources located in non-attainment areas must use most stringent controls and emissions offsets that compensate for residual emissions.</p>	<p>Air toxics regulation increases cost of controlling numerous air emissions produced by metal finishers, increasing incentives for waste reduction.</p> <p>Restriction on CFCs limit some chemicals used by metal finishers and force use of alternatives including aqueous and semi-aqueous degreasers.</p> <p>Offsets can be achieved through pollution prevention.</p>
<b>Clean Water Act</b>	<p>Imposes technology-based effluent limits on pollutants for specific industries. Standards can require in-plant water treatment systems.</p>	<p>Effluent limits raise cost of treatment and disposal, creating financial incentives for source reduction.</p> <p>In-house controls provide process/procedural modifications that achieve waste reduction.</p>
<b>Emergency Planning and Community Right-to-Know</b>	<p>Requires select industries to report environmental releases of specified toxic chemicals including metal fabricating and other industries that conduct metal finishing.</p>	<p>Reporting requirements have created a strong incentive for reducing waste generation and releases for all industries.</p> <p>Release data have spurred increased industry and public scrutiny of waste generation and manufacturing operations.</p>
<b>Executive Order 12843</b>	<p>Requires federal agencies to implement the Montreal Protocol and the phase-out of ozone-depleting substances including chemicals used by the metal finishing industry.</p>	<p>Requires the phase-out of ozone-depleting chemicals such as 1,1,1-trichloroethane. Forced metal plating operations to identify replacements such as aqueous and semi-aqueous degreasers.</p>
<b>Resource Conservation and Recovery Act</b>	<p>Directly regulates several metal finishing wastes as hazardous wastes.</p> <p>Requires all hazardous waste generators, including metal finishers, to certify that they have a program in place to reduce the volume or quantity and toxicity of the waste they generate.</p>	<p>Rigorous regulatory scheme applicable to metal finishing wastes that are hazardous wastes. Creates strong financial and liability incentives to pursue source reduction.</p>

operating functions (e.g., facility equipment and process modifications). If these companies make no such modifications, they remain subject to the electroplating standards only. All new facilities are subject to the metal finishing standard.

### Metal Finishing Standard

The Effluent Guidelines and Standards for Metal Finishing are applicable to wastewater generated by any of the following processes:

- ◆ Electroplating
- ◆ Electroless plating
- ◆ Anodizing
- ◆ Coating
- ◆ Chemical etching and milling
- ◆ Printed circuit board manufacturing

If a facility performs any of the processes listed above, it is subject to this standard. In addition, discharges from 40 additional processes including cleaning, polishing, shearing, hot dip coating, and solvent degreasing could be subject to this standard.

The metal finishing and electroplating standards include daily maximum and monthly maximum average concentration limitations. The standards, which are based on milligrams per square meter of operation, determine the amount of wastewater pollutants from various operations that can be discharged (EPA 1995b).

### Electroplating Standard

The Effluent Guidelines and Standards for Electroplating cover wastewater discharges from electroplating and related metal finishing operations. This standard was developed prior to the metal finishing standard and has less stringent requirements than the metal finishing standard. Facilities that are currently regulated by the electroplating standard can become subject to the more stringent metal finishing standard if they make modifications to their facility's operations. EPA has made some exceptions to this rule, for example printed circuit board manufacturers (primarily to minimize the economic impact of regulation on these relatively small firms). EPA defines independent printed circuit board manu-

facturers as facilities that manufacture printed circuit boards primarily for sale to other companies. Also excluded from the metal finishing standard are facilities that perform metallic platemaking and gravure cylinder preparation within printing and publishing facilities.

Operations similar to electroplating that are specifically exempted from coverage under the electroplating standards include:

- ◆ Continuous strip electroplating conducted within iron and steel manufacturing facilities
- ◆ Electrowinning and electrefining conducted as part of non-ferrous metal smelting and refining
- ◆ Electrodeposition of active electrode materials, electro-impregnation, and electroforming conducted as part of battery manufacturing
- ◆ Metal surface preparation and conversion coating conducted as part of coil coating
- ◆ Metal surface preparation and immersion plating or electroless plating conducted as part of porcelain enameling
- ◆ Surface treatment including anodizing and conversion coating conducted as part of aluminum forming

Congress is considering reauthorization of the CWA that could change the standards affecting metal finishing operations. In addition to possible congressional changes to the CWA, EPA also is reviewing the Effluent Guidelines and Standards for Electroplaters and Metal Finishers, which were promulgated in the 1970s and amended in the 1980s.

EPA also is developing effluent guidelines and standards for a related industry, the metal products and machinery industry. Phase 1 of these regulations was due in May 1996. These regulations would have set new effluent limits for some metal finishers. However, as a result of comments received, EPA is considering combining Phases 1 and 2 of these regulations and promulgating them in 2 years. Although this standard contains only cleaning and finishing

operations as captive processes, it is likely that EPA might integrate the new regulatory options for metal finishing processes into this guideline. Under this scenario, electroplaters and metal finishers would most likely reference appropriate sections of the Products and Machining Industry Guideline to determine their effluent limits. What is not clear is how this guideline will affect job shop operations, which are not considered part of this industry. If job shops are not included, different requirements could be developed for them.

## Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) of 1976 addresses solid (Subtitle D) and hazardous (Subtitle C) waste management activities. Regulations promulgated under

Subtitle C establish a "cradle to grave" system that governs these wastes from point of generation to disposal. A material is classified under RCRA as a hazardous waste if the material meets the definition of solid waste and exhibits one of the characteristics of a hazardous waste (i.e., corrosiveness, flammability, toxicity, or reactivity, designated with the code "D") or if it is specifically listed by EPA as a hazardous waste (designated with the code "F"). Metal finishers generate a variety of hazardous wastes during the plating process. Within RCRA subtitle C, EPA includes hazardous waste from non-specific sources in a series of "F" listings. Table 4 presents the F-listed wastes that might be relevant to the electroplating industry.

The universe of RCRA listed wastes is constantly changing. In some states, the list of specific

Table 4. RCRA Listed Wastes (EPA 1995a)

Listing	Waste Description
F001 F002 F003 F004 F005	Listings F001 through F005 are for halogenated solvents. The listing for a particular site will depend on the type of solvent used.
F006	Wastewater treatment sludges from electroplating operations. This category refers to sludges produced during the treatment of spent plating baths and rinsewaters. Wastewater treatment sludges from specific operations <u>not</u> included in this classification system are: <ul style="list-style-type: none"> <li>•Sulfuric acid anodizing of aluminum</li> <li>•Tin plating or carbon steel</li> <li>•Zinc plating (segregated basis) on carbon steel</li> <li>•Aluminum or zinc-aluminum plating on carbon steel</li> <li>•Cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel</li> <li>•Chemical etching and milling of aluminum.</li> </ul>
F007	Spent cyanide plating bath solutions from electroplating operations.
F008	Sludges and residues from the bottom of plating baths where cyanides are used in the process.
F009	Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.
F011	Spent cyanide solutions from salt bath pot cleaning from metal heat-treating operations.
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum.



wastes might be different because they have added to EPA's list of hazardous chemicals.

A waste can exhibit one or more of the RCRA Subtitle C characteristics but not be listed as a specific waste. Waste generated in electroplating operations that are not specifically listed but might exhibit a RCRA characteristic include:

- ◆ Plating bath sludges (not generated from cyanide baths), which might be toxic because of metal content
- ◆ Alkaline cleaning baths, which might be corrosive because of high pH
- ◆ Rinsewater, which might have a low or high pH depending on the contents of the preceding bath
- ◆ Spent plating baths or cleaning and pickling solutions containing acids, which might be corrosive because of low pH or dissolved metal content (EPA 1994)

To determine what a plater must do to comply with RCRA requirements, the facility first must determine its generator status. Generator status is based upon the amount of waste generated on a monthly basis. The following criteria determine the quantity of waste that is regulated by RCRA:

- ◆ Material remaining in a production process is not counted as waste until it is no longer being used in that process.
- ◆ Waste discharged directly and legally to a POTW in compliance with CWA pretreatment standards is not counted toward RCRA generation total.
- ◆ Any material that is characteristic or listed as a hazardous waste, and is accumulated after its removal from the process before being sent off site for treatment, storage, or disposal, is counted toward RCRA Subtitle C generation total.

In general, there are three classes of generators. Although individual states might have different names for them, EPA classifies them as:

- ◆ Large quantity generators: Facilities that generate more than 1,000 kilograms (2,200

pounds) of hazardous waste per month or that generate or accumulate more than 1 kilogram (2.2 pounds) of acute hazardous waste at one time.

- ◆ Small quantity generators: Facilities that generate between 100 kilograms (220 pounds) and 1,000 kilograms (2,200 pounds) of hazardous waste in any calendar month.
- ◆ Conditionally exempt small quantity generators: Facilities that generate less than 100 kilograms (220 pounds) of hazardous waste per month or that generate less than 1 kilogram (2.2 pounds) of acute hazardous waste in any calendar month.

Each state has varying degrees of regulation for the three generator classes. At a minimum, however, EPA requires each class to comply with the requirements listed in Table 5.

## Toxics Release Inventory Reporting

Metal finishers must publicly report many of the chemicals they use in plating under the federal Toxic Release Inventory (TRI) reporting requirement. Facilities report information on a TRI data form (Form R) for each toxic chemical that is used over the threshold amount. Basic information that is reported in a Form R includes:

- ◆ Facility identification
- ◆ Parent company information
- ◆ Certification by corporate official
- ◆ SIC code
- ◆ Chemical activity and use information
- ◆ Chemical release and transfers
- ◆ Off-site transfer information
- ◆ On-site waste treatment
- ◆ Source reduction and recycling activities

The releases and transfers reported on a Form R include:

- ◆ Emissions of gases or particulates to the air

Table 5: EPA Regulations for the Three Generator Classes

Category	Requirements
<b>Large Quantity Generators</b>	<ul style="list-style-type: none"> <li>◆ Notify the EPA and obtain an EPA ID number</li> <li>◆ Store waste for no more than 90 days</li> <li>◆ Comply with container standards and tank rules</li> <li>◆ Prepare and retain a written Contingency Plan</li> <li>◆ Prepare and retain written training plan including annual training of employees</li> <li>◆ Prepare a written waste minimization plan</li> <li>◆ Dispose of hazardous materials only at a RCRA permitted site</li> <li>◆ Only use transporters with EPA ID numbers</li> <li>◆ Use proper Department of Transportation (DOT) packaging and labeling</li> <li>◆ Use the full Uniform Hazardous Waste Manifest</li> <li>◆ Place a 24 hour emergency number on all manifests</li> <li>◆ Report serious spills or fires to the National Response Center</li> <li>◆ Obtain a DOT registration number for shipments over 5,000 pounds</li> <li>◆ Keep all records for 3 years</li> <li>◆ Make sure that any treatment or recycling done onsite is permitted</li> <li>◆ Report missing shipments in writing</li> <li>◆ Submit biennial reports of hazardous waste activities, including waste minimization</li> </ul>
<b>Small Quantity Generators</b>	<ul style="list-style-type: none"> <li>◆ Notify the USEPA and obtain an EPA ID number</li> <li>◆ Store waste for no more than 180 days (270 days if the waste is shipped more than 200 miles)</li> <li>◆ Comply with container standards and tank rules</li> <li>◆ Dispose of hazardous materials only at a RCRA permitted site</li> <li>◆ Only use transporters with EPA ID numbers</li> <li>◆ Use proper Department of Transportation (DOT) packaging and labeling</li> <li>◆ Use the full Uniform Hazardous Waste Manifest</li> <li>◆ Place a 24 hour emergency number on all manifests</li> <li>◆ Post emergency response telephone numbers near telephones</li> <li>◆ Provide informal employee training</li> <li>◆ Make sure that any treatment or recycling done onsite is permitted</li> <li>◆ Report missing shipments in writing</li> <li>◆ Keep all records for 3 years</li> </ul>
<b>Conditionally Exempt Small Quantity Generators</b>	<ul style="list-style-type: none"> <li>◆ Avoid accumulating more than 1,000 kilograms (2,200 pounds) of hazardous waste onsite at any one time</li> <li>◆ Send waste to a facility that is at least approved to manage municipal or industrial solid waste</li> </ul>

- ◆ Wastewater discharges into rivers, streams, and other bodies of water
- ◆ Releases to land on site including landfill, surface impoundment, land treatment, or other mode of land disposal
- ◆ Disposal of wastes in underground injection wells
- ◆ Transfers of wastewater to POTWs
- ◆ Transfers of wastes to other off-site facilities for treatment, storage, and disposal

A facility must fill out Form R if it:

- ◆ Is included in SIC codes 20 to 39
- ◆ Has 10 or more full-time employees
- ◆ Manufactures, processes, or "otherwise uses" any listed material in quantities equal to or greater than the established threshold for the calendar year

The manufacturing and processing thresholds have dropped over the reporting years from 75,000 pounds in 1987 to 25,000 pounds in 1989. For a chemical "otherwise used," the threshold amount is 10,000 pounds. The following list presents the top 22 chemicals in the TRI database for metal finishing (SIC 3471) from 1987 through 1990 (the list ranks the chemicals in order of decreasing release quantities with national TRI rankings presented in parentheses):

#### Acids

- Sulfuric acid (1)
- Hydrochloric acid (2)
- Nitric acid (7)
- Phosphoric acid (17)

#### Metals

- Nickel compounds (8)
- Zinc compounds (11)
- Chromium compounds (12)
- Zinc (14)
- Nickel (16)
- Copper (20)
- Chromium (22)
- Copper compounds (23)

#### Solvents

- 1,1,1-trichloroethane (3)
- Dichloromethane (methylene chloride) (9)
- Tetrachloroethylene (13)
- Methyl ethyl ketone (15)
- Toluene (9)
- Xylene (21)

#### Cyanide

- Cyanide compounds (24)

#### Other

- Freon 113 (10)

Technical assistance providers can use TRI data to develop an aggregate picture of the releases and transfers from the metal finishing industry.

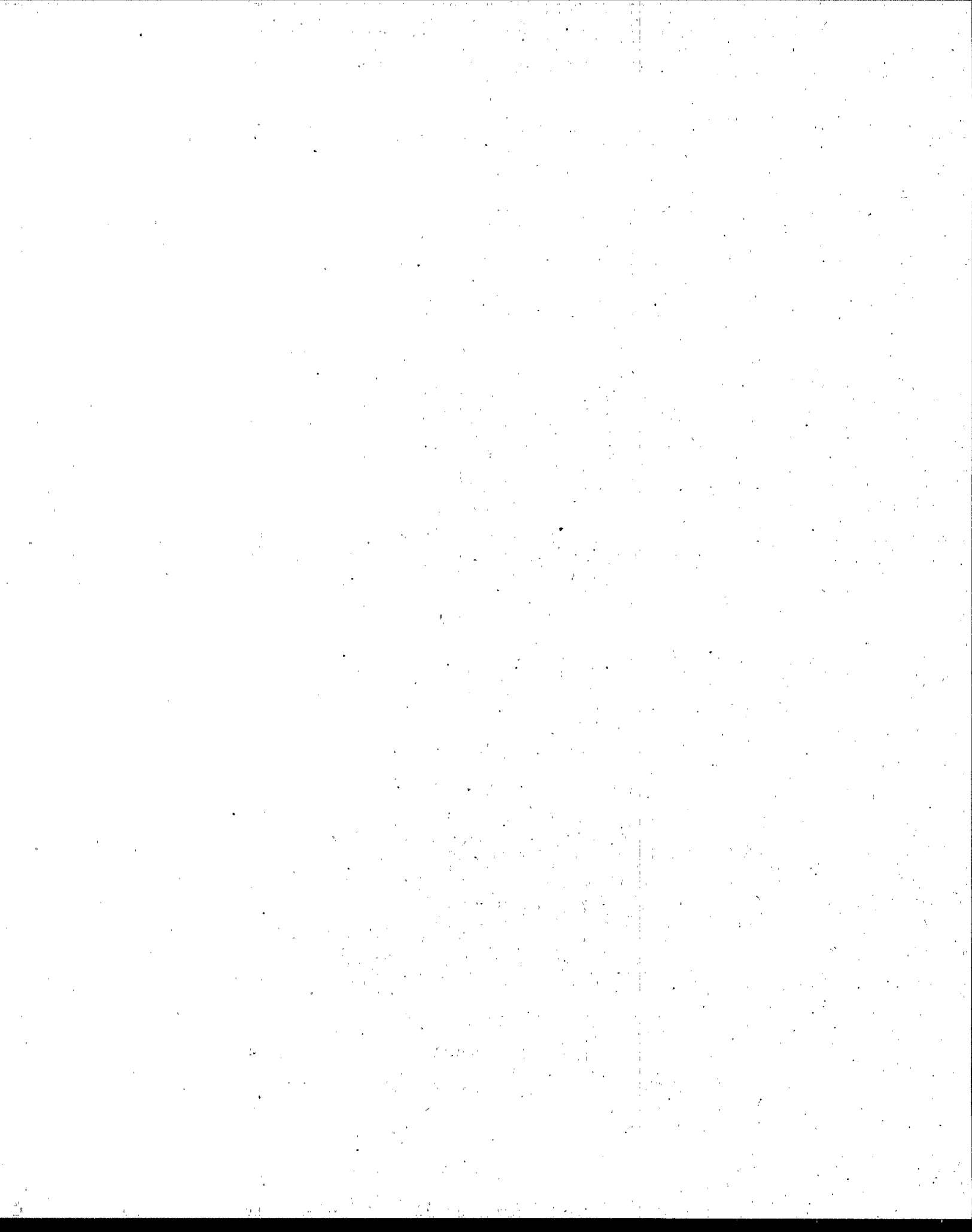
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# 3 Planning Pollution Prevention Programs at a Metal Finishing Facility

How can assistance providers and regulatory compliance staff sell pollution prevention options to a metal finisher? The most important point that an assistance provider can make to a metal finisher is that pollution prevention can help them achieve regulatory compliance while saving money. The savings associated with recapturing and reclaiming precious metals are obvious; the value of the recovered metal in many cases outweighs the cost of reclamation processes. Overall, the benefits associated with pollution prevention include:

- ◆ Reduced operating costs/overhead: These savings result in reduced utility charges, water/sewer fees, wastewater treatment costs, waste disposal expenses, permit discharge fees, analytical monitoring and reporting costs, and increased potential for chemical recovery.
- ◆ Reduced manufacturing costs: Facilities can save money on reduced materials costs (e.g., reduced plating bath solution purchases), water costs, and anode loss.
- ◆ Product quality improvements: Pollution prevention techniques often increase the quality of rinsing, reducing spotting and staining of the workpiece. Often pollution prevention increases the process controls of the plating operation, improving the predictability/performance of process solutions and decreasing reject rates.
- ◆ Environmental risk reduction: Pollution prevention projects can result in reduced non-compliance enforcement actions; environmental and worker health liability; and risk of on-site contamination via spills, releases, and leaks.

A facility potentially can realize other benefits from the implementation of a comprehensive pollution prevention program. Source

reduction can lower insurance costs, protect property values, and improve relationships with financial institutions. Even though pollution prevention has clear economic advantages and the techniques are simple, inexpensive, and time proven, many facilities still do not have significant source reduction programs (Haveman 1995).

## Planning

One of the keys to developing a successful pollution prevention program is planning. Assistance providers can work with facilities to implement planning programs, assist in establishing baseline measures, and identify potential pollution prevention projects. The key steps to starting a pollution prevention program include:

- ◆ Obtaining management support and involvement
- ◆ Establishing an in-house pollution prevention team
- ◆ Getting companywide involvement

## Management Support

The support of company management is essential for developing a lasting and successful pollution prevention program. The level of success that a metal finishing plant can achieve in reducing waste generation appears to depend more on management interest and commitment than on technical and economic feasibility, particularly for source reduction technologies that require process modifications or housekeeping improvements (Noyes 1989).

At the outset of the program, management endorsement is needed to help identify the pollution prevention team and give credence to the planning effort. Throughout the program, company management can support the team by endorsing goals and implementation efforts, communicating the importance of pollution

prevention, and encouraging and rewarding employee commitment and participation in the effort (Dennison 1996).

Some companies see only the barriers they face in implementing a project and use these as excuses for not implementing pollution prevention. Other firms find solutions to overcome obstacles and reap the benefits of a successful pollution prevention project. Technical assistance providers should stress to management that a successful program has a wide range of benefits. These benefits include cost savings as well as reduced liability and enhanced company image. Assistance providers also should inform management that an initial labor cost is incurred in organizing and implementing a pollution prevention program. Using a technical assistance provider can minimize these costs but an up-front resource commitment must still be made. Case studies often can highlight the benefits that other companies have realized from implementing pollution prevention programs.

Providers can help facilitate management support by developing a plan that sells pollution prevention to a company's executives. The presentation on pollution prevention drivers and barriers in Chapter 1 should help users of this manual to find the appropriate basis for selling pollution prevention. Successful management initiatives that have promoted pollution prevention include developing a corporate policy that makes pollution prevention a mandate, incorporating pollution prevention success into performance evaluations, and offering financial incentives for meeting pollution prevention goals or for finding pollution prevention opportunities.

Obviously, each firm is different and, therefore, the assistance provider's approach to each company's leadership should attempt to address their specific interests and priorities as manifested by the corporate culture. Identifying these interests and priorities is a challenge for any assistance team. Many technical assistance programs require active management participation in the assistance process as part of their agreement to conduct an on-site visit. On these visits the teams discuss their priorities and pollution prevention in relation to those

priorities. Technical assistance providers should also stress to management that planning is an ongoing task. Once the initial plan is completed the facility should continue to re-evaluate their facility to identify areas that can be improved (CAMF 1995).

## Establishing the Team

A successful pollution prevention program requires not only support from management, but also input and participation from all levels of the organization. To champion the effort, every pollution prevention program needs an effective pollution prevention coordinator. Assistance providers can identify the team leader and work with them on developing their team and suggesting ways for the facility to implement its pollution prevention program.

The pollution prevention team should include employees who are responsible for planning, designing, implementing, and maintaining the program. A team approach allows these tasks to be distributed among several employees and enables staff from different parts of the company to have input into the planning process. Members of the team are typically responsible for:

- ◆ Working with upper management to set preliminary and long-term goals
- ◆ Gathering and analyzing information relevant to the design and implementation of the program
- ◆ Promoting the program to employees and educating them on how they can participate in the effort
- ◆ Monitoring and reporting to management on the progress of the program (Dennison 1996)

The ideal size of the team depends on the size of the organization. In small companies, the team can consist of one person who wears many hats or the company manager and a technical person. In larger companies, the team might include environmental managers, building supervisors, technical staff, maintenance staff, marketing staff, purchasing staff, and other interested employees (Dennison 1996).

External personnel such as technical assistance providers or consultants can complement the team by providing expertise. These people often can offer auditing expertise as well as knowledge of pollution prevention and environmental laws and regulations. However, external people will be unfamiliar with the facility's operation. Once the team is established, assistance providers and regulatory staff should encourage the facility to take the following steps to properly evaluate the options for reducing pollution:

- ◆ Define and identify the facility's objectives: Clearly identify, quantify, and rank the facility's objectives. For example, at some facilities compliance with effluent limits and quality rinsing are primary concerns while optimized worker efficiency and cost are secondary concerns.
- ◆ Define criteria for evaluating pollution prevention options: Clearly define what constitutes a feasible option. Items to consider beyond technical feasibility include economic feasibility, quality standards, and the effect of the option on the overall process.

## Assessing the Facility

Once the team has defined its objectives and criteria for a pollution prevention program, the next step is to assess the facility. Beyond the facility tour, useful information for the assessment can be obtained from sources such as:

- ◆ Engineering interviews and records
- ◆ Accounting interviews and records
- ◆ Manifest documents
- ◆ Vendor data
- ◆ Regulatory documents
- ◆ Sampling data

The following pages provide an overview of the typical steps involved in a facility assessment.

### Characterize the Facility

Locate or prepare drawings of the layout of the process and storage areas. These drawings

should be to scale, showing the location of all relevant equipment and tanks and identifying:

- ◆ Floor space of facility
- ◆ Plating and other process lines
- ◆ Gutters, sumps, and sewer lines
- ◆ Water lines, control valves, and flow regulators
- ◆ Available rinse stations
- ◆ Location of each process tank

Piping plans should be reviewed for cross connections and illegal connections. Facilities can also use this information to develop process flow diagrams to which baseline information can be added, resulting in a diagram that represents current operating practices.

## Gather Baseline Information

Review all operations of the facility that relate to chemical or water use. Some of the information that should be collected includes:

### General Facility Information

- ◆ Estimates of production units such as square meters plated and number of parts, barrels, or racks to pass through a line sequence
- ◆ Types of parts plated
- ◆ Chemical purchases
- ◆ Chemical inventory
- ◆ Chemical use rates (where each chemical is used and how much is used in each process)
- ◆ Quality of makeup water
- ◆ Facility-wide water use rates
- ◆ Wastewater treatment operating procedures
- ◆ Wastewater content
- ◆ Sludge management procedures
- ◆ Sludge content analysis
- ◆ Waste management costs
- ◆ Raw material costs

- ◆ Compliance problems
- ◆ Control processes
- ◆ Sampling and analysis information
- ◆ General amount of drippage onto the floor

#### From Each Line

- ◆ Rack/barrel design and condition
- ◆ Actual operating procedures
- ◆ Operating parameters
- ◆ Production rates (i.e., square feet processed per hour)

#### From Each Plating Process Bath

- ◆ Batch dumps that result from the process
- ◆ Dragout rates from each process tank
- ◆ Bath evaporation rates
- ◆ Process solution composition
- ◆ Actual operating parameters for each process tank
- ◆ Dump schedule for each process tank

#### From Each Rinsing Process

- ◆ Rising and draining times on automatic lines or efficiency of operator on manual lines
- ◆ Dragout measurements
- ◆ Dragin/contaminant loading rates
- ◆ Rinsewater quality requirements
- ◆ Flow control techniques
- ◆ Wastewater flow rate from each rinse tank
- ◆ Dragout reduction techniques used (Hunt 1988)

Table 5 summarizes the types of data and information that is useful for conducting an assessment.

### Evaluate the Design of the Facility's Process

Some technologies might require the addition of tanks or modifications to the plating process. The facility should evaluate its ability to

optimize the process and to accommodate changes to the process (Ferrari 1995).

## Developing a Process Flow Diagram

Once all the information has been gathered and a map of the facility exists, a process flow diagram can be developed. Process flow diagrams break down the facility into functional units, each of which can be portrayed in terms of material inputs, outputs, and losses. Developing a process map helps the facility understand how the production process is organized, providing a focal point for identifying and prioritizing pollution prevention opportunities (EPA 1996).

The process map should cover the main operations of the metal finishing facility and any ancillary operations (e.g., shipping and receiving, chemical mixing areas, and maintenance operations). Separate maps can be generated for ancillary operations. Another important area to cover is "intermittent operations" or operations that do not occur on a regular basis. The most common intermittent operation is cleaning and maintenance. A great many pollution prevention opportunities can be found by examining intermittent operations (EPA 1996).

It is also useful and important to include operations that are upstream and downstream of the metal finishing operation. Pollution and waste issues often cross facility boundaries. An understanding of where the pollution originates from can assist in identifying pollution prevention opportunities.

## Identifying Pollution Prevention Opportunities

Using the information obtained in the facility assessment, the team should compile a list of technically feasible options. Brainstorming sessions with the team can provide innovative ideas. Researching case studies of other companies also can provide valuable information. Other potential sources of ideas include suppliers and consultants. At this point, all ideas should be taken seriously and none should be rejected automatically for reasons such as "that's already



Table 6. Overview of Assessment Information (BCDNRP 1994)

Process	Data
<b>Production Processes and Operational Procedures</b>	<ul style="list-style-type: none"> <li>◆ Production rates</li> <li>◆ Process description and efficiencies</li> <li>◆ Condition of process equipment</li> <li>◆ Sources or potential sources of leaks/spills</li> <li>◆ Operating procedures</li> <li>◆ Maintenance procedures and schedules</li> <li>◆ Energy/utility use and costs</li> <li>◆ Operating and maintenance costs</li> </ul>
<b>Material Use, Handling, and Storage</b>	<ul style="list-style-type: none"> <li>◆ Material inventory</li> <li>◆ Raw material accounting (how much of the material is used in the process, how much is lost through evaporation or other means, and how much enters the wastestream)</li> <li>◆ Raw material costs</li> <li>◆ Material transfer and handling procedures</li> <li>◆ Storage procedures</li> <li>◆ Sources of leaks or spills in transfer and storage areas</li> <li>◆ Condition of pipes, pumps, tanks, valves, and storage/delivery areas</li> </ul>
<b>Wastestream</b>	<ul style="list-style-type: none"> <li>◆ Activities, processes, or input materials that generate wastestreams</li> <li>◆ Physical and chemical characteristics of each stream</li> <li>◆ Hazardous classification of each wastestream</li> <li>◆ Rates of generation of each wastestream and variability in these rates</li> </ul>
<b>Waste Management</b>	<ul style="list-style-type: none"> <li>◆ Current treatment and disposal system for each wastestream</li> <li>◆ Cost of managing wastestream (e.g., fees, labor, and disposal costs)</li> <li>◆ Operating procedures for waste treatment units</li> <li>◆ Efficiency of waste treatment units</li> <li>◆ Quantity and characteristics of all treated wastes, sludges, and residues</li> <li>◆ Wastestream mixing (hazardous wastes mixed with non-hazardous waste)</li> </ul>
<b>Waste Reduction</b>	<ul style="list-style-type: none"> <li>◆ Current waste reduction and recycling methods being implemented</li> <li>◆ Effectiveness of those methods</li> </ul>

been tried" or "it will never work" or "it's too expensive."

After all options have been identified, the team should screen the options based upon the objectives and criteria set in the assessment phase. It is likely that each option will fit into one of the following categories:

- ◆ Impractical idea
- ◆ Ideas needing more detailed information and study
- ◆ Ideas that can be implemented with a minimum of effort and cost

Each company will weigh an option differently based upon its criteria (e.g., cost and compliance issues). This initial evaluation will assist the company in identifying a subset of options that deserve further investigation. Generally, the number of options requiring detailed information and study should be pared to a minimum (Ferrari 1995).

When screening ideas keep in mind that an important principle of manufacturing excellence is maximizing the productivity of the plating cycle. Some pollution prevention options can increase productivity while others can increase the cycle time, sometimes substantially. Productivity and output in plating operations are influenced by a number of factors. Technical assistance providers should be aware of how their suggestions can affect the productivity of the plating process when screening options. The following is a description of the major factors that can affect plating line efficiency:

- ◆ **Part geometry:** The shape and size of the workpiece will greatly influence the throughput of a plating line. Larger complex pieces usually must be rack plated whereas small parts can be barrel plated together. Part geometry also is an important factor in determining dragout rates.
- ◆ **Solution concentration and temperature:** A change in the concentration of the plating solution can have a critical impact on the plating process. Concentrations that are not high enough can result in increased reject

rates, while higher concentrations can increase dragout and waste generation.

- ◆ **Plating specifications:** Plating thickness, corrosion resistance, and brightness are the primary quality specifications in electroplating. These specifications and the steps needed to accomplish them will greatly affect the productivity of the line and the waste generated.
- ◆ **Masking or plugging:** The amount of masking and plugging required to plate the workpiece correctly also affects productivity. Masking or plugging prevents metals from being deposited on inappropriate areas of the part. In many electroplating applications only a portion of the part might need to be plated.
- ◆ **Single load versus long runs:** The need to change processes frequently to accommodate different plating jobs will reduce productivity when compared to scheduling long runs of the same part.
- ◆ **Rinsing methods:** Productivity also is affected by the type of rinsing method used. For instance, countercurrent rinsing increases cycle time significantly when compared with other rinsing methods.
- ◆ **Unfamiliar parts:** Familiarity with certain substrates, process chemistries, particular production specifications, or similar workpiece geometries will assist a facility in increasing productivity. Although production specifications often are available and provide guidance, working with an unfamiliar plating line can decrease plating productivity (Haveman 1995).

By gaining information on these types of issues, technical assistance providers can provide better suggestions on pollution prevention options when assessing a facility.

## Analyze and Select Options

Once a short list of options has been identified, the team should begin the process of deciding which options are appropriate for the facility. During this phase, the team should be clear on

the company's objectives and criteria. Depending on the goals of the company, cost effectiveness might not be the overriding goal. Option screening should consider these questions:

- ◆ Which options will best achieve the goal of waste reduction?
- ◆ What are the main benefits to be gained by implementing this option?
- ◆ Does the technology exist to develop the option?
- ◆ How much does it cost?
- ◆ Can the option be implemented without major disruptions in production?
- ◆ Does the option have a good track record?
- ◆ What are other areas that might be affected by implementation of the option?

In addition, a company that believes cost effectiveness is critical should consider the long-term costs associated with a particular option. For instance, the team might be inclined to disregard an option because the initial capital outlay is high, however, upon examining the total cost associated with the measure, the team might find that it could yield impressive savings in several years (Dennison 1996). In order to identify the total costs associated with both existing processes and new processes, the facility might have to consider costs that traditionally have not been incorporated into capital acquisitions. For more information on identifying these costs, assistance providers can refer to a training manual developed by the Northeast Waste Management Officials' Association for conducting financial assessments of pollution prevention projects.

### Pilot Test or Validate Preferred Options

Once the facility has determined its preferred option(s), it should pilot test the program prior to full facility implementation. A pilot test can highlight any installation or implementation issues. At this point, the technical assistance provider has completed his or her job. However, if issues arise in the pilot test phase, he or she

can be called in to troubleshoot or suggest other alternatives.

### Procure/Implement New System

Once the new system is installed, employees should be informed about the project and the importance of their cooperation and involvement. Operators should be trained on how to properly operate the system. Companies should update employees on the expected benefits and the progress made in achieving the goals of the system. Frequent updates on the progress of the program can increase staff's stake in the program. In order to sustain employee interest in the program, facilities should encourage employees to submit new ideas for increasing the effectiveness of the program. By working with employees as a team, assistance providers can aid in the development and successful implementation of a pollution prevention program.

Following these steps can provide the facility with the necessary information for determining the best opportunities for implementing pollution prevention projects. This methodology is useful because the cost to correct a failed system can greatly exceed the cost of proper initial implementation. A few critical rules should be kept in mind when helping a company consider new projects:

- ◆ No single system or process is right for all applications. A vast range of variables can affect the physical and chemical characterization of process baths and rinses which in turn affects the selection and performance of a pollution prevention system. Specific variables include process bath formulations, work type, work loading rate, and workpiece geometry.
- ◆ Unless the scope of the application is small, the new system will likely involve more than one process unit or subsystem.
- ◆ Prior to investing in any new system, the team should take the time to evaluate and understand the process, preferably including a rigorous pilot test in the facility.

- ♦ The team should recognize that the provider of any new system (including designer and sales staff) is a new partner at the facility (Ferrari 1995).

The Canadian Association of Metal Finishers prepared a detailed document on planning a pollution prevention program in a metal finishing facility. Information on the document can be found by calling The Metal Finishing Centre. Their telephone number is located in the resource section in Appendix B.

## Keeping the Program Going

If the technical assistance provider uses the team approach described earlier, many individuals from all areas of the company will have a chance to share their perspective on waste problems and solutions. Working from the process map, the team will go onto the plant floor to discuss the process with those directly involved (i.e., supervisors and front-line production workers) and develop a baseline to measure all future efforts. The assistance providers can suggest to the facility that they develop a mechanism for soliciting input from all employees in the future. Communicating the success of the program also can keep employees involved. The facility can use the baseline information developed from the facility assessment phase to communicate progress that the facility has made.

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# 4 Common Pollution Prevention Practices

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Pollution prevention has emerged as an effective tool for companies to attain compliance with environmental requirements. As stated in the previous chapter, using pollution prevention as the primary technique for attaining compliance also can reduce operating costs and increase profits. Metal finishing firms have achieved widespread success in reducing pollution using everything from improved housekeeping to advanced technologies.

The primary goal of this manual is to describe the major pollution prevention techniques used in the metal finishing industry. Some of the technologies involve simple installations, for example, retrofitting pipes or drainboards. These methods are cost effective and can be implemented in house without outside consultation. Other methods such as metal removal from liquids and total recycling in a closed-loop system require large capital expenditures. Although EPA and the states do not mandate recycling or zero discharge, urging companies to plan new equipment purchases with these goals in mind should prove cost effective in the long run and help companies sustain environmental compliance and profitability.

This manual does not attempt to make blanket judgments as to the economic feasibility of the pollution prevention options that are presented. The conditions in each facility vary, and the characteristics and quantities of the platables are diverse. However, loss of raw materials in metal finishing can affect at least five distinct cost categories. Facilities should consider the following in any financial evaluation of pollution prevention options:

- ◆ Replacement of raw materials
- ◆ Removal of the materials from the waste water before discharge (i.e., pretreatment)

- ◆ Disposal of removed materials
- ◆ Replacement of water
- ◆ Processing of wastewater by local sewer authorities

Assistance providers should take advantage of the expertise and knowledge of local conditions that a facility operator possesses when working with a firm. Assistance providers should also keep in mind that current practices are often the result of employee training. Employees might not know why the facility uses certain work practices. In some cases, the real reason for a practice no longer applies to the current situation.

The following sections present some of the overall strategies that a company should incorporate into a successful pollution prevention program including employee training, housekeeping, leak prevention, spill prevention, inventory management, chemical sample testing, and water quality monitoring.

## Employee Training

Employee training can provide workers with the information necessary to minimize waste generation. Companies should train employees in the proper handling of chemicals and the reasons for implementing safer techniques. Employee training should also cover safety, rinsing techniques, and chemical hazards. For instance, only trained employees should be responsible for mixing bath solutions and setting flow levels.

Companies should realize that they might experience increased training costs to capture these benefits (APPU 1995). In general, this training produces a quick payback.

### *Employee Training Case Study*

EPA documented a firm that achieved a 32 percent reduction in sludge and a savings of \$2,000 in off-site treatment costs by a facility that implemented an employee training program in plating and wastewater treatment operations. The changes improved control of water levels in rinse tanks, improved sludge separation, and resulted in higher levels of surfactant being recycled back into the process. No capital or operating costs were incurred. (EPA 1989a)

In addition, firms could consider designating specific employees to be responsible for specific tasks and properly training them in appropriate work practices so that they can do the job correctly. The tasks could include inspections of tanks, raw material distribution, and bath mixing. Properly trained employees are more likely to:

- ◆ Understand how to operate baths at peak efficiency
- ◆ Minimize spill generation
- ◆ Improve the consistency of solution formulation and minimize the number of bad baths

## **Housekeeping and Preventative Maintenance**

Although the benefits of improved housekeeping can be difficult to quantify, simple housekeeping improvements often can provide low-to-no-cost opportunities for reducing waste. Preventative maintenance and proper equipment and materials management can minimize leaks, spills, evaporative losses, and other releases of potentially toxic chemicals. A plant can reduce waste by developing inspection and maintenance schedules, controlling the purchasing and handling of raw materials, removing dropped parts quickly from baths, keeping filters and other process equipment in good working order, and authorizing a limited number of employees to accept and test samples from chemical suppliers (UNCE 1995).

Employees should quickly remove dropped parts and tools from process baths to reduce contami-

nation of the bath. Firms can help speed up such removal by having rakes located in handy places. Shops also should coordinate maintenance schedules with inspection schedules to ensure that equipment is operating at optimal efficiency. Some of the benefits of improved housekeeping and preventative maintenance include:

- ◆ Optimal efficiency of machinery and equipment
- ◆ Prevention of production losses
- ◆ Reduced reject rate
- ◆ Reduced effluent violations
- ◆ Decreased amounts of waste from spills occurring as a result of equipment failure
- ◆ Increased worker safety

Companies that have effective maintenance programs can see an increase in up-front labor costs, however; these costs usually are offset by decreased downtime (APPU 1995).

## **Leak Prevention**

Inspecting tanks and pipes for leaks can lead to immediate reductions in waste at little or no cost. Firms should inspect production, storage, and waste treatment facilities regularly to identify leaks, improperly functioning equipment, and other items that could generate waste. Inspections can be as simple as walking by tanks and visually inspecting them or as complex as formal inspections that include checklists and a log of findings. Frequent inspections can identify problems before they become significant. Piping systems, filters, storage tanks, defective racks, air sparging systems, automated

### *Leak Prevention Case Study*

EPA documented a firm that achieved a 40 percent reduction in solvent loss and savings of \$4,800 annually in raw material and disposal costs by changing operating procedures and scheduling of two in-line degreasers that use tetrachloroethylene (TCE). Prior to implementation, 3,510 gallons of TCE were lost per year. No capital costs or operating costs were incurred and the payback period was immediate. (EPA 1994)

flow controls, and even operators' production procedures (including drain time and rinse methods) should be inspected regularly. Inspection routines could include setting up calibration schedules on all temperature, speed controls, and pH meters; instituting an employee training program; or implementing a computerized tracking system for preventative maintenance procedures (Cushnie 1994).

## Spill Prevention

Spills can be reduced by training personnel in improved material handling and spill prevention methods. Training should include proper use of spouts, funnels, and drip pans during material transfer; design of drainboards to eliminate spills and reduce dragout; maintenance of liquid levels in tanks to reduce overflow spills; use of mops or pigs to clean up spills (as opposed to the use of an absorbent that must be treated or disposed of as a hazardous waste); and use of containment berms to contain spills. Training employees in proper spill prevention techniques can assist in reducing waste generation and disposal costs by eliminating spills and overflows (APPU 1995).

### Spill Prevention Case Study

EPA documented a firm that achieved a 25 percent reduction in hazardous waste shipments, a 50 percent reduction in chrome waste production, and a 95 percent reduction in chromic wastes as a result of several improvements. These improvements included installing a rain cover for outdoor tanks, repairing leaks in tanks and pipes, and installing a new treatment system that uses caustics and sodium bisulfite at a metal finishing facility. The capital cost was \$30,000 and disposal and feedstock savings were \$15,000 annually.

(EPA 1994)

## Inventory Management: Chemical Purchasing, Tracking, Storage, Use, and Handling

Controlling the purchasing and handling of materials can significantly reduce waste generation. Firms should purchase chemicals in the smallest possible quantities, reducing stockpiles of raw materials. Chemicals that are bought in

### Chemical Handling Case Study

EPA documented a company that achieved a 49 percent reduction in wastes from 310 to 152 tons per year with a savings of \$7,200 in disposal and feedstock costs. The company limited access to solvents to the foreman and reused solvent from upstream operations in downstream machine shop operations. Prior to implementation, waste consisted of reactive anions, waste oils, and halogenated solvents.

(EPA 1989b)

bulk can be cheaper up front, but material remaining after the product has expired will require disposal. Companies should store materials in a locked space and limit access to a few designated employees. By controlling access to raw materials, operators will ensure that containers are completely empty before new containers are opened (Cushnie 1994).

Companies should label materials with shelf life dates to ensure that they have not degraded. Companies also should use a first-in, first-out policy. These practices will reduce the potential for spills, decrease the likelihood of mixing poor process baths, and minimize waste generated from the disposal of obsolete materials. Management also should establish standard operating procedures for inventory control and purchasing, working with suppliers to take back empty or off-spec containers (UNCE 1995).

In addition, firms should develop strict procedures for mixing chemicals. Mixing procedures should be designed to minimize spills, to provide correctly mixed baths, and to ensure that the baths are operated at the lowest possible concentration to reduce dragout loss.

## Chemical Sample Testing

Many suppliers provide metal finishers with a variety of process chemicals for testing. However, the material that the company does not use stockpiles at the site and must eventually be disposed of, increasing waste generation. If possible, metal finishers should stipulate that test samples will be accepted only if the supplier agrees to take back leftover samples. The unused portion of analytical samples taken from

process baths should be returned to the process baths. Furthermore, using a bench test rather than implementing a full-scale test in a process bath will reduce waste generated by chemical testing (Cushnie 1994).

## Maintaining Incoming Water Quality

Surprisingly, few metal finishers scrutinize the quality of incoming water in their facility. Companies use water throughout the finishing process, in the cleaning process, and, most importantly, in the rinsing process. Water also is used as process bath makeup. Water quality can impact process efficiency and waste generation significantly. Whether a problem exists is based on many factors including the level of water cleanliness, the sensitivity of the plating chemistry, and the evaporation rate of the system. Hardness in the water decreases the ability of the water to rinse effectively and creates scales on heated surfaces. Some surface water contains high concentrations of calcium, magnesium, chloride, and other soluble contaminants that can build up in the bath and possibly reduce bath life and increase sludge generation. Companies should examine the quality of their incoming water to determine if some treatment of the water is required prior to use in the metal finishing process. For instance, in the Midwest the use of deionized water is more common mainly because of the presence of hard water. Companies can correct this problem by using water softeners that are relatively inexpensive or by deionizing their tap water (Gallerani 1990).

In many baths, the total dissolved solids content of the water tends to accumulate in the rinsing system and plating bath. For example, in closed-loop systems, impurities from many sources tend to build up in process baths. Common contaminants from tap water are calcium carbonate or bicarbonate and, to a lesser degree, chlorides or sulfates. Alkaline baths especially tend to absorb carbon dioxide from the air. Carbon dioxide combines with carbonate contamination in tap water and can cause carbonate levels in these baths to rise quickly. When a firm is not able to discharge

### Deionized Water

#### Advantages

- ◆ Improves plating quality
- ◆ Extends bath life
- ◆ Increases rinsing efficiency
- ◆ Reduces water use
- ◆ Reduces sludge generation

#### Disadvantages

- ◆ Increased costs

(APPU 1995)

bath as dragout, as is the case in closed-loop systems, the level of carbonates will tend to rise requiring additional treatment for the bath. In this case, normal procedures for sodium baths would be to chill a side stream from the bath to precipitate the carbonates and regain control.

Similar problems exist for almost all baths in one way or another. For example, metal impurities can build up from dropped parts or anode impurities. Organic additives combined with metals in the tap water can increase contamination. In each case, the question is the same: How can the bath be treated, and does the problem occur rapidly? In some cases, the problem might never occur or might occur so slowly that bath life is not a concern. For example, baths that degrade themselves, such as chromating baths, normally are changed frequently so that water quality problems never occur. As with all pollution prevention technologies, facilities have to examine their situation and determine whether they prefer using deionized water.

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# 5

## Pre-Finishing Operations

Virtually all products that are finished require some pre-finishing procedure such as cleaning, stripping, or pickling. Without a properly cleaned surface, even the most expensive coating will fail to adhere or protect the workpiece. Depending on the process being performed, the degree of cleanliness will vary. Finishing operations such as phosphating, chromating, or electropolishing do not require as high a degree of cleanliness as electroplating or electroless plating. For example, it would be unreasonable to set up the same system for phosphating and electroplating operations because the cleaning prior to phosphating is not as critical to achieving a finish of high quality. In some cases, cleaners that contain acids or alkalis can actually reduce the quality of the finishing process. In other words, the cleaning process should match the finishing operation so that cleaning is performed in the most economical way to meet requirements (Innes 1993).

### Assessing the Cleaning Process

Technical assistance providers should help companies determine feasible options by examining the overall cleaning operations of a facility. Often workpieces in plating lines are cleaned several times using water, acids, caustics, and detergents. An analysis of an entire finishing process can identify redundant or unnecessary cleaning steps. The cleanliness requirements also should be evaluated to see if they are too stringent. Second, assess the technical feasibility of the alternatives. To determine the best alternative, ask the following questions:

- ◆ What are the cleanliness requirements of the part?
- ◆ Does the alternative meet customer specifications?
- ◆ Is the part/material/coating compatible with the cleaning process?

- ◆ Can the new process meet required production volumes?
- ◆ Is the process easily installed, operated, and maintained?
- ◆ How does the new process affect subsequent production steps?

Then, compare the economics of technically feasible options. When comparing the economics, consider capital outlay, process operating costs, permit requirements, waste disposal costs, labor costs, and energy costs. Many facilities have substantially reduced waste generation by implementing alternative cleaning systems. Finally, consider any potential new regulatory requirements that might be required if the new process is installed (NFESC 1995).

### Factors Affecting Cleaning Operations

In order to properly assess the cleaning operation, four parameters must be analyzed: the substrate, the degree of cleanliness required, the nature of the soil, and incoming water quality.

#### Substrate

The composition, physical properties, and chemistry of the base metal influence the selection of the cleaning procedure. Hardness, porosity, thermal coefficient of expansion, conductivity, melting point, specific heat, and the effect of hydrogen embrittlement must be considered. For instance, hardened steels and other metals, such as titanium, can become embrittled by hydrogen. For this reason, these metals must be handled appropriately to minimize embrittlement (Innes 1993).

The condition of the base metal is equally important. For example, a piece of metal with heat or welding scale requires more processing than nonoxidized cold rolled steel. The cleaning medium must be designed so that it is compatible with the metal being processed. A cleaning

process that attacks the metal surface is undesirable. Therefore, select a process that does not attack the metal or does so in a desirable way (e.g., a satiny or frosty appearance might be desirable on aluminum substrates). Other problems can be encountered when working with metals that have low melting points (200 degrees Fahrenheit). Such alloys cannot be cleaned in boiling aqueous solutions. Other metals can be distorted or bent in heated solutions (Innes 1993).

### Degree of Cleanliness Required

The degree of cleaning required varies depending on the particular surface treatment it will receive. For instance, parts plated with a cyanide-based solution usually do not need a high level of cleaning because cyanide-based plating solutions clean the part during the plating operation. For a nickel plate to adhere to a metal surface, however, the surface must be extremely clean. Because the plating bath does not contain cyanide, it does not clean the part. Therefore, thorough and rigorous cleaning operations are needed prior to plating (EPA 1990).

### Nature of the Contamination

In order to properly design the cleaning system and sequence of baths or other operations, it is important to know the composition of the contaminants on the material surface. Generally, soils can be broken down into two categories: organic and inorganic.

**Organic:** Saponifiable — animal and vegetable oils  
Unsaponifiable — mineral oils and waxes  
Miscellaneous — contaminants either formed in situ or inhibitors from certain pickle acids redepositing on the metal

**Inorganic:** Scale and smut — oxide and metallic residues  
Polishing compounds — abrasive, grinding, and polishing residues or grits  
Miscellaneous contaminants — shop dust or soldering flux

Other soils are paints, cleaning residues, fingerprints, inorganic coatings, and rust preventatives.

The method and medium used for soil removal depends on the composition and condition of the soil as well as its physical and chemical properties. Often a cleaning procedure can be recommended based on the chemical properties of the soil providing that a chemical change has not occurred after application because of age or drying out. For instance, alkaline cleaners often are used to remove heavy soils and some solid oils while caustics are good stripping agents. Acid cleaners and abrasives are used mainly to remove oxidation and rust. When parts have been contaminated with several materials, sequencing of cleaning operations can be important. For instance, a layer of oily contamination might be removed by an alkaline cleaner before abrasives are used to remove a rust layer (EPA 1990).

### Water Quality

The condition of the incoming water often is overlooked in metal cleaning. Hard water can decrease the effectiveness of a cleaning system. Water with a hardness exceeding 25 grains is definitely a problem and must be treated in order to operate most cleaning systems adequately. Many of the chemical additives that are used in cleaning can be neutralized by minerals found in tap water. Filtration and deionizing can be used to correct water quality problems (Innes 1993).

### Cleaning Processes

Four types of metal cleaning can be used by the metal finishing industry: solvents (both halogenated and nonhalogenated), alkaline cleaners, electrocleaning, and acid cleaners. Alkaline and acid cleaners are generally referred to as aqueous cleaners. Mixtures of solvents and alkalines frequently used. Mixtures where water-immiscible solvent is emulsified in water are termed emulsion cleaners (EPA 1990). Electrocleaning uses electrical current to clean the workpiece.

Frequently, no one cleaning operation can be specified as the best. Several cleaning methods often appear appropriate and only through experimentation can one be selected. Some

cleaning techniques involve the application of organic solvents to degrease the surface of the workpiece. Other techniques such as emulsion cleaning use common organic solvents dispersed in an aqueous medium.

The cleaning process generally can be divided into three distinct phases: immersion, power spray, and electrocleaning. The purpose of immersion and spray cleaning is to remove the bulk of or all soil contamination prior to electrocleaning, phosphating, pickling, or chromating. In some cases, the spray cleaner also can be an activation process. In other cases, spray cleaners can be used individually or in conjunction with one another. In fact, in a number of cleaning operations, success ultimately depends upon the soak and spray combination (Innes 1993). An immersion or spray cleaner can fall into any of the following categories:

- ◆ Solvent
- ◆ Emulsifiable solvent
- ◆ Emulsion of oil in water (o/w) or water in oil (w/o)
- ◆ Diphase
- ◆ Acid
- ◆ Detergent
- ◆ Alkaline-built detergent

## Solvent Cleaning

The most common form of cleaning in metal finishing operations is chlorinated solvent vapor degreasing and ambient-temperature solvent immersion cleaning. The Clean Air Act Amendments of 1990 required new standards for vapor degreasing. These new regulations are pushing metal finishers to investigate alternative cleaning methods or improve current operating practices. The University of Tennessee Center for Industrial Services has developed a manual to assist manufacturers in complying with the CAAA standards for vapor degreasing.

Traditionally, vapor degreasing using chlorinated solvents such as trichloroethylene (TCE) or

perchloroethylene (PERC) has been used to remove oils, grease, and wax-based soils. Unlike other cleaning processes involving water, vapor degreasing does not require downstream drying because the solvent vaporizes from the workpiece over time. However, vaporization results in significant VOC emissions and solvent losses.

Conventional open-top vapor cleaners (OTVCs) use an open tank where solvent vapor is maintained. A perforated basket containing soiled parts is retained in this vapor layer for a few minutes and rotated to expose all part surfaces to the vapor. As vapor condenses on the parts, the soil is dissolved and carried away by condensate. When the parts reach the temperature of the vapor, no more condensate is generated and the parts are removed (Ford 1994).

## Methods for Improving Solvent Vapor Degreaser Efficiency

Certain equipment-related and operational factors can reduce emissions from traditional OTVCs including:

- ◆ Installing of refrigeration coils in addition to or as replacements for water chillers; coils can help to reduce vapor generation by 40 percent or more in some cases.
- ◆ Covering the degreaser at all possible times. Placing a cover on the OTVC opening during idling and shutdown reduces emissions significantly. The best type of cover is a motor-controlled cover that can be closed automatically.
- ◆ Keeping the tip of the spray wand below the vapor level during spraying operations.
- ◆ Removing parts from the degreaser unit slowly. Lowering and raising the basket of soiled parts gently (with a hoist) reduces convective losses by minimizing turbulence. The recommended hoist/withdrawal speed is 11 linear feet per minute.
- ◆ Racking parts so that the solvent drains out of the holes, joints, crevices, etc. Retaining the basket of soiled parts over

the tank opening for a short time allows solvent condensate to drip back into the tank instead of being dragged out.

- ◆ Increasing the freeboard ratio (the height of the tank walls above the vapor layer) from 0.5 to 0.75 or 1.0 feet can cut vapor loss in half (Freeman 1995).

## Alternatives to CFC Solvent Cleaning

With the phaseout of chlorofluorocarbon (CFC)-based cleaners, facilities have been investigating chemical, mechanical, and specialty alternatives. Chemical alternatives include replacement solvents for use in existing cold cleaning and vapor degreasing systems. In contrast, mechanical alternatives commonly require replacement of an entire process. Generally, higher initial costs are offset by a safer workplace and reduced operating costs. Specialty alternatives include processes such as plasma systems and supercritical cleaning. Table 6 lists several methods to reduce the use of chlorinated solvents.

### Chemical Alternatives

Many alternatives to methylchlorofluorocarbons (MCF) and CFC-113 are available for

use in cold cleaning and vapor degreasing applications such as wipe cleaning, dip cleaning, immersion soaking, pressure washing, and vapor degreasing. Some solvents are recommended only for specific applications while others are used for many applications. In general, the following properties are desirable when considering solvent alternatives: low surface tension to penetrate small spaces, high density to remove small particles, high volatility to provide rapid drying, good solvency to readily improve organic soils, low cost, low toxicity, non-flammable, little residue, and easy cleanup and disposal (NFESC 1995).

Drop-in solvent replacement of traditional solvents such as MCF and CFC-113 usually is not possible. However, because vapor degreasing is effective at cleaning delicate parts, facilities might want to consider maintaining the process with a substitute solvent. Some possible CFC-free alternatives include:

- ◆ Aliphatic hydrocarbons: Aliphatic compounds comprise a wide range of solvents such as mineral spirits and kerosene. These solvents have superior cleaning ability and are compatible with most plastics, rubbers, and metals and reusable when distilled. However, aliphatic hydrocarbons are

Table 7. Alternatives for Chlorinated Solvent Cleaning (NFESC 1995)

Contaminant	Possible Alternatives
Corrosion Inhibitors	Consider alkaline-soluble compounds Protective packaging can eliminate the need to clean
Fats and Fatty Oils	Hand wipe or use alkaline cleaners
Fingerprints	Handle all fabricated parts with gloves Use alkaline compounds for hand wiping
Ink Marks	Use water-soluble inks Remove ink with water Use labels or tags until final marking is applied
Hydrocarbon Greases and Oils	Hand wiping stations remove enough soil for alkaline cleaning Use water-soluble compounds
Machining (cutting fluids)	Substitute water-soluble fluids for use in machining
Polishing Compounds	Use water-soluble compounds Clean at polishing station

flammable, slow to dry, and have low occupational exposure limits. As a result, aliphatics have not been a desirable substitute for traditional solvents.

- ◆ Other chlorinated solvents: The main advantage to using a chlorinated solvent such as trichloroethylene, perchloroethylene, or methylene chloride is their similarity to CFC solvents in both physical properties and cleaning effectiveness, especially in vapor degreasing. However, all of the above three have been classified as Hazardous Air Pollutants (HAPs) by EPA and are targeted by the Emergency Planning and Community Right-to-Know Act as well. Furthermore, spent solvents are classified as a hazardous waste. As a result, handling and disposal of these solvents is more involved and expensive than other cleaning alternatives. Future regulations might ban the manufacture of all chlorinated solvents.
- ◆ Other organic solvents: Organic solvents such as ketones, alcohols, ether, and esters are effective, but dangerous. Many are HAPS while others have very low flash points. For example, acetone has a flashpoint of 0 degrees Fahrenheit. Extreme caution is required when handling organic solvents. Additionally, organic solvents can be toxic and malodorous and, as a result, are not generally used in vapor degreasing.
- ◆ N-methyl-2-pyrrolidone: Also known as M-pyrrol or NMP, N-methyl-2-pyrrolidone has high purity, a high flash point, and low volatility. It is very effective in ultrasonic applications.
- ◆ Volatile methyl siloxanes: Volatile methyl siloxanes (VMS) compounds are relative newcomers to solvent cleaning. They are low molecular-weight silicone fluids available in a variety of blends, exhibiting good compatibility with plastics and elastomers. However, all blends are either flammable or combustible and somewhat toxic. Advantages of VMS include good cleaning capabilities for a wide variety of contaminants, rapid drying without leaving residue on the workpiece, rapid spreading, and good penetration into tight spaces. This alternative can use existing equipment. Another

advantage of VMS fluids is that they can be distilled for reuse.

- ◆ Hydrochlorofluorocarbons: While, hydrochlorofluorocarbons (HCFCs) are similar to CFC-113 and MCF in solvency and cleaning effectiveness, the use of HCFCs is severely restricted because of their ozone depleting potential and health effects. A production ban on HCFCs is scheduled for the year 2010, but could be accelerated at any time. Emission controls are required for safe operating conditions (NFESC 1995).

## Aqueous Cleaning

Aqueous cleaning uses a solution of water, detergents, and acidic or alkaline chemicals to clean parts. These cleaners also are made up of builders, surfactants, inhibitors, and chelators. Most cleaners include a variety of ingredients, many of which are not needed for a firm's cleaning process and can actually cause problems with cleaning systems. Before a facility purchases any equipment for aqueous cleaning, it should first identify an acceptable aqueous cleaner. Some vendors will work with a facility to develop a cleaner tailored to their application. Below are some common additive types, what they do, and the advantages and disadvantages of each (FL DEP 1995).

- ◆ Builders: A builder is the basic ingredient of an aqueous cleaner. The most common builders are sodium hydroxide, potassium hydroxide, and sodium silicates. All of these are alkalines and are difficult to rinse. Remember that proper rinsing is the key to effective aqueous cleaning. Silicate-based cleaners tend to be easier on substrates and reduce worker exposure when compared to hydroxides (FL DEP 1995).
- ◆ Surfactants and emulsifiers: Surfactants, also known as surface active agents or wetting agents, are used to reduce the surface tension of the cleaning solution. Unfortunately, most surfactants are also emulsifiers. Emulsifiers take oils into solution and keep them from re-contaminating the workpiece. Traditional aqueous cleaners work by breaking down organic soils with caustic and/or solubilizing them with emulsifiers; either method tends to leave a large amount

of spent useless wastewater. Before disposal, the emulsion must be "cracked" or processed via ultrafiltration to remove the emulsified oils. Cracking requires either heat or acid treatment.

The newest aqueous cleaners clean by subverting the soil. Non-emulsifying surfactants have a higher affinity for the substrate than the soil. The surfactant lifts the soil from the part without chemically reacting with it. Non-emulsifying cleaners work well in spray applications. If a settling tank and oil skimmer are added to the system, soils can be removed and the cleaning solution can be reused, sometimes indefinitely without contaminating the part. In an immersion tank, however, non-emulsified oils rise to the surface. Parts can be contaminated with oils as they are withdrawn from the tank. This may be desirable because the oil can act as a rust inhibitor, but is not acceptable in most situations.

Weak emulsifiers offer the best of both worlds. This type of cleaner will keep the oils in suspension as long as the solution is agitated, but the emulsion breaks when the agitation stops, either in a holding tank or when the system is shut down. The soils can be removed and the solution can be reused.

- ◆ **Inhibitors:** Inhibitors are used to reduce the effect of highly alkaline or acidic cleaners on sensitive substrates. Inhibitors are also used to prevent rusting or oxidation of parts after cleaning. Chromates and silicates are commonly used pH inhibitors, but chromates have obvious environmental disadvantages. Hydroxides and silicates prevent rust. Inhibitors can make rinsing more difficult and can adversely affect subsequent plating operations.
- ◆ **Chelating agents:** Chelators are designed to keep metal ions in solution. These can cause major problems with wastewater treatment. Chelating agents should be avoided if possible. A number of surfactants are also chelators. For more information on chelators, refer to Chapter 6.

- ◆ **Sequestering agents:** Many alkaline cleaners are sensitive to the condition of incoming process water. Sequestering agents are used to capture hard water ions such as calcium and magnesium, allowing the cleaner to work at maximum efficiency.
- ◆ **Saponifiers:** Highly alkaline cleaners can convert insoluble fatty oils to water soluble soils. This will keep the soils in solution and the additional soap can aid cleaning, however, it also causes disposal problems similar to those for emulsified solutions. Soaps created by saponification can cause foaming problems in spray and ultrasonic applications.

The three most common equipment configurations of conventional aqueous processes for metal finishing are: immersion with ultrasonic agitation, immersion with mechanical agitation, and spray washing. Aqueous immersion cleaning with mechanical agitation or ultrasonics and spray methods are being used most widely as substitutes for solvent cleaning. Aqueous cleaners are generally better than solvent cleaners at removing soils or particulate matter. However, when oils or greases are part of the contamination, other steps might be needed to provide adequate cleaning. The rinsing and drying steps are of particular concern, especially with parts that have complex geometries or that are susceptible to corrosion because water can remain on the part and cause flash rust.

Advantages of these systems include increased safety and flexibility, decreased material and waste disposal costs, and multiple cleaning mechanisms (chemical reaction, displacement, emulsification, dispersion, and others). Aqueous cleaning solutions can be tailored for specific parts and contaminants. When compared with solvents, aqueous systems generally have higher capital costs and require elaborate rinsing and drying procedures as well as tighter process controls for optimum cleaning (NFESC 1995).

Alkaline tumbling and hand-aqueous washing are most often used although automated processes are available. In alkaline tumbling, the soiled parts are placed in an open, tilted vessel



and an aqueous cleaning solution is introduced. As the vessel rotates, the parts tumble over each other. The cleaning solution overflows and clean tap water is added to rinse the parts.

In the hand-aqueous process, the workload (perforated basket of parts) is dipped into a series of tanks containing (successively) surfactant solutions and rinsewater. A continuous clean water flow must be maintained through the final rinse tanks, but the surfactant and dragout tank contents can be used for an entire day without changing. Both aqueous processes require drying at the end before further surface finishing treatment (Freeman 1995).

Automated aqueous washers use a helical screw to transport soiled parts through the five compartments. The parts are sprayed successively with solutions from the holding tanks. The helical screw agitates the parts as it carries them forward. The automated washer is used mostly for parts small enough to be conveyed by the helical screw. For larger parts, such as engines and transmissions, power washers can be used. The part(s) are placed on a turntable for the automatically timed cleaning cycle. High-pressure, high-temperature water, usually containing a detergent, blasts the parts clean. Rotation on the table and the number and angle of the sprays enable the water to reach all surfaces (Freeman 1995).

#### *Regeneration of Aqueous Cleaners*

Some of the cleaners used in aqueous cleaning can be regenerated for further use. Alkaline cleaners, for example, often are regenerated with microfiltration. In microfiltration, the membrane is a physical barrier with a pore size of approximately 1 to 2 microns. The microfiltration membranes reject grease, oils, and dirt while allowing the cleaning solution to pass through. For a detailed discussion of microfiltration, see Chapter 7.

#### *Wastewater Treatment from Aqueous Cleaning Systems*

In many instances because of local, state, or federal regulations, wastewater from aqueous or semi-aqueous processes must be treated before discharge to a municipal wastewater treatment

plant. Contaminants of concern include organic matter (grease and oil), metals (dissolved or in suspension), and alkaline cleaners, which raise the pH to an unacceptable level. Pretreatment technologies include gravity separators, ultrafiltration, chemical treatment, precipitation, and carbon adsorption. For more information on these technologies, refer to Chapter 6.

#### *Acid Aqueous Solutions*

Acidic solutions effectively and rapidly remove rust, scale, and oxides from metal surfaces. The solutions actually etch the surface of the metal and can improve coating adhesion. Inhibitors are used to control the etching rate. However, acid solutions are classified as hazardous waste and can cause hydrogen embrittlement as hydrogen gas formed during surface etching penetrates the metal and reduces its strength (KSBEAP 1996).

#### *Aqueous Alkaline Cleaning*

In alkaline cleaning, the cleaning action relies mainly on the displacement of soils rather than the breakdown of the soil, as is the case with organic solvents. Most alkaline cleaning solutions are comprised of three major types of components: builders such as alkali hydroxides and carbonates, which make up the largest portion of the cleaner; organic and inorganic additives, which promote better cleaning or act to affect the metal surface in some way; and surfactants. Other additives can include antioxidants and stabilizers as well as a small amount of solvents.

Mild alkaline detergent solutions such as sodium hydroxide, sodium carbonate, sodium phosphate, sodium metasilicate, and borax are used to clean many substrates because no hydrogen embrittlement results from alkaline cleaning (IHWRIC 1992). Alkaline cleansers also remove rust, scale, and oxides from metal surfaces. In general, the stronger the solution, the faster it cleans. However, relatively mild solutions often are used to easily accomplish thorough rinsing (KSBEAP 1996). Aqueous processes apply to a wide range of products and are environmentally safer than chlorinated solvent processes. Some disadvantages of aqueous cleaning are its high water consumption rate and its hazardous wastewater discharges (Freeman 1995).

Alkaline cleaning often is assisted by mechanical action, ultrasonics, or by electrical potential (e.g., electrolytic cleaning). Alkaline cleaning also can be used for the removal of organic soils. Alkaline cleaners and strippers are used to remove soil from metal parts, old paint, and plating. These types of solutions are beginning to be used in acid cleaning as well.

#### Regeneration of Alkaline Solutions

Most cleaning formulations resist treatment because they are designed to keep dirt and oil in suspension. If the concentration of cleaning chemicals is high enough in an effluent, it can prevent efficient removal of the precipitated metals. Slugs of alkaline cleaner passing through treatment systems are well known to upset the systems.

While alkaline solutions are not currently regulated by wastewater programs, they can have a significant impact in wastewater systems. In certain cases, large finishing operations on small sewer systems or small receiving streams might have a problem meeting organic content requirements because of wetting agents and detergents. Cleaners are also important contributors to a facility's total dissolved solids load in their effluent.

#### Ultrasonic Cleaning

This method uses high-frequency sound waves to improve the cleaning efficiency of aqueous and semi-aqueous cleaners. By generating zones of high and low pressure in the liquid, the sound waves create microscopic vacuum bubbles that implode when the sound wave moves and the zone changes from negative to positive pressure. This process, called cavitation, exerts enormous localized pressures (approximately 10,000 pounds per square inch) and temperatures (approximately 20,000 degrees Fahrenheit on a microscopic scale) that loosen contaminants and actually scrub the workpiece, especially in hard-to-reach areas. Ultrasonic cleaning has allowed aqueous/non-chlorinated degreasing to be practiced in applications where solvents had been the only effective degreasing tool. Ultrasonic cleaning can be used on ceramics, aluminum, plastic, and glass as well as electronic parts, wire, cables, rods, and detailed items that might

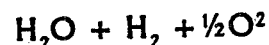
be difficult to clean by other processes (Freeman 1995). Ultrasonic cleaning can be used to increase the efficiency of virtually any immersion cleaning process.

#### Semi-Aqueous Cleaning

Semi-aqueous cleaning, a combination of a non-aqueous cleaner with an aqueous rinse, is used frequently in metal cleaning, especially where aqueous methods alone are ineffective on heavy grease, tar, and soils. However, precision and electronics applications are limited. Primary concerns generally focus on the properties of the non-aqueous cleaners: volatility, flammability (especially in heated applications), exposure risks, residues requiring rinsing, and high costs of disposal. A nitrogen blanket can reduce the risk of combustion. Hydrocarbon and surfactant mixtures, alcohol blends, terpenes, and petroleum distillates are solutions available for semi-aqueous cleaning. Advantages include compatibility with most metals, plastics, and rust inhibitors. Other benefits include potential decreases in solvent purchases, decreases in evaporative losses, and reduction in metals entering the waste stream because of the non-alkaline nature of the cleaner.

#### Electrocleaning

Electrocleaners are basically heavy-duty alkaline types and are always used with an electric current either reverse, direct, or periodic reverse. These systems are designed for soil removal and metal activation. These solutions are heavily alkaline and often heated. Typically, an initial cleaning step precedes this operation, although electrocleaning alone will suffice. In electrocleaning, the work is immersed in the solution and current is applied. When water is electrolyzed by electric current, the following reaction occurs:



The objective of electrocleaning is to remove all soils and activate the metal surface. Activation is usually obtained by using reverse-current electrocleaning. The gas scrubbing of the oxygen assists in the removal of soils while the reverse current aids in soil removal and prevents the deposition of any metallic film or non-

adherent metallic particles. A dilute mineral acid dip usually follows the final cleaner to neutralize the alkaline film on the metal surface.

### Reverse or Anodic Cleaning

In reverse cleaning, the workpiece is made the anode. In this case, oxygen gas is evolved at the surface of the piece and assists in oil and dirt removal. Because of the reversed current, any metallics in the bath cannot deposit on the piece, making this method of cleaning preferable to others (Ford 1994). In this process, the current density, temperature, and concentration, particularly on non-ferrous materials, must be controlled to avoid etching and tarnishing. This type of cleaning is not recommended for use on aluminum, chromium, tin, lead, or other metals that are soluble in alkaline electrocleaners (Innes 1993).

### Direct or Cathodic Cleaning

If the workpiece is the cathode, the cleaning is considered to be direct. In this case, hydrogen gas is liberated at the surface of the workpiece. The volume of hydrogen liberated is twice that of oxygen liberated at the anode for a given current density. Therefore, more gas scrubbing is achieved at the cathode than at the anode. For this reason, cathodic cleaning is sometimes used as a precleaner followed by anodic cleaning (Innes 1993). However, any positively charged particles (especially metallics) in the solution will tend to adhere to the workpiece forming a smut. This type of cleaning is generally used when reverse cleaning is harmful to the work (Ford 1994).

Any workpiece that is subject to hydrogen embrittlement should not be cleaned with this method unless adequate steps are taken after processing to remove the hydrogen. Generally, heat treatment for 1 hour at 400 degrees Fahrenheit immediately after processing will remove the embrittling effect of hydrogen.

Cathodic cleaning is used for the following applications:

- ◆ To clean metals such as chromium, tin, lead, brass, magnesium, and aluminum.

These metals are dissolved or etched by anodic cleaning.

- ◆ To buff nickel prior to chromium plating. The oxidation action of anodic cleaning produces a passive film on the nickel. This prevents the deposition of bright chromium.

### Periodic Reverse

Periodic reverse cleaning alternately makes the workpiece anodic and cathodic. This cleaning technique is used in oxide removal where acidic processes are harmful to the base material (Ford 1994). This method of cleaning generally is used to remove smut, oxide, and scale from ferrous metals. One of the advantages of this method is the elimination of acid on certain types of work (hinges) where entrapment of acid aggravates bleed-out during and after alkaline plating (brass, copper, zinc, cadmium, and tin). Oxides also can be removed without the danger of etching or the development of smut usually encountered from acid pickling (Innes 1993).

Solutions used in these types of cleaning operations often are sent off site for disposal because the chemical nature of the surfactants, wetting agents, inhibitors, and wetting compounds is such that they directly interfere with waste treatment operations.

### Acid Cleaning (Pickling)

Acid cleaning, or pickling, often is used to remove contaminants from the workpiece using an acid. Acid pickling is used to remove oxides (rust), scale, or tarnish as well as to neutralize any base remaining on the parts. Acid pickling uses aqueous solutions of sulfuric, hydrochloric, phosphoric, and/or nitric acids. For instance, most carbon steel is pickled in sulfuric or hydrochloric acids although hydrochloric acid can embrittle certain types of steel and is used only in specific applications. In the pickling process, the workpiece generally passes from the pickling bath through a series of rinses and then onto plating. Acid pickling is similar to acid cleaning, but is more commonly used to remove the scale from semi-finished mill products whereas acid cleaning is usually used for near-final preparation of metal surfaces prior to finishing.

## Regeneration of Pickling and Bright Dipping Solutions

### Copper and Alloys

Straight electrolytic recovery as described earlier is highly effective on many copper pickling and milling solutions including sulfuric acid, cupric chloride, and ammonium chloride solutions. Solutions based on hydrogen peroxide generally are regenerated best by crystallization and removal of copper sulfate with the crystals sold as byproducts or redissolved for further treatment by electrolytic metal recovery (Steward 1985).

Highly concentrated bright dipping nitric/sulfuric acids are a difficult challenge for regeneration because of the small quantities (5 to 25 gallons) used and the high dragout losses. Regeneration is possible by distillation of nitric acid and removal of copper salts, however, the economics are usually not favorable.

### Sulfuric and Hydrochloric Acid

Both sulfuric and hydrochloric acids are used commonly for cleaning steel. Sulfuric acid can be regenerated by crystallizing ferrous sulfate. Hydrochloric acid can be recovered by distilling off the acid and leaving behind iron oxide. These techniques have been used for many years in large facilities. The economics of these processes, however, usually are not favorable for smaller facilities (Steward 1985).

Waste pickle liquors from these operations often can be of use to sanitary waste treatment systems for phosphate control and sludge conditioning. Some industrial firms can use spent process waste from pickling operation. Iron in the waste is used as a coagulant in wastewater treatment systems (Steward 1985).

## Specialty Alternatives

### Vacuum De-oiling

A vacuum furnace uses heat and a vacuum to vaporize oils from parts. Vacuum furnace de-oiling can be applied where vapor degreasing typically is used to clean metal parts. It also can

remove oil from nonmetallic parts. Although capital costs for vacuum de-oiling are high, the operating costs are low. Unlike other clean technologies, vacuum de-oiling does not leave the cleaned parts water-soaked so they do not need to be dried. Because the time and temperature of the de-oiling process depends on the material to be cleaned and the oil to be removed, adjustments might be needed for each new material, oil, or combination. Also, the parts must be able to withstand the required temperature and vacuum pressure (Freeman 1995).

### Laser Ablation

In this method, short pulses of high-peak-power laser radiation are used to rapidly heat and vaporize thin layers of material surfaces that form a dense cloud of hot vapors that will condense and recontaminate the surface if not removed immediately. Ablation must be carried out in an inert gas environment to avoid further contamination. Laser ablation can do localized cleaning in a small area without affecting the entire part. Laser ablation meets waste minimization goals with no solvents or even aqueous solutions needed. The only waste is the small amount of material removed from the surface of the item being cleaned (Freeman 1995). The use of laser ablation to clean metal surfaces is being explored by Sandia National Laboratories.

### Pressurized Gas

This method uses clean, dry, inert gas or air that is fed to a pressurized gas gun to physically remove the contaminant from the substrate surface. Advantages of this process are low capital cost and the fact that nonflammable gases are generally used. However, this technology might not be effective in removing all soils, and it might damage the substrate (Freeman 1995).

### Supercritical Fluid Cleaning

This process involves the application of supercritical fluids at temperatures and pressures above their critical point to remove contaminants from parts. Carbon dioxide ( $\text{CO}_2$ ) is the most commonly used fluid in this process because it is widely available and considered to be environmentally sound. Supercritical fluid cleaning is compatible with stainless steel, copper, silver, porous metals, and silica. It leaves no solvent

residue after cleaning and has low operating costs. However, capital costs are very high (Freeman 1995).

### Plasma Cleaning

This method uses an electrically charged gas containing ionized atoms, electrons, highly reactive free radicals, and electrically neutral species to remove soils. Plasmas can be used in a wide range of temperatures and pressures. The advantages of this process include low operating costs and lessened disposal costs. However, initial capital costs can be high (Freeman 1995).

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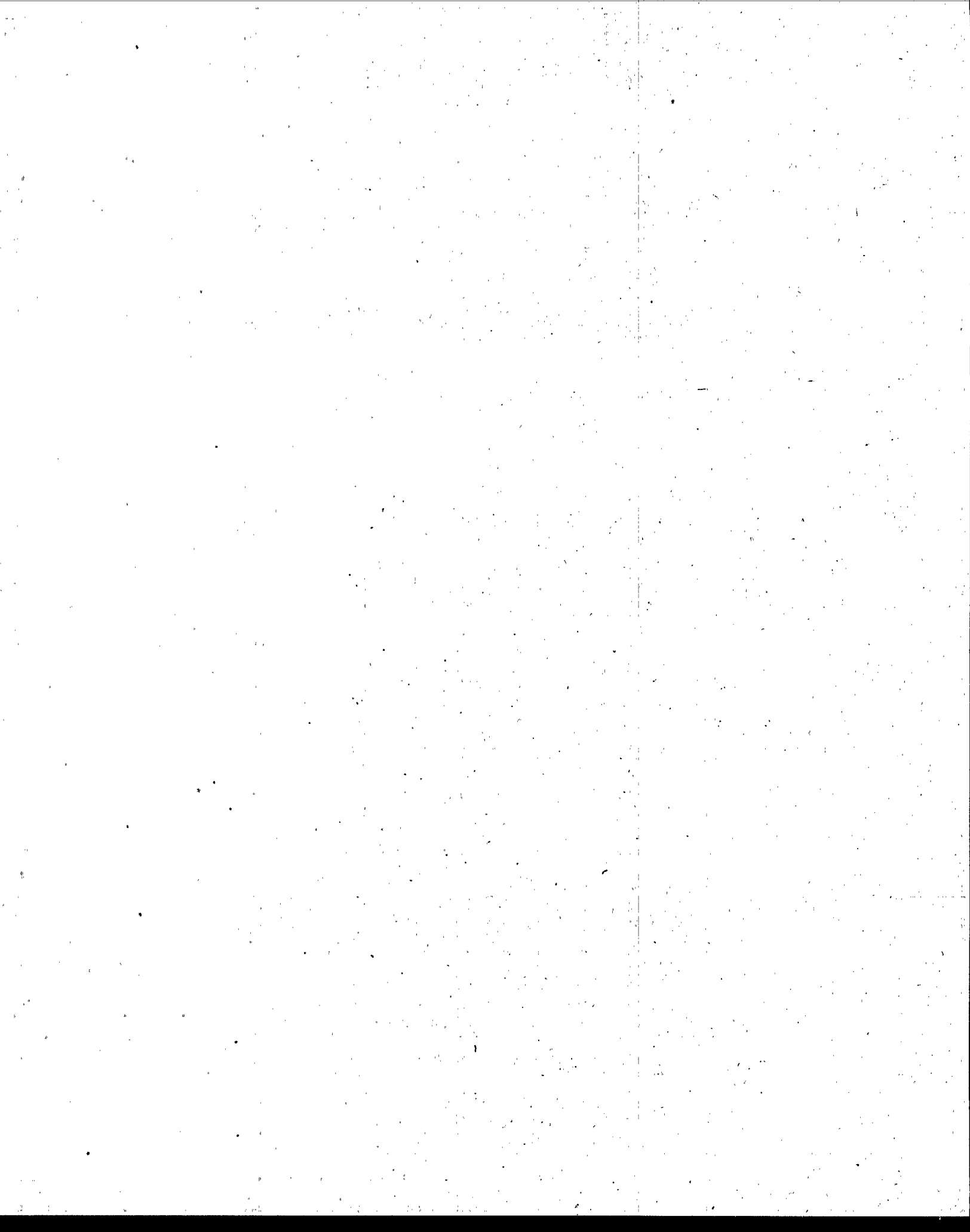
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# 6 Pollution Prevention in the Plating Process

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This chapter provides an overview of pollution prevention techniques that apply to plating lines within metal finishing operations. As described in Chapter 1, the plating line is the part of the metal finishing process where metal is applied to a substrate.

The first section of this chapter describes general pollution prevention techniques for plating solutions and covers housekeeping, monitoring, additives, equipment modification, and on-site recycling and recovery. The next section covers general issues in pollution prevention for cyanide-based plating. The next seven sections cover pollution prevention options for plating specific metals such as brass, cadmium, chromium, copper, nickel, precious metals, and zinc. The sections that follow cover additional types of plating including electroless, aluminum, chemical and electrical conversion, and others.

## General Pollution Prevention Techniques for Plating Solutions

Chapter 4 presented a number of general pollution prevention techniques for all types of metal finishing operations. These general techniques can apply in a variety of ways to plating lines. The following are some specific applications of these techniques to plating baths.

### General Housekeeping

Keeping the plating areas clean and preventing foreign material from entering or remaining can prolong the life of a bath. Companies can use a number of simple and inexpensive techniques to reduce contamination of the process bath. A part that falls off the rack into a bath should be removed quickly to reduce contamination. Operators should maintain racks so that they are

clean and free of contaminants. Firms should avoid using broken or cracked racks because they can increase the amount of process solution that is dragged into the rinse process, increasing sludge generation. Other general housekeeping methods include protecting anode bars from corrosion, using corrosion-resistant tanks and equipment, and filtering incoming air to reduce airborne contaminants. A clean process area also makes detecting problems such as leaking tanks or pipes much easier. For more information on these techniques, refer to Chapter 4.

## Monitoring Bath Composition/Chemistry

Proper control of bath operating parameters can result in more consistent workpiece quality as well as longer bath life. This strategy is simple: determine critical operating parameters and maintain them within the acceptable limits. The first step in this process is to determine optimum operating parameters for the process. The next step is to ensure regular monitoring of bath chemistry, which is essential in determining the proper amount of chemicals to add to maintain efficient operating parameters. For many solutions, simple field test kits are available. Determining operating parameters on an individual plating line basis is important because suppliers sometimes set concentration specifications for levels higher than is required for effective operation. Higher concentrations mean increased dragout and waste generation. Many plating facilities rely heavily on suppliers to provide them with optimum operating parameters. In some cases, shops send samples on a monthly basis to their vendors in addition to the daily analyses performed at facilities. The following sections describe the operating parameters that a facility should establish and the ways to determine those values (IAMS 1995).

### High Process Bath Operating Temperature

#### Advantages

- ◆ Reduces volume of dragout loss
- ◆ Allows the use of lower solution concentrations

#### Disadvantages

- ◆ Increases energy costs
  - ◆ Increases evaporation as more water will be needed to replenish process bath
  - ◆ Can increase worker exposure because of higher emissions from process bath (e.g., cyanide baths)
- (APPU 1995)

### Process Bath Operating Temperature

Increased bath temperatures will reduce the viscosity of the plating solution, enabling faster drainage from the workpiece and reducing the amount of solution that is dragged into subsequent baths. Operators, however, should avoid using very high temperatures because many additives break down in high heat, and carbonate buildup increases in cyanide solutions. Excessive temperatures also can cause the process solution to dry onto the workpiece during removal, increasing dragout, water use, and labor costs (APPU 1995).

Higher operating temperatures also will increase the evaporation rate of the process solution. A facility can take advantage of the increased evaporation rate by using solution from the process line rinse tanks to replenish the process bath and to maintain the proper chemical equilibrium. This replenishment reduces wastewater and recovers dragout while maintaining a stable plating solution. A facility might consider using deionized water when operating plating solutions at higher temperatures since deionized water will minimize the natural contaminant buildup in the process bath. Increasing the operating temperature also can increase energy costs (EPA 1992).

### Plating Solution Concentration

Facilities should determine the lowest concentration of chemicals that can be used to obtain a quality finish. If the process line is operated at higher temperatures, lower concentrations can be used to obtain results equivalent to higher concentrations at lower temperatures. Generally,

### Lower Plating Solution Concentration

#### Advantages

- ◆ Reduces dragout losses
- ◆ Reduces chemical use and costs
- ◆ Reduces sludge generation rates

#### Disadvantages

- ◆ Decreases tolerance to impurities
  - ◆ Might not be an option if contractual specifications require a certain concentration
- (APPU 1995)

the greater the concentration of chemicals in a solution, the greater the viscosity and dragout. As a result, the film that adheres to the workpiece during removal from the process bath is thicker and does not drain back into the process bath as quickly. Reducing the concentration of the plating solution can increase the ability of process solution to drain efficiently from a workpiece (EPA 1992).

Many chemical product manufacturers recommend an operating concentration that is higher than necessary. To determine the lowest possible process bath concentration, a facility should mix a new process bath at the median recommended concentration. As the process bath is replenished, operators can continue to reduce the chemical concentration until product quality begins to deteriorate. Alternatively, operators can mix the new bath at a low concentration and gradually increase the concentration until the bath cleans, etches, or plates the test pieces adequately. Facilities can operate fresh cleaning process baths at lower concentrations than used baths. Makeup chemicals can be added to the used bath increasing the concentration gradually to maintain effective operation (EPA 1992).

### Lower Concentration Plating Solution Case Study

EPA documented a firm that used low concentration plating solutions instead of mid-point concentrations in order to reduce total mass of chemicals dragged out. This case involved five nickel tanks and an annual dragout of 2,500 gallons. The capital cost was \$0 and disposal and feedstock savings were \$1,300.

(APPU 1995)



## Additives for Plating Baths

Platers commonly use several chemical additives to aid in the plating process and to reduce waste generation. Most of these chemicals are used to reduce dragout of solution into rinsewater. Some of the more common additives are described below.

### Wetting Agents

Metal finishers have used wetting agents for years in process solutions to aid in plating. A wetting agent is a substance, usually a surfactant, that reduces surface tension. The addition of a very small amount of surfactant or wetting agents can reduce dragout by as much as 50 percent (EPA 1992). However, platers should be careful to use only non-ionic wetting agents. The use of certain ionic wetting agents can reduce plating quality and limit reclamation of metals in wastewater. If a shop is considering the use of wetting agents for dragout reduction, they should conduct experiments to determine the potential benefit and to ensure compatibility with bath chemistry, especially for hard chromium plating.

Wetting agents also can create foaming problems in process baths and might not be compatible with waste treatment systems. For these reasons, impacts on both the process bath and treatment system should be evaluated prior to use (Ford 1994).

#### Wetting Agents

##### Advantages

- ◆ Reduces dragout loss by as much as 50 percent
- ◆ Can improve quality of finish

##### Disadvantages

- ◆ Can create foaming problems in process bath
- ◆ Some bath chemistries are not compatible with wetting agents

(APPU 1995)

## Non-Chelated Process Chemicals

Firms use complexers, including chelators, in chemical process baths to control the concentration of free metal ions in the solution beyond their normal solubility limit. Chelators are usually found in baths used for metal etching, cleaning, and electroless plating. However, once chelating compounds enter the wastestream, they inhibit the precipitation of metals and additional treatment must be used. These treatment chemicals end up as sludge and contribute to the volume of hazardous waste. For example, when platers use ferrous sulfate, a popular precipitant, the volume of sludge increases significantly. For some applications, operators add ferrous sulfate at an 8:1 ratio. Also, many of the spent process baths containing chelators cannot be treated on site and are put into containers for off-site disposal, adding to waste disposal costs (EPA 1992).

Metal finishers use a variety of chelators in different processes. In general, mild complexors such as phosphates and silicates are used for most cleaning and etching processes. Electroless plating baths typically are chelated with stronger organic acid chelating compounds including citric acid, maleic acid, and oxalic acid. Some firms also use ethylenediaminetetraacetic acid (EDTA), but with less frequency than the other chelators (PRC 1989). However, EDTA is a common component in many cleaning solutions.

Operators must make a trade off between extending bath life and removing chelated process chemicals from wastewater to meet required discharge levels. Often, the pH of wastestreams must be adjusted to break down the metal complexes formed by the chelators. EDTA, for example, requires lowering the pH below 3.0 and adding treatment chemicals (PRC 1989). In some cases, even this form of treatment does not enable metals to precipitate.

### Wetting Agents Case Study

EPA documented a firm that used wetting agents to reduce dragout by 50 percent. An additional dragout reduction of 67 percent was achieved by increasing drainage time. No savings information was available, although operating and maintenance costs of \$15 per 200 grams of wetting agents and \$15 per gallon misting reduction additives was reported. (EPA 1989a)

Firms can use non-chelated process chemistries for processes (e.g., alkaline cleaning and etching) in which keeping the metals removed from the workpiece surfaces in solution for later treatment might not be necessary. An application of the above is dummy plating. In such cases, the metals can be allowed to precipitate and the process bath can be filtered to remove the solids. However, non-chelated chemicals are not used for electroless plating because the chelators play a significant role in allowing the plating bath to function (PRC 1989).

Non-chelated process cleaning baths usually require continuous filtration to remove the solids. These systems generally have a filter with pore sizes 1 to 5 microns thick with a pump that can filter the tank contents once or twice each hour (PRC 1989). The cost of a filter system ranges from approximately \$400 to \$1,000 for each tank. Operating costs include filter element replacement as well as disposal and maintenance costs. However, firms will realize savings in reduced waste treatment, sludge handling, and disposal costs for spent baths. Another important advantage of non-chelated process chemicals is that the metal removal capability of wastewater treatment usually is improved and the treated effluent is more likely to meet discharge limits (EPA 1992).

## Equipment Modifications to Prevent Pollution

A facility can implement several modifications to reduce contamination of the process bath, extending its life and reducing waste generation. These techniques include using the proper anode care, purified water, and ventilation/exhaust systems.

### Anodes: Purity, Bagging, and Placement

Anodes used in the plating process often contain impurities that can contaminate a process bath. Anodes with higher grades of purity do not contribute to bath contamination, however, their cost might be higher than less pure anodes. In addition, some contaminants are added to the anode to aid in the plating process. Therefore, properly matching the anode to the process is critical. One method for reducing contamination from anodes is placing cloth bags around them.

This technique can prevent insoluble impurities from entering a bath. However, the bags must be maintained and made of a material that is compatible with the process solution (EPA 1992). For some process solutions, such as copper cyanide, bagging is not a feasible option. Facilities also can experiment with the placement of the anode in the process bath. Proper placement of the anode can increase the quality of the plating process resulting in fewer rejects, and can reduce the need to rework workpieces.

### Purified Water

Firms can use deionized, distilled, or reverse osmosis water to replace tap water for process bath makeup and rinsing operations. Natural contaminants such as calcium, iron, magnesium, manganese, chlorine, carbonates, and phosphates can reduce rinsewater efficiency, minimizing the potential for dragout recovery and increasing the frequency of process bath dumping. These contaminants also contribute to sludge volume when removed from wastewater during treatment (EPA 1992). Further information on issues related to purified water are included in Chapter 4 in the section on water quality monitoring.

### Ventilation/Exhaust Systems

Scrubbers, de-misters, and condensate traps remove entrained droplets and vapors from air passing through ventilation and exhaust systems. If segregated, operators can return some wastes from scrubbers to process baths after filtering. Updraft ventilation allows mist to collect in the duct work and flow back to the process tank. For example, hard chromium plating baths can benefit from an updraft ventilation system (EPA 1992).

Process baths that generate mist (e.g., hexavalent chromium plating baths and air-agitated nickel/copper baths) should be in tanks that have more freeboard in order to reduce the amount of mist in the ventilation system. The added space at the top of the tank (i.e., the freeboard) allows the mist to return to the bath before entrainment in the air entering the exhaust system. Platers also can use foam blankets or floating polypropylene balls in hard or decorative chromium baths to keep mists from reaching the exhaust system (EPA 1992).

## Chemical Substitution

A plater can use several chemical substitutes to reduce the amount of toxic materials. Detailed information on these substitutes is presented in Chapters 5 and in upcoming sections in Chapter 6. Substitutes are used most commonly for cyanide because of its toxicity.

### Replace Cyanide-Based Plating with Non-Cyanide-Based Processes

Converting process baths to non-cyanide process chemistries can, in some cases, simplify wastewater treatment, reduce treatment costs, and decrease sludge generation. Alternatives are available for most cyanide-containing processes including silver, cadmium, zinc, gold, and copper plating. However, drawbacks often are associated with switching to non-cyanide process plating. For a more detailed description of cyanide alternatives, refer to the Pollution Prevention for Cyanide-Based Plating section in this chapter.

### On-Site Recycling and Recovery

Several opportunities exist for platers to recycle or reuse solutions in baths either within the same tanks or in other processes. This section covers acid solution regeneration, reactive rinsing, and spent solution reuse.

#### Acid Solution Regeneration

Firms can regenerate acid solutions using several processes including distillation, acid sorption, membrane electrolysis, crystallization, and diffusion dialysis. Technologies such as membrane electrolysis and diffusion dialysis rely on the ability of a membrane to selectively diffuse anions and hydrogen while at the same time rejecting metals. Diffusion dialysis functions by passing water in a countercurrent flow to the

spent acid stream. The two streams meet at a membrane where anions and hydrogen diffuse through the membrane into the water. Operators end with an acid solution at the approximate strength with which they started and a dilute acid waste that contains the metal component. The acid then is reused and the waste is treated or sent off site for disposal. Acid solution regeneration technologies are discussed in further detail in Chapter 7.

#### Spent Acid Bath Reuse (Reactive Rinsing)

Companies might have opportunities to reuse spent process baths in other facets of a metal finishing operation. Used acid and alkaline cleaners from the cleaning process are the most common example of this technique. For example, rinsewater from an acid dip process can be piped to the alkaline cleaning process for use as rinsewater (or vice versa). If both systems have the same flow rate, water use would be reduced by 50 percent. This system also can increase rinsing efficiency by reducing the viscosity of the alkaline dragout (EPA 1992). However, facilities should make sure that rinse tanks, pipes, plumbing, and bath chemistries are compatible with the rinse solution (EPA 1992).

Another use for spent acid cleaning rinsewater is as an influent for rinsing after a mild etch process. Furthermore, rinsewater from final or critical rinses, which tend to be less contaminated, can be used in rinsing operations where a high degree of rinsing efficiency is not required. Costs for implementing a system to reuse water can vary greatly. Simple systems can cost as little as a few hundred dollars while a complex system can cost hundreds of thousands. Figure 6 illustrates rinsewater reuse for an alkaline cleaning, mild acid etch, and acid cleaning line.

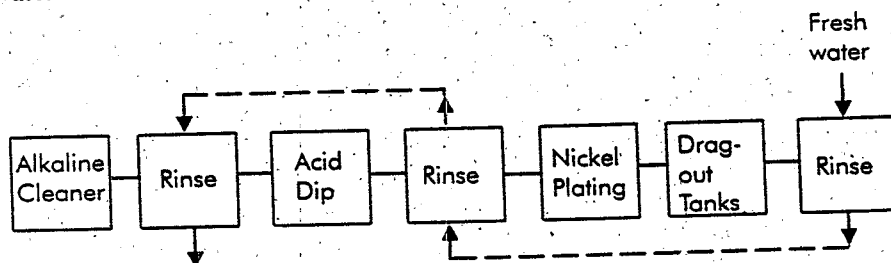


Figure 6. Multiple Reuse of Rinsewater (EPA 1992)

## Spent Solution Bath Reuse

Process baths that have become too contaminated to be used for plating operations often are dumped. However, these solutions can have valuable uses in other metal finishing operations such as:

- ◆ **Metal precipitation:** Non-chelated caustic solutions can be used to precipitate metals. However, cleaning solutions that contain detergents, surfactants, and high concentrations of wetting agents tend to destroy the flocculating/settling ability of the precipitated metal (Ford 1994).
- ◆ **Chrome treatment:** Solutions can act as pH adjusters in a precipitation tank (precipitation is discussed in the next section). For example, acid solutions can be used to adjust the pH in chromium reduction treatment. However, because these solutions typically have a high metal content, they should not be used for final pH adjustments. As with reusing spent rinsewater, facilities should check to make sure that the spent process bath solutions are compatible before they are used (EPA 1992).
- ◆ **Chelated metals treatment:** Spent acids, particularly those high in iron content such as ferric chloride etchants and steel and iron pickling solutions, are particularly desirable for pH adjustment (Ford 1994).
- ◆ **Cyanide treatment:** Non-chelated caustic solutions can be used to raise the pH in the first stage of cyanide treatment. In the second stage, the pH can be lowered with spent acid, but care must be taken not to use spent acids that contain nickel or iron as these metals form complexes with cyanide that are extremely refractory to alkaline chlorination (Ford 1994).

## Waste Segregation

Platers can extend the life of process solutions by removing impurities from the bath. The following sections provide an overview of removal techniques including filtration, carbonate freezing, precipitation, electrolysis, and carbon treatment.

## Removal of Solids via Filtration

Filtration is one of the most common techniques available for maintaining process bath purity. Most frequently, platers use cartridge filters as either in-tank or external units to remove suspended solids from the process solution. The majority of cartridges in use are disposable. However, reusable filters also are available. Filter systems also can be used on pre-finishing operations (mainly on larger tanks). The cost varies depending on the size and type of filter the shop uses (Cushnie 1994).

## Removal of Salts via Carbonate Freezing

Cyanide baths are adversely affected by the formation of carbonate buildup during the breakdown of cyanide. An excessive carbonate concentration can affect the smoothness of deposits, plating efficiency, and plating range.

### Filtration

#### Advantages

- ◆ Extends bath life
- ◆ Reduces chemical purchases for bath makeup and neutralization
- ◆ Reusable filters decrease operating costs

#### Disadvantages

- ◆ Takes up tank space

(APPU 1995)

### Filtration Case Study

An in-tank filtration unit reduced one company's chemical costs and waste generation by 50 percent. Capital costs for a 1,200 gallon per hour in-tank filter was \$500. Operation and maintenance costs were \$1,391 with a payback period of less than 5 months. Annual savings were approximately \$2,781. (APPU 1995)

Salt buildup can increase process solution dragout by as much as 50 percent.

Carbonate freezing can prevent the buildup of salts. The carbonate freezing process takes advantage of the low solubility of carbonate salts in the bath. Bath temperature is lowered to approximately 26 degrees Fahrenheit to

### Carbonate Freezing Case Study

The United States Army has developed a process to reduce carbonate concentration in cyanide baths using a technique that involves freezing the carbonates out of solution. A metal box containing dry ice and acetone is immersed in the plating bath. Carbonates are precipitated directly onto the outside metal surface of the box. The box is removed and the carbonates scraped off the box and discarded as solid waste. (Cushnie 1994)

crystallize the salts. This process also can remove sodium sulfate and sodium ferrocyanide. Carbonate freezing is used most often in cadmium cyanide plating, zinc cyanide plating, copper cyanide plating, and copper cyanide strike. Sodium cyanide baths can be treated by carbonate freezing or crystallization. However, potassium cyanide baths must be treated by precipitation rather than freezing (Cushnie 1994).

### Removal of Metal Contaminants via Precipitation

Metal finishers use precipitation as an alternative to carbonate freezing for cyanide baths. Table 7 lists common bath contaminants and precipitators that platers can use to remove contaminants. The process generally is performed in a spare tank where the solution is chemically treated and filtered and then returned to the original tank. For example, in a zinc bath, zinc sulfide can be used to precipitate lead and cadmium; the precipitant then is removed via filtration. In addition, iron and chromium contamination is

### Precipitation

#### Advantages

- ◆ Extends bath life

#### Disadvantages

- ◆ Eventually the process is no longer effective and bath will need to be dumped

(APPU 1995)

common in acidic nickel baths. In most formulations, these contaminants can be removed with peroxide combined with pH elevation and batch filtration. As with all chemical reactions, facilities must take care to ensure that the precipitation reagents are compatible with the bath constituents (Cushnie 1994).

### Removal of Metal Contaminants via Low-Current Electrolysis (Dummy Plating)

A common problem with plating baths is the introduction of metal contaminants into the bath that reduce the effectiveness of the solution. Copper is a common metal contaminant that builds up in plating baths. Copper can be removed from zinc and nickel baths through a process called dummy plating. Dummy plating is an electrolytic treatment process in which metallic contaminants in a metal finishing solution are plated out using low current density electrolysis. The process is based on the electrolytic principle that copper can be plated at a low electrical current (Ford 1994).

When the copper concentration in a process bath becomes too high, an operator can place an

Table 8. Precipitators for Common Plating Solutions (ASM 1982)

Plating Bath	Contaminant	Precipitator
Silver Cyanide	Carbonates	Lime
Cyanide Baths	Zinc and lead	Sodium sulfide
Nickel	Misc. metal contaminants (e.g., iron and aluminum)	Nickel hydrate
Acid Chloride Zinc	Soluble ferrous iron	Hydrogen peroxide
Zinc	Iron	Potassium permanganate
Electroless Nickel	Phosphorous compounds	Lime

electrolytic panel in the bath (the bath must be inoperative for 1 or 2 days). A trickle current then is run through the system, usually at a current density of 1 to 2 amperes per square foot. At this current, the copper in the plating bath solution will plate out onto the panel, but the plating bath additives are unaffected. Some of the plating metals also might be removed inadvertently, but the savings from extending the life of the bath usually justifies the metal loss. For more information on this process, refer to the recovery techniques section in Chapter 7.

### Removal of Organics Using Carbon Treatment

Carbon treatment of plating baths is a common method of removing organic contaminants. The carbon absorbs organic impurities that are present as a result of introducing oil or breaking down bath constituents. Carbon treatment can be used on both a continuous and batch basis. Various filtration methods are available, including carbon filtration cartridges (restricted to use on small applications), carbon canisters, pre-coat filters, and bulk application/agitation/filtration. Typical dosages are 1 to 4 pounds of carbon per 100 gallons of solution (Cushnie 1994).

#### Carbon Filtration Case Study

EPA documented a company that used activated carbon filtration to regenerate plating baths. This method consisted of a holding tank, a mixing tank, and a MEFIAG paper-assisted filter operating in a batch mode. This project reduced the volume of plating baths disposed and the amount of virgin chemicals purchased by 47 percent. The batch size was 2,400 gallons. Approximately 4 to 5.5 barrels of solids are generated annually from this process. Capital cost for the activated carbon filtration unit was \$9,192 and operational/maintenance costs were \$7,973 per year. Savings came from \$67,420 in reduced waste disposal costs and \$55,000 in chemical purchases savings. Waste generation was reduced by 10,800 gallons a year. The payback period was 3 months.

(APPU 1995)

## Cyanide-Based Plating Processes

Perhaps the single most toxic chemical used in metal finishing on a weight-for-weight basis is cyanide. Electroplaters are most at risk for exposure to hydrogen cyanide (HCN) through ingestion and inhalation, either through a catastrophic event or low levels associated with processing. Skin contact with dissolved cyanide salts is somewhat less dangerous but will cause skin irritation and rashes (Mabbett 1993).

This section contains information on the available alternatives to cyanide plating. The first part discusses general information regarding the substitution of non-cyanide solutions for traditional cyanide-based baths. The next section addresses specific plating solutions (e.g., brass, cadmium, copper, precious metals, and zinc) and provides information on alternative bath chemistries and successful implementation of recycling and recovery technologies.

Substitution of cyanide can have profound effects on a metal finisher. Cyanide, in the form of sodium or potassium cyanide, has been a key component of plating solutions for many years, particularly in plating copper, zinc, and other metals. Cyanide is an excellent complexer and has a wide tolerance for impurities and variations in bath composition. Cyanide's principle disadvantages are toxicity and the high cost of wastewater treatment (Ford 1994).

For these reasons, EPA and many states severely limit the discharge of cyanide. Platers typically use an alkaline chlorination process requiring sodium hypochlorite or chlorine to treat wastestreams containing free cyanide. These chemicals can contribute substantially to sludge generation (Braun Intertec 1992). For complex cyanides, platers typically use ultraviolet (UV)/ozone or UV/peroxide treatment. This process is simple and cost effective (Gallerani 1996).

### Overview of Non-Cyanide Substitutes

Many metal platers are seeking alternatives to traditional cyanide-based plating. Concerns over

occupational health and safety, waste treatment costs, regulatory compliance requirements, and potential liability have encouraged process managers to investigate new, non-cyanide plating technologies. The earliest and most complete cyanide substitution that has taken place in the industry is the conversion from zinc cyanide to zinc chloride or zinc alkaline (TURI 1994).

Non-cyanide alternatives generally have proven to be base specific and, therefore, are not simple to substitute. Also, non-cyanide plating solutions are less forgiving than cyanide baths to soils left on parts for plating. Firms must maintain higher cleaning standards if they switch to non-cyanide solutions. Another disadvantage of non-cyanide substitutes is that they tend to cost more than conventional baths (Ford 1994). Also, some of the common recovery technologies are more difficult to use with non-cyanide substitutes.

Using non-cyanide process chemistries can reduce hazardous waste sludge by eliminating a treatment step. However, many non-cyanide processes are difficult to treat and produce more sludge than cyanide baths. Some platers also have found that they need to install more than one process line to replace a single cyanide line. Usually, no substitute will meet all the requirements for replacing the single cyanide line. Multiple substitutes must be used, and some applications have no available substitute (TURI 1994).

Non-cyanide-based alternatives are available for cyanide copper, zinc, and cadmium plating processes. These substitutes can reduce regulatory reporting requirements, lower risks to workers, decrease environmental impact, and decrease corporate liability. Platers should weigh the advantages and disadvantages of non-cyanide baths for specific applications (Braun Intertec 1992).

The following list describes the factors that technical assistance providers should consider when recommending changes to a non-cyanide solution:

- ◆ Often, several non-cyanide solutions replace the single cyanide line.

- ◆ Process controls and cleaning practices must be maintained within tighter limits.
- ◆ Without the complexing ability of cyanide, periodic removal of iron and other potential contaminants might be required to ensure deposit quality. Filtration generally is necessary when using non-cyanide processes.
- ◆ The color shades obtained in chromating non-cyanide deposits do not always match those obtained with the same color chromates over cyanide deposits. Customers should be notified when segregating products with color shade differences is important.
- ◆ Some non-cyanide processes do not satisfactorily adhere to all surfaces and tend to become brittle at high temperatures.
- ◆ Alkaline non-cyanide processes generally provide more ductile deposits for subsequent forming operations than do acid non-cyanide processes.
- ◆ In both acid and alkaline non-cyanide processes, higher levels of organic or non-organic brightening agents are required to achieve a more cosmetically appealing finish. However, residue left on the workpiece can cause problems in future finishing processes such as chromating.
- ◆ Acid substitutes require an appropriate liner such as plastic (TURI 1994).

Technical assistance providers should make sure that companies that are considering a conversion to a non-cyanide substitute understand the inherent dangers in converting a cyanide line. Many problems can be averted as long as companies develop a well thought-out plan. A majority of the accidents involving cyanide in metal finishing operations have occurred because of badly planned conversions of a plating line from cyanide to non-cyanide operations (Gallerani 1996).

The following sections provide detailed descriptions of commonly used cyanide plating

processes (brass, cadmium, copper, precious metals, tin, and zinc) and the available alternatives.

## Brass Plating

### Common Uses

Brass plating is one of the most common alloy plating processes in use today. Brass can be plated in many applications and in varying thicknesses. Another property of brass plating is its ability to provide good adhesion to steel and rubber. Brass is, therefore, commonly used in the manufacture of steel wire cord for use in tires. Other applications of brass plating include a variety of decorative and engineering finishes (Strow 1982).

Brass plate comes in variety of colors from yellow to various shades of bronze and brown. In some cases, platers use brass as a very thin plate over other bright plates. Nickel often is used under a brass plate to level the surface. A brass plate then is applied over the nickel to provide a bright brass surface. Yellow brass is the most common material used in brass plating. Gold-colored brass often is used as a decorative plate. The main problem in applying a brass finish is rapid tarnishing. The conventional solution to this problem is to apply a protective layer of clear transparent powder coat or lacquer (Strow 1982).

### Common Bath Solutions

Typical brass plating solutions are cyanide-based. The basic ingredients of a cyanide brass plating solution are sodium cyanide, copper cyanide, and zinc cyanide. Other constituents include ammonia and carbonate. In some cases, platers also add sodium carbonate to provide a buffering action so that the plate color is consistent. The ratio of cyanide to zinc is the key element in controlling plate color and alloy composition (Strow 1982).

### Bath Content

Plating efficiency is controlled by copper content (i.e., the higher the copper content, the higher the efficiency). Temperature also plays a key role in the efficiency of the bath solution. For example, plating at 95 degrees Fahrenheit is twice as

efficient as plating at 75 degrees Fahrenheit. Process lines operated at higher than 95 degrees Fahrenheit require more frequent additions of ammonia; lines below 95 degrees require less frequent additions (Strow 1982).

### Alternative Bath Solutions for Brass Plating

Various non-cyanide brass solutions have been developed in the past, however, cyanide brass solutions are still the most prevalent solutions used by metal finishers today. Some of the original non-cyanide solutions had some problems including insufficient color in the deposit, poor appearance, narrow operating ranges, or bath instability. One of the most critical disadvantages is the lack of uniformity of color or appearance of the non-cyanide brass deposit (Fujiwara 1993b). Currently, not much literature is available for alternatives to brass cyanide baths.

#### *Brass Pyrophosphate*

Among the non-cyanide brass plating baths, pyrophosphate appears to be one of the most promising. However, field reports have stated that additives are necessary to operate this application properly. Otherwise, problems develop with unalloyed zinc getting contained in the deposit. Metal finishers have used the additive histidine in a pyrophosphate solution successfully. The deposits have shown similar qualities to the traditional copper zinc alloy deposits (Fujiwara 1993a).

#### *Brass Pyrophosphate-Tartare*

Tests have been completed on an alkaline pyrophosphate-tartare bath containing histidines as an alternative to brass cyanide solutions. Tests on these solutions have found that their alloy composition was almost constant over a wide range of current densities. Moreover, bright brass deposits having a uniform composition and color were obtained over almost the entire cathode area. The tests were performed on a bath solution that had a pH of 12.0 and a constant temperature of 30 degrees Celsius.

#### *Zirconium Nitride*

Zirconium nitride is a coating that has similar characteristics to brass and is applied using an



alternative deposition process. This compound is much easier than brass to plate and does not tarnish. The surface has a metallic appearance and a brass color tone. The solution uses a deposition process called sputterion plating. Sputterion plating involves coating a thin film in an even layer on a material to form a strong atomic bond. The film provides good wear resistance without color variation that can result from tarnishing. In this process, all or some portions of the material to be deposited enter a gas phase and condensation of the material takes place under constant ion bombardment (Kopacz 1992). For additional information on sputterion plating, refer to Chapter 8.

## Alternative Deposition Methods

### *Electrocoating*

The electrocoating process has been used as an alternative to brass electroplating. This process places the metal coating on the substrate via electrocoating. It comes in a brass color and is clear and can be used for some decorative applications. It does not involve metal plating, however, the finished surface resembles a plated finish. This finish provides excellent resistance under salt spray tests. A plater in Illinois is using this process on zinc die castings as a replacement for brass plate (Peden 1996).

## Cadmium Plating

Cadmium is extremely toxic and tightly regulated by EPA and OSHA. Because of its regulatory status and the high cost of cadmium plating, many platers are substituting cadmium with zinc where possible. Metal finishers have found some problems with finding substitute bath solutions or low-cyanide cadmium solutions for many applications. No single cadmium substitute has stood out as a drop-in solution. The primary problems with cadmium substitutes are customer acceptance, the characteristics of the finish, and the higher cost of the plating solution in some cases (Davis 1994).

### Common Uses

Cadmium exhibits superior corrosion resistance (especially in marine environments), lubricity, and other specific engineering properties. Cadmium also is easily welded. Moreover, a

because of its toxicity, fungus or mold growth is not a problem. Often, cadmium-plated material is chromated to increase corrosion resistance. The largest segment of the cadmium plating market is the military, which is beginning to change its specifications to less toxic products (Haveman 1994).

## Common Bath Solution

The most common method for electroplating cadmium is an alkaline cyanide bath. Cadmium is supplied to the bath in the form of metallic cadmium and cadmium compounds. An all-purpose, bright cadmium bath has a sodium cyanide to cadmium ratio of 5:1. Sodium hydroxide and sodium carbonate also are used in the bath solution. Operating temperatures range from 24 degrees Celsius to 32 degrees Celsius. A current density of 20 to 40 amperes per square foot is required to achieve a uniform plating thickness (ASM 1982).

## Alternative Process Solutions for Cadmium Plating

Cadmium plating solutions that do not use cyanide are commercially available. These include cadmium acid and cadmium alkaline plating solutions. Given the toxicity of cadmium, however, the most environmentally preferable substitutes do not use either cadmium or cyanide. Replacing cyanide-based cadmium coatings with one of the non-cadmium, non-cyanide alternatives eliminates workplace exposure to both cadmium and cyanide and reduces environmental releases of both chemicals. Tables 8 and 9 present an overview of the available alternatives. These alternatives include several non-cyanide based cadmium baths, various combinations of zinc-based chemistries, and two tin-based alternatives. Some of the alternatives have improved performance when compared to cadmium. These benefits include:

- ◆ Zinc substitutes exhibit improved corrosion resistance
- ◆ Zinc-nickel alloys have better wear resistance
- ◆ Zinc-cobalt deposits show good resistance to atmospheres containing sodium dioxide

Table 9. Alternatives to Cadmium Cyanide—Product Quality Issues (TURI 1994)

Alternatives	Corrosion Protection	Finish Appearance	Chromate Colors	Ductility
<b>Cadmium Neutral or Acid Sulfate</b>	(+) Good	(+) Satisfactory	Full line available	(+) Good; little hydrogen embrittlement
<b>Cadmium Acid Fluoroborate</b>	(+) Good	(+) Satisfactory	Full line available	(+) Good; little hydrogen embrittlement
<b>Zinc-Nickel Alkaline</b>	(+) Excellent with chromate conversion coating	(+) Good	Specialized chromates: bronze, yellow, iridescent, and black	(+) More ductile than acid zinc
<b>Zinc-Nickel Acid</b>	(+) Good	(+) Good brightness at higher efficiency	Specialized chromates: bronze, yellow, iridescent, and black	(-) Less ductile because of higher brightener levels
<b>Zinc-Cobalt Acid</b>	(+) Good	(+) Excellent (+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, and black	(+) Fair; lower hydrogen embrittlement than alkaline
<b>Zinc-Cobalt Alkaline</b>	(+) Good	(+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, and black	(+) Better than acid bath
<b>Zinc-Iron Acid</b>	(+) Good, but not recommended for high-temperature applications	(+) Provides deep uniform black without use of silver	Black; other limited based on bath conditions	(+) Good
<b>Tin-Nickel Acid or Near Neutral</b>	(+) Good resistance to corrosion and tarnish	(+) Can be decorative in appearance	N/A	(+) Good
<b>Tin-Zinc Acid, Alkaline or Neutral</b>	(+) Good with chromate applied (+) Does not undergo bimetallic corrosion	(-) Fair	Limited to yellow	(+) Excellent (soft deposit)

Table 10. Alternatives to Cadmium Cyanide—Process Issues (TURI 1994)

<b>Alternatives</b>	<b>Plating Uniformity</b>	<b>Process Considerations</b>	<b>General Comments</b>
<b>Cadmium (Neutral or Acid Sulfate)</b>	(-) Poor throwing power	(-) Liners required for acid; preferred for neutral	(-) High toxicity, low discharge limits for cadmium; not preferred toxic use reduction (TUR) option
<b>Cadmium Acid Fluoroborate</b>	(-) Poor throwing power	(+) High cathode efficiency at high current densities (+) Good stability	(+) Good data available; widely used in barrel plating (-) High toxicity, low discharge limits for cadmium; not preferred TUR option
<b>Zinc-Nickel Alkaline</b>	(+) More uniform thickness and alloy distribution than tin-nickel (+) Good throwing power	(-) Chiller required to maintain optimum temperature (-) Slower plating speed than zinc-nickel acid (+) Faster plating speed than alkaline nickel	(+) Good corrosion properties maintained after forming and heat treating (-) Might contain chelators
<b>Zinc-Nickel Acid</b>	(-) Poor thickness distribution; alloy variation from high to low current density	(-) Requires additional inert anodes and segregated rectification (+) Faster plating speed than alkaline nickel	(+) Good corrosion properties maintained after forming and heat treating (-) Might contain chelators
<b>Zinc-Cobalt Acid</b>	(-) Poor throwing power (-) Variable current density	(+) Good plating speed (+) High cathode efficiency	(+) No silver required for black chromating (-) Might contain chelators
<b>Zinc-Cobalt Alkaline</b>	(+) More uniform than zinc-cobalt acid	(-) Lower efficiency than zinc-cobalt acid	(+) No silver required for black chromating (-) Might contain chelators
<b>Zinc-Iron Acid or Alkaline</b>	(+) Good throwing power	(-) Iron content must be controlled to prevent blistering	(+) No silver required for black chromating (-) Might contain chelators
<b>Tin-Nickel Acid or Near Neutral</b>	(+) Deep throwing power	(-) Chiller required (-) Lined tanks recommended	(+) Good hardness (between nickel and chromium) and wear resistance, low contact resistance (+) Able to retain oil film for lubrication
<b>Tin-Zinc Acid, Alkaline or Neutral</b>	(-) Poor throwing power (+) Excellent covering power	(-) Chiller required	(+) Excellent solderability properties

Some of the limitations of cadmium alternatives include:

- ◆ Increased electrical contact resistance for zinc coatings
- ◆ Reduced lubricity
- ◆ Decreased throwing power
- ◆ Decreased corrosion resistance in marine environments

#### *Cadmium Neutral or Acid Sulfate/Cadmium Acid Fluoroborate*

Three non-cyanide, cadmium-based alternatives are available: neutral sulfate, acid fluoroborate, or acid sulfate. However, these cadmium-based alternatives do not have the throwing power of cadmium cyanide processes. The only substitute that is capable of high cathode efficiency is acid fluoroborate, but only at high current densities. Since cadmium is also a highly regulated substance, non-cyanide alternatives that still use cadmium are not as preferable as those substitutes that contain neither cadmium or cyanide (Pearlstein 1991).

#### *Zinc Alloys*

Numerous zinc alloy processes are commercially available including zinc-nickel, zinc-cobalt, zinc-tin, and zinc-iron. The use of zinc alloys has grown because of their potential to replace cadmium, particularly in countries such as Japan where the use of cadmium has been strictly curtailed or prohibited. Zinc alloys were introduced in the Japanese and German automotive industry for use in fuel lines and rails, fasteners, air conditioning components, cooling system pumps, coils, and couplings. Improved warranty provisions in 1989 from vehicle manufacturers such as Honda, Toyota, and Mazda further boosted the use of zinc-nickel and zinc-cobalt in the automotive industry. Other industries that use zinc alloys as a substitute for cadmium include electrical power transmitting equipment, lock components, marine, and aerospace industries. Metal finishers also have substituted zinc-nickel coatings for cadmium on fasteners for electrical transmission structures and on television coaxial cable connectors (EPA 1994).

Plating with zinc alloys requires that operating parameters are controlled and maintained at much tighter standards than with cadmium cyanide plating. Critical parameters include pH, chemistry, temperature, and agitation level. Zinc-nickel alloys can be plated from a chloride-based process that is similar to chloride zinc baths or from an alkaline non-cyanide zinc solution. Brightening agents and other additives make these alloy processes more expensive to purchase and operate than cadmium baths. The alloying metal usually is added as a chemical concentrate, which is purchased from the supplier. Zinc anodes generally are used with this solution because alloy anodes are not readily available (Altmayer 1993a).

For cadmium applications that require enhanced corrosion resistance to salty environments, zinc alloys are suitable substitutes. Pure zinc also can be used as a substitute for heavy cadmium deposits (more than 1 millimeter thick). However, zinc alloy deposits can fail to be suitable substitutes when cadmium is specified for the following characteristics: enhanced lubricity, solderability, low electrical contact resistance, ease of disassembly after corrosion has occurred, or inhibition of fungus or mold growth (Bates 1994).

Treatment of rinsewater from zinc alloy electroplating usually is simply adjusting the pH, eliminating the need for cyanide oxidation. The zinc-cobalt, zinc-tin, and zinc-iron processes do not add any metals to the process that are presently regulated under federal water programs (Altmayer 1993a). The following sections provide a brief description of several of the most common zinc alloys.

#### *Zinc-Nickel Alkaline*

Alkaline zinc-nickel baths produce a deposit that tends to favor applications that do not require bendability. Those applications are better suited for the laminar structure of acid baths. Alkaline zinc-nickel coatings, however, provide one of the highest corrosion protection ratings available with a chromate conversion coating. High corrosion protection is a result of the chromate solution dissolving some of the zinc from the

surface, leaving a nickel-rich layer. Zinc-nickel finishes provide good corrosion properties after parts-forming operations and heat treating. Other features of alkaline zinc-nickel are low metal formulation, limited range of chromate colors, difficulty in chromating because of nickel content, and temperature constraints that require a chiller for control (Zaki 1989).

#### Zinc-Cobalt

Zinc-cobalt deposits contain approximately 1 percent cobalt and 99 percent zinc. The acid bath has a high cathode efficiency and high plating speed. The deposit also has reduced hydrogen embrittlement when compared to alkaline systems. Thicknesses of the deposits tend to vary substantially with the current density of the process bath (Murphy 1993).

#### Zinc-Iron Acid or Alkaline

The primary advantage of zinc-iron is its ability to develop a deep uniform black conversion coating. Additionally, the alloy is easily welded and machined and is used easily on strip steel. This coating has been used successfully as a base

coat prior to painting. The primary disadvantage of zinc-iron coatings is their limited ability to provide corrosion resistance (Murphy 1993).

#### Zinc-Nickel Acid

Zinc-nickel acid solutions provide bright coatings that exhibit high throwing power. Good corrosion properties are maintained after parts-forming operations and heat treating because acid zinc-nickel delivers a higher nickel content than the alkaline zinc bath, which tends to increase corrosion. Unfortunately, acid solutions also tend to produce deposits with poorer thickness distribution and greater alloy variation between high and low current density areas than its alkaline counterpart. Other disadvantages include the limited range of chromate colors, required use of additional inert anodes, and segregated treatment systems. For workpieces that are being chromated after a cadmium plate, this solution is difficult to work with because higher brightener levels and nickel content create a more brittle coating, making it more difficult to chromate (Zaki 1989).

#### Tin-Zinc Alloy

A tin-zinc alloy has been developed in the United Kingdom as an alternative for cadmium plating. The proprietary solution, Stanzac, was developed by the International Tin Research Institute (ITRI) in Uxbridge, Middlesex, United Kingdom. It contains 75 percent tin and 25 percent zinc and can be used in either rack or barrel plating. Research is underway to develop a high-speed tin-zinc plating line for the continuous plating of steel strip (Plating and Surface Finishing 1994).

#### Zinc Chloride

Zinc chloride process baths were tested to assess the feasibility of using this solution as an alternative for cadmium cyanide in rack plating operations. Performance results demonstrated that while the zinc chloride finish was similar to the cadmium finish, the cadmium-plated parts, however, exhibited superior corrosion resistance. The main advantage of using the zinc chloride over cadmium is a greatly reduced hazard risk at the facility. High capital costs (\$2 million for the purchase of new equipment, cleanup costs for old equipment, and waste disposal costs) gave this investment a payback period of 115 years.

#### Substituting Zinc-Cobalt for Cadmium Case Study

The Foxboro Company, a manufacturer of industrial process controls located in southeastern Massachusetts, employs 3,500 people in three facilities. The company manufactures a wide range of production processes, from electronic assembly to cleaning, plating, painting, degreasing, and machining.

In 1992, the company focused attention on eliminating the use of cadmium in its plating operations. This was accomplished by eliminating unnecessary plating and substituting zinc-cobalt solution for cadmium cyanide. The change did not require any new plating equipment and the vendor of the new plating bath provided technical support and worker retraining to facilitate the switch. The switch not only eliminated health and safety problems associated with cyanide, but also permitted the facility to eliminate an entire process from waste treatment operations. It is estimated that the change in operations saves the company \$35,000 annually. (MA OTA 1995)

The process change, therefore, cannot be justified on economics alone (PNWPPRC 1996).

### *CorroBan*

CorroBan was developed by Boeing scientists in the early 1980s. It is a proprietary zinc-nickel alloy that is electrodeposited from a cyanide-free solution. The process was licensed to Pure Coatings, Inc. The zinc provides galvanic protection similar to cadmium while the nickel imparts extra hardness. Deposits from this process pass 2,600-hour salt spray tests and ASTM F 519 hydrogen embrittlement tests and are compatible with aluminum. This deposit also has lubricity (torque-tension) characteristics similar to cadmium. Testing also has shown that CorroBan provides better sacrificial corrosion protection than cadmium because of the improved electrode potential of the coating in a sodium chloride solution (EPA Region 2 1995).

### **Alternative Deposition Processes for Cadmium Plating**

#### *50/50 Zinc-Cadmium Alloy Using In-situ Reclaim*

The 50/50 zinc-cadmium alloy using an alternative deposition processes has shown promise as an alternative to cadmium plating. This alloy uses 50 percent less cadmium, but exhibits superior corrosion resistance. The coating is applied using a dry plating technique developed by IonEdge Corporation for use specifically with this alloy. In this dry plating process, simultaneous plating of zinc and cadmium species is conducted under neutral gas-flow discharge conditions. Details of the process are of a proprietary nature and, therefore, further information is not available (Sunthakar 1994).

#### *Ion Vapor Deposition of Aluminum*

Aluminum coatings deposited through ion vapor deposition (IVD) can replace cadmium coatings in some applications, eliminating both the use of cadmium and cyanide. This technology is suited especially to applications that require cadmium to protect steel substrates from corrosion and to inhibit the growth of organisms such as mold and fungus. Ion Vapor deposition aluminum coatings can be applied to a wide variety of metallic substrates including aluminum alloys and plastic/

composite substrates. This process does not use or create any hazardous materials.

This technology has been used mainly on high-strength steels in the aerospace industry and in marine applications. Some facilities have converted to IVD coatings, eliminating the anodizing process on aircraft components that are subject to fatigue (EPA 1994). Ion Vapor Deposition aluminum has found applications in naval aircrafts, particularly those manufactured by McDonnell Douglas Corporation. This company has found IVD aluminum coatings are especially suited for parts where temperatures can exceed 450 degrees Celsius and/or when contact with titanium parts is expected. This process also is used when working with high-strength steels that preclude using cathodic processes such as electroplating. However, IVD coatings lack the frictional properties of cadmium and are expensive to implement (Lansky 1993).

The advantages of IVD aluminum coatings include the uniformity in finish thickness and excellent throwing power. Deposits can be plated on difficult-to-reach places, making IVD attractive for coating complex shapes. The process is limited, however, in its ability to deposit coatings into deep holes and recesses, particularly in configurations where hole depth exceeds the diameter (Pearlstein 1991). IVD processes are discussed in more detail in Chapter 8.

## **Copper Plating**

### **Common Uses**

Copper plating is widely used as an underplate in multi-plate systems and as stop-offs for carburizing as well as in electroforming and the production of printed circuit boards. Although relatively corrosion resistant, copper tarnishes and stains rapidly when exposed to the atmosphere. Copper alone is rarely used in applications where a durable and attractive surface is required. Copper plating is used generally as an underplate or pre-plate before a final finishing operation such as nickel or gold. Bright copper is used as a protective underplate in multiple

layer systems or when a decorative finish is desired. The copper finish often is protected against tarnishing and staining by the application of a clear lacquer. Copper plating can change the appearance, dimensions, or electrical conductivity of a metal part. Jewelry manufacturing, aerospace, and electronics often use copper plating (ASM 1982).

### Common Bath Solutions and Waste Treatment

The major constituents of copper cyanide baths are potassium cyanide, potassium hydroxide, and copper cyanide. Cyanide copper plating requires a two-stage waste treatment procedure. The first step is cyanide destruction using either chlorine gas or less hazardous, but more expensive, hypochlorite treatment. The second step is precipitation of metals (i.e., pH adjustment with a caustic). The sludge produced from this treatment contains trace amounts of cyanide, increasing disposal costs significantly (ASM 1982).

The benefits of replacing cyanide-based copper plating baths with a non-cyanide solution include reduced environmental exposure and employee health risks. Non-cyanide copper has the following benefits:

- ◆ Greatly reduces safety risks to workers
- ◆ Can reduce the costs and complexity of treating spent plating solutions
- ◆ Poses no risk of hydrogen cyanide (HCN) evolution from dragout to an acidic bath
- ◆ Can increase plating speed
- ◆ Eliminates a listed hazardous wastestream
- ◆ Eliminates or reduces Toxics Release Inventory (TRI) reporting requirements
- ◆ Can reduce sludge generation because of reduced metal concentrations
- ◆ Might not require treatment for carbonates in the plating solution (EPA 1994)

### Issues Related to Non-Cyanide Substitutes

Non-cyanide copper plating requires more frequent bath analysis and adjustment than cyanide-based plating. Cyanide-based copper

plating baths are relatively forgiving to bath composition because they remove impurities. Non-cyanide baths are less tolerant of poor surface cleaning so thorough cleaning and activation of the surface is critical to obtain a quality finish. Personnel should be capable of operating the non-cyanide process as easily as the cyanide-based process (EPA 1994).

Operating costs of the bath are substantially higher for the non-cyanide processes than the cyanide process, however, replacing the cyanide-based bath with a non-cyanide bath eliminates the need for treatment of cyanide-contaminated wastewaters. This reduces substantially the difference in cost between the two solutions. Given the higher operating costs, a facility might not be able to justify this conversion on economics alone unless the facility faces substantial treatment costs for cyanide emissions.

### Reported Applications

The use of non-cyanide copper plating baths is not widespread. The number of companies running non-cyanide trials is small, but growing (Altmayer 1993). An application where non-cyanide plating could be attractive from a cost perspective is selective carburizing. This process is used widely in the heavy equipment industry for hardening portions of coated parts such as gear teeth. Gears must be hard at the edges, but not throughout because hardness throughout could cause the part to become brittle. To achieve this selective hardening, the plater applies a copper mask to that portion of the part that is not targeted for hardening. The part then is treated with carbon monoxide and other gases (EPA 1994).

### Limitations

Alkaline non-cyanide processes are unable to deposit adherent copper on zinc die castings and zincated aluminum parts without a copper strike. The one exception is a supplier that claims to be able to plate these parts using a proprietary process. Several facilities are currently testing this method on a pilot scale (Altmayer 1993). Of these pilot tests, two facilities reported that costs are approximately two to three times more than other processes, even when waste treatment and disposal costs are considered. One of these

facilities has discontinued the use of the process while the other facility has continued with the process believing that the benefits of increased safety and compliance are worth the cost (EPA 1994).

For plating copper, certain non-cyanide alkaline baths of proprietary composition have been developed. Four widely known alternatives to copper cyanide plating are copper acid sulfate, copper acid fluoroborate, copper alkaline, and copper pyrophosphate. Table 10 provides a brief overview of these four alternative bath solutions.

### Specific Non-Cyanide Alternatives

#### *Copper Alkaline Solutions*

Non-cyanide alkaline baths yield fine grained, dense deposits similar to cyanide copper deposits. The one area where they might differ is in the purity of deposit. Additives in copper alkaline solutions incorporate a trace of organic material into the deposit. This solution is ideally suited for workpieces that require thick deposits such as those used as heat treating (carburizing)

stop-off on steel parts. The dense deposit is an excellent diffusion barrier for carbon (Braun Intertec 1992).

The non-cyanide alkaline copper solution uses cupric copper ions while the cyanide process contains monovalent copper. The chemical composition of monovalent copper results in faster plating at the same current density levels. Platers can operate alkaline copper baths at higher current densities than cyanide solutions to yield faster plating overall. The throwing power of the non-cyanide process is superior to the cyanide process, especially in barrel plating. This process uses one-quarter to one-half of the copper contained in cyanide solution, resulting in lower sludge generation because of lower metal concentrations (Mabbett 1993).

The alkaline substitute has significant drawbacks. Copper alkaline non-cyanide baths operate at significantly lower pHs (8.0 to 8.8) than traditional cyanide copper lines. Despite the lower pHs, non-cyanide baths have trouble tolerating zinc contamination and have not been

Table 11. Overview of Alternatives for Copper Cyanide Plating (TURI 1994)

Alternatives	Finish Appearance	Ductility	Plating Uniformity	Process Considerations	General Comments
Copper Alkaline	(+) Good appearance	(+) Good	(+) Better throwing than cyanide	(+) Operating pH 8.0 to 8.8	(+) Can be used as heat treat maskants (+) Less corrosive (+) Might be used as a strike bath
Copper Acid Sulfate or Fluoroborate	(+) Good appearance (+) Excellent leveling	(+) Good to excellent	(-) Less macro-throwing power than alkaline (+) More micro-throwing power than alkaline	(-) Lined tanks and appropriate anode baskets required (+) Fluoroborate allows use of higher current densities	(+) Good use data available
Copper Pyrophosphate	(+) Good, fine grained, and semi-bright	(+) Good	(+) Good throwing power	(+) Operating pH of 8.0 to 9.8 (-) More sensitive to organic contaminants than acid copper (-) Might require longer plating time	(+) Might be used as strike bath (-) Might contain ammonia



successful at plating copper over zinc surfaces. The alkaline copper process also is more sensitive to impurities and the chemistry can be difficult to control. In addition, changing over to alkaline copper requires a lined tank and, in some cases, the addition of a purification tank. Overall, the cost for substitution is fairly high when compared to the cost of copper cyanide solutions (Mabbett 1993).

### *Copper Acid Sulfate*

The copper sulfate bath is the most frequently used of the acid copper electrolytes. An acidic copper plating bath using sulfate ions has proved versatile. However, the low pH can sometimes

and electroforming operations and for the application of copper as an undercoating for chromium. By altering the composition of the bath, platers can use copper sulfate in through-hole plating of printed circuit boards where a deposit ratio of 1:1 is desired. With additives, the bath produces a bright deposit with good leveling characteristics or a semi-bright deposit that is easily buffed (Braun Intertec 1992).

In contrast to heavy copper cyanide plating baths, copper sulfate baths are highly conductive and have simple chemistries. Sulfate baths are economical to prepare, operate, and treat. Previous sulfate bath problems have been overcome with new formulations and additives. The copper cyanide strike might still be needed for steel, zinc, or tin-lead base metals (Braun Intertec 1992).

### *Copper Fluoroborate*

Fluoroboric acid is the basis for another copper plating bath that provides enhanced solubility and conductivity as well as high plating speeds. This bath is simple to prepare, stable, and easy to control. Operating efficiency approaches 100 percent. Deposits are smooth and attractive and can be easily buffed to a high luster. The addition of molasses to the bath, when operated at 120 degrees Fahrenheit, results in deposits that are stronger and harder (Weisenberger 1982). Additional agents must be used to avoid excessive porosity in thicknesses greater than 20 mils. The drawbacks of this bath solution are that it is more costly, has fewer additive systems available, and is more hazardous to use than other non-cyanide alternatives. Treatment of wastewater also is more costly (Murphy 1993).

### *Copper Pyrophosphate*

Copper pyrophosphate is used primarily to produce thick deposits. These baths are used for decorative multi-plate applications, through-hole plating of printed circuit boards, and a stop-off in selective case hardening of steels. The types of plates obtained with this solution are similar to those obtained with a high efficiency cyanide bath. However, a strike is required if plating over steel, magnesium, aluminum, or zinc. Alkaline pyrophosphate baths exhibit good throwing power, plating rates, and coating

### **Substituting Copper Alkaline Solutions for Copper Cyanide Case Study**

Tri-Jay Company is located in Johnston, Rhode Island. The facility employs 45 people and occupies an 11,000 square foot facility. Tri-Jay provides the jewelry industry with job shop plating services. In conjunction with the Rhode Island Department of Environmental Management, Tri-Jay tested the feasibility of replacing their copper cyanide lines with an alkaline plating solution manufactured by Zinex Corporation of Oxnard, California.

In testing the solution, parts were placed in rack and barrel processes under controlled conditions. Based on limited production runs, the baths were scaled up to higher production quantities. The bath conditions were optimized and data was taken on plate conditions after quality control.

Tri-Jay concluded that while the bath had promise, the operation needs close monitoring and the solution might not be well suited for job shop applications. The process proved to be trouble-free in plating brass and, with proper cleaning, steel as well. Castings, however, presented too many contamination problems for this solution to be economically feasible. For the electronics and automotive industries and for reel-to-reel plating operations, this solution might be extremely feasible. (RI DEM 1995a)

attack the substrate and increase iron concentration in the process bath. The process is used primarily in printed wire board manufacturing

ductility. In addition, the bath normally operates at an almost neutral pH. Deposits from this bath are fine-grained and semi-bright. The main disadvantage of copper pyrophosphate is that the chemistry is expensive and wastewater is harder to treat when compared to traditional copper cyanide wastewater (Braun Intertec 1993).

### Acid Copper Versus Alkaline Copper Solutions

Plating of copper from acid baths is used extensively for electroforming, electrorefining, manufacturing of copper powder, and decorative electroplating. Acid copper plating baths contain copper in bivalent form and are more tolerant of ionic impurities than alkaline baths. However, they have less macro-throwing power and poorer distribution rates than alkaline solutions. Acid baths have excellent micro-throwing power, which can be effective in sealing porous die castings. As with the alkaline baths, the plater must apply a strike to a workpiece prior to plating on steel or zinc (Braun Intertec 1993).

### Alternative Deposition Processes for Copper Plating

The Department of Defense is testing the feasibility of depositing copper using new deposition technologies such as plasma spraying, ion plating, and sputter deposition. For more information on these technologies, refer to Chapter 8.

### Waste Treatment of Alkaline Non-Cyanide Copper

Wastewater treatment of non-cyanide copper solutions is simpler than those for copper cyanide processes because of the elimination of cyanide removal. Another benefit is reduced sludge generation because the non-cyanide process contains one-half to one-fourth as much copper as a full-strength cyanide copper bath. Furthermore, non-cyanide alternatives eliminate the two-stage chlorination system that uses chemicals such as chlorine or sodium hypochlorite that can increase sludge generation. One potential disadvantage of the non-cyanide bath is that it frequently can become contaminated beyond control (as happened in pilot test), requiring increased treatment and disposal for the process line (Freeman 1995).

## Separation Technologies for Copper Plating

This section provides specific examples of recycling and recovery technologies for copper plating including ion exchange, electrodialysis, electrolytic recovery, and reverse osmosis. A more in-depth discussion of individual recycling technologies is included in Chapter 7.

### *Ion Exchange*

Copper platers can use ion exchange to recover a high percentage of the copper from contaminated plating baths and rinsewaters. For example, a Montreal plating shop sent rinsewater with copper concentrations of about 300 parts per million from a copper sulfate plating solution (acid copper) to an ion exchange resin unit. The unit reduced the concentration of copper to about 1 part per million. Every 20 to 30 minutes, the resin would be regenerated with dilute sulfuric acid, exchanging copper ions in the resin with hydrogen ions. The concentrated copper sulfate solution produced from the regenerating process was added to the plating tank as needed. Through this ion exchange process, the company recovered 95 percent of the copper from the running rinse (RI DEM 1995a).

### *Electrodialysis*

Used on a stagnant rinse line, electrodialysis can recover 90 to 95 percent of the dragout from heated copper plating solutions. This concentrated dragout goes back into the plating tank while the dilute stream is returned to the rinse tank. Electrodialysis can run continuously without regeneration, requires only a DC power source for operation, and consumes relatively small amounts of electricity. A disadvantage of electrodialysis is that it recovers plating bath impurities along with the copper. The membranes in this process also are prone to fouling from either solids in the bath or from compounds forming on the sheets (RI DEM 1995b).

### *Electrolytic Recovery*

This process recovers only the metals that are dragged into the rinsewater. Enough metal must be present in the solution to form a usable strip. A homogenous copper deposit requires the rinse solution to have concentrations of 2 to 10 grams

per liter. Cathodes with greater surface area can recover copper from much lower concentrations (in the 10- to 50-milligrams-per-liter range).

An electroplater in Providence, Rhode Island, reported recovery of 85 grams per minute over 9 days using a 5-square-foot electrode. The unit received flow from a dragout tank and returned the clean water to the same tank. This particular tank's copper concentrations dropped from 150 to 10 milligrams per liter. Other companies have experienced similar reductions of approximately 88 percent of the copper from both standing rinse tanks and running rinses (RI DEM 1995a).

### *Reverse Osmosis*

EPA performance tests have shown reverse osmosis (RO) to be successful in recovering metals from both acid copper and copper cyanide plating baths. Reverse osmosis membranes used in cyanide applications might need pretreatment. A copper cyanide plater reported that its RO unit recovered 98 to 99 percent of the copper from its plating wastes and 92 to 98 percent of the cyanide. The type of membrane used is a major factor in determining the effectiveness of RO. Cellulose membranes cannot withstand cyanide and solutions with either high or low pH. However, many membranes are resistant to these conditions (RI DEM 1995a).

## **Copper Strike**

Copper strikes often are used to deposit a thin intermediate layer (strike) of copper over a variety of substrates including steel and zinc die castings before those metals are plated with other metals. This layer is required for successful plating because it promotes adhesion on difficult-to-plate metals and protects some substrates from degradation in subsequent plating solutions. Because copper strikes are applied frequently, finding replacements for cyanide solutions can greatly assist facilities in reducing the amount of cyanide that they use (Hughes 1991).

### **Copper Strike Alternatives**

#### *Copper Pyrophosphate*

Dilute copper pyrophosphate has been viewed as a feasible replacement for the cyanide strike because the solution does not degrade substrates.

The main disadvantage of this chemistry is that it usually takes three times longer to plate than traditional cyanide solutions (Hughes 1991). For more information on this alternative, refer to the previous section on copper cyanide plating in this chapter.

#### *High-pH Nickel*

High-pH nickel plating solutions have been available for a long time as a substitute for cyanide copper strike on zincated surfaces and zinc die castings. To obtain optimum results with high-pH nickel, the plater must balance the ratio between nickel sulfate and sodium sulfate. The proper ratio depends on several factors including part geometry; parts with complex shapes require higher sodium sulfate concentrations than parts with simple geometry. For plating operations above a 5.4 pH, platers use ammonium hydroxide and sulfuric acid for pH control. Zinc contamination should be removed continuously through low current density dummyming in a purification cell. Cleaning parts prior to plating is more critical in high-pH nickel plating than traditional copper cyanide strikes. Because the bath chemistry is not proprietary and requires no additives, facilities can mix their own solutions. This makes the cost of operating this bath lower than operating cyanide copper strike lines and significantly lower than the cost of operating alkaline non-cyanide copper baths (Freeman 1995).

Using sodium in the bath will affect the deposit characteristics of the strike. The higher the sodium content of this nickel-plating bath, the more brittle the deposit becomes. The bath, therefore, should be used only as a strike before conventional nickel or copper plating. Parts that undergo fatigue cycles or extreme temperature changes can experience early fatigue failures and less corrosion resistance (Freeman 1995).

Substituting high-pH nickel for a copper cyanide strike will eliminate a cyanide wastestream. However, the ammonium ion present in the high-pH nickel formulation can cause waste treatment problems unless the concentration can be minimized through dragout recovery techniques. Another disadvantage of this technique is that the bath contains a higher metal content than the

cyanide copper process and twice the metal content of the alkaline non-cyanide process. Sludge volume from wastewater treatment would be affected accordingly (Freeman 1995).

## Precious Metals

The electrodeposition of precious metals for decorative and engineering purposes is an important part of the metal finishing industry. Given the high cost for a gallon of precious metal solution, platers have used many methods to conserve and recover precious metal solutions. Because of this, more information is available on recovery technologies for precious metals than common metals (e.g., copper, nickel, and zinc). Common forms of metal recovery in precious metal operations include ion exchange or electrowinning (Ford 1994).

## Gold Plating

### Common Uses

Until recently, gold plating was used primarily for decorative purposes in jewelry and flatware. Currently, gold is widely used in the electronics industry because of its good electrical contact properties as well as corrosion and oxidation resistance. Typical applications for gold plating include printed circuit boards, contacts, connectors, transistor bases, and integrated circuit components. Gold plating also is widely used in the chemical industry for reactors and heat exchangers (ASM 1982).

Traditionally, gold has been plated from potassium gold cyanide solutions, although many different types of gold and gold alloys are available. However, gold plates can be broken down into eight general classes:

- ◆ Class A: Decorative 24K gold flash (2 to 4 millionths thick) plated in rack and barrel operations
- ◆ Class B: Decorative gold alloy flash (2 to 4 millionths thick) plated in rack and barrel operations
- ◆ Class C: Decorative gold alloy flash (20 to 40 millionths thick) plated in rack operations
- ◆ Class D: Industrial/electronic high-purity soft gold plated in rack, barrel, and selective plating operations
- ◆ Class E: Industrial/electronic hard, bright, and heavy 99.5 percent gold (20 to 200 millionths thick) plated in rack, barrel, and selective plating operations
- ◆ Class F: Industrial/electronic gold alloy heavy (20 to 400 millionths thick) plated in rack and selective plating operations
- ◆ Class G: Refinishing, repair, and general; deposits are pure bright alloys (5 to 40 millionths thick) plated in rack and selective plating operations
- ◆ Class H: Miscellaneous including electro forming of gold and gold alloys, statuary, and architectural applications (Weisberg 1993)

In general, platers use high gold contents at heavy thickness because this permits higher current densities and higher cathode efficiencies. Other methods that platers can use to increase plating speed include higher operating temperatures and increased agitation (ASM 1982).

### Common Bath Solutions

The four general groups of gold plating solutions are alkaline gold cyanide, neutral gold cyanide, acid gold cyanide, and non-cyanide solutions (generally sulfite-based). Alkaline cyanide baths have been used for the past century. Because of the complexing action of cyanide, however, obtaining consistent co-deposit of gold alloys is difficult unless the process is operated at high current densities. As a result, platers have limited the use of alkaline cyanide baths to flash deposits. Around the 1950s, bright baths were developed using silver and selenium as alloying agents. Some success has been demonstrated with neutral baths. Free of cyanide at the start, these baths build up potassium cyanide by adding gold potassium cyanide to replenish the gold in the process bath (Braun Intertec 1992). Each of the groups can be paired with the different classes of plating operations discussed above.

- ◆ Alkaline gold cyanide: Class A, B, C, D, occasionally F, G, and H
- ◆ Neutral gold cyanide: This is usually used to achieve high-purity gold plated for Class D and G.
- ◆ Acid gold cyanide: This is used for bright, hard gold and gold alloy plating. It is used occasionally for Class B, C, E, F, and G.
- ◆ Non-cyanide gold: Occasionally, it is used for Class A, B, C, D, F, G, and H (Weisberg 1993).

### Alternative Gold Plating Solutions

The high cost of gold has made conservation critical and has led to a search for substitutes. Table 11 provides an overview of the alternatives to gold cyanide plating.

#### Gold Sulfite

In gold plating, firms can substitute a sulfite bath for a cyanide bath. For example, a study performed at Sandia National Laboratories compared coatings on microelectronic circuits produced by the gold cyanide process and the gold sulfite process. The test results showed that gold sulfite plating solutions are compatible with a wide variety of substrates used in electronics including quartz, aluminum oxide, silicon, glass, cordierite, duriod, and gallium arsenide. The study also found compatibility with surface treatment compounds. The sulfite bath formed a gold plate with similar weld bond strength and a coat density similar to pure gold. The study concluded that the gold sulfite bath produced nearly equal, if not slightly better, coatings and

was far less hazardous to use. Another study found that a non-cyanide sulfite gold plating solution is capable of stable operations at pH values as low as 4.0. At pH values lower than 6.5, sulfur dioxide is released at a controlled level during operation (Hughes 1991).

#### Palladium

Palladium, a precious metal, has emerged as a feasible substitute for hard gold and, in some instances, soft gold finishes within the last decade. Palladium's attributes include lower cost, lower specific gravity, comparable attributes to gold, and solution composition. Palladium and palladium-nickel alloys have been used primarily for separable connectors and printed wiring board fingers. Recently, many additional applications have been found including contact finishing for edge card connectors, lead frames for IC packaging, solderable contact and end terminations for multi-layered ceramic capacitors, semiconductor optoelectronic devices for packing, etch resists for printed wire boards, battery parts, and decorative items for jewelry and consumer hardware. These applications all take advantage of palladium's lower cost and material properties, which, in many instances, are superior to gold. The use of palladium also eliminates the use of cyanide because palladium is plated from non-cyanide solutions. The two major solutions for palladium are ammonia-based and organic amine-based (Abys 1993).

### Alternative Deposition Processes for Gold Plating

Several facilities are testing the use of alternative deposition processes for gold plating. Processes

Table 12. Overview of Alternatives for Gold Cyanide Plating (Braun Intertec 1992)

Alternative Solution	Advantages	Disadvantages	Outlook for Solution
<b>Gold Sulfite</b>	Excellent throwing power Can plate on complex parts Performs as well as gold cyanide solutions	Solutions are less stable, therefore, require more monitoring and conditioning	For electronic applications, more research is required
<b>Cobalt-Hardened (No Free Cyanide) Gold*</b>	Works well on slide wear applications	Deposits are brittle and thermal shock can cause cracking	More research is required

\*Little information on this solution is available

such as ion plating and sputter deposition are being tested. For more information on these processes, refer to Chapter 8.

### Recovery Technologies for Gold Plating

Because of the high cost of the metal salts for gold plating, recovery technologies are widely used. Even with the high cost of some of the technologies, it still is economically feasible for companies to use technologies such as ion exchange and reverse osmosis.

## Silver

### Common Uses

The largest use of silver plate is in the flatware and hollowware trade. The second largest use is in the electronics industry where large amounts of silver are plated onto conductors, wave guides, and similar items because of silver's unsurpassed electrical conductivity. In most of these applications, silver is plated over copper and copper alloys. The aerospace industry uses silver as a plate over steel in aircraft engine manufacturing (SME 1985).

### Common Bath Solutions

Commercial silver electroplating has been practiced since the middle of the nineteenth century. The plating bath contains silver in the form of potassium silver cyanides and free potassium cyanide. Platers also can use sodium cyanide, but they generally prefer the potassium form. The amount of free cyanide in silver solutions is extraordinarily high. For example, a common copper-cyanide bath has 2 to 4 ounces of free cyanide per gallon while the amount of free cyanide in silver solutions commonly is 16 to 22 ounces. Large quantities of cyanide are required to increase the throwing power of the solution. Usually, a small amount of potassium carbonate and/or potassium hydroxide also is added to the bath. Silver baths usually are operated at room temperature although high-speed plating has been performed at temperatures as high as 120 degrees Fahrenheit (SME 1985).

When hard, bright silver deposits are desired, proprietary additives containing metals or organic brighteners generally are used. Some

### Closed-Loop Metal Recovery for Jewelry Manufacturer Case Study

Howard H. Sweet and Son is a 125-worker jewelry manufacturer specializing in the production of silver, gold, and gold-filled beads and chains. The company's operations are widely integrated spanning the design and manufacture of the working parts for its chain-making machines, the stamping of flat stock and tubing, and bead and chain making to the soldering, plating, and assembly of finished jewelry. In late 1995, the company faced new regulations that required them to implement further pollution controls. The company determined that a major source of hazardous waste was a burn-out room where copper used in the fabrication of gold beads was stripped.

Faced with this requirement, the company first examined traditional wastewater treatment options. Problems with space and cost immediately became apparent. The company chose to invest in an ACCA system, a virtually closed-loop recovery system for gold and copper. During the first year of operation, Sweet's new system recovered 263 troy ounces of gold and 2,144 pounds of copper.

The total capital and engineering costs for the ACCA Technologies system was \$95,000. The payback period from the recovery of additional gold and copper was 12.6 months. After the first year, the system yielded \$95,000 annually in recovered metals. In addition, the need for sludge disposal was eliminated.

(Plating and Surface Finishing 1993)

additive combinations increase the tarnish resistance of the silver deposit. As with all bright solutions, the metal and free cyanide content of the bath must be closely monitored (SME 1985).

### Alternative Solutions for Silver Cyanide

Given the large amounts of cyanide used in silver plating, finding suitable alternatives could greatly reduce cyanide levels in wastewater. Several attempts have been made to introduce non-cyanide alternatives. Most of these solutions are based on ammonium, halide, and aminothio complexes containing silver and a variety of conductivity salts and brightening agents. In almost all cases, the non-cyanide

solutions have had problems especially in producing thick, bright deposits. Many of the alternatives that have been tested are unsuitable because of photosensitivity. However, some proprietary formulations are worthy of mention. Table 13 provides an overview of the alternatives for silver cyanide plating.

#### *RCA Silver Solution*

RCA, Inc. obtained a patent for silver iodide in 1977. Silver iodide is a stable and easy-to-use solution. However, the solution was unsuitable for electronics and decorative coating because of sensitivity to light and the high cost of the solution. Another problem with this solution is that it is toxic and is likely to complicate waste treatment operations (Braun Intertec 1992).

#### *Silver Ammonium*

In 1968, IBM, Inc. obtained a patent for a bath that uses silver ammonium complexes. This solution's optimum performance was found to be

in the pH range of 11.0 to 12.5. At this pH level, the bath generates ammonium hydroxide, which poses a concern for employee health and safety (Braun Intertec 1992).

#### *Silver Methanesulfonate-Potassium Iodide*

Researchers have investigated a silver methanesulfonate-potassium iodide bath to study the effects of additives. This bath produced a deposit with a fine grain structure and appearance that was comparable to or better than a conventional cyanide bath. However, this solution has not been tested on a commercial scale (Braun Intertec 1992).

#### *Technic Non-Cyanide Silver Solution*

Some platers have successfully applied Technic Inc.'s proprietary non-cyanide silver solution for applications where a thin deposit is required. However, it has not been applied universally. A facility in New York tested Technics, Inc.'s non-cyanide silver solution, Technic-Silver CyLess,

Table 13. Overview of Alternatives for Silver Cyanide Plating (Braun Intertec 1992)

Alternative Solution	Advantages	Disadvantages	Outlook for Solution
<b>Ammonium Silver*</b>		Bath generates ammonium hydroxide which poses an exposure concern for line operators	Not promising because of worker health and safety issues
<b>Amino or Thio-Complex Silver</b>		<ul style="list-style-type: none"> <li>◆ Readiness of thiosulfate ions to be oxidized</li> <li>◆ Low current density area might be discolored</li> </ul>	Not promising; at one time widely marketed but withdrawn
<b>Halide Silver</b>	Very stable Easy to operate	<ul style="list-style-type: none"> <li>◆ Light-sensitive solution</li> <li>◆ Initial cost is high for decorative and electronic applications</li> <li>◆ Solution is toxic</li> </ul>	Limited application; solution is fairly unstable
<b>No Free Cyanide Silver</b>	<ul style="list-style-type: none"> <li>◆ Developed specifically for electronics applications</li> <li>◆ Good contact properties</li> <li>◆ Less susceptible to tarnishing</li> <li>◆ Silver can be precipitated and reused</li> <li>◆ Neutral pH and no free cyanide allows for free rinsing</li> </ul>		Limited test application Developed for high-speed electronics plating

\*No additional information on this solution is available

as a replacement for their bright silver cyanide line. The facility decided not to implement this system for the following reasons:

- ◆ Alternative is cost prohibitive: The facility estimated that the cost of operation for the non-cyanide system is three to four times more expensive than a conventional silver cyanide system.
- ◆ Difficult-to-polish surface: The non-cyanide silver plating process produces a surface that is difficult to polish and not as bright as conventional silver cyanide deposits. Customer specifications require that the facility's silver-plated products are bright.

More work on Technic's non-cyanide solution is being performed by Lawrence Livermore National Laboratory through a cooperative research and development agreement.

### Silver in the Electronics Industry

Researchers have developed a new silver plating bath with no free cyanide especially for high-speed plating in the electronics industry. This solution also can be formulated for standard systems. Silver coatings from the no free cyanide bath have good contact properties and are less susceptible to tarnishing than those from conventional alkaline cyanide silver baths. These solutions are easy to maintain and require less complicated waste treatment procedures. Silver can be precipitated as silver cyanide and reused. The neutral pH and no free cyanide properties cause the system to be less likely to leave residuals on parts, a property known as free rinsing (Braun Intertec 1992).

### Alternative Deposition Processes for Silver Plating

Several facilities are testing alternative deposition processes for silver plating. Processes such as sputter deposition are being tested. For more information on this process, refer to Chapter 7 in this manual.

### Recovery Technologies for Silver Plating

Because of the high cost of the metal salts used in silver plating, recovery technologies are widely practiced. Even with the high cost of the some of the technologies, it is still economically

feasible for companies to use technologies such as ion exchange and reverse osmosis. Silver cyanides can be quite problematic because the complexed cyanide is somewhat resistant to oxidation using conventional alkaline chlorination.

### *Electrolytic Recovery Technology for Silver Cyanide Recycling*

Wastewater generated from the rinsing of silver cyanide parts contain silver and cyanide-containing compounds. The wastestream requires pretreatment to reduce these toxic materials prior to discharge. Electrolytic recovery technology uses an electrical current to plate out the silver metal and oxidize the cyanides in spent rinsewater. The silver metal is recovered from the electrolytic recovery unit (ERU) as a metal foil that can be returned to the plating process bath as an anode source. The purity of the recovered silver should meet the specifications for anode purity as long as the water from the rinse tanks is used to rinse parts that are plated only in the silver cyanide tank. The ERU should be plumbed to a static rinse tank in a closed-loop fashion. The cyanides are partially oxidized to cyanates in the electrolytic process. This technology can be used to remove more than 90 percent of the silver metal in the rinsestream and oxidize 50 percent of the cyanides (NFSESC 1995).

The benefits of electrolytic recovery for silver cyanide recycling include cost savings and reduced hazardous waste generation. The cost savings will vary for each installation, however, cost savings can be expected from reduced use of treatment chemicals for cyanides and heavy metals in the wastewater treatment plant, reduced costs for silver anodes and chemicals, and reduced cost for disposal of hazardous waste sludge generated from the treatment process. For more information on electrolytic recovery, refer to the recycling/recovery section in Chapter 7.

### *Silver Recovery with Ion Exchange and Electrowinning*

Ion exchange systems can be used to remove silver cyanide complexes from rinsewater. These metal complexes are strongly retained by anion resins and are difficult to remove with



conventional strong base regeneration. Often, the exhausted resin is simply shipped off site for silver recovery by incineration, resulting in high operating costs for the ion exchange unit because of resin costs. A study done in Wisconsin found that by combining ion exchange and electrowinning technology facilities can expect that:

- ◆ Greater than 99 percent of the silver cyanide can be removed from electroplating rinsewater using a strong base anion exchange resin.
- ◆ Ion exchange resins can be effectively regenerated using sodium thiocyanate at a dosage of 40 to 50 pounds per cubic foot of resin.
- ◆ Silver can be completely recovered from spent thiocyanate regenerant using electrowinning. Thiocyanate destruction during electrowinning is fairly minimal so that regenerant can be reconstituted for reuse. Electrowinning also can be used to remove 67 percent of the copper contamination.
- ◆ Budgetary estimates for a 2 gallons-per-minute system indicate a 3- to 4- year payback is feasible (Lindstedt 1992).

For more information on ion exchange and electrowinning, refer to the recovery/recycling section in Chapter 7.

#### *Polymer Filtration*

A new technology is under development at Los Alamos National Laboratory to selectively recover silver ions from electroplating rinsewaters. The silver ions are recovered in a concentrated form with the appropriate counter ions ready for return to the original electroplating bath. The technology is based on the use of specially designed water-soluble polymers that selectively bind with silver ions in the rinse bath. The polymers have such a large molecular weight that they can be separated using ultrafiltration technology. The advantages of this technology are high metal selectivity with no sludge formation, rapid processing, low energy, low capital costs, and small size.

## Zinc Plating

The electroplating industry uses approximately 88,000 tons of zinc in the United States per year. Approximately 40 percent is used in cyanide baths and another 40 percent is used in chloride zinc solutions. The remainder is used in alkaline non-cyanide baths (Davis 1994).

### Common Uses

Zinc plating is versatile and used for many different applications. Because zinc is relatively inexpensive and readily applied in barrel, tank, or continuous plating, platers prefer it for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective (Ford 1994).

### Common Bath Solutions

As stated above, zinc is deposited electrolytically from three different solutions: a cyanide bath, an acid chloride bath, and an alkaline non-cyanide (or zincate) bath. Zinc is also used in the galvanizing process. Workpieces usually are chromated after plating. The conventional zinc coating is dull gray in color with a matte finish. Another common zinc coating is bright zinc with a bleached chromate conversion coating or a clear lacquer coating, which is sometimes used as a decorative finish (Mabbett 1993).

### Alternatives to Cyanide Zinc Baths

Two bath solutions are currently used as alternatives to zinc cyanide plating: zinc alkaline and zinc acid chloride. Tables 13 and 14 present these alternatives and their characteristics. Proper matching of the bath solution to the substrate characteristics is important to successfully implement a non-cyanide zinc plating system. Regular steel and leaded steel substrates are both compatible with acid chloride and alkaline non-cyanide processes. Substrates other than steel tend to be more compatible with acid chloride zinc than alkaline zinc (TURI 1994).

#### *Zinc Alkaline*

Alkaline non-cyanide electrolytes consist of sodium and zinc hydroxide. In the absence of cyanide, platers sometimes use proprietary

Table 14. Alternatives to Zinc Cyanide—Product Quality Issues (TURI 1994)

Alternatives	Corrosion Protection	Finish Appearance	Chromate Colors	Ductility
<b>Zinc Alkaline</b>	(+) Good, greater protection in difficult-to-rinse areas	(+) Good brightness	Full line available	(+) Good, can be reduced at higher thickness
<b>Zinc Acid Chloride</b>	(+) Good, but less protection in difficult-to-rinse areas	(+) Excellent brightness and leveling	Full line available	(-) Higher brightener levels can reduce ductility (+) Little hydrogen embrittlement

Table 15. Alternatives to Zinc Cyanide—Process Issues (TURI 1994)

Alternatives	Plating Uniformity	Process Considerations	General Comments
<b>Zinc Alkaline</b>	(+) Good uniform in high and low density areas (+) Good throwing power	(-) Narrow optimum operating range of bath parameters (-) Lower conductivity than zinc	(+) Better for some forming operations (-) Harder to plate on cast iron and carbon nitride steel
<b>Zinc Acid Chloride</b>	(-) Variable with current density	(-) Liners necessary in steel or porous tanks (+) High cathode efficiency at high current densities (-) Agitation required	(+) Higher conductivity results in energy savings (-) Bleed out of entrapped plating solution can limit use for complex parts (+) Plates readily on cast iron and carbon nitrated steel

sequestering agents to yield grain refinement. When operated with concentrations and other parameters in control, zinc alkaline baths perform as well as cyanide-based baths and are the least expensive of all the zinc plating baths. This solution has excellent throwing power and rinsewater generally is easy to treat. Also, sludge generation is low because of the low metal content of the solution (Murphy 1993).

A common problem with alkaline baths is the control of the zinc metal level. During idle periods, the caustic is aggressive toward the zinc anodes and metal concentration rises. Platers often are forced to remove anode baskets at the end of a work shift or prior to the weekend. Some opt to store the solution in an anode-free

storage tank. In the past, yellowing of the plate has been a problem, however, advances in technology have resolved this issue and many proprietary bath solutions can provide excellent brightness and good color. Another drawback often cited about zinc alkaline baths is low cathode efficiency. While this is a problem for barrel platers, those that rack plate actually can find that an increase in cathode current density can provide excellent metal distribution on parts with intricate designs. Blistering also can be a problem with this solution, especially in thicker deposits. Blistering can be attributed to poor cleaning or high brightener levels. Good house-keeping is imperative to avoid this problem (Natorski 1992).

Alkaline zinc baths also form carbonate similar to cyanide solutions. Symptoms of this include yellows in blue bright chromate, a drop in brightness, and poor coverage. If carbonate levels become too high, platers should consider one of the following options:

- ◆ Decant the bath and rebuild to specifications
- ◆ Freeze out the carbonate
- ◆ Mix the bath with a compatible barrel plating bath to equalize carbonate

### *Zinc Acid Chloride*

Chloride zinc baths have been available since the 1960s. The original baths used chelates or ammonium chloride. Today, however, most baths use either potassium or ammonium chloride. The advantages of the chloride systems include brilliant deposits, high cathode efficiency, good leveling properties, low energy consumption, and easily treated non-toxic electrolyte. The disadvantages are poor throwing power, higher initial equipment investment, and higher brightener costs compared to the alkaline processes. In the past, chloride solutions had a foaming problem, especially in air-agitated rack plating. However, new surfactants in the solution produce low-foaming electrolytes. Facilities using atmospheric evaporators should use low-foaming solutions. Another advancement in chloride solutions are their ability to plate efficiently at higher temperatures (Murphy 1993). Higher temperature baths increase the number of potential recycling/recovery applications that this process can use.

### **Alternative Deposition Processes**

#### *Autophoretic Coatings*

A number of electroapplied organic coatings, also known as Ecoat, and at least one commercially available autophoretic coating are feasible as non-metallic substitutes for zinc electroplated coatings, especially when they are used for corrosion resistance on steel substrates (Altmayer 1993a).

### **Replacing Zinc Plating for Auto Deposition Case Study**

Steelcase, Inc., replaced four zinc plating lines with an autophoretic autodeposition line at its Desk Division in Grand Rapids, Michigan. Steelcase began investigating alternatives in 1987 when it determined that its plating lines were outmoded and no longer efficient. Various coating processes were tested for hardness, abrasion resistance, corrosion resistance, finish consistency, and environmental impact. The company chose to install the autodeposition line. Capital investment was similar to the cost of installing four new zinc lines. The new single line process, however, has doubled the production capacity of the four original plating lines. Maintenance and waste treatment costs have been reduced substantially as a result of the new process line. Other savings include energy costs, labor costs, and reduced reject rates. (Ohio EPA 1994)

### **Separation Technologies**

#### *Reverse Osmosis*

In August 1988, Plating Inc., a subsidiary of Superior Plating, installed a 5 gallons-per-minute reverse osmosis system on their automated zinc cyanide line to recover rinse and process bath solution. In a 7-month study funded by the Minnesota Waste Management Board, the system achieved its objectives. It maintained rinse quality standards, recovered 2,480 gallons of plating solution, avoided shipment of thousands of gallons of dead rinse for treatment, and was projected to eliminate the need for shipment of 700 cubic feet annually of resins containing cyanide. Payback for the system was expected to be less than 1 year (Rich 1989).

### **Non-Cyanide-Based Plating Processes**

While cyanide is a major contributor to pollution generation at a metal plating facility, other constituents are of concern because of the toxicity of the metal contained in the solution. Most common of these processes include nickel, tin, and chrome. The following section covers nickel and chromium plating.

## Chromium Plating

Electroplating processes and aluminum finishing use chromium plating heavily. The most common hexavalent chromium-bearing solutions include decorative and hard chromium, aluminum conversion coating, bright dipping of copper and copper alloys, chromic acid anodizing, aluminum deox/desmut, chromate conversion coatings on cadmium and zinc, and copper stripping with chromic acid. This section will cover hard and decorative electroplating. Conversion coatings such as anodizing and chromating are covered in this chapter. Chromium use with aluminum and stripping are covered in this chapter.

Because of hexavalent chromium's high toxicity and cost for treatment and disposal, the industry has focused on reducing or eliminating its use. Hexavalent chromium is a known carcinogen and a designated hazardous air pollutant. Approximately 80 percent of the available power supplied to hexavalent chromium processes generates hydrogen gas. Evolution of the gas produces a mist of fine water particles with entrained hexavalent chromium. This mist is regulated under the Clean Air Act and the Occupational Safety and Health Administration (OSHA). Protection of employee health and safety as well as the environment requires a high level of emissions control (PTAPS 1995). Chromium, especially hexavalent, also is very easy to operate in a closed-loop system using simple technologies (Gallerani 1996).

### Common Uses

When the plater's goal is a pleasing appearance that has durability, the plating is considered decorative. Decorative chromium plate is almost always applied over a bright nickel-plated deposit, which is usually deposited on substrates such as steel, aluminum, plastic, copper alloys, and zinc die casting. Chromium has a pleasing appearance when plated over bright nickel. Decorative chromium plating typically ranges from 0.005 mils to 0.01 mils in thickness. Decorative chromium plating can be found on numerous consumer items including appliances, jewelry, plastic knobs, hardware, hand tools, and automotive trim (EPA 1994).

When chromium is applied for almost any other purpose, or when appearance is an incidental or lesser feature, the process is commonly referred to as hard chromium plating or functional chromium plating. Functional chromium plating normally is not applied over bright nickel plating although, in some cases, nickel or other deposits are applied first to enhance corrosion resistance. Functional chromium plating tends to be relatively thick, ranging from 0.1 mils to more than 10 mils. Common applications of functional chromium include hydraulic cylinders and rods, crankshafts, printing plate/rolls, pistons for internal combustion engines, molds for plastic and fiberglass parts manufacture, and cutting tools. Functional chromium commonly is specified for rebuilding worn parts as rolls, molding dies, cylinder liners, and crankshafts (Chessin 1982).

### Common Bath Solutions

The traditional chrome plating process is the 100:1 bath, which means that the ratio of chromic acid ( $\text{CrO}_3$ ) to sulfate ( $\text{SO}_4$ ) should be 100:1 by weight, that is, 250 g/l  $\text{CrO}_3$  to 2.5 g/l  $\text{SO}_4$ . Excess sulfate in these solutions can affect plating quality and should be removed by the addition of barium carbonate. The addition of this chemical causes the formation of barium sulfate, which can be precipitated. This solution contains chrome in the hexavalent form, which is regulated far more stringently than trivalent chrome. For this reason, development of trivalent chromium plating solutions is proceeding rapidly (Ford 1994).

### Alternative Solutions

To function as a suitable substitute for chromium, an alternative coating must offer a combination of wear resistance, corrosion resistance, lubricity, high-temperature tolerance, low friction coefficient, heavy thickness deposition, and high impurity tolerance. No single coating can replace the properties and processing ease of traditional hexavalent chromium, however, several alternatives have shown promise in replacing chromium for specific applications.

#### *Trivalent Chromium*

In some applications, especially decorative plating, the use of trivalent chromium has been

proven successful as an alternative for hexavalent chrome for certain thicknesses. Use of trivalent chrome eliminates misting problems and the added reduction step in wastewater treatment. Adherence, throw, and coverage also are improved. Higher rack densities also can be achieved because bath concentration is much lower, dragout is less, and the amount of sludge produced by wastewater treatment is reduced substantially. However, plating thickness is limited to 0.1 mil; coatings thicker than this usually have problems with cracking and palling. Therefore, this technique usually is not suitable for hard chromium coatings, which can require finish thicknesses of 20 mils or more. Although the color tones of trivalent chromium coatings are different from those of hexavalent chromium, additives to the trivalent chromium bath often can ameliorate the difference. One of the main barriers for increased use of this solution is customer acceptance. Primarily, customer concern is related to the color of the deposit (Shahin 1992).

#### *Electroless Nickel Phosphorous*

The use of electroless nickel finishes from conventional hypophosphite solutions has been investigated as an alternative. The use of electroless nickel as an alternative is limited by its somewhat poorer physical properties including lessened hardness and abrasion resistance. The corrosion and wear properties depend on the phosphorous content, which can vary from 1 to 12 percent. Electroless nickel deposits from borohydride chemistry rather than from hypophosphite chemistry have shown better wear, lower friction, and improved hardness (Lindsay 1995). Additionally, heat treatment is required to achieve full hardness. Brittleness of the deposits makes some final finishing applications, such as grinding, difficult on thick deposits. Also, thick deposits of electroless nickel cannot be plated as cost effectively as chrome. However, electroless nickel plates more evenly so that the need for substantial overplating often can be eliminated. An advantage of electroless nickel is that the deposit follows all the contours of the substrate without excessive buildup at the edges and corners, which is a common problem in chrome plating (Meyers 1994).

#### **Trivalent Chrome Case Study**

Foss Plating in Sante Fe Springs, California, is a family-run chrome plating shop that has been in business more than 40 years. Today about 30 people are employed in the shop. Their current plating line is a fully automated single chrome-cell (III) system that was converted from a hexavalent chromium line in 1989. The cost of conversion was approximately \$30,000.

As a result of the conversion, Foss Plating realized a return on their investment within the first year of operating the chrome (III) system. They saw an increase in productivity, greater system efficiency, fewer rejects, and lower treatment costs. The better throwing power and covering power of chrome (III) allowed them to increase the surface area on the racks by 70 percent. At the same time, they experienced a more than 90 percent decrease in the number of rejected parts and eliminated almost all need for color buffing. Foss also found that chrome (III) plated more efficiently from an energy standpoint.

The two biggest disadvantages Foss Plating experienced with chrome (III) were discoloration from impurities in the bath and the need to passify the non-plated areas of the parts.

(CDTSC 1995)

The process bath, however, is more sensitive to impurities than the chrome plating bath. As a result, it must be monitored closely to maintain the proper concentrations and balance of the metal ions and reducing agents. In addition, the bath life is finite and requires frequent disposal and replenishment, especially when thick deposits are being applied. Deposition rates and coating properties are affected by temperature, pH, and metal ion-reducing agent concentrations (Meyers 1994).

Electroless nickel has been well accepted for ground-based hydraulic component use; however, it has not been used in aerospace applications. For more information on electroless nickel, refer to the section on electroless plating in this chapter.

### *Nickel-Tungsten Electroplating*

Two nickel tungsten-based alloy electroplating processes are available as potential alternatives to chrome plating: nickel-tungsten boron (Ni-W-B) and a nickel-tungsten silicon carbide composite (Ni-W-SiC). The two processes are similar in that they are both electrolytic and they deposit a coating of nickel and tungsten with minor percentages of either boron or silicon carbide to enhance the coating's properties (Meyers 1994).

Both substitutes use less energy than chrome plating both for rectification and heating, resulting in reduced energy costs. Additionally, the deposits are more uniform than chrome, increasing plating line throughput and reducing reject rates. Each coating exhibits many of the same desirable properties as chrome plating, but additional testing is needed before widespread use can be expected. The major disadvantages of these two processes are their lack of maturity, potential for increased chemical costs, and their reliance on nickel (a metal targeted by EPA for reduction) (Meyers 1994).

### *Nickel-Tungsten-Boron Alloy*

Following several years of development, an alloy of nickel, tungsten, and boron has been introduced recently under the trade name AMPLATE. The plating solution is mildly alkaline and far less toxic than chromium. The alloy is reflective and has an appearance similar to chromium, bright silver, or bright nickel. The coating has favorable chemical and abrasion resistance, high ductility, a low coefficient of friction, and a uniform finish (Meyers 1994). Unlike most metals that exhibit a crystalline structure at ambient temperatures, the AMPLATE alloy is structureless so that the plate replicates the appearance of the substrate. For instance, if the substrate has a bright appearance so will the finish, but if the substrate is etched or patterned, the plated workpiece will appear etched (Scruggs 1992).

### *Nickel-Tungsten Silicon Carbide*

This technology has been patented by Takada Inc. to replace functional (hard) chromium coatings. Nickel-tungsten silicon carbide is similar to nickel-tungsten-boron, except that it uses silicon carbide particles interspersed in the

matrix to relieve internal stress and improve coating hardness (Meyers 1994). Nickel and tungsten ions become absorbed on the suspended silicon carbide particles in the plating solution. The attached ions are then adsorbed on the cathode surface and discharged. The silicon carbide particle becomes entrapped in the growing metallic matrix (EPA 1994).

This process has several advantages over hard chromium plating including higher plating rates, higher cathode current efficiencies, better throwing power, and better wear resistance. The main disadvantage of this process is its susceptibility to metallic and biological contamination. Much is still unknown about this process including its susceptibility to hydrogen embrittlement, fatigue, and corrosion as well as its maximum finish thickness, lubricity, grinding characteristics, and facility requirements (EPA 1994).

### *Tin-Cobalt Alloy*

Tin-cobalt alloys provide a finish that is similar in appearance to chromium. The tin-cobalt appearance ranges in color from a bright, chromium appearance to a warm, silvery gray color. Color is controlled by varying the percent of tin in the alloy. To achieve the appearance of a chromium plate, the optimal tin-cobalt ratio in solution is 50:50. This ratio results in a plate that is 80 percent tin and 20 percent cobalt. Reducing the cobalt content of the plate below 17 percent results in a matte gray appearance. Additional operating parameters include a pH of approximately 8.5 and an operating temperature of between 38 and 43 degrees Celsius. The tin-cobalt finish provides a hardness and wear resistance that is sufficient for most indoor, decorative applications. The process, either in rack or barrel operations, uses an alkaline sulfate system with optional wetter/amine-based liquid brighteners. Current applications of this plating alternative for chromium include automotive interior parts, computer components, bicycle spokes, flexible shower hoses, and screws (Davis 1994).

### *Tin-Nickel Acid or Near Neutral*

Tin-nickel alloy plating can be used as a replacement for decorative chromium plating for both indoor and outdoor applications because of its

faint rose pink cast. This alloy is resistant to corrosion and tarnish and has good contact and wear resistance. Tin-nickel's hardness lies between that of chromium and nickel. Other advantages of this coating include excellent frictional resistance and ability to retain an oil film on its surface. Tin-nickel alloy plating solutions have a high throwing power, which enables the solution to function where plating chromium in deep recesses is a problem (Plating and Surface Finishing 1994).

## Alternative Deposition Methods

### *Aluminum Ion Vapor Deposition*

Ion vapor deposition (IVD) produces a multi-purpose coating that has excellent corrosion protection and no embrittlement problems. This technology has been used as an alternative to chromium coating in several applications. Extensive testing has shown that IVD aluminum protects substrates better than electroplated or vacuum-deposited chromium in acetic salt fog and outdoor environments. IVD also provides greater resistance to cracking (Muehlberger 1983). For more information on IVD, refer to the section on IVD in Chapter 8.

### *Metal Spray Coating*

Several metal spray coatings processes have shown promise as potential alternatives to chrome plating. These technologies are not new, however, recent regulation of chrome has made these technologies economically desirable. Variations on the spray technologies include arc spray, flame spray, plasma spray, and high velocity oxy-fuel (HVOF) spray. From a materials standpoint, HVOF spray results in coatings with the best properties (Meyers 1994).

HVOF coatings are used currently in many industrial applications because they develop very hard, wear-resistant surfaces that are comparable to those of chrome plating. In HVOF coating application, an explosive gas mixture ignites the barrel of the spray gun, which melts a powdered coating material and propels it at supersonic speeds toward the substrate. The superior properties achieved using this technology are a result of the high speed of the material. The higher the velocity, the greater the force of

impact on the substrate, resulting in fewer voids in the coating. Several of the potential alternatives contain chromium, yet the HVOF coating will generate a significantly smaller mass of chromium-containing waste and will emit less chromium. The powdered overspray can be captured and recycled easily by a dry filter system and, unlike conventional chrome electroplating, no chemicals are added to the total waste volume when precipitating the metals (Meyers 1994).

A disadvantage of the HVOF process is that the application is limited to line-of-sight areas of the part. Complex shapes, threads, and bores/holes cannot be coated. Unlike the chemical substitutes that use conventional finishing methods, metal spray coatings will require changes in finishing and grinding operations. Given the hardness of the coating, stripping and reworking these finishes might prove difficult (Meyers 1994). For more information on this process, refer to Chapter 8.

### *Physical Vapor Deposition*

Physical vapor deposition (PVD) is one of the many emerging replacements for chromium electroplating. PVD encompasses several deposition processes in which atoms are physically removed from a source and deposited on a substrate. Thermal energy and ion bombardment methods are used to convert the source material into a vapor. Specific processes for applying chromium include ion plating and sputtering. For more information on PVD, see Chapter 8.

Titanium nitride using PVD is a prime replacement for chromium coatings. This material exhibits greater hardness than chromium and can be applied cost effectively in a thinner coating. Titanium nitride applied with PVD is not subject to hydrogen embrittlement. However, because of its hard nature, titanium nitride coating cannot replace chromium in highpoint or line-load applications. This material also does not provide the corrosion protection of the thicker chromium plates (Lindsay 1995).

### *Other Emerging Technologies*

The government is evaluating several other technologies as alternatives to hexavalent

chrome under the Environmental Technology Initiative including:

- ◆ Alloy deposition of hard coatings (nickel-tungsten silicon carbide and electroless nickel-tungsten)
- ◆ Deposition of powdered chromium with an inductively coupled radio-frequency plasma torch
- ◆ Sputterion deposition using hard chromium (Lindsay 1995)

For more information on these alternative deposition processes, refer to Chapter 8.

### Process Modifications for Chromium Plating

#### *Mist Reduction*

Inhibiting the release of chromium into the air by forming a physical barrier atop the plating bath with plastic balls or mist suppressants or by altering the chemistry of the bath with the addition of wetting agents is one way to prevent pollution from a chromium plating line (PTAPS 1994).

#### *Floating Plastic Ball*

Placing solid polypropylene balls 3/4 to 1½ inches in diameter on top of the plating bath will retard mist formation and evaporation. The balls can prevent up to 70 percent of the mist from escaping the plating solution and can be used effectively in both decorative and hard chrome plating processes. Polypropylene is reasonably resistant to chromic acid solutions at temperatures of up to 140 degrees Fahrenheit. Higher temperatures can cause the balls to break. Platers should use solid balls because hollow ones tend to trap solution inside from seam leakage (PTAPS 1994).

Polypropylene balls cost approximately \$45 to \$200 per 1,000 balls depending on the ball size and the total quantity purchased. An average tank requires about 2,500 balls. There are no additional operating costs for using this method. However, some of the balls might need to be replaced on an annual basis depending on the operating conditions of the tank (PTAPS 1994).

When using balls in a plating solution, pre-cleaning of parts is essential. Small amounts of oil and grease from workpieces can float onto the bath surface and adhere to the balls. As parts are raised and lowered in the bath, oil-covered balls can drag across the workpiece surface and prevent effective plating and rinsing, resulting in a flawed coating.

The most common problem associated with this method is that the balls become trapped in recessed areas of parts or equipment (e.g., barrels) and prevent plating or cause burning or dulling of the plated workpiece. Whether the balls become entrapped usually is associated with their size. To help prevent entrapment of balls, platers can use plastic mesh bags. The bags can keep the balls together on the surface and reduce the likelihood of balls being carried into subsequent tanks (PTAPS 1994).

#### *Mist Suppressants*

A mist (or fume) suppressant is a chemical that forms a barrier on the surface of the bath solution to prevent mist from escaping. During operation of the plating or anodizing process, the mist suppressant generates a foam blanket and traps the process gases either between the bath surface and the blanket or within the foam blanket. Mist suppressants can be more than 99 percent effective in reducing emissions from decorative chrome plating and anodizing (PTAPS 1994).

Suppressants are chemical additives that can affect the chemical balance of the plating or anodizing solution. For this reason, a generic suppressant is not available for widespread use. Depending on the various types of baths within a shop (e.g., hard, decorative, or proprietary), a different mist suppressant or concentration of suppressant might be required for each bath to achieve the desired result. Some mist suppressants must be replaced because of the degradation of the active ingredient. These are known as temporary suppressants. Other mist suppressants only have to be replaced when they are diminished because of bath dragout (PTAPS 1994).

Another factor to consider when deciding whether to use mist suppressants is the amount of foam generated during bath use. Too much



mist suppressant will cause a large foam blanket that can result in excessive dragout into subsequent rinse tanks. This dragout will lead to an increase in the amount of materials necessary to replenish the suppressant in the tank. The foam blanket also can be drawn into the exhaust system, increasing the likelihood that a more concentrated chromium mist will be released from the stack. Finally, too much mist suppressant can spill onto the facility floor or into other tanks, generating large amounts of waste that require clean up and increase treatment and disposal costs (PTAPS 1994).

Because hydrogen is the primary gas formed during plating, dissipation of the gas is important. Build up of hydrogen with the foam or under the foam poses a serious explosion risk, especially when the parts are removed while "hot" (i.e., the electric current is still on). When hot parts are removed, the hydrogen gas can ignite spontaneously, resulting in equipment damage, serious personal injury, and an increased risk of fire (PTAPS 1994).

Mist suppressants come in liquid and free compressed-powder form and range in cost from \$10 per pound to \$60 per pound. The amount of mist suppressant chemical necessary to form a sufficient barrier varies depending on the type of chemical mist suppressant, tank size, and frequency of plating. According to manufacturers' instructions for different mist suppressants, the recommended amount of chemical to add ranges from 0.001 percent of the total volume of the plating bath to 0.1 percent (approximately 1 ounce per 500 gallons initially with infrequent additions thereafter). When used in the appropriate amount, dragout and replenishment costs are minimal. Because mist suppressants also are stand alone emission controls, utility requirements are nonexistent, except perhaps for makeup water in the case of free-form powders (PTAPS 1994).

When using mist suppressants, operators should start with half the manufacturer's recommended amount and increase levels slowly to determine the actual amount required to achieve the desired

### Scrubber Modifications Case Study

C&R Hard Chrome is a small chrome and electroless nickel plating company specializing in plating and plastic injection molding apparatus and machined tool parts. To reduce the high costs associated with proper disposal of waste generated at the facility, the company sought ways to keep wastes and liabilities to a minimum.

To control emissions from the chrome plating operation, the company installed a wet-packed fume scrubber with a recirculation system in 1990. The system collected chromium concentrate from two plating tanks. The company, however, experienced several problems with this system including contamination of the chrome concentrate from the steel ducts that transported the washout. To address this issue, the company installed polyvinyl chloride (PVC) pipes. The new system employed a moisture extractor, double-baffle mesh pad eliminator, and an in-line vertical mist eliminator. The plating fumes are collected by two plenum arms on either side of the tank. The tops of these arms slant toward the tank to return dragout to the solution. The collected fumes are directed to a moisture extractor located above the tank. Moisture removal is accomplished centrifugally as air passes through the set of stationary blades. A spray system periodically washes these blades and the solution is returned to the plating tank.

The final treatment involves an in-line vertical mist eliminator. A mesh pad was installed as a protection in case the washdown spray does not engage. A blower operating at a rate of 5,250 cubic feet per minute is used for this system. Now, the chromium can be recaptured by the fume scrubbers and recirculated back to the solution.

The PVC fume-scrubbing system eliminated the need to send 1,840 gallons of chromium concentrate and wastewater off site each year for treatment. Chromic acid use fell by almost 90 percent, from 5,400 to less than 600 pounds annually. Chromium emissions fell by 98 percent, from 61.4 to less than 0.2 pounds per year. The capital outlay for the system was \$95,000 with an annual savings of \$12,000 per year. (NCDEHNR 1995)

result. The necessary amount of suppressant often depends on the activity of the plating line. Less active plating lines might require the use of more suppressant while a similar amount on a busy day might generate an unmanageable foaming problem (PTAPS 1994).

### *Wetting Agents*

Reduction of surface tension of the chrome plating or anodizing bath reduces the rate of mist generation by causing the gas bubbles to burst with less intensity. For chrome finishing, decreasing the surface tension to 40 dynes per centimeter will achieve excellent chromium emission reductions. However, wetting agents can affect the quality of the deposit; too much can cause burning, pitting, or poor adhesion; too little can result in little or no reductions in emissions (PTAPS 1994). For a complete description of wetting agents, refer to the first section in this chapter.

### *Static Rinse Tank*

Many facilities use a static rinse tank (often known as dead rinse) after the process bath. Water from this tank is used as makeup water in the process bath. Using this method has assisted many facilities in closing the loop on chromium contamination.

### *Tank Covers*

Thin plastic sheets can be placed over the plating bath to reduce emissions by trapping and condensing vapors from the tank. The cover can be placed almost directly on the chromic acid solution, resulting in little free space between the cover and the solution. Tank covers can be constructed of plexiglass or other suitable plastic and cut to fit the size of the tank. The facility should determine how to remove the cover when transferring workpieces during plating or anodizing operations. Rigid covers are most easily made by using anchors and hinges that operate like a window or door. Platers can use flexible sheeting by mounting it on one side, rolling it over the top, and anchoring it to the other side like a window shade. A drawback of this method is that chromium can dry out or corrode plastics. Another consideration is how the cover will affect the movement of parts through the process line (PTAPS 1994).

## Recycling and Recovery Technologies for Chromium Plating

### *Porous Pots*

For hexavalent chromium plating baths, firms can use porous pots to extend bath life. During plating, the concentrations of iron and other cationic impurities build up in a hexavalent chromium bath so that the finish is unsatisfactory. When the solution reaches this point, operators can use porous pot technology to purify the process solution. This technology uses a porous pot in which a semi-permeable membrane separates a cathode from an anode along with an applied power source. In this operation, the iron and other contaminant metal ions pass through the membrane and accumulate in the cathode chamber. Once the contaminants are contained in the chamber, they can be removed periodically for disposal. Chromate ions remain in the anode compartment as part of an anolyte that, after purification, can be returned to the plating tank for further use. Using this technique, companies not only reduce waste but also use less chromium. The liquid in the cathode compartment must be handled as waste (IAMS 1995).

Two basic design configurations exist for this technology. One type consists of a tank holding four to eight pots. Plating solution is pumped to the tank on a continuous basis and returned by gravity flow to the plating tank. The cells are powered by a rectifier (1,000 to 2,000 amperes) that is dedicated to the purification unit. A second type of unit exists that consists of a single pot that is suspended directly in the plating bath. This unit is powered by the tank rectifier and draws up to 240 amperes. The advantage of the smaller unit is that it does not require extra equipment (e.g., rectifier, fume exhaust system, and overhead hoist). However, there are disadvantages to the smaller units. They include limited capacity and operation that only occurs when the tank is energized. For more information on this technology, refer to Chapter 8.

### *Membrane Electrolisis*

Membrane electrolisis is similar to the ion transfer technology used in porous pots, however, this technology is primarily used in chrome

### Porous Pots Case Study

C&R Hard Chrome is a small chrome and electroless nickel plating company specializing in plating plastic injection mold apparatus and machined tool parts. To reduce the high costs associated with proper disposal of wastes generated at the facility, the company sought ways to keep wastes and liabilities to a minimum. One of the problems in the facility was that the chrome plating solution was being contaminated from the workpieces. The contaminants reduced solution life and lowered plating efficiency. The reduced lifespan required frequent replacement and disposal of the chromium solution while lower plating efficiency reduced plating quality and increased power consumption and plating time. In 1987, the company purchased a chrome solution purifier called a porous pot. During plating operations, impurities collect in the pot rather than the solution. The porous pot used the concept of electrodialysis in conjunction with ceramic membranes. The continual removal of impurities significantly increased the bath life. Since the installation of the porous pots, they have collected 55 gallons of contaminant sludge and prevented the disposal of at least four chrome baths (2,300 gallons of solution). The payback time on the \$600 pot was less than three months. Annual savings for this project are approximately \$2,375 a year. (NC DEHNR 1995)

applications. The unit employs a separate tank and power source for operation. Plating solution is circulated through the unit, which contains an anode compartment and 10 cathode modules. When the unit is energized, bath cations pass through the membrane and deposit on the cathodes. The membrane is not anion or cation selective. Selectivity is a result of the electrical force. This selectivity distinguishes this technology from electrodialysis equipment. For more information on this technology, refer to the recycling/recovery section in Chapter 7.

### Ion Exchange

Ion exchange has been applied to chromium solutions for the removal of trivalent chromium, iron, and other metallic contaminants. Facilities using this technology usually treat the solution on a batch basis, requiring a shutdown of the chromium line. However, a continuous process

has been used. Generally, the plating solution is cooled and diluted prior to treatment.

Eco-Tec Inc. in Canada has developed an ion exchange system for use in hexavalent chrome plating operations. Initial results are promising, however, other platers have had problems in the past with other ion exchange systems. Problems usually are a result of fouling membranes and sensitivity to chromium concentrations (Cushnie 1993). For more information on ion exchange, refer to Chapter 7.

## Nickel Plating

Companies have plated nickel since 1842, but modern nickel plating began in 1916 with the introduction of the Watts formulation. Typically, nickel ingots or balls are dissolved into a metal salt solution that is used in the plating baths. However, nickel salts have some negative characteristics including allergenic properties and carcinogenicity (ASM 1982).

### Common Uses

Nickel plating commonly is used to impart corrosion resistance or to act as an intermediate layer prior to plating silver, chrome, or gold. Nickel also is valued for its leveling and brightening properties. Because of these properties, nickel can eliminate the need for polishing work and can improve the quality of an inferior substrate. Several types of electrolytic nickel plating are available including sulfamate nickel and bright nickel. Many industries use nickel plating for decorative or functional purposes including jewelry, automotive parts, tools/dies, and lighting fixture manufacturing (RI DEM 1995c).

### Common Wastes

Typical wastes from nickel plating operations include nickel-contaminated water from running rinses and excess dragout solution. If a plater uses traditional chemical precipitation to treat the nickel-laden wastewater prior to discharge, the resulting sludge automatically is classified as a F006 hazardous waste. Iron and chromium contamination is common in acidic nickel baths. In most formulations, this contamination can be removed with peroxide combined with pH elevation and batch filtration (SME 1985).

## Common Bath Solutions

### *Sulfamate Nickel*

Sulfamate nickel, also known as dull nickel or engineering nickel, is used for engineering (usually non-decorative) applications to produce low-stress deposits. This plate is ductile and can be used in many applications. This bath also is useful for electroforming and for parts that are susceptible to fatigue failure. The primary constituents of this bath are nickel sulfamate, nickel chloride, and boric acid (Ford 1994).

### *Bright Nickel*

Another common nickel plate is bright nickel, sometimes referred to as a Watts bath. This solution imparts a bright and hard finish, which is used mainly for decorative purposes. The process bath in nickel plating contains both inorganics (i.e., nickel salts and acid) and organics (i.e., brighteners and wetting agents). Additional chemicals ultimately determine the characteristic of the plate. These include brightening and wetting agents that account for the brittle nature of the deposit (Ford 1994).

## Alternative Metal Processes Baths for Nickel Plating

Alternatives to nickel as intermediate layers include bronze, palladium, and cobalt. Like nickel, however, cobalt is under examination as an allergen and carcinogen and might be regulated in the future.

### *Yellow/White Bronze*

Processes available for white or yellow bronze deposits include cyanide or alkaline-based systems. Like the nickel baths, operators can add buffers, brighteners, and levelers to the bath to create the needed characteristics. Bronze exhibits better throwing power than nickel, resulting in a more evenly distributed thickness. This alloy can be used when superior solderability, hardness, corrosion resistance, brightening properties, thickness distribution, wear resistance, or diamagnetic properties are needed. Bronze alloys also kill bacteria, just like copper, and have better bactericide properties than silver, making them attractive plating materials for bathroom fittings and door handles (Simon 1994).

White bronzes are hard and tarnish resistant. This metal also is corrosion resistant. Yellow bronzes are hard, but do not have the corrosion resistance properties of white bronze because of their high copper content. Yellow bronzes, however, have the brightening and leveling effects of nickel plating. Platers use a layer of white bronze on top of a yellow bronze to replace bright nickel of the same layer and thickness (Simon 1994).

Bronzes can provide a surface that is harder than nickel and, in decorative applications, protect workpieces from deterioration or tarnishing. However, for technical applications where the workpiece will be subjected to high temperatures, bronzes are not an appropriate substitute.

### *Palladium*

Metal finishers can use palladium as a substitute for nickel as an intermediate layer when nickel's property as an allergen is a consideration. Some platers also consider palladium a feasible replacement for gold because of palladium's lower cost. One of the benefits associated with substituting palladium is that it is not listed as a chemical that facilities must report under the TRI reporting requirement.

A relatively new system for using palladium chloride as a palladium salt combined with proprietary additives exists. This system produces ductile deposits that are crack-free and bendable as well as resistant to corrosion. To avoid contamination of the electrolyte, a gold strike or palladium strike is recommended before applying the main palladium layer (Simon 1994).

### *Issues Concerning Palladium and Bronze as Nickel Substitutes*

Many questions remain unanswered about the feasibility of replacing nickel with bronze and palladium, but some advantages are well known. Bronzes and palladium are comparable to nickel with regard to hardness, color, corrosion protection, solderability, further plating ease, and wear resistance. Bronzes, especially the yellow-white combination, are superior to palladium in this area. However, palladium is similar to nickel in its diffusion properties. The use of bronze as a diffusion barrier is limited to decorative

purposes. In regard to ductility, bright nickel is the most brittle of the three applications. Palladium is ductile, yellow bronze has average ductility, and white bronze is brittle. With regard to cost, palladium is the most expensive of the three processes (Simon 1994).

### Recycling/Waste Reduction Technologies

Common pollution prevention options in nickel plating include electrolytic dummieing, spill and leak prevention (especially from filtration systems), countercurrent rinsing, evaporation, and ion exchange. This section covers particular recycling/recovery technologies for nickel plating. For more detailed information on a specific recycling/recovery technology, refer to Chapter 7.

#### *Electrodialysis Reversal Process (EDR) in Nickel Plating*

Electrodialysis is an electrochemical separation process in which ions are transferred through a pair of ion-selective membranes from a less concentrated to a more concentrated solution as a result of the flow of direct electric current. Initially, these systems could only transfer ions in one direction. Typical problems associated with the system included membrane fouling and organic buildup. Newer electrodialysis systems, however, eliminate these problems by allowing the flow to periodically reverse itself in order to clean the membrane. Recently, electrodialysis has been considered a promising method for the recovery of nickel ions from rinsewater, recycling them back to the plating solution and simultaneously generating clean water for reuse in the plant. Important parameters to evaluate include limiting current density, current efficiency, and water transport through the membranes (RI DEM 1995c). Small-volume shops might find that the costs associated with electrodialysis are too high. But effort to build smaller systems that are feasible for all manufacturers is increasing (Girasole 1996).

#### *Electrolytic Recovery in Nickel Plating*

Nickel can be recovered from a variety of concentrated solutions including dragout tanks, ion exchange regenerants, and concentrated membrane fluids. The metal that is recovered can be sold as scrap metal or, as some facilities

#### Atlantic Seaboard Case Study

Atlantic Seaboard realized they were losing 80 to 100 pounds of nickel per day as a result of dragout from barrel plating operations following the installation of modern control equipment. Atlantic Seaboard installed an EDR unit and reduced their annual costs for purchasing plating chemicals by approximately \$110,000 based on costs of nickel sulfate at \$1.10 per pound, nickel chloride at \$1.40 per pound, and boric acid at \$0.41 per pound. Annual sludge disposal costs also were reduced by \$6,600 per year (sludge disposal costs were \$250 per ton at 95 percent solids). The company also realized savings of \$2,200 from reduced sodium hydroxide use. The total annual savings amounted to more the \$118,000.

(Ohio EPA 1994)

have done, returned as reclaimed material to the plating bath for use as a solid material in the anode. Electrolytic recovery works best in nickel plating applications when pH values are between 3 and 9. Generally, high energy is required (100 to 500 amperes). Anode and cathode materials are important design parameters for this technology. Stainless steel or graphite are the best choices. Trace metal contamination in the electrowinning solution can sometimes affect the overall efficiency of this operation (Girasole 1996).

Electrolytic recovery of nickel cannot eliminate nickel because the nature of the process makes it less efficient with low metal concentrations. However, it will have a significant effect on sludge generation: In general, for every pound of metal reclaimed, sludge generation is reduced by 4 pounds (Girasole 1996). For more information on electrolytic recovery, refer to Chapter 8.

#### *Ion Exchange in Nickel Plating*

Ion exchange is a frequently used and effective method to recycle nickel rinsewaters and capture nickel metal either for reuse or recycling. Specifically made resins are manufactured to remove particular metal ions from the solution through the exchange of similarly charged ions. At some point, the resin becomes saturated with the metal ions and must be regenerated with an acid to remove the captured metals. The metals some-

times can be reused in the nickel plating tank if the ion exchange regenerant is matched correctly because the residual material consists of concentrated nickel salts. Some companies also choose to send the saturated resin off site for metal recovery (RI DEM 1995c).

The final rinse in a nickel plating line can be continuously processed through the resin columns to ensure a nickel-free final rinsewater. The upstream rinses and dragouts are returned to the plating tank to make up for evaporative losses. As a result, platers can reduce generation of F006 hazardous waste sludge. Initial capital costs for ion exchange can vary depending on the size of the shop, and setup costs can range from several thousand dollars for a small line to \$10,000 to \$20,000 for a larger facility. Operating expenses include chemical costs and labor (RI DEM 1995c).

#### *Reverse Osmosis in Nickel Plating*

While ion exchange is used more frequently, interest among platers in reverse osmosis (RO) is growing. Nickel is the most common plating salt reclaimed with RO because it is expensive and the pH and temperature requirements are handled easily by a RO system. Reverse osmosis can separate dissolved components such as nickel ions, significantly reducing or possibly eliminating F006 sludge. Depending on the type of RO membrane used, the recycled rinsewater might still contain some metal ions. While a perfect membrane theoretically could separate 100 percent of metal ions, the commercially available membranes are usually 95 to 99 percent effective. Whether this is clean enough depends on the ultimate use of the plated part (Cushnie 1994).

For many non-decorative products, water produced by RO is clean enough to return to the process. However, in decorative and electronic applications where nickel is a base for precious metals, a nickel-free final rinse is necessary to avoid contaminating the precious metal plating solution. Modifying the RO process to ensure a nickel-free final rinse is possible with the addition of a small ion exchange system. Operating costs for these systems include membrane replacement, electricity, and labor. Average

labor costs can total \$2,000 to \$3,000 per year. Systems for smaller units are not yet commercially available, however, they are under development (RI DEM 1995c).

#### **Recycling Nickel Rinsewater Using Low-Temperature Evaporation and Reverse Osmosis Case Study**

A Connecticut facility evaluated low-temperature evaporation and reverse osmosis (on a pilot scale) for their ability to process rinsewater collected from a nickel electroplating operation. Each system offers advantages under specific operating conditions. The low-temperature evaporation system appeared best suited to processing solutions with relatively high nickel concentrations. The RO system appeared best adapted to conditions where relatively dilute rinsewater solutions must be concentrated to levels acceptable for replacement in the plating bath. The company found that a combination of the two technologies might provide the best process alternative. Initially, the RO system would be used to concentrate the feed solution followed by low-temperature evaporation processing to concentrate the solution to levels acceptable for replacement in the plating bath.

(EPA 1995)

## **Electroless Plating**

### **General Issues in Electroless Plating**

Electroless plating is a growing segment of metal finishing, especially in the electronics industry. In electroless plating, metals are deposited onto the surface of a part without the use of electricity as a source of electrons. Instead, the bath solution supplies the electrons for the deposition reaction. These baths are extremely complex using a variety of chelating and/or complexing agents that hold the metals in solution. Common chelating agents include ethylenediaminetetraacetic acid (EDTA), citrates, oxalates, cyanides, and 1,2-diaminocyclohexanetetraacetic acid (DCTA). Nickel, copper, cobalt, and gold are the most common metals plated in this process. Deposition rates are controlled by the amount of reducing agent present and the type of chelating agent

used. Figure 7 presents a flowchart of a typical electroless plating process.

Electroless plating results in a fine-grained metal deposit similar to traditional electroplating finishes. Industries use this process to plate on non-conductors such as plastic, electroformed dies, and printed circuit boards or to obtain an extremely uniform plate (ASM 1982).

Waste segregation is especially important in electroless systems because of the presence of chelators. Chelated metal solutions are not responsive to conventional neutralization, precipitation, flocculation, and settling treatment techniques. Therefore, electroless platers require alternate treatment methods. Because of the affinity of metallic ions for chelating agents, combining waste streams will cause unchelated metallic ions to mix with unreacted agents, increasing the load of difficult-to-break chelated metals to the recovery equipment (Jordan 1985).

Although extremely similar to electroplating, electroless operations feature four rather distinctive characteristics:

- ◆ Electroless plating demands much tighter control over process parameters than electroplating. Critical parameters include metal concentration, reducer concentration, pH, temperature, agitation, and contamination control. Improper control over these process variables can result in increased reject rates of workpieces and substantial waste.
- ◆ Chemical reactions in the electroless process bath cause plate-out in which everything coming into contact with the process solution, including the tank itself, is coated with the plating material. To treat plate-out, the plating line must be taken off-line and stripped. In the case of electroless nickel, stripping is accomplished with nitric acid. In some shops, stripping is done every few days. The nitric acid stripping process can cause significant air releases of nitrous oxides (NOX) if the stripping solution is too dilute. The resulting nitric acid/nickel waste also is difficult to treat for disposal because of its high metal content.

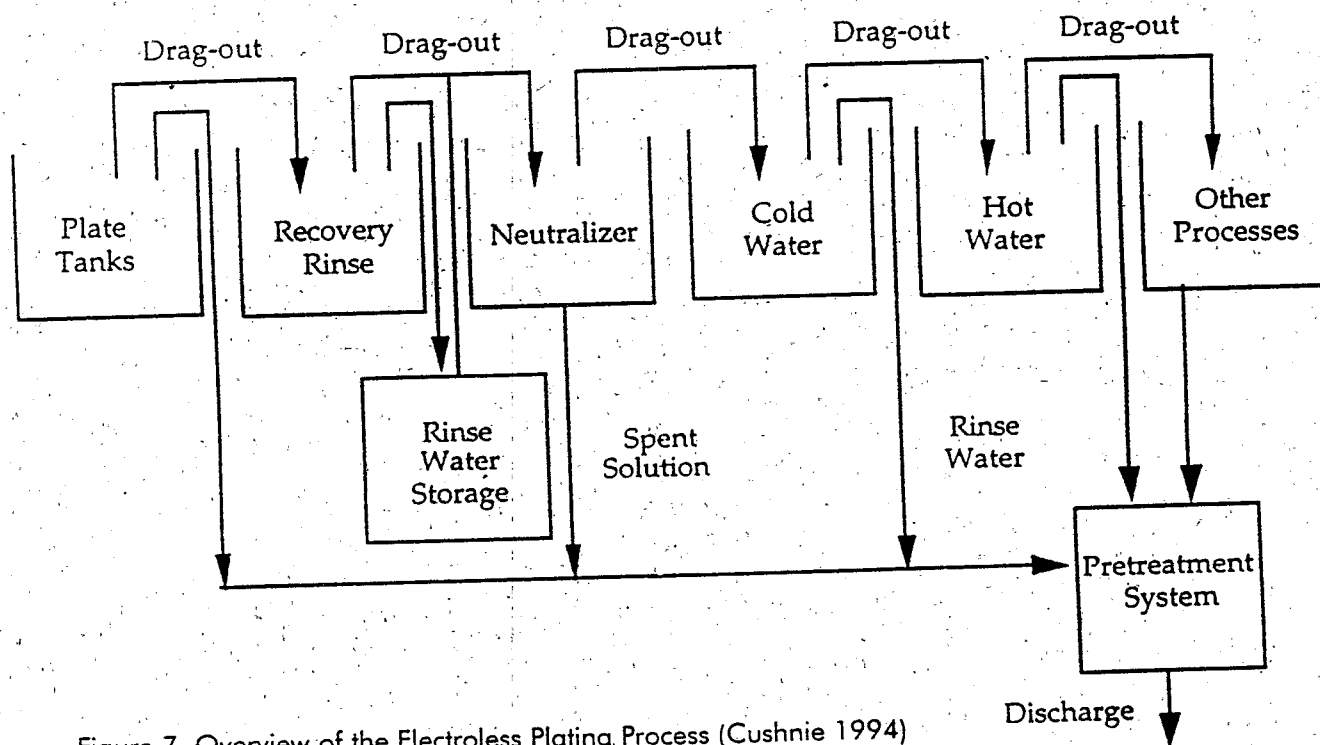


Figure 7. Overview of the Electroless Plating Process (Cushnie 1994)

- ◆ The frequency of dumping electroless baths is greater than that of electroplating. Electroless baths are extremely sensitive to contamination, especially those that are brought into the solution (drain). Turnover is a measure of the age of electroless plating baths and is the term used for the number of times the starting mass of metal at makeup is replenished. Current process bath technologies typically allow up to 10 to 12 turnovers, although 5 to 6 is common.
- ◆ The concentration of organics in electroless process chemistries can create special wastewater treatment problems. The focus for most metal finishers is metals. For electroless platers, the level of chlorinated organics can be a problem as well. The amines used in the process can break down to form chlorinated organics when combined with other chemicals in the pretreatment process (Haveman 1995).

### Precipitators

A common method of treating electroless wastes is the addition of reducing agents such as sodium borohydride, sodium hypophosphite, or sodium hydrosulfite at elevated temperatures to reduce the soluble metals to their metallic or oxide forms. Sludges produced in these processes contain relatively impure metal powders that are susceptible to air oxidation and require further treatment because of the presence of interstitial water containing relatively large amounts of free chelating agents. Over a relatively short period of time, these chelates can cause redissolution of some of the metal oxide in the sludge. As a result, platers must consider this sludge a hazardous waste and manage the waste accordingly (Richmond 1991).

### Housekeeping in Electroless Plating

Electroless solutions are especially susceptible to impurities affecting the process solution. Impurities in the solution can cause reduced ductility and corrosion resistance as well as pitting, adhesion, and roughness problems. Facilities should identify sources of contamination and take steps to avert them including worker

training or equipment modifications. Common sources of contamination include cleaners, pickling solutions, airborne particulates, hard water, and defective equipment (ASM 1982).

### Metal Recovery in Electroless Plating

#### *Electrolytic Recovery*

Electrolytic techniques use high surface-area cathodes and/or non-conductive fluidized beds to recover metal that can be sold for scrap. The process uses a high surface-area cathode that attracts the metallic ions out of solution. Platers then must strip the cathodes and treat the resulting solution by chemical or conventional electrolytic means to remove the remaining metal content. In some cases, concentrate can be returned to the process solution. Using a process such as this will result in decreased sludge generation and increased production rates from the electroless bath (Jordan 1985). Chapter 7 presents a more thorough review of electrolytic recovery.

#### *Electrodialysis*

Electrodialysis uses a membrane that allows for the separation, removal, or concentration of ionized chemicals. These functions are accomplished by selective transport of ions through ion exchange. Electrodialysis uses two different membranes: an anionic permeable (AP) membrane that allows passage of only anions and a cationic permeable (CP) membrane that allows cation ions to pass through. The result is two streams: a demineralized rinsewater stream suitable for reuse and a concentration of metallic salts usually returned directly to the plating solution. For example, electroless nickel and copper plate rinsewaters generated during the production of printed circuit boards can be directed to an electrodialysis unit. Processed concentrate can be returned to the plating tank and water reused in the rinse process (Kamperman 1991).

#### *Ion Exchange in Electroless Plating*

The use of conventional ion exchange systems as well as newly developed resin technology has been proposed for the treatment of electroless wastes. Conventional cation exchange resins are extremely inefficient. Systems involving these



resins, therefore, require large columns and frequent regeneration. Most chelating resin systems available today are not effective on all chelators. In addition, the regenerant from most ion exchange or chelate resin systems requires further treatment in order to reclaim or otherwise remove the metal content (Cushnie 1994).

## Electroless Copper

### Common Uses

Electroless copper is used commonly to plate parts for engineering applications, particularly to provide conductivity for electronics and printed circuit boards or plastics that are going to receive further plates for decorative applications (ASM 1982).

### Common Process Solutions

Electroless copper uses copper salt as the metal salt, often cupric chloride, EDTA as a chelating agent, and formaldehyde (a suspected carcinogen) as the reducing agent. The reductive reaction is favored at high pHs so caustic soda is used to keep the pH above 11.0. Reducing agents often react with the bath, resulting in slower deposition rates and poorer deposit quality. This also can mean that the bath will need to be rejuvenated after several metal turnovers.

This solution also is subject to spontaneous decomposition. Copper built up on the tanks from the process solution must be stripped with an etching solution (e.g., sulfuric acid/hydrogen peroxide etchant). This results in an additional wastestream of copper and etching solution (Ford 1994).

### Alternatives to Electroless Copper

#### Carbon Technology

The printed circuit board industry is testing a proprietary technology, called the Blackhole Process, as an alternative to electroless copper plating. This process uses conventional plating equipment and aqueous black carbon that is dispersed at room temperature. The carbon film that is obtained provides the conductivity needed

for the through-holes. The following qualities make Blackhole environmentally attractive:

- ◆ Reduced process steps
- ◆ Reduced health and safety concerns
- ◆ Reduced waste treatment costs
- ◆ Reduced water use
- ◆ Reduced air pollution

The chemistry in the Blackhole process avoids the use of metals (i.e., copper, palladium, and tin) and formaldehyde (a suspected carcinogen) used in electroless copper plating. Compared to conventional electroless copper plating, the Blackhole technology uses fewer individual steps than electroless plating. The smaller number of process steps reduces the use of rinsewater, decreasing waste treatment requirements (EPA 1994).

Printed circuit boards are prepared prior to carbon coating in the same manner as electroless copper including etchback. Immediately prior to carbon coating, the boards are cleaned with proprietary cleaners and conditioning solutions which are alkaline and contain weak complexing agents. The carbon coating solution also is slightly alkaline and contains extremely fine carbon particles. The process has been available commercially since 1989. It is used in many printed circuit board facilities and has been approved by the United States Military (MIL-55110D) as a substitute for electroless copper in military applications (Altmayer 1994). Making the transition from an electroless copper plating system to the Blackhole technology requires only the disposal and cleaning of the existing electroless line and purchasing of the new solutions (EPA 1994).

Elimination of electroless copper removes a chelated process from wastewater, however, the substitute might have some disadvantages. The extremely fine, suspended carbon might cause problems in wastewater treatment operations by clogging filters, coating probes, and interfering with clarifier operations. Carbon cannot be removed by precipitation and must be controlled

at the source. Carbon in wastewater will increase loading to the publicly owned treatment works (POTW) significantly. The carbon also can act as an organic collector, increasing total organic concentrations in the wastewater. In areas where POTWs have excessive coloration regulations, discharges containing carbon are unlikely to meet this requirement (Altmayer 1993).

## Electroless Nickel

### Common Uses

Electroless nickel is used normally as an engineering coating to impart corrosion and wear resistance to a workpiece. Platers also commonly use the process on aluminum to provide a solderable surface and to improve lubricity and the release of molds and dies. Because of these properties, this technology is used widely in petroleum, chemicals, plastics, optics, printing, mining, aerospace, nuclear, automotive, electronics, computers, textiles, paper, and food machinery manufacturing (Fields 1982).

### Common Bath Solutions

Metal finishers have used electroless nickel since the 1950s. The most common baths use nickel sulfate salts with sodium hypophosphite as the reducing agent. Platers frequently use hypophosphite in metal applications and a warm, alkaline hypophosphite solution in plastics applications. In either case, decomposition of the sodium hypophosphite during the reduction reaction results in the formation of a compound that increases deposition rates. Generally, this occurs between five and seven metal turnovers (Fields 1982).

### Process Characteristics

Some advantages of this process include:

- ◆ Uniform deposition without variances in thickness
- ◆ Platable on non-conducting materials such as plastic
- ◆ Solderability
- ◆ Good wear
- ◆ Corrosion resistance

Some disadvantages of the system include:

- ◆ High chemical costs
- ◆ Embrittlement
- ◆ Poor welding characteristics of nickel phosphorous deposits
- ◆ Copper strike needed to plate certain alloys
- ◆ Slow plating rates

Another disadvantage is that the baths have a tendency to decompose spontaneously causing the entire tank to become nickel plated. When this occurs, the tank must be drained of the plating solution and filled with a nitric acid solution to dissolve the metal and repacify the tank. The nitric acid solution can be retained and used several times, but at some point it must be disposed (Davis 1992).

### Bath Life Extension

Because of the frequency of bath change-out, the primary pollution prevention goal in electroless nickel baths is bath life extension. Bath life extension technology performs two functions: removal of the chemical byproducts formed during the processing of parts and the continuous addition of bath chemicals to maintain the overall chemical balance of the bath. Typical byproducts of the process are orthophosphite, sulfate, and sodium ions. Process bath chemicals and operating parameters such as nickel concentration, hypophosphite, reducing agents, complexing agents, pH, temperature, and bath stabilizers influence the effectiveness of different bath life extension methods (DoD 1996).

Recovery technologies such as ion exchange and reverse osmosis have been used to remove contaminants. Other methods include the precipitation of orthophosphite contaminants with calcium or magnesium ions, however, this method is only useful if the sulfate ion also is removed. Some treatments have extended the bath life from seven to ten times the original life (extensions such as these can reduce waste generation by 90 percent) while others have claimed increases of 50 times the original. Facilities should be aware that the concentration of inhibitors, catalysts, and exaltants will change

as the lifetime of the bath is extended, requiring monitoring and additions of the chemicals (Bishop 1993).

### Regeneration of Electroless Nickel Baths

Electroless nickel solutions are degraded by the buildup of orthophosphite, a breakdown product of sodium hypophosphite that platers use in the solution as a reducing agent. Studies are underway to see if electrodialysis is capable of removing the orthophosphite selectively, increasing the life of the solution vastly. Initial results for this are not promising, however, research centers such as the Toxics Use Reduction Institute continue to work with companies on making this technology feasible (Palepu).

### Prolonging Bath Life with Lime

A pilot-scale study was conducted by TecKote, in Brampton, Canada, to determine if it is possible to precipitate out phosphite contamination of electroless nickel baths using lime. The test procedure was as follows:

- ◆ A plating bath was prepared using a proprietary electroless nickel solution
- ◆ Nickel salt and hypophosphite solution were mixed with deionized water
- ◆ Parts (i.e., activated steel panels) were immersed in the solution
- ◆ A 15-percent lime slurry was pumped into the plating bath at a constant rate of 20 milliliters per minute.

The plating run lasted 44 hours and yielded some promising results. The test found that the addition of lime slurry doubled the life expectancy of the plating solution, however, the process also produced a sludge that was determined to be hazardous. The study did not determine whether this process would yield cost savings for plating facilities (Richmond 1991).

## Immersion (Displacement) Plating

Immersion plating is a process similar to electroless plating. In this process, the metal finish is placed on the workpiece by displacing base metal from the workpiece with another metal ion

in the plating solution. The metal ions in the plating solution have a lower oxidation potential than the displaced metal. This process, like electroless plating, uses chemical reactions to apply a metal finish to the substrate. Immersion plating differs from electroless plating in that the reducing agent is the base metal of the workpiece and not a chemical additive, as is the case in electroless plating (Davis 1994).

The thickness of deposits obtained in immersion plating is limited because deposition stops when the entire surface of the base metal is coated. Higher temperatures and agitation can increase the reaction rate of the immersion process. These baths usually are inexpensive to operate and deposit well. Other benefits of immersion include its ability to deposit on difficult surfaces such as bores or holes. When working with this solution, be aware of the safety hazards associated with bases and acids (Hirsch 1993). Table 16 identifies deposit-base pairs that can use this plating technique without a cyanide solution.

## Chemical and Electrical Conversion

Chemical and electrochemical conversion treatments are designed to deposit a coating on metal surfaces that perform corrosion protection and/or decorative functions and, in some cases, to prepare for painting. Processes include anodizing, chromating, passivation, phosphating, metallic coating, and electropolishing. The converted surface is not superimposed on the underlying metal, but rather is a strongly adherent chemical entity formed at the interface by an interaction between the chemical coating solution and the ions formed from the metal surface immersed in the solution.

### Anodizing

As mentioned in the previous section, anodizing is a specialized electrolytic surface finish for aluminum that imparts hardness, resists corrosion, increases paint adhesion, provides electrical insulation, imparts decorative characteristics, and aids in the detection of surface flaws on the aluminum. This process employs electrochemical means to develop a surface oxide film on the workpiece, enhancing corrosion resistance.

Table 16. Immersion Plating Formulations (Hirsch 1993)

Type of Deposit	Base Metal	Bath Ingredients
Bronze	Steel	Stannous sulfate, copper sulfate, and sulfuric acid
Cadmium	Aluminum	Cadmium sulfate and hydrofluoric acid
	Copper alloys	Cadmium oxide and sodium hydroxide
	Steel	Cadmium oxide and sodium hydroxide
Copper	Aluminum	Copper sulfate and ethylenediamine or hydrofluoric acid
	Steel	Copper sulfate and sulfuric acid
	Zinc	Copper sulfate, tartaric acid, and ammonia
Gold	Copper alloys	Hydrogen tetrachloroaurate and ethanol
Nickel	Copper alloys	Nickel sulfate, ammonium nickel sulfate, and sodium thiosulfate
	Steel	Nickel sulfate
	Zinc	Nickel sulfate and sodium chloride
Silver	Copper alloys	Silver nitrate, ammonia, and sodium thiosulfate
Tin	Aluminum	Sodium stannate
	Copper alloys	Stannous chloride, thiourea, and sulfuric acid
	Steel	Stannous sulfate and sulfuric acid
	Zinc	Stannous chloride
Zinc	Aluminum	Zinc oxide and sodium hydroxide
	Steel	Zinc chloride and ammonium chloride

Anodizing differs from electroplating in two ways. First, the workpiece is the anode rather than the cathode as in electroplating. Second, rather than adding another layer of metal to the substrate, anodizing converts the surface of the metal to form an oxide that is integral to the substrate (SME 1985).

Industry uses three principal types of anodizing: chromic acid anodizing (called Type I anodizing), sulfuric acid anodizing (called Type II anodizing), and hard coat anodizing, a combination of sulfuric acids with an organic acid such as oxalic acids (called Type III anodizing). Because of the structure, the anodized surface can be dyed easily. These dyes are organic or organometallic and often contain chrome in the trivalent state. Whether the pieces are dyed or not, they need to be sealed. Sealing can be performed with hot water, nickel acetate, or sodium dichromate, depending on the required properties (SME 1985).

#### *Type I (Chromic Acid) Anodizing*

Chromic acid anodizing takes place in a solution of chromic acid. The hexavalent chrome solution creates a thin hard coating (Ford 1994).

#### *Type II (Sulfuric Acid) Anodizing*

Sulfuric acid anodizing takes place in a 15-percent solution of sulfuric acid. During the anodizing process, aluminum dissolves off the surface of the part and changes the surface characteristics to an oxide coating. This process creates a surface structure that is both porous and harder than the base aluminum. Sealing this coating provides greater corrosion protection. When the aluminum concentration in the bath solution builds up to a certain level (15 to 20 gallons per liter), the process becomes less efficient and requires treatment (Ford 1994).

#### *Type III (Hard Coat) Anodizing*

Hard coat anodizing is a form of sulfuric acid anodizing in which the acid content is slightly

higher (20 percent) and an organic additive is added to the bath. This additive helps to create a tighter pore structure that increases the hardness of the oxide coating. Hard coat anodizing has a high resistance to abrasion, erosion, and corrosion. This type of coating also can be applied in much thicker layers than Type I or Type II anodizing (Ford 1994).

Platers use various methods to treat wastes generated from anodizing bath solutions. Technologies that have been employed successfully include evaporation systems operating under reduced pressure, sedimentation, reverse osmosis, filtration, and anion and cation exchangers.

### Substituting Type I Chromic Acid Anodizing with Type II Sulfuric Acid Anodizing

Because of federal and state mandates being imposed on operations using hexavalent chrome, researchers have investigated the feasibility of substituting Type I anodizing with Type II sulfuric acid anodizing. The results of a NASA study indicate that in applications where anodizing is used to impart corrosion protection on aluminum, Type II sulfuric acid anodizing is superior to Type I chromic acid anodizing (Danford 1992).

Conversion from chromic acid to sulfuric acid anodizing is not a simple chemical substitution according to suppliers. The conversion requires a complete changeover of anodizing equipment and partial modifications to downstream waste treatment facilities. Replacement of the anodizing tank often is required because of the differences in acidity between sulfuric acid and chromic acid. Sulfuric acid anodizing processes also have different voltage and amperage requirements, necessitating replacement of the rectifier. The operating temperature of the electrolytic bath also is different for the two processes. The chromic process is usually maintained by steam heat at an operating temperature of 90 to 100 degrees Fahrenheit whereas the sulfuric acid process must be chilled using cooling water to an operating temperature of 45 to 70 degrees Fahrenheit.

Operation and maintenance costs are typically much lower for sulfuric acid anodizing than for

chromic acid because of lower energy requirements. Wastewater treatment costs are lower as well because sulfuric acid only requires removal of copper whereas chromic acid requires more complex chrome reduction techniques. The change in materials also means that the cost of sludge disposal is greatly reduced.

### Substituting Chromic Anodizing with Sulfuric Acid Case Study

In December 1988, General Dynamics replaced a 35-year-old chromic acid/aluminum anodizing system with a new computerized sulfuric acid anodizing system that used computerized hoists and on-demand rinsing. The new system, supplied by NAPCO, Inc., enabled General Dynamics to eliminate a major source of chromium emissions. In addition to the chemical substitution to eliminate chromium releases, automated hoist and on-demand water rinse systems helped to reduce wastewater treatment requirements. The computerized automated hoists monitor the time intervals during which the parts are treated and allowed to drain. Compared with manual immersion and draining of parts, this system reduces treatment requirements by avoiding unnecessary dragout of immersion fluids to downstream rinse tanks. Subsequently, the on-demand water system reduces rinsewater use and wastewater treatment requirements by reducing water consumption and monitoring the conductivity of the rinsewater in the tank. Unlike manually operated rinse tanks, which have constant overflows, the on-demand system adds water only when the conductivity of the tank exceeds a set value. (US EPA 1995)

### Ion Vapor Deposition as a Substitute for Anodized Coatings

The brittle nature of anodized coatings can cause fatigue failure on aluminum alloy structures. However, the soft ductile ion vapor deposition (IVD) aluminum coating will not affect mechanical properties of the base metal detrimentally. In addition, the IVD coating offers excellent sacrificial and stress-corrosion protection, increasing the service life of products using this coating. This coating can allow for stronger

constructions that save weight, particularly important in the design of new aircraft (Muehlberger 1983). For more information on IVD coatings, refer to Chapter 8.

### Chromic Acid Regeneration

Chromic acid anodizing solutions can be regenerated by the use of a cation exchanger which removes the accumulating aluminum together with other impurities such as copper. The life expectancy is much shorter than on normal waste treatment applications, but the method is still practical and economical (Steward 1985).

#### Chromic Acid Case Study

NASA conducted a case study comparing the corrosion protection between Type I (chromic acid) anodizing and Type II (sulfuric acid) anodizing. After using several analytical techniques, the study found the corrosion protection obtained by Type II anodizing superior to Type I anodizing. (Danford 1992)

### Sulfuric Acid Anodize Regeneration with Ion Exchange

Traditionally, platers use ion exchange to remove metallic contaminants from wastewater streams. However, ion exchange resins remove the hydrogen and sulfate components of the sulfuric acid/aluminum anodizing solution. As the solution passes through the columns, the acid is removed. Then the wastestream, which consists of a small amount of acid plus all the aluminum from the anodizing solution, flows to the wastewater treatment system. To recover the acid, platers use water to flush the acid components from the resin, which forms a sulfuric acid solution that is low in dissolved aluminum and can be used again in the anodizing process (Ford 1994).

Chromic acid anodizing solutions can be regenerated by the use of a cation exchanger that removes the accumulating aluminum together with metal impurities such as copper. The life expectancy of the resin is much shorter than for normal waste treatment applications, but the method is still practical and economical (Kostura 1990).

### Sulfuric Acid Anodize Regeneration with Electrodialysis

Electrodialysis removes metal ions (cations) from solutions using a selective membrane, an electrical current, and electrodes. This technology uses a chemical mixture (catholyte) as a capture and transport media for metal ions. This catholyte will form a metal sludge and will require periodic change-outs. The recovered sludge is hazardous, however, companies might want to work with an outside firm to recover the metal in the sludge. Using electrodialysis, facilities can remove all the metal impurities from the anodizing bath, maintaining it indefinitely. By keeping the concentration of contaminants in the process bath low, the rinsewater potentially can be recycled back to the bath, closing the loop on the process. The cost to operate this system will depend on the size of the acid anodizing bath, the level of metal concentration, the metal removal capacity of the electrodialysis unit, and the ability to reclaim metals in the sludge. For more information on this technology, refer to the recycling/recovery section in Chapter 7.

### Sulfuric Acid Anodize Regeneration Using Acid Retardation

Theoretically, sulfuric acid anodize solution and the phosphoric acid bright dip bath can both be regenerated using acid retardation, which is a sorption process using ion exchange resins. The cost for such a recovery operation is likely to be economically feasible for only very large operations. For more information on acid sorption technologies, refer to Chapter 7 (Steward 1985).

It is also possible to collect sludges from rinse-water neutralization and from treatment of batch dumps of anodizing and caustic soda etch, press the sludges as dry as possible, and then dissolve the sludge in sulfuric acid to make a concentrated alum solution, which can be sold as a byproduct for coagulation in wastewater treatment operations. Facilities should ensure that they have a market for the alum cake prior to undertaking this option (Steward 1985).

## Blackening (Antiquing)

### Common Uses

Creating an antique finish by coating a workpiece with a black substance and mechanically relieving it so that the only black remains in recesses has been a common practice in jewelry electroplating shops for many years. Typically, the black is applied in one of several ways: as a paint, as an oxide coating (usually applied by immersion), or as an electroplated deposit (METFAB 1995).

### Common Bath Solutions

The paints are solvent-based, the oxide solutions often contain hazardous materials (e.g., arsenic, lead, permanganate, antimony, and dichromate), and the most popular electroplating process can contain more than 1 pound per gallon of solution of free sodium cyanide (METFAB 1995).

### Alternative Bath Solutions for Blackening

The Versy Black process by Zinex Corporation of Oxnard, California, is a feasible alternative for traditional antiquing operations. This process does not contain any cyanide or chelators and contains only small quantities of zinc, copper, and cobalt. Substitution of this process for existing blackening operations eliminates cyanide, arsenic, antimony, permanganate, dichromate, and tellurium from a facility's wastestream. The proprietary nature of the Zinex product imposes limits on discussing the chemistry behind it (METFAB 1995).

The Rhode Island Department of Environmental Management in conjunction with METFAB Sales and Service tested the Versy Black solution over a 14-month period at several locations. The study showed that Versy Black is not only a feasible alternative, but also a superior product. Versy Black outperformed traditional blackening in the following ways:

- ◆ Easier to control
- ◆ Easy to relieve
- ◆ Easy to lacquer
- ◆ Stable chemistry

- ◆ Excellent adhesion
- ◆ Easier to rework
- ◆ No safety risk
- ◆ No environmental risk

Waste treatment of this process is simple. Because the process uses no chelators, treatment can be accomplished simply by precipitation with caustics (pH adjustment). The absence of chelators in the process also means that treating the metals that enter the wastestream from other processes is less troublesome. Chelators make the precipitation less effective because of their ability to keep metals from reacting with caustics to form insoluble hydroxides (METFAB 1995).

## Chromating

Platers often use chromate coatings to minimize rust formation and to guarantee paint adhesion after anodizing aluminum parts. These coatings also are used over zinc and cadmium to simulate the appearance of bright nickel and chromium. Other applications include use as a coating over zinc or cadmium-plated parts to prevent the formation of white rust. Depending on the color, chromating takes place in a solution of chromic acid and additives. Although these baths contain hexavalent chrome, they are not electrolytic baths and, therefore, do not generate the same level of mist/fumes of chrome electroplating or anodizing. For this reason, the chromating process is not regulated under the Chrome MACT standard (Katz 1992).

### Process Description

The operator immerses anodized parts in a solution that contains a hexavalent chrome salt, either chromic acid or chromate, and an acid, often nitric acid. This solution dissolves the outer layers of the substrate and causes a pH increase at the surface-liquid interface. This change results in the precipitation of a thin complex chromium gel on the surface. The gel is composed of hexavalent and trivalent chromium and the substrate itself. These chromate films provide further corrosion resistance and are formed in a wide range of colors: clear, yellow, gold, and drab olive (Ford 1994). Table 17 presents an overview of the common chromating uses for different substrates.

Table 17. Common Uses of Chromate Conversion Coatings (Freeman 1995)

Metal	Corrosion Resistance	Paint Base	Chemical Polish	Metal Coloring	Remarks
Aluminum	X	X		X	Economical replacement for anodizing if abrasion resistance is not required Used to touch up damaged areas on anodized surfaces
Cadmium	X	X	X	X	
Copper	X	X	X	X	Thin coatings prevent spotting out of brass and copper electrodeposits No fumes generated during chemical polishing
Magnesium	X	X			
Silver	X				
Zinc	X	X	X	X	

Unfortunately, like chromium plating, chromating involves highly carcinogenic and toxic materials. If inhaled, chromate mists can eventually cause lung cancer. Health and safety considerations and the increasing cost of disposal of chromium-containing wastes have prompted users to evaluate alternative treatments. A number of alternatives exist, however, few provide the corrosion protection of chromate conversion coatings. Sulfuric acid anodizing can be substituted for some chromium conversion coatings although the coatings are more brittle and significantly thicker than those produced with chromate (Freeman 1995).

### Alternatives for Chromating

#### *Cobalt/Molybdenum*

Cobalt/molybdenum (Alodine 2000) is a developmental conversion coating process that was originally developed and patented by Boeing Aircraft Company. The process is being developed further by Parker+Amchem in preparation for commercial availability. The process uses an undisclosed proprietary formulation identified generally as cobalt- and molybdenum-based. The cobalt and molybdenum ions are much less

hazardous than chromium and behave similarly. The coating does not have the ability to inhibit pitting corrosion as effectively as chromium, therefore, a second step is required to meet military specifications. The second step is an organic emulsion seal (Alodine 2000) that enhances corrosion resistance and paint adhesion characteristics. The process is estimated to cost two to three times more than conventional chromating. The process also requires an additional tank for the sealing process (Meyers 1994).

#### *Gardolene VP 4683*

A new chrome-free, post-rinse called Gardolene VP4683 has been developed for use on phosphated steel zinc, and aluminum surfaces prior to painting. The rinse contains only inorganic metallic compounds as the active ingredient with no hexavalent or trivalent chrome. The rinse is applied at temperatures up to 100 degrees Fahrenheit and at a slightly acidic pH. The manufacturer describes corrosion protection and paint adhesion as equal to that of hexavalent chrome (Finishers Management 1991).



### *Oxide Layer Growth in High-Temperature Deionized Water*

The oxide layer growth system was developed and refined within the past decade. The process coating is applied in a series of steps, including an oxide layer growth step in boiling deionized water, to build a corrosion-resistant paint base on aluminum. Both immersion and steam spray methods are being developed. The process does not use any hazardous materials and is completely inorganic and non-toxic. Depleted bath and rinsewaters require limited treatment before discharge to a sanitary sewer. The process can withstand greater temperature exposure than the chromate conversion coating and is thin, yet abrasion resistant. The chemical solutions used to apply the coatings are very dilute, facilitating long solution life and simple monitoring and control (Meyers 1994).

The major drawback with the oxide layer growth process is cost. The process requires many additional steps involving numerous tanks of chemicals at elevated temperatures. Consequently, energy and capital costs increase substantially. While energy costs are offset by waste disposal reductions, this technology is estimated to cost up to ten times more than conventional chromating methods. A variation on the process involves spray application within a cabinet coater. This device is a chamber or series of conveyerized chambers. This method reduces some of the associated heating and chemical requirements and requires much less floor space (Meyers 1994).

### *Non-Chromate Passivation of Zinc*

The Centre for Advanced Electroplating in Denmark has developed two different treatment

methods, both based on passivation using molybdate and phosphate (referred to as MolyPhos) as alternatives to chromating. Chromated zinc often is used in the automotive, aerospace, and electronics industries. Platers can use MolyPhos for passivation of electroplated zinc instead of chromate. Depending upon the zinc substrate and the environment in which the workpiece will be placed, this method will function similarly to yellow chromate. MolyPhos performs well in outdoor exposure tests, adhesion tests, and CMT tests, but does not fair well in salt spray tests. The results of numerous corrosion tests are summarized in Table 18 (Tang 1993).

### *SANCHEM-CC*

Another promising alternative is the SANCHEM-CC chromium-free aluminum pretreatment system. The following is a summary of the process:

- ◆ Stage One: Boil in deionized water or steam to form a hydrated aluminum-oxide film.
- ◆ Stage Two: Treat in a proprietary aluminum salt solution for at least 1 minute at a minimum of 205 degrees Fahrenheit.
- ◆ Stage Three: Treat in a proprietary permanganate solution at 135 to 145 degrees Fahrenheit for at least 1 minute.

In cases where maximum corrosion resistance for certain aluminum alloys is required, the process requires a fourth stage. The developers claim that this process closely matches the

Table 18. Results of Molyphos as a Substitute for Chromating (Tang 1993)

Substrate	Yellow Chromate	MolyPhos 33	MolyPhos 66
Cyanide Zinc	Very good	Very good	Good
Acidic Zinc	Good	Not possible	Very good
Zinc/Nickel (15% Nickel)	Good	Bad	Good
Zinc/Cobalt (0.8% Cobalt)	Very good	Good	Good

performance of a chromate conversion process (EPA 1994).

### *Zirconium Oxide*

Zirconium oxide, an organic conversion coating, is an alternative to chromating for some applications. This coating is one of the only commercially available non-chromating treatments for aluminum. This process usually involves immersion of the substrate in an aqueous solution containing a polymeric material and a zirconium salt. The zirconium deposits on the surface in the form of zirconium oxide. These coatings have been used on aluminum cans for some time, but they have not been tested in the kinds of environments in which chromate conversion coatings are typically used. Wider application of this coating as a total replacement for chromating must be based on further testing (EPA 1994).

### **Alternative Conversion Coating Case Study**

A facility using a traditional chromate system generated many forms of hazardous waste (airborne and wastewater). The facility replaced their chromating process with a dry-in-place waterborne emulsion conversion coating. The product is completely chromium-free and adaptable to heat spray applications. The permanganate-based product is considered environmentally safe at ambient temperatures. In fact, small residual amounts of the potassium salt that are deposited as a primary coat are desirable in the industrial wastewater treatment system because they aid in treatment of other common wastewater contaminants.

Replacement of the chromate conversion coating process resulted in a coating that bonded strongly to the metal surface and provided good corrosion resistance. Uniform coverage was achieved easily, and the unpainted surface does not rub off on worker's hands or emit toxic fumes when welded. The parts can be painted immediately, which reduces the time required to complete the finishing process.

(Freeman 1995)

### *Other Chromate Conversion Coating Alternatives*

Several additional processes might prove feasible in eliminating chromium from conversion coatings. These include SBAA and other emerging technologies.

SBAA, developed by Boeing, might prove valuable as a replacement for chromating on certain aircraft parts. The process imparts excellent paint adhesion and corrosion protection at a cost that is comparable to chromating. However, because SBAA is an anodic process, it might not be technically feasible to use it on all parts, especially parts with steel inserts or those having sharp edges, crevices, or areas that entrap fluids (Meyers 1994).

Several experimental and developmental technologies might lead to breakthroughs as replacements for chromium in conversion coatings. These technologies include hydrated alumina coating, hydrated metal salt coating, oxyanion analogs, potassium permanganate, rare earth metal salts (cerium), zirconium oxide/yttrium oxide in aqueous polymeric solution, and lithium-inhibited hydrotalcite coatings.

### **Regeneration of Chromating Solutions**

Both ion exchange and electrochemical methods have been demonstrated as effective methods to regenerate spent chromates; however, in almost all cases, the metal finisher relies on a proprietary chemical supplier for the appropriate balance in the chromating bath. Either of these regenerating technologies make the metal finisher responsible for the overall chemical maintenance of all constituents in the bath. Proprietary suppliers might provide this service to further assist finishers in maintaining a proper balance when one of these techniques is used (Steward 1985).

### **Passivation**

Passivation is a process by which protective films are formed on metals through immersion in an acid solution. In stainless steel passivation, embedded ion particles are dissolved and a thin oxide coat is formed by immersion in nitric acid.

which sometimes contains sodium dichromate. During forming, machining, tumbling, lapping, and other processing operations, iron particles can be embedded or smeared onto the surface of stainless steel. If these remain, the iron corrodes and gives the appearance of rust spots on the stainless steel. In order to prevent this, platers immerse the parts in a solution of nitric acid that sometimes contains oxidizing salts (generally sodium dichromate) depending on the alloy. Generally, 300-series stainless steel and chromium steel with 17 percent or more chromium are passivated in a solution of nitric acid. Series-400 stainless steel with less than 17 percent chromium is passivated in nitric acid and sodium dichromate (Ford 1994).

### Chelant-based Solutions for Passivation

Nitric acid is a fuming, suffocating, and corrosive liquid. The acid's fumes are toxic and the liquid causes severe tissue burns. Because of these attributes, Cal-chem of South El Monte, California, has developed a safer substitute solution for use with passivation on steel. The solution contains chelants as opposed to nitric acid. Chelants provide an attractive alternative because they are non-toxic and biodegradable, however, platers need to be careful of this solution in waste treatment (Microcontamination 1993). For more information, refer to the first section of this chapter.

### Phosphate Coatings

Phosphating is used to treat various metals (mainly steel and iron) to impart corrosion resistance and to promote the adhesion of finishes such as paint and lacquers. Phosphating treatments provide a coating of insoluble metal phosphate crystals that adhere strongly to the base metal. Generally, phosphating solutions are prepared from liquid concentrations containing one or more divalent metals, free phosphoric acid, and an accelerator (Ford 1994).

Iron and zinc phosphate coatings often are used as paint bases and manganese phosphate coatings are applied chiefly to ferrous parts for break-in and galling (e.g., engine parts). Other metallurgical uses for phosphate coatings are aiding in the forming of steel, wear resistance, and corrosion protection (with the addition of oils or

waxes). The choice of iron or zinc phosphate coating depends on product specifications. In general, the more extensive multi-stage zinc phosphate processes provide better paint adhesion, corrosion protection, and rust protection than iron phosphate processes. Zinc phosphate baths, however, tend to be more expensive, require more maintenance, and often result in more sludge disposal (SME 1985).

The phosphating process consists of a series of application and rinse stages typically involving the application of either an iron, manganese, or zinc phosphate solution to a substrate. A simple iron phosphating system is comprised of two stages: an iron phosphate bath that both cleans the part and applies the conversion coating followed by a rinse bath to remove dissolved salts from the treated surface. An advanced zinc phosphating line might feature seven stages of spray/dip and rinse baths. In addition, a final seal rinse comprised of a low-concentrate acidic chromate or an organic non-chromate often is applied to further enhance corrosion resistance. Following the conversion application, the parts are dried to prevent flash rusting (Ford 1994).

### Pollution Prevention in the Phosphating Process

Since the 1970s, a trend in the metal finishing industry toward reducing heating costs, improving working conditions, prolonging equipment life, reducing sludge, and reducing processing steps has resulted in low-temperature iron and zinc phosphate coatings and, to a limited degree, solvent phosphating solutions.

### Regeneration of Phosphating Baths

Precipitates are formed continuously in phosphating operations presenting maintenance headaches. Often, this results in dumping of the solution. Usually, the precipitates accumulate in the tank, primarily on the heating coils. When the solution is removed from the tank, this accumulation of sludge can be manually removed. The solution should be decanted back into the tank to minimize waste because this uses space and time; this is rarely done. A more efficient system involves the use of a continuous recirculation system through a clarifier with gentle agitation in the sludge blanket zone. This

### Ultrafiltration in the Phosphating Process Case Study

R.B. White, Inc., of Bloomington, Illinois, operates a sheet-metal fabrication facility that manufactures painted steel shelving units. The company uses a single stage, aqueous iron phosphating/degreasing system to improve worker safety and reduce the generation of organic solvent emissions and hazardous waste. Although the switch eliminated the risks and liabilities associated with organic solvents, it introduced a new waste disposal problem. Simultaneous degreasing and phosphating in the same bath formed an oil-water emulsion. With extended use, the buildup of oil in the bath reduced cleaning and phosphating efficiency and product quality was compromised. Additionally, dragout of oil from the bath into the rinsewater eventually pushed oil and grease levels in the discharge over the allowable limit.

In the past, the company used oil skimmers to control oil slicks on the surface and prolong the life of the bath, but the skimmers were only partially effective. When oil in the bath began to sacrifice product quality and discharge levels edges closer to the maximum allowable limit, the bath had to be replaced. Depending on production rates, the bath typically lasted 3 to 4 months. Replacing the bath required losing a full day of production time to take the process off-line, arranging with a waste transporter to drain and dispose of the contents, and recharging the tank with 5,000 gallons of fresh water and raw materials. Disposal costs alone were \$15,000.

The plant implemented a full-scale, in-plant field test of an ultrafiltration system provided by Koch membrane equipped with four 1-inch tubular PVDF membranes. When the field test began, the iron phosphating/degreasing bath had not been replaced in more than 3 months. The aqueous solution was murky with dirt and oil, and large patches of free oil floated on the surface. Over the next 11 days, ultrafiltration produced dramatic changes. Surface oil slicks disappeared and were replaced by a clean, light foam. The bath solution was visibly clearer and plant personnel testified that it looked like a freshly recharged bath. Results of total organic carbon (TOC) analysis for the full-scale test showed a change in oil and surfactant concentrations during the test.

The company analyzed the costs and benefits associated with installing the ultrafiltration system to determine the economic feasibility of this technology. Based on the estimated expenditures and savings, the payback period for this technology was only 6.9 months. The net present value and internal rate of return indices were \$152,143 and 178 percent, respectively.

In summary, the findings of the evaluation indicated that:

- ◆ The application of ultrafiltration produced significant reductions in hazardous waste, especially significant when compared to earlier methods that used separate degreasing and phosphating tanks and organic solvent.
- ◆ In most phosphating applications, ultrafiltration is economically attractive although capital investment is required. Applications for recycling/reusing wastewater via ultrafiltration have good potential for pollution prevention improvements as well as good economics. However, firms first should carefully investigate highly sensitive parameters such as fouling on small-scale systems and identify variability in their operation and its effect on the process.

(EPA 1995)

allows for indefinite use of the solution and allows easy removal of dewatered sludge from the bottom of the clarifier (Steward 1985).

## Issues Related to Aluminum Finishing

Aluminum finishing uses mainly anodizing and chromating treatments. Prior to anodizing or chromating, a workpiece usually proceeds through a cleaning and etching process. Both anodizing and chromating use similar cleaning schemes. If required, platers perform solvent or less toxic immersion cleaning. The cleaner used for aluminum workpieces should not contain sodium hydroxide because this chemical attacks aluminum. An example of an acceptable cleaning solution is borax (sodium tetraborate). Technical assistance providers should be aware that, even if a cleaner is made of a non-toxic substance, if the cleaning solution becomes contaminated with oils and lubricants, the spent solution can be classified as a hazardous waste (SME 1985).

The next step prior to finishing is etching. The surface is etched by an alkaline or acid-based etchant. Platers perform this etch step to thoroughly clean and prepare the surface for further treatment. The caustic etch used in many aluminum finishing lines and the chemical milling solution used for aircraft components can both be regenerated by crystallization and removal of sodium aluminate. However, the process must be carefully controlled and maintained. Many operations might not find this option economically feasible because the technology is capital intensive (DOD 1993).

During the etching process, smut often is formed on the aluminum workpiece. The smut must be removed prior to further treatment. Usually this treatment is accomplished with a nitric or nitric/hydrofluoric acid dip, otherwise known as desmutting (Cushnie 1994). The desmutting process involves the use of large amounts of acids. Several products currently on the market use approximately 10 percent of the usual amount of nitric acid. Commonly, ferric nitrate is substituted as a desmutting agent in the presence of small amounts of nitric acid. The

rate and desmutting action of ferric nitrate are comparable to the traditional 50-percent nitric acid bath (Ford 1994).

## Stripping

Occasionally, workpieces that have a metallic coating must be stripped to the base metal. Most immersion stripping is accomplished with cyanide, which does not attack steel substrates but dissolves many of the metals used as coatings. There are seemingly as many different stripping solutions as there are base metal/applied coating combinations. In general, they tend to be either acid-, alkali-, or cyanide-based. They can be chelated heavily or not at all. The most important property of these solutions (besides the ability to strip the coating) is that they must not attack the base metal. The use of cyanide-based metal strippers results in the generation of cyanide-contaminated solutions and a host of associated occupational health and hazardous waste compliance issues. These solutions require special treatment and disposal procedures. Interestingly, stripping can be a part of the finishing process, particularly for complex parts that only require plating on certain surfaces. The entire part is plated and then the areas where plating should remain are masked off and the entire part is immersed in the stripping solution to remove the undesired finish (Ford 1994).

## Pollution Prevention in Stripping Operations

As the baths used in stripping are similar to those used in plating, similar techniques of pollution prevention and waste minimization are applicable. Attention to cleanliness and process control are important in reducing stripping wastes. Stripping usually is accomplished either by chemical immersion or by electrolytic processes. Although mineral acids, suitably inhibited, are useful for stripping some coatings, they tend to attack the metal substrates and, therefore, are limited in their application.

## Alternatives to Cyanide Stripping

Several non-cyanide alkaline immersion stripping baths are available to remove copper or nickel from various substrates. These baths

typically use either the ammonium ion or an amine to provide complexing. Persulfate or chlorite anions can be used as well as proprietary formulations. The use of non-cyanide strippers eliminates cyanide from the spent stripper solution. In general, these non-cyanide strippers are less toxic than their cyanide-based counterparts and are more susceptible to biological and chemical degradation, resulting in simpler and less expensive treatment and disposal costs. In addition, the use of a non-cyanide stripper can simplify the removal of metals from spent solutions. These metals are difficult to remove from cyanide-based solutions because they form a strong complex with the cyanide ligand (EPA 1994).

Because non-cyanide stripping solutions are typically proprietary formulations, the detailed chemistry of coating removal is not available for most solutions. Stripping solutions are available for a wide variety of coating metal/base metal combinations and processing characteristics can vary widely (EPA 1994).

### Reported Applications

Non-cyanide strippers have been available for many years. The major drawbacks of this technology include lack of speed, etching of some substrates, and the need for electronic current. As the disposal costs for cyanide strippers increase, many companies have converted to non-cyanide stripping and have adjusted production cycles accordingly for the slower stripping speed (EPA 1994).

### Operating Features

The wide variety of non-cyanide strippers makes it difficult to generalize about operating parameters. Some strippers are designed to operate at ambient bath temperatures whereas others are recommended for operating temperatures as high as 180 degrees Fahrenheit. Stripping processes range from acidic to basic. Bath life is longer because higher metal concentrations can be tolerated. In general, the same equipment can be used for cyanide-based and non-cyanide stripping, however, acidic solution tank liners might be needed to prevent corrosion (EPA 1994).

### Costs

The impacts on costs when using non-cyanide strippers are:

- ◆ No large capital outlay is required
- ◆ Costs of makeup solution is likely to increase slightly
- ◆ Waste treatment costs are reduced because of reduced cyanide treatment (EPA 1994)

Facilities should be aware that treatment costs might not change or might increase if cyanide is still used in other processes in the facility.

### Hazards and Limitations

Non-cyanide metal strippers have some disadvantages. The stripping rates for some coatings might be lower than for comparable cyanide strippers. Some strippers can produce undesirable effects on substrate metals even if the stripper has been recommended by the manufacturer. Also, for some non-cyanide strippers, the recommended operating temperatures are high enough to cause safety concerns and reduced temperatures can lead to slower stripping times and reduced effectiveness (EPA 1994).

A major use for non-cyanide strippers is the removal of nickel coatings. Advances in non-cyanide alternatives have been spawned by the difficulty in treating nickel cyanide waste-streams. Opportunities for further improvement still remain though as the non-cyanide process is significantly slower than cyanide (8 hours versus 1 hour) (EPA 1994).

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# 7 Pollution Prevention in Rinsing

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**R**insing follows cleaning, plating, and stripping operations. Adequate rinsing is a critical step within the plating process. Rinsing prepares a part for subsequent finishing operations, stops the chemical reaction, and prevents cross contamination of subsequent plating tanks. Poor rinsing can result in staining, spotting, blistering, or peeling of the workpiece. Therefore, rinsing must be effective and efficient. Alternative rinsing practices succeed only if they are properly designed, operated, and maintained. In some cases, the only practical means of preventing or reducing pollution is by improving, modifying, or installing recovery/reuse technologies to the rinsing process (Pinkerton 1984).

Most of the hazardous waste in a metal finishing operation comes from the wastewater generated by rinsing operations. Two general strategies to reduce waste from rinsing operations are preventing rinse contamination, and recovering and recycling materials from the rinsing process. Facilities should evaluate alternative rinsing practices prior to investigating recovery technologies. Nevertheless, facilities might need to use a combination of the two strategies for an effective rinsing system that complies with the regulations.

## Alternative Rinsing Practices

The goals of alternative rinsing practices are two-fold: (1) to control the dragout of solution from process baths into the rinsewater and (2) to minimize water consumption. These two goals have a significant effect on the amount of waste, mainly sludge, generated by waste treatment systems. The amount of wastewater sludge generated is directly proportional to the amount of metal, organic, and other bath constituents in the rinsewater. Therefore, any technique for

reducing dragout also will reduce sludge generation (EPA 1992).

## Dragout Reduction

Dragout, the bath solution that is carried out of the process bath and into succeeding tanks, is the primary source of contamination in rinsewater. Reducing dragout can be the single most effective way to reduce waste and conserve water in rinsing operations. Figure 8 illustrates typical generation of dragout.

Reducing dragout extends the life of the process baths and reduces sludge generation. The rate of dragout varies considerably among different parts and processes. For instance, barrel plating commonly carries 10 times more solution into the rinsing process than a typical rack plating operation (Ford 1994). Several factors contribute to dragout including workpiece size and shape, bath viscosity and chemical concentration, surface tension, and temperature of the process solution.

Most dragout reduction methods are inexpensive to implement and, in most cases, have short payback periods. Savings are mainly in the area of reduced use of plating and processing chemicals. Additional savings, often many times the cost of the pollution prevention project, include decreased operating costs of pollution control systems. Many of the methods to reduce dragout require only the cost to properly train employees with no capital expenditures. For example, removing workpiece racks at a slower rate or allowing the rack to drain over the process tank for a longer time does not require capital outlays, but the method does require a conscientious, properly trained operator. Such procedures should not significantly affect production and should result in reducing process chemical

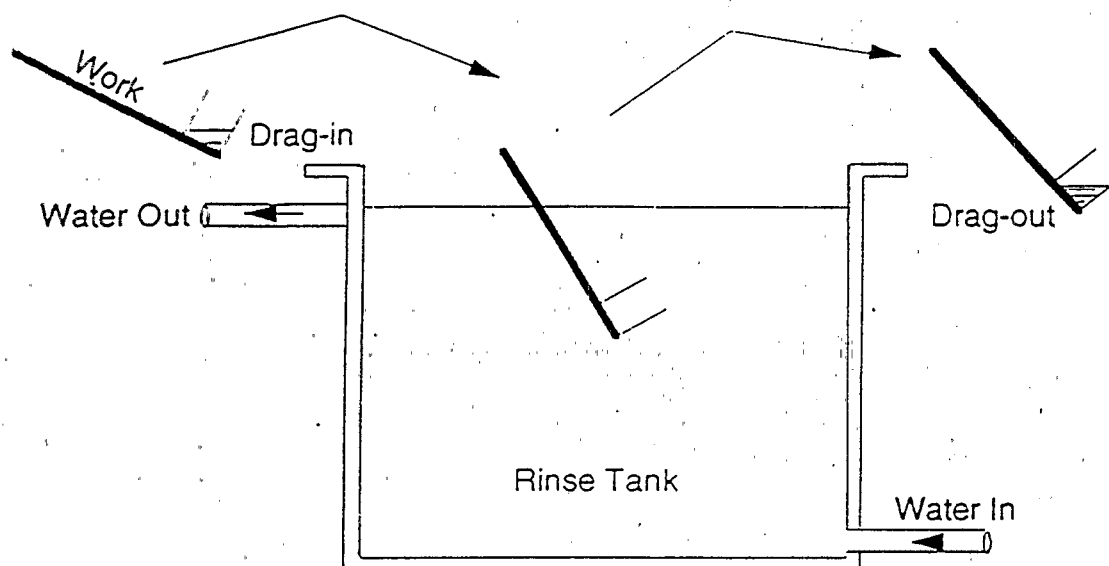


Figure 8. Illustration of Dragout (IAMS 1995)

purchases, water and sewer use fees, treatment chemical purchases, and sludge handling costs (Cushnie 1994).

### Measuring the Dragout Rate

Measuring dragout allows facilities to determine the extent of the problem and to monitor the effectiveness of reduction techniques. Facilities can use several methods to effectively monitor dragout rates. Some facilities use a tensiometer to measure surface tension. A tensiometer measures the force necessary to lift a metal wire ring off the surface of a liquid. The cost for this tool is approximately \$2,000. A second method for determining surface tension is a stalagmometer. While stalagmometers are much less expensive than tensiometers, they are more difficult to use. For instance, plating solution tends to dissolve the ink marks on the meter that are used to calculate surface tension.

Facilities also can use a conductivity meter to determine dragout rates. Using conductivity measurements to generate information on rinsing can greatly reduce analytical fees and eliminate the lag time between sampling and results since samples do not need to be sent to a lab. Most plating facilities have combination pH/conductivity meters that can be used for this purpose or

they can purchase a portable unit for \$200 to \$300 (Cushnie 1994).

### Methods to Reduce Dragout

Platers can reduce dragout using a variety of techniques that involve a combination of employee retraining and relatively simple technology. These methods include:

- ◆ Decreasing workpiece withdrawal while increasing drain rates
- ◆ Changing the bath concentration and temperature
- ◆ Improving racking and rack design
- ◆ Using drainboards and dragout tanks
- ◆ Rinsing over the plating tank
- ◆ Using air knives
- ◆ Improving barrel plating

These techniques are described in detail in the following sections.

### Workpiece Withdrawal and Drain Rates

The speed at which workpieces are removed from the process bath can have a substantial impact on dragout volume. The more slowly a

workpiece, is removed from the bath, the thinner the film of process solution is on the workpiece, and the less solution is dragged into rinse tanks. The effect is so significant that many experts believe that most of the time allowed for draining should instead be used for withdrawing the workpiece. A recent case study demonstrated that a drain time of 10 seconds reduced dragout by 40 percent compared to the industry average of 3 seconds (IAMS 1995).

Facilities can control drain times by posting them on tanks as a reminder to employees on manual lines or by building delays into automated process lines. Smooth, gradual removal of parts from the solution is the preferred method. A bar or rail above the process tank can ensure adequate drain time prior to rinsing. If platers use drip bars, employees can work on more than one rack during an operation. In rotation plating, an

operator removes a rack from a plating bath and lets it drain above the process tank while other racks are handled. Increased drain time, though, can have some negative effects such as drying, which is especially problematic with hot cleaners because it can cause spotting on the workpiece (Cushnie 1994).

### Bath Concentration and Temperature

Lowering the viscosity of the bath can reduce dragout. Facilities can lower the viscosity of a plating solution in two ways: (1) reducing the chemical concentration of the process bath or (2) increasing the temperature of the process bath. For further information on this option, refer to the general pollution prevention section on plating baths in Chapter 6.

### Racking

The placement of workpieces on racks can have a significant impact on the chemicals carried into the rinse tanks. Positioning pieces so that solution drains freely without being trapped in grooves or cavities reduces dragout. Positioning workpieces so that they face downward also can improve drainage efficiency. However, proper placement must take into account both proper plating and rinsing. For example, a saucer-shaped object placed upside down would drain well, but the plating solution would not entirely coat the inside of the cup because of entrapped gas bubbles. Therefore, an angled position is the most efficient. This placement allows for proper plating and efficient draining. Proper racking also can reduce surface tension and improve draining. The following are some suggestions for properly orienting and positioning workpieces (EPA 1992):

#### Workpiece Withdrawal Case Study

The Institute of Advanced Manufacturing Sciences increased the drain time to 10 seconds for workpiece withdrawal and found that dragout was reduced by more than 40 percent. The more slowly the workpiece was removed from the solution, the less solution was removed with the workpiece. This practice also reduced the amount of hazardous waste generated. No information was available in the case study on savings. Costs include training personnel or slowing down automatic process lines. (APPU 1995)

#### Decreased Workpiece Withdrawal Rates

##### Advantages

- ◆ Less contaminants in the rinsewater
- ◆ Posting drainage times on a tank will assist operators in using the optimal drainage time

##### Disadvantages

- ◆ Hard to control drainage time if workpieces are removed manually
- ◆ Takes training if done manually
- ◆ Quality control problems could occur if allowed to dry
- ◆ Might cause production delays (depending on production schedule) (APPU 1995)

- ◆ Parts should be tilted so that drainage is consolidated. The part should be twisted or turned so that fluid will flow together and off the part by the quickest route.
- ◆ Where possible, avoid positioning parts directly over one another.
- ◆ Tip parts to avoid table-like surfaces and pockets where solution will be trapped.

If a workpiece is designed so that it does not drain easily, facilities can work with their designers or, in the case of job shops, their

### Improved Racking

#### Advantages

- ◆ Improves drainage
- ◆ Reduces rinsewater contamination
- ◆ Little or no cost

#### Disadvantages

- ◆ Might require some time to seek innovative measures to improve workpiece drainage
- ◆ Might require redesign of customer workpiece

(APPU 1995)

customers to see if modifications are possible. For example, a plater asked his customer whether he could drill four holes in the workpiece to improve drainage. The customer agreed and the pollution prevention technique was successfully implemented (IAMS 1995).

### Design and Maintenance of Racks

Improving the design of racks, baskets, or barrels can reduce the amount of dragout. If equipment is not properly maintained, it can increase contamination both in terms of increased dragout and contamination from residue on racks. These contaminants include rust and salt deposits that form on racks, barrels, and baskets. Keeping racks clean can reduce contamination of process baths and rinsewaters (Ford 1994).

### Drainboards

Metal finishing operators can use drainboards to collect dragout and drippage when transferring racks from one tank to the next. Boards should

be mounted so that they cover the entire space between the two tanks, allowing the solution to drain back into the previous bath. This method prevents chemical solutions from dripping onto the floor. Figure 9 presents the typical set up of a drainboard. Many operators prefer removable drainboards because they permit access to plumbing and pumps. Drainboards should be made of a compatible material such as polyvinylchloride (PVC). Use of drainboards is a cost-effective technique for reducing chemical consumption and rinsewater contamination (IAMS 1994).

### Drainboards

#### Advantages

- ◆ Reduces chemical consumption
- ◆ Reduces amount of rinsewater needed

#### Disadvantages

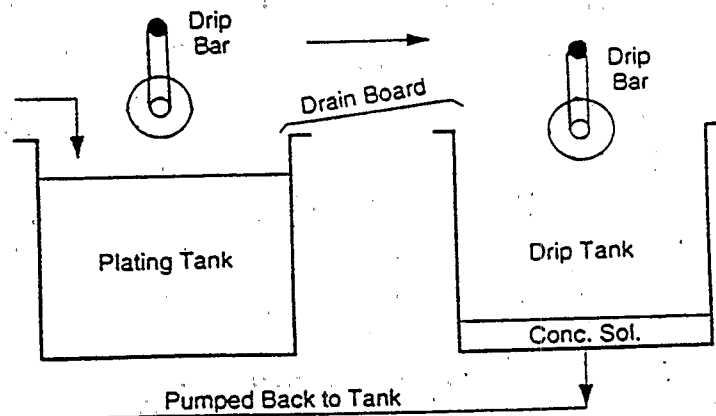
- ◆ Might limit access to pipes and plumbing

(APPU 1995)

### Drainboard Case Study

An EPA case study found that the use of drainboards to reduce dragout, combined with deionized water for bath makeup, reduced waste generation by 50 percent at one company. Prior to implementation, 300 to 400 gallons of sludge were pumped out periodically and disposed of as waste. Capital costs were \$315, the payback period was 1.3 months, and disposal and new material savings were \$2,892. (APPU 1995)

Figure 9. Illustration of Drainboards (IAMS 1995)



### Static Rinse Tank Case Study

PRC Environmental stated that since static rinse tanks are not used as flow-through tanks, they could be set up without plumbing. They returned dragout solution to the process bath, reducing waste generation. Capital costs were \$400 to \$1,500 depending upon tank capacity. No other cost information was available.

(APPU 1995)

### Dragout Tanks (Dead or Static Rinse Tanks)

Dragout tanks are essentially rinse tanks that operate without a continuous flow of feed water. The workpiece is placed in the dragout tank before the standard rinsing operation. Dragout tanks are used primarily with process baths that operate at an elevated temperature.

Chemical concentrations in the dragout tank increase as the operator passes the work through the tank. Because dragout tanks do not have feed water flow to agitate the rinsewater, air agitation often is used to enhance rinsing. Eventually, the chemical concentration of the dragout tank solution will increase so that it can replenish the process bath. Adding the dragout solution back to the process bath compensates for evaporative losses that occur because of high evaporation rates (EPA 1992).

#### Static Rinse Tanks

##### Advantages

- ◆ Replenishes bath with dragout solution
- ◆ Reduces chemical replacement costs
- ◆ Reduces rinsewater use by as much as 50 percent

##### Disadvantages

- ◆ Returned solution can contaminate some process baths, requiring the baths to be dumped (e.g., electroless copper baths).
- ◆ Pretreatment step required before dragout is returned to process tank

(APPU 1995)

The cost of a dragout tank depends on the size of the tank. Since these tanks are not used as flow-through tanks, they can be installed without plumbing. Typically, dragout solutions are

added back to the process bath manually. However, automation is more efficient as it maintains the best concentration in the dragout tank (EPA 1992).

### Rinsing Over the Plating Tank

If the process tank has a high evaporation rate, workpieces can be rinsed directly over the process solution, returning water and chemicals directly to the process tank. This form of rinsing requires a high evaporation rate so that the work can be done without splashing solution onto the equipment. Rinsing often is practiced over electroless plating tanks because they have no buss bars or rectifiers that can be splashed. However, operators can rinse over other plating tanks if they are careful (EPA 1992).

### Air Knives

Metal platers use air knives to blow air across the surface of workpieces as they are withdrawn from process or rinse solutions, physically pushing liquid off of workpieces. This technique returns solution directly to the process bath, reclaiming dragout and reducing the amount of rinsewater required to clean the workpiece, which enhances the drying process. In some applications, however, this rapid-dry method can cause poor bonding, spotting, and staining (APPU 1995).

#### Air Knives

##### Advantages

- ◆ Enhances drying process
- ◆ Reduces amount of rinsewater used
- ◆ Returns solution to process tank

##### Disadvantages

- ◆ Can cause poor bonding, staining, and spotting

(APPU 1995)

### Specific Techniques for Reducing Dragout in Barrel Plating Operations

In barrel plating, floor spills are less likely to occur since automation typically moves the barrel from one tank to the next. However, barrels potentially create more dragout since they hold more solution. In addition, although the barrels are perforated, complete drainage can be

### Air Knives Case Study

US EPA, Mexico's SEDESOL, and the Institute of Advanced Manufacturing Science found that air knives reduced dragout by 75 percent at a particular facility because they pushed water off of the workpiece back into the tank. This technique reclaimed dragout and reduced water use. The study found that facilities must properly filter the compressed air to remove contaminants. Capital costs were \$500.

(APPU 1995)

difficult. As with rack plating, extending drip times reduces dragout.

In order to reduce dragout, the correct barrel must be used for the parts being plated. For example, if the average part is 2 inches in diameter and the barrel contains holes that are too small (less than  $\frac{1}{2}$  inch) drainage can be too slow, resulting in significant dragout. In general, using a barrel with the largest holes possible minimizes dragout. Operators should make sure that barrel holes are not plugged. If they become plugged, they should be cleaned or redrilled and deburred to ensure maximum drainage. The most important technique for reducing dragout in barrel plating is proper hole size and rotation of the barrel in the upright position (Gallerani 1996).

Angled withdrawal from the plating solution also can result in reduced dragout. However, no producer/vendor of angled barrel technology has been found for large, horizontal double-hung barrels. Nevertheless, one of the following modifications of existing barrels might prove useful in minimizing dragout:

- ◆ Lengthen or shorten one arm so as to create an off-horizontal position that allows for quicker runoff
- ◆ Attach a drip bar at the bottom of the barrel edges to facilitate droplet collection and runoff
- ◆ Design a slope at the top of barrel carriers

Prior to implementing an angled or sloped barrel technique, platers should check the design of all tanks to ensure proper clearance for the modified system (IAMS 1995).

## Alternative Rinsing Methods

This section presents alternatives to traditional rinsing techniques. Two strategies for reducing water use are improving the efficiency of the rinsing operation and controlling the flow of water to the rinsing operations. Contact time and agitation influence the effectiveness of the rinsing operations.

### Improving Rinsing Efficiency

Platers can use several methods to improve rinsing efficiency. These methods include finding the optimal amount of contact time and the correct level of agitation.

#### Contact Time

Contact time refers to the length of time workpieces are in the tank. For a given workpiece and tank size, the efficacy of rinsing varies with contact time. Production rate, however, varies inversely with contact time. Through experimentation, the operator should find the contact time that satisfies production requirements while providing the highest rinsing efficiency (IAMS 1995).

#### Increased Contact Time

##### Advantages

- ◆ Improves rinsing efficiency
- ◆ Reduces contamination
- ◆ If combined with agitation, can shorten contact time

##### Disadvantages

- ◆ Rinse efficiency varies with contact time
- ◆ Experimentation is needed to find the optimal rinse efficiency
- ◆ Can reduce production rate (this factor varies and the production process should be analyzed to see the effect of this technique on production) (APPU 1995)



### Contact Time Case Study

PRC Environmental documented that by increasing rinsewater contact time and agitating workpieces manually, the rate of rinsewater flow can be reduced significantly without affecting rinse efficiency. The only capital costs incurred for this project were for training personnel, however, no financial costs or savings were provided in the case study. (APPU 1995)

### Agitation

Rinses that are agitated reduce the required amount of contact time and improve the efficiency of the rinsing process. Rinsewater can be agitated by pumping either air or water into the rinse tank. Air bubbles create the best turbulence for removing chemical process solution from the workpiece surface. However, misting as the air bubbles break the surface can cause air emissions problems (Cushnie 1994).

A finishing shop can use many methods to agitate rinse tanks. In manual plating, the operator lifts and lowers the workpiece in the rinse tank, creating turbulence. In other tanks, the most effective form of agitation involves a propeller-type agitator, but this method requires extra room to prevent parts from touching the agitator blades. Good agitation also can be obtained with the use of a low-pressure blower. The following is a list of other effective agitation methods:

- ◆ Filtered air pumped into the bottom of the tank through a pipe distributor (air sparger)
- ◆ Ultrasonic agitation for complex parts
- ◆ Mechanical agitation
- ◆ Recirculation of a sidestream from the rinse tank
- ◆ An in-tank pump (a process known as forced water agitation) (EPA 1992)

Air spargers, water pumps, or agitators can be installed in existing rinse tanks. Installation of an air sparger with a blower costs approximately \$200 to \$325 for a 50 gallon tank. Air blowers

can reduce costs because they eliminate the need for air cleaners and filters to remove oils in compressed air systems. An in-tank pump for forced water agitation can be purchased for \$200 to \$1,000 depending on the flow rate

### Increased Agitation

#### Advantages

- ◆ Improves rinsing efficiency by removing process chemicals using turbulence (they remain in the tank instead of being dragged out)
- ◆ Reduces water fees, sewer fees, treatment chemical costs, and sludge generation

#### Disadvantages

- ◆ Manual system requires operators cooperation
- ◆ Compressed air needs to be contaminant-free otherwise contaminants could enter the water supply and affect work quality (oil-free, low-pressure blowers reduce the likelihood of contamination)
- ◆ Might need an additional tank for water reuse (APPU 1995)

desired. Selection of the optimum method of agitation entails balancing capital and operating costs against revenues from increased production rates and decreased water use (IAMS 1995).

### Controlling Water Flow to Rinses

The following sections present rinsing methods that use less water and increase the efficiency of the rinsing operations.

#### Countercurrent Rinsing

Countercurrent rinsing uses sequential rinse tanks in which the water flows in the opposite direction of the work flow (dirtiest to cleanest). Fresh water is added only to the final rinse station and is conveyed, normally by gravity overflow, to the previous rinse tank. Wastewater exits the system from the first rinse tank. Figure 10 illustrates a three-stage countercurrent rinse system. In some cases, the water contained in the first rinse can be used as makeup water for the process bath (see discussion of water quality in Chapter 4). Many shops have used this technique successfully to minimize water consumption. The amount of water conserved will

depend on the number of tanks installed for countercurrent rinsing. In some cases, countercurrent rinsing can achieve 95 percent reductions

#### Countercurrent Rinsing Case Study

EPA documented a company that installed a countercurrent rinse system with conductivity controls. The system reduced rinsewater from 43,000 to 8,000 gallons per day. Operation and maintenance costs were \$10 per 1,000 gallons, and disposal and feedstock savings were \$170,000. (APPU 1995)

in rinse flow if the facility uses three rinse tanks; 90 percent is possible with two tanks (Hunt 1988).

Limitations governing the use of countercurrent rinsing include:

- ◆ Shop floor space and/or line space
- ◆ Increased cycle time
- ◆ General resistance to change

Limited shop floor space can present a significant problem for the electroplater. However, careful review of the shop often can reveal opportunities for added rinse stations. The following list presents some of the ways a shop can make room for countercurrent rinsing:

- ◆ Reduce the number of plating stations by one or two in order to increase space for rinse tanks.
- ◆ Eliminate obsolete processes (e.g., bright dipping before chromating or nickel activation before chrome plating).
- ◆ Evaluate rinse station sizing. Single station rinses often are sized arbitrarily to match plating tanks. In many cases, platers can install baffles in oversized rinse tanks to create multiple rinse stations.
- ◆ Review shop floor layout and seek opportunities to combine processes.
- ◆ Extend the line and add rinse stations (Gallerani 1990).

#### Static Rinsing (Recovery Rinsing)

If direct countercurrent rinsewater overflow to the process tank is not possible, the first rinse tank after a process bath can be a static rinse that builds up a concentration of dragin. Static rinse tanks used with low-temperature processes can be used as pre-dip or post-dip rinses to recover dragout (as much as 80 percent). Periodically, the accumulation in this bath should be concentrated enough for reuse/recycling into the process bath (EPA 1992).

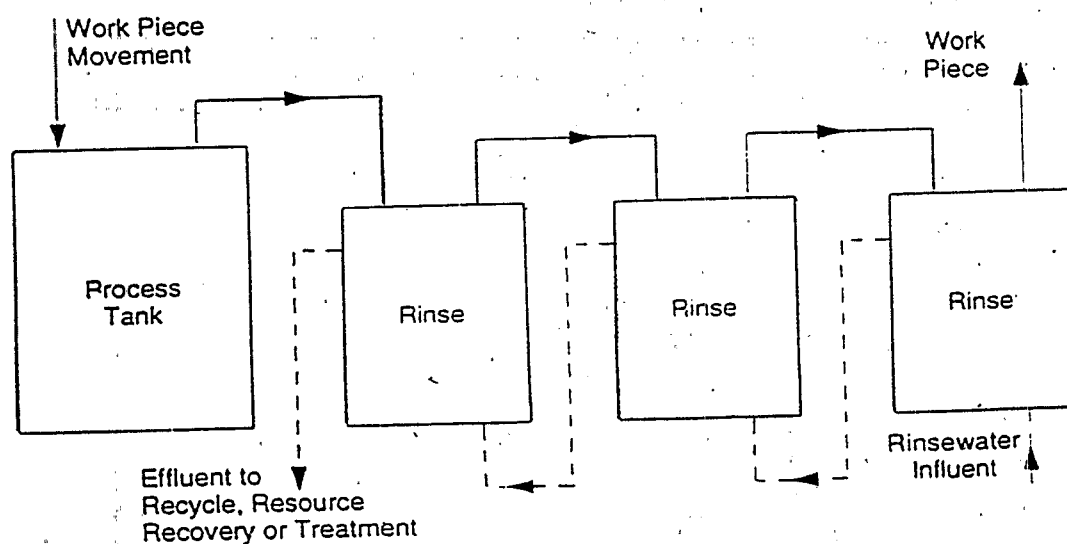


Figure 10. Three-Stage Countercurrent Rinsing (IAMS 1995)

## Multistage Static Rinsing

Multistage static rinsing uses multiple dead tanks rather than a system where the water flows from one rinse tank to the other. This process often is used in cadmium plating to keep the metal from entering the waste treatment system. Solution from the first rinse tank can be used to replenish the process bath. However, the solution might need treatment prior to reuse such as filtration to remove contaminants.

### Multistage Static Rinsing

#### Advantages

- ◆ Increases contact time between the workpiece and rinsewater; improves rinse efficiency
- ◆ Reduces water use

#### Disadvantages

- ◆ Needs more process steps
- ◆ Needs additional tanks
- ◆ Needs more work space
- ◆ Should use deionized water to reuse rinsewater

## Warm Rinsing

Warm rinsing is effective particularly in the case of alkaline solutions such as cleaners and cyanide plating baths. Alkaline solutions tend to freeze onto parts when immersed in cold water, making effective cleaning difficult. Warm rinses reduce freezing rate and increase rinsing effectiveness (Ford 1994).

## Reactive Rinsing

Reactive rinsing uses less water and saves chemicals. Most cleaning lines use an alkaline cleaner followed by an acidic pickle. Taking

advantage of the chemical nature of the pickle liquors and alkaline cleaner, reactive rinsing feeds the water from the acid pickle to the alkaline rinse. This step neutralizes the cleaner, and also prevents alkaline material from being dragged into the acid, prolonging the life of the pickle solution. Reactive rinsing cuts water use in half, and, in some cases, enables the plater to plumb more than two rinses in a series. However, acidic water should never be fed into a rinse that contains cyanide solution (Hunt 1988).

In the example in Figure 11, nickel rinsewater is recycled back to the acid dip-rinse tank, allowing nickel plating solution dragged out of the process bath to be dragged back into the bath. Such a modification will not harm the rinse step and will allow the fresh water feed to the acid rinse to be turned off. The acid rinsewater then can be recycled to the alkaline cleaner rinse tank. Advantages include allowing the feed water to be shut off, improving the rinsing efficiency by neutralizing the dragged-in alkaline solution, and prolonging the life of the acid rinse bath as the rinsewater dragin already will be partially neutralized. This concept can be taken one step further and the rinsewater can be recycled among process lines (Hunt 1988).

The reuse of rinsewater cannot be indiscriminate. Facilities must avoid contaminating the process baths and reducing the plating quality (e.g., pitting). However, following careful evaluation, reactive rinsing can produce significant water and chemical savings (Gallerani 1990).

## Spray or Fog Rinsing

Installation of fixed or movable rinse spray nozzles over the process tank can replace separate rinse tanks. Overspray is returned to the

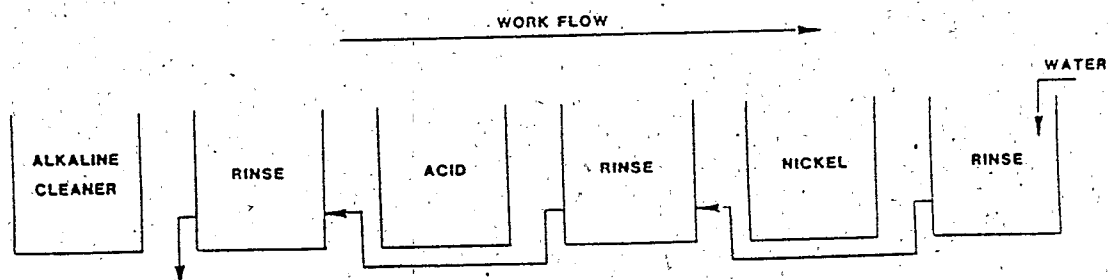


Figure 11. Example of Reactive Rinsing (Hunt 1988)

process tank, resulting in reduced dragout. This spray or fog rinsing can be used for either rack or barrel plating (IAMS 1995).

Spray rinsing uses between 10 to 25 percent less water than dip rinsing. However, this method is not always applicable to metal finishing because the spray rinse might not reach all of the parts of the workpiece. The effectiveness of spray rinsing depends upon part geometry and complexity. Spray rinsing compares favorably with single-dip rinses, but is not as effective as countercurrent rinsing. To address this problem, spray rinsing can be combined with immersion rinsing. In this technique, the workpiece is spray rinsed over the process tank as soon as the part is removed from the process solution. The part then is submerged in an immersion tank. As a result, the spray rinse removes much of the dragout, returning it to the process bath before the workpiece is placed in the dip rinse tank. This allows facilities to use lower water flow rates and reduce dragout (EPA 1992).

Platers also can use spray or fog rinse systems above heated baths to recover dragout solutions. Spray rinsing washes process solutions through impact and diffusion forces and can reduce water use by 75 percent. If an operator can adjust the spray rinse flow rate to equal the evaporation loss rate, the spray rinse solution can be used to replenish the process bath. Purified water should be used for the spray systems to reduce the possibility of contamination entering the bath. Fog rinsing uses water and air pressure to reduce concentration of dragout films. This method is most useful in finishing simple pieces (Cushnie 1994).

### Spray/Fog Rinsing

#### Advantages

- ◆ Reduces dragout by as much as 75 percent
- ◆ Reduces waste management costs (i.e., lower sewer bills and less sludge generation)
- ◆ Greater quality control (i.e., less chemical use and cleaner rinses)

#### Disadvantages

- ◆ Might not be effective in rinsing certain workpieces and might not work in all plating operations (APPU 1995)

### Spray/Fog Rinsing Case Study

EPA documented a 50 percent reduction in hazardous waste generation with spray rinsing, and a savings in disposal and feedstock costs of \$5,280. Capital costs were \$11,685 with no operation or maintenance costs and a payback period of 26 months. Prior to implementation, 650,000 gallons of waste were generated daily with 5 percent from cyanide-based plating operations. (APPU 1995)

## Rinsewater Flow Controls

An important concept in rinsewater conservation is to use only as much water as you need. Many electroplaters use far more water than they need. Reducing water flow also can make certain recovery technologies (such as reverse osmosis) economically feasible because of the linear relationship between cost and flow rate. In fact, most of these technologies will only be cost effective if water flow rates are reduced to the lowest possible levels.

Typically, a rinse tank uses a wide-open, unrestricted water feed. Installing flow restrictors or conductivity cells can result in a significant reduction in water use. The operator should first determine the current flow rate and then the optimum flow rate at which the facility should be functioning.

### Determining the Appropriate Flow Rates

Platers should size rinsewater flow requirements according to contaminant loading (process dragout) and required final rinsewater purity or concentration. In a multiple rinse setup, the flow requirements should be exponentially lower than those in static tanks. Operators can determine the required rinsewater flow for a single station rinse using the following equation:

$$D \times C_p = F \times C_r$$

D = Dragin rinse or process dragout

C<sub>p</sub> = Concentration of dragin

F = Rinsewater flow

C<sub>r</sub> = Concentration of the rinse  
(Gallerani 1990)

Once platers have determined the appropriate flow rate, they can use several methods to control flow rates in their facilities including flow restrictors, conductivity cells, and pH meters.

## Methods to Restrict Water Flow

A number of simple methods are available to restrict water flow and conserve water including flow restrictors and conductivity controllers.

### Flow Restrictors

Flow restrictors limit the volume of rinsewater flowing through a rinse system by limiting the volume of water that can enter the rinse system. This method will maintain a constant flow of fresh water to the rinse process. Since most small- and medium-sized metal finishers operate batch process operations, pressure-activated flow

#### Flow Restrictors

##### Advantages

- ◆ Reduces water use
- ◆ Maintains flow rates at predetermined levels

##### Disadvantages

- ◆ Unable to adjust flow restrictors
- ◆ Increases operator responsibility
- ◆ Need to coordinate among operators to survey the rinse tanks and shut off the flow to tanks not in use
- ◆ Might not be suitable for shops where flow rates are variable. (APPU 1995)

#### Flow Restrictor Case Study

Alpha Metal Finishing in Dexter, Michigan, is a large job shop that specializes in chromate conversion. The president of the company, Robert Wood, designed a company plan to minimize water use. The company's greatest waste reduction success is the decrease in the volume of wastewater discharged to a POTW. By reconfiguring rinse tanks and decreasing water flow rates, Alpha Metal reduced its wastewater discharge by 50 percent. Following an intern's recommendation, the facility installed flow restrictors on the rinse tanks. The installation resulted in direct savings of more than \$18,000. Wastewater discharge decreased from a daily average of 40,000 to 11,000 gallons. (OWRS 1992)

control devices as foot-pedal-activated valves or timers can be helpful to ensure that water is not left on after completion of the rinse operation (EPA 1992).

### Conductivity Cells/pH Meters

Platers can use conductivity controllers in place of flow restrictors on a rinse system where drag-in is highly variable or where monitoring the bath for extreme conditions (over or under concentration) is desirable. Figure 12 shows a typical application of conductivity cells. These devices control water flow through a rinse system by means of a conductivity sensor that measures the level of ions in the rinsewater. When the ion level reaches a preset minimum, the sensor activates a valve that shuts off the flow of fresh water into the rinse system. When the concentration builds to a preset maximum level, the sensor opens a valve to resume the flow of fresh water. These meters can alert production line staff to imbalances in rinsewater concentration so that they can be replenished on an as-needed rather than a continuous basis. These systems are relatively expensive and require a good deal of maintenance (Gallerani 1990). If these systems are not maintained consistently, water use actually can increase. If the solenoid valve becomes clogged, it will remain open, allowing water to flow freely. A conductivity meter equipped with the necessary solenoid valve can cost approximately \$700 to \$4,000 per system.

#### Conductivity Cells/pH Meters

##### Advantages

- ◆ Reduces the amount of overflow water
- ◆ Extends bath life

##### Disadvantages

- ◆ Expensive maintenance costs for sensing probes because of the need for regular cleaning and maintenance

## Rinsewater Recycling and Recovery Techniques

Water conservation and metal recovery techniques have become an integral component of pollution prevention programs for platers. Many techniques to recover water, metals, or acids that have contaminated rinsewater are available. In

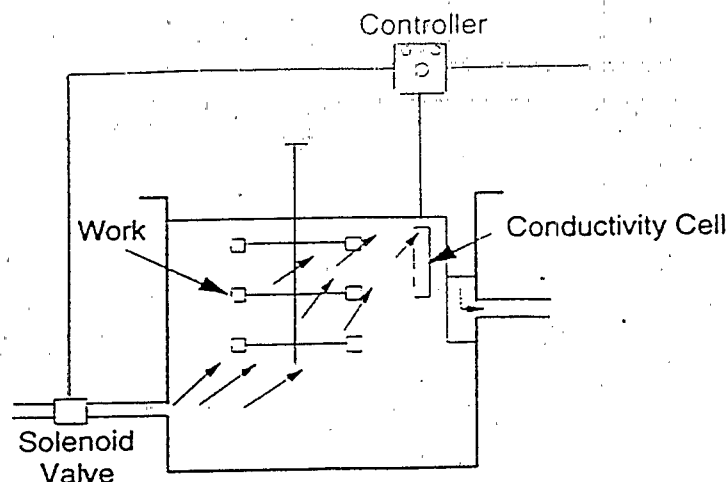


Figure 12. Application of Conductivity Cells (IAMS 1995)

some cases, the technologies merely recover materials so that they can be sent off site for easier disposal. In other cases, the technology can return the material back to the process line for reuse.

### Rinsewater Recycling

Rinsewater can be recycled in either a closed- or open-loop system. In a closed-loop system, the treated effluent is returned to the rinse system. Recycling rinsewater can reduce water use and the volume of water discharged to the wastewater treatment system significantly. Closed-loop systems discharge a small amount of waste. An open-loop system allows the treated effluent to be reused in the rinse system, but the final rinse is fed by fresh water to ensure high-quality rinsing. Therefore, some treated effluent will continue to be discharged to the sanitary sewer (EPA 1995). These two systems are shown in Figure 13.

To improve the economic feasibility of closed- or open-loop systems, platers should first implement rinsewater efficiency techniques. In the past, material recovery from metal finishing was not considered economical. However, effluent pretreatment regulations and treatment and disposal costs are now a significant financial factor. As a result, metal finishers now might find reusing rinsewater as well as recovering metals and metal salts from spent process baths and rinsewater are cost effective.

After rinse solutions have become too contaminated for their original purpose, they can be used in other rinse processes. For example, effluent from a rinse system following an acid cleaning bath sometimes can be reused as influent to a rinse system following an alkaline cleaning bath (reactive rinsing). If both rinse systems require the same flow rate, 50 percent less rinsewater could be used to operate the system.

### Chemical Recovery

Facilities can manage the captured dragout solution from rinsewater recovery in three ways: (1) recycling solution back into the process, (2) on-site recovery, and (3) shipment off site for disposal or recovery. The choice will depend upon the type of process bath, composition of the dragout, and the cost of the technique.

Platers must understand the chemical properties of a wastestream to assess the potential for reusing the waste as a raw material. Although the properties of process bath or rinsewater solutions might make them unacceptable for their original use, the waste material might still be valuable for other applications. A common reuse option in multiple-use rinses is using rinsewater from one process as rinsewater in another. For example, rinsewater from a cleaning rinse can be reused in a plating rinse line. The primary cost associated with rinsewater reuse is replumbing. Depending on the design of the rinse system, firms also might need to purchase storage tanks and pumps.

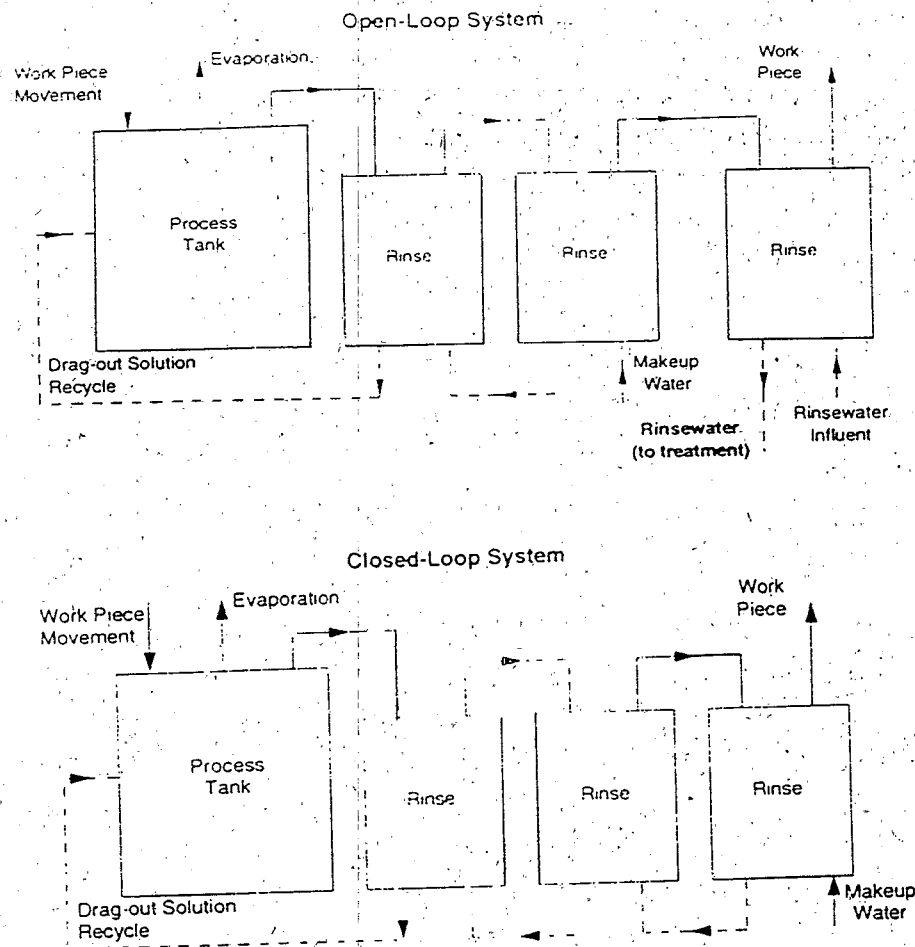


Figure 13. Configuration of Rinsewater Recycling in Open- and Closed-Loop Systems (IAMS 1995)

Typically, operators dump spent acid or alkaline solutions when contaminants exceed an acceptable level. However, these solutions might remain sufficiently acidic or alkaline to act as pH adjusters. For example, alkaline solutions can be used to adjust the pH in a precipitation tank while acid solutions can be used in chromium reduction treatment. The operator must ensure that the spent solutions are compatible. For example, because spent cleaners often contain high concentrations of metals, they should not be used for final pH adjustments. Facilities should check with chemical suppliers to determine whether they have reclamation services for plating baths. Be aware that some states classify reclamation as treatment under the RCRA program, requiring compliance with additional regulatory requirements (in some cases, an abbreviated treatment license).

## Metal Recovery

Every year, the plating industry pours millions of dollars down the drain in valuable metals. Closed-loop systems reduce rinsewater volumes and facilitate the recovery of metal salts for reuse in plating baths, using separation processes such as evaporation, ion exchange, reverse osmosis, electrolysis, and electrodialysis. An industry consultant recently estimated that it would be economically feasible to recover 80 to 90 percent of copper, 30 to 40 percent of zinc, 90 to 95 percent of nickel, and 70 to 75 percent of chromium presently disposed of as sludge (Gallerani 1990). Recovered metals can be reused in several ways:

- ◆ Returned to bath as makeup
- ◆ Sold or returned to suppliers

- ◆ Sold to a reclaimer
- ◆ Used on site as plating metal anode materials

The savings achieved through metal recovery are site-specific. Factors that determine whether metal recovery is economically justified include:

- ◆ The volume of waste that contains metals
- ◆ The concentration of the metals
- ◆ The potential to reuse some of the metal salts
- ◆ Treatment and disposal costs

Table 19 highlights different technologies that can be used for chemical recovery, metal recovery, and chemical solution maintenance.

Table 20 provides an overview of technologies for recovering metals, plating solutions, and water.

## Recovery Technologies

A number of rinsewater recovery technologies are available to platers. Many platers already use these systems. The recovery systems include various types of electrolytic recovery and evaporators.

## Electrolytic Metal Recovery

Electrolytic metals recovery (EMR) is used to recover the metallic content of rinsewater. EMR, one of the most common methods of recovering metal from finishing operations, is capable of recovering 90 to 95 percent of the available metals in gold, silver, tin, copper, zinc, solder alloy, and cadmium plating operations (Bennati and McLay 1983). The basic unit of this technology is an electrolytic cell with two electrodes (an anode and a cathode) placed in the solution. Ions in the solution move toward the charged electrode. The dissolved metal ions are reduced and deposited on the cathode. The material that is deposited onto the cathode is removed either by mechanical or chemical means and then is sent off site for refining, recycling, or disposal (Cushnie 1995). Table 20 provides a summary of the metals and their potential for successfully applying electrowinning. The table also includes an indication of the use of EMR for certain groups of metals.

As shown in Table 21, some metals are not particularly suited to EMR. The only common metal salt that cannot use electrowinning is chromium. This technology can recover nickel, but it requires close monitoring of the pH. Platers also can use electrowinning in electroless

Table 19. Overview of Applications for Recycling and Recovery Equipment (Hunt 1988)

Recycling/Recovery Method	Chemical Recovery	Chemical Solution Maintenance	Metal Recovery
Acid Sorption		X	
Diffusion Dialysis		X	
Evaporators	X		X
Electrolytic Metal Recovery	X		X
Electrodialysis	X		X
Ion Exchange	X	X	X
Ion Transfer		X	
Microfiltration		X	
Membrane Electrolysis		X	



Table 20. Overview of Recovery/Recycling Technologies (Hunt 1988)

Method	Advantages	Disadvantages	Successful Applications
<b>Electrolytic Metal Recovery</b>	<ul style="list-style-type: none"> <li>◆ Recovers only metals</li> <li>◆ Results in salable, non-hazardous products</li> <li>◆ Energy efficient</li> <li>◆ Low maintenance</li> </ul>	<ul style="list-style-type: none"> <li>◆ Solution concentration must be monitored</li> <li>◆ Fumes can form and can require hood scrubbing system</li> <li>◆ Solution heating encouraged to maximize efficiency</li> </ul>	Cadmium cyanide, copper cyanide, copper pre-etch, copper final etch, acid copper, electroless copper, gold, electroless nickel, watts nickel, silver, tin, and zinc
<b>Reverse Osmosis</b>	<ul style="list-style-type: none"> <li>◆ Achieves modest concentration</li> <li>◆ Small floor space requirement</li> <li>◆ Less energy intensive than evaporation</li> </ul>	<ul style="list-style-type: none"> <li>◆ Limited concentration range of operation</li> <li>◆ Fouled membranes because of feeds high in suspended solids</li> <li>◆ Feed filtration essential</li> <li>◆ Membrane sensitive to pH</li> <li>◆ Some materials fractionally rejected</li> <li>◆ Might require further concentration</li> </ul>	Copper, nickel, and zinc
<b>Ion Exchange</b>	<ul style="list-style-type: none"> <li>◆ Low-energy demands</li> <li>◆ Handles dilute feed</li> <li>◆ Returns metal as metal salt solution</li> </ul>	<ul style="list-style-type: none"> <li>◆ Requires tight operation and maintenance</li> <li>◆ Equipment complex</li> <li>◆ Limited concentration ability</li> <li>◆ Might require evaporation to increase concentration</li> <li>◆ Excess regenerate required</li> <li>◆ Feed concentration must be monitored closely</li> </ul>	Chromium, chromium etch, copper pre-etch, copper final etch, acid copper, gold cyanide, nickel, electroless nickel, silver, tin, and zinc
<b>Electro-dialysis</b>	<ul style="list-style-type: none"> <li>◆ Achieves higher concentration than reverse osmosis or ion exchange</li> <li>◆ Energy efficient</li> <li>◆ Organics not concentrated</li> <li>◆ Inorganic salts transport at different rates</li> <li>◆ Minimizes return of unwanted inorganics</li> </ul>	<ul style="list-style-type: none"> <li>◆ Feed must be filtered</li> <li>◆ Membrane sensitive to flow distribution, pH, and suspended solids</li> <li>◆ Equipment uses multi-cell stacks</li> <li>◆ Incurs leakage</li> <li>◆ Chemical adjustment of recovered material</li> <li>◆ Membrane life uncertain</li> <li>◆ Solution concentration must be monitored</li> </ul>	Cadmium cyanide, copper cyanide, gold, iron, nickel, silver, tin, zinc cyanide, and zinc chloride
<b>Evaporators</b>	<ul style="list-style-type: none"> <li>◆ Established and proven technology</li> <li>◆ Simple to operate</li> <li>◆ Widely applicable</li> <li>◆ Can exceed bath concentration</li> </ul>	<ul style="list-style-type: none"> <li>◆ Some units are energy intensive</li> <li>◆ Multistage countercurrent rinsing essential</li> <li>◆ Returns impurities to bath</li> <li>◆ Additional treatment might be needed to control impurities</li> <li>◆ Might require pH control</li> </ul>	Cadmium cyanide, chromium, chromium etch, acid copper, copper cyanide, gold, iron, lead, nickel, silver, tin, and zinc

Table 21. Potential of Metal Using Electrolytic Recovery (Cushnie 1994)

Potential of Electrolytic Recovery	Metals	Widespread Use
<b>High Potential for Success</b>	Brass cyanide, cadmium cyanide, copper acid, copper cyanide, gold cyanide, silver cyanide, and zinc cyanide	Yes
<b>High Potential for Success</b>	Antimony, cadmium ammonium sulfate, iridium, lead acid, palladium, ruthenium, rhodium, selenium, tin acid, and tin alkaline	No
<b>Moderate Potential for Success</b>	Cobalt, electroless copper, copper strong acid, copper ammoniacal etch, gold strip, indium, lead fluoroborate, nickel watts and woods, nickel sulfamate, electroless nickel, silver thiosulfate, tin/lead fluoroborate, zinc acid	No
<b>Low Potential for Success</b>	Aluminum, barium, beryllium, boron, calcium, cadmium strip, chromium, iron, magnesium, manganese, mercury, molybdenum, silicon, tantalum, titanium, tungsten, vanadium	No

plating operations. However, this application is not as straightforward because of the presence of chelated metals, reducing agents, and stabilizers (Cushnie 1994). The most common applications of EMR include acid copper plating, cyanide cadmium plating, cyanide zinc plating, and cyanide copper plating (Freeman 1994).

Electrolytic recovery is most effective when metal concentrations are high. Platers can take the residual metals and sell them or recycle them in the plating process. Because plating becomes inefficient at low metal-ion concentrations, it alone is not suitable for producing wastewater that complies with discharge regulations. EMR can be an effective reclaim/recycle method with lower capital costs in conjunction with another technique such as ion exchange (EPA 1995).

Metal finishers also can use EMR for spent plating bath solutions, recovered spills, discharge from static rinse tanks, and regeneration solutions from ion exchangers. Firms generally use EMR for reducing the amount of inexpensive regulated metals and cyanide that they discharge to treatment systems or for recovering expensive

metals, both common and precious. In either case, companies use EMR for gross metal recovery from concentrated solutions such as dragout rinses or ion-exchange regenerant (Cushnie 1994). Figure 14 illustrates the EMR process.

#### Electrolytic Case Study

Pioneer Industries of Stratford, Connecticut, is a job shop that uses both rack and barrel plating operations. The company, which employs 10 people, works with nickel and gold electroplating and electroless nickel plating.

In 1989, Pioneer Industries conducted a pilot-scale test of the lonnet electrolytic recovery unit to plate out nickel from wastewater. They processed nickel-bearing wastewater through the unit until the nickel concentration was less than 20 parts per million. The pilot test was successful and Pioneer expected that full-scale implementation of this project would save the firm \$17,000 per year in waste treatment costs. The payback period on the \$11,900 investment was 8.4 months.

(ConnTAP 1992)

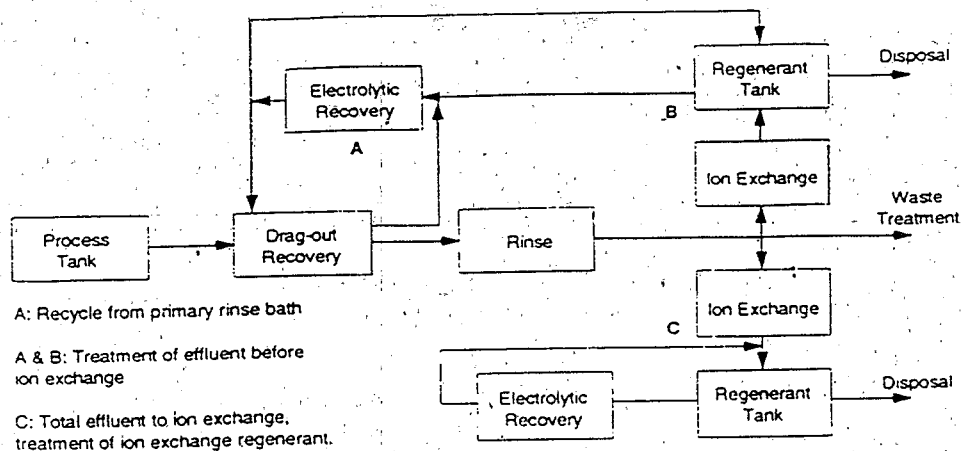


Figure 14. Electrowinning (IAMS 1995)

Several basic design features, which are well known to the electroplating industry, are used in electrolytic recovery:

- ◆ Expanded cathode surface area
- ◆ Close spacing between cathode and anode
- ◆ Recirculation of the rinse solution (Cushnie 1994)

Two electrolytic recovery methods are conventional metal cathode (electrowinning or dummy plating) and high surface-area cathode (HSAC). Conventional electrowinning involves the placement of a cathode and an anode in the rinse solution. As the current passes between the cathode and the anode, metallic ions deposit onto the cathode, generating a solid metallic slab that can be reclaimed or used as an anode in an electroplating tank. Electroplaters can make their electrowinning units by closely spacing parallel rows of anodes and cathodes in a plating tank and circulating rinse solutions through the tank (Cushnie 1994).

In HSAC, the operator pumps the metal-containing solution through a carbon fiber cathode or conductive foam polymer, which is used as the plating surface. To recover the metals, the carbon fiber cathode assembly is removed and placed in an electrorefiner, which reverses the current and allows the metal to plate onto a

stainless steel starter sheet. These systems recover a wide variety of metals and regenerate many types of solutions. Platers use HSAC recovery mainly with dilute solutions such as rinsewater effluent.

The types of cathodes used in electrowinning can be classified into three categories in order of increasing surface area: (1) flat plate; (2) expanded metal, wire mesh, or reticulate plate;

### Electrowinning

#### Advantages

- ◆ Recovers metals that can be recycled or reused in process, sometimes up to 90 to 95 percent
- ◆ Uses no chemicals
- ◆ Recovers only metals
- ◆ Maintenance is low
- ◆ Misapplication is rare because of similarity with plating process

#### Disadvantages

- ◆ Energy inefficient at very low metal-ion concentrations
- ◆ Segregation of the rinsewater is needed to prevent contamination of the anode with mixed metals
- ◆ Incomplete recovery (will not recover total metal content)
- ◆ Might have high energy consumption
- ◆ Might cause spontaneous combustion of plated metal

(Ohio EPA 1994 and Freeman 1995)

and (3) porous or woven carbon and graphite plate. Platers use flat plates for applications of gross metal recovery from concentrated solutions including expanded metal, wire mesh or reticulate plates, and porous or woven types for recovering metals with lower concentrations. Facilities also use cathodes to recover metals from spent process baths prior to wastewater treatment (Cushnie 1994).

### Restrictions on Applications

Strong oxidizing substances, such as nitric acid or fluoroboric acid, generally are not feasible options for electrowinning primarily because of the short life of the anodes in such environments. Hydrochloric acid or other compounds containing the chloride ion also might not be suitable because of the generation of chlorine gas at the anodes. However, ventilation can control gas formation (EPA 1995).

### Costs

In general, capital cost for electrolytic recovery equipment is low. A unit equipped with a 100-ampere rectifier can cost between \$8,000 and \$15,000 depending on the type of anodes and cathodes. Such a unit can remove up to 500 grams of metal per day from a dragout tank (EPA 1995).

Electricity, electrode replacement, and maintenance costs are the most significant operating costs. Electricity costs per unit mass of metal recovered vary with the concentration of metal in the electrolyte. A low concentration of metal ions leads to lower efficiency and higher energy costs. Anodes require replacement every 1 to 5 years depending on the nature of the electrolytes being electrowinned. The cost of anodes varies widely, from \$600 to more than \$3,000 per square meter for platinum-coated titanium types, although some anodes rarely require replacement. For example, flat plate steel cathodes can be reused after being scraped free of metal deposits. Wire mesh and reticulate cathodes usually are rated to hold more than 1 kilogram of metal and generally cost less than \$100 per square meter. The labor costs for operating and maintaining an electrowinning unit are generally low. Besides daily checks for electrical settings

and overall operation, many installations require little scheduled maintenance (EPA 1995).

## Evaporators

Evaporation is widely used by platers to recover a variety of plating bath chemicals. This technology separates water from dissolved solids such as heavy metals. Evaporators create additional room in a process bath so that dragout can be returned to the process tank. They also can concentrate rinsewater so that less volume goes back to the process tank. Evaporators often return recovered dragout to the process tank in higher concentrations than that of the original process solution. This technology is used most often in decorative chromium, nickel, and copper cyanide plating, although it is not limited to these applications (Freeman 1995).

Evaporators are most economical when the amount of water is small and the product concentration is high or when natural atmospheric evaporation can be used. For instance, evaporation is efficient with multistage countercurrent rinsing because the quantity of rinsewater to be processed is small. However, this energy-intensive technology is expensive when used for large volumes of water. Another problem with this technology is that when the water volume is

### Evaporation

#### Advantages

- ◆ Reuses recovered chemicals
- ◆ Uses no chemicals
- ◆ Reduces liquid waste for treatment and disposal
- ◆ Requires no maintenance
- ◆ Widely applicable
- ◆ Low in cost
- ◆ Can reuse rinsewater

#### Disadvantages

- ◆ Energy intensive
- ◆ Needs multi-stage countercurrent rinse system to be economical
- ◆ High in cost
- ◆ Plating chemicals can be corrosive to evaporator
- ◆ Atmospheric evaporators can degrade plating bath chemistry because of high temperatures.

(Ohio EPA 1994)

high, sludge generation rates increase as the flow volume increases. Effective rinsing and reduced dragout, however, increases the effectiveness of evaporation (see Section 1 in Chapter 6 for more information). In cases where large volumes of water have low metal concentrations, ion exchange, reverse osmosis, or electrodialysis are more cost effective than evaporation. In some cases where water volume is high, even precipitation, settling, and resolubilization can be more efficient procedures (Veit 1989).

Evaporators should not be confused with drying devices, which produce a solid or semi-solid product. While both dryers and evaporators use volatilization, evaporators are designed to concentrate a solution to no greater than one-half to three-quarters solubility (Veit 1989).

#### Evaporation Case Study

EPA documented a case in which evaporators reduced waste generation by 50 percent from 56,000 to 28,000 pounds per year, and all plating chemicals were recovered. Prior to implementation, rinsewater was treated with neutralization, flocculation, clarification, settling, filtration, and compaction. The capital costs for two evaporators were \$12,500 and the operation/maintenance costs were \$24,741. The payback period was 7 months. Disposal and feedstock savings were \$24,000 for the first year and \$36,000 for the second. (APPU 1995)

Two types of evaporation systems are atmospheric and vacuum.

#### Atmospheric Evaporators

Atmospheric evaporators operate by spraying the dilute wastestreams over packing media, grids, or plates, and then blowing air from the facility to vaporize water. These units consist of a heater which preheats the rinsewater (most commonly, the process tank's heating system), a pump which transfers the fluid to the evaporation chamber, and the chamber which consists of fins or a packing surface to increase the surface area of the air-fluid interface. The source of air in these systems is important because the bath can absorb airborne impurities. Evaporation rates depend on the size of the chamber, the solution

temperature, and the humidity of the air blown across the chamber. The most common units are designed for less than 150 gallons per hour. However, units are available in a large range of sizes (Cushnie 1994).

#### Applications and Restrictions

Metal finishers generally use atmospheric evaporators on a variety of plating processes including nickel, chrome, and acid zinc plating. Figure 15 illustrates the application of atmospheric evaporators to high- and moderate-temperature rinse systems. Atmospheric evaporators commonly are applied to a heated process bath to increase the evaporation rate and to make room in process tanks for water return in a countercurrent rinse system. The system directs rinsewater from the system to an off-line tank where it circulates through the evaporator. Operators then return the concentrated fluid to the process tank. Ambient temperature baths require a similar configuration, but operators must circulate some fluid to the off-line tank and evaporator to make room in the process tank. Evaporators are most efficient when used in plating baths that are already heated between 49 and 65 degrees Celsius (Cushnie 1994).

Atmospheric evaporators are not appropriate for process fluids or additives (e.g., brighteners) that degrade with heat or solutions degraded by aeration such as cyanide or tin plating baths. A major disadvantage of atmospheric evaporators is their inability to evaporate on days when air humidity levels reach 80 to 90 percent unless a heating system is installed. Another disadvantage of atmospheric evaporation is that all dragout, including bath contaminants, is returned to the process tank, increasing the potential for contamination of the process solution. This problem can be minimized if deionized water is used. If evaporators are used with cyanide solutions, the rate of carbonate buildup will increase because of carbon dioxide adsorption from the entrained air and thermal breakdown of cyanide (Freeman 1994).

Capital costs of evaporators vary. A typical atmospheric evaporator that processes 40 to 75 liters per hour costs less than \$10,000. Installation costs can be high depending on plumbing

### Atmospheric Evaporators Case Study

Quality Rolling & Deburring Co., Inc., of Thomaston, Connecticut, installed two NAPVAP atmospheric evaporators supplied by NAPCO Inc. on its nickel plating line. Quality Rolling & Deburring employs 70 people and serves the aircraft, automotive, medical, and consumer products industries. The production department focuses on high-volume throughput using barrel nickel plating, mass finishing, alkaline finishing, vapor degreasing, and mechanical plating. The company reduced the amount of chemicals that they purchased and the flow of rinsewater to the wastewater treatment system with the evaporators.

The company purchased the two evaporators at a total cost of \$5,000. The company saved \$510 per week in raw materials costs alone and substantially more in off-site disposal costs. The company experienced a 6-month payback on this project. (ConnTAP 1990)

and duct modification requirements. Operating costs (e.g., electricity and labor) average \$0.25 to \$0.35 per gallon. Many companies prefer atmospheric evaporators to other types of evaporators because they are relatively inexpensive (EPA 1995).

### Vacuum Evaporators

Vacuum evaporators are closed systems that use one or more vacuum chambers to reduce the boiling point of water to volatilize water from the wastestream. In practice, platers pump preheated fluid into the vacuum chamber where it quickly vaporizes. These units do not require large air volumes and generally produce distilled water as a byproduct. A number of different designs are available. They differ in how the vacuum is achieved (i.e., eductor or vacuum pump) and how much energy is used (i.e., single effect or double effect). These systems take advantage of the depression of the boiling point of water as air pressure decreases. The higher

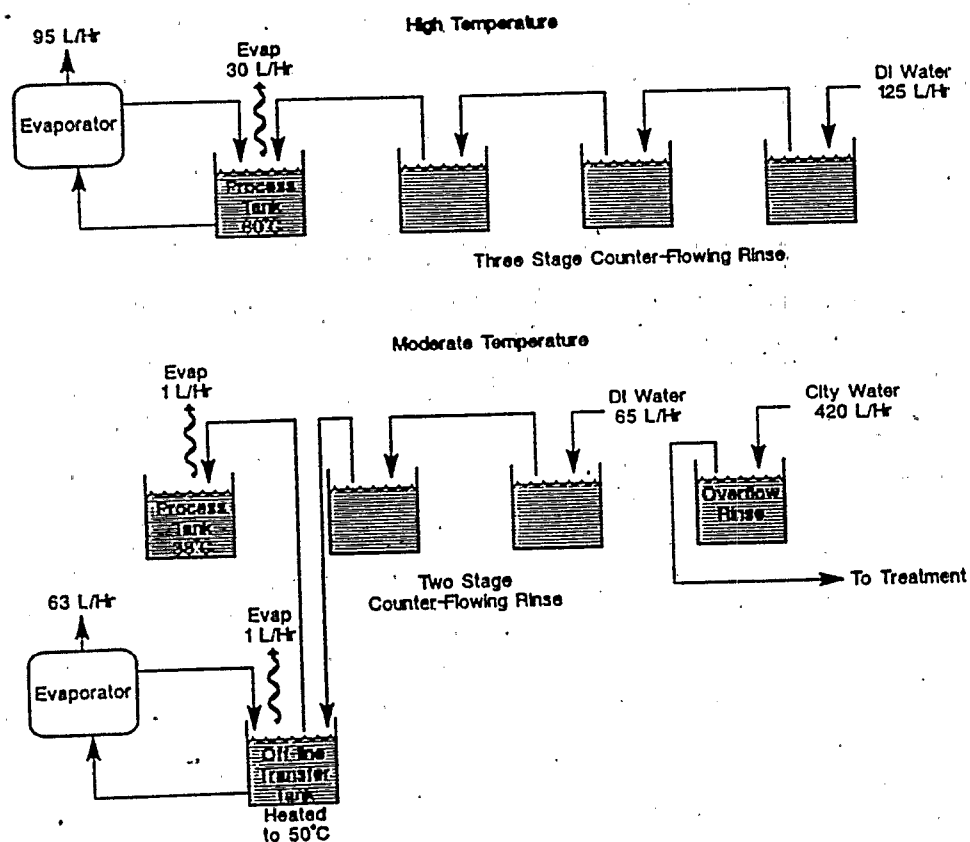


Figure 15. Two Common Configurations of Atmospheric Evaporators (EPA 1995)

### Atmospheric Evaporators Case Study

In 1989, the Ilco Unican facility in Rocky Mount, North Carolina, plated 800,000 key blanks per day with nickel. Typically, rinse tanks become contaminated with dragout from the nickel process solution, resulting in a hazardous sludge that required costly treatment.

To eliminate this problem, Ilco Unican began using an inexpensive and low-maintenance atmospheric evaporator system. Sufficient water is evaporated so that rinsewater can be reused in the plating bath. Ilco was using a carbon filtration system in the plating bath already to remove contaminants from the process bath. Since adding the evaporator equipment, Ilco Unican has reduced the use of nickel chloride by 6,400 pounds and nickel sulfate by 22,000 pounds. The in-line recycling loop also recovered 80 percent (7,040 pounds) of the boric acid used. The only waste generated is plating bath sludge from the filtration system.

The installation of two evaporator systems cost approximately \$12,200. Maintenance and energy costs are \$24,741 per year. Reduction in nickel chloride, nickel sulfate, and boric acid saved the company \$9,280, \$19,360, and \$3,328, respectively. The project also eliminated rinse tank sludge. Disposal and handling of this waste cost \$25,131 annually. Given these savings, the payback for the project was 7.3 months with subsequent annual savings of \$36,223 per year.

(NCDHSE 1995)

the vacuum, the lower the boiling point for water. By lowering the boiling point, vacuum evaporation protects some of the ingredients in the processing solution from degrading.

The four types of vacuum evaporators include:

- ◆ **Single-effect evaporators:** A single-effect unit usually uses steam or high-temperature hot water to heat the process liquid to its boiling point. The steam is passed through a coil or jacket and the vapors produced by the boiling liquid are drawn off and condensed. The concentrated liquid then is pumped from

the bottom of the vessel. This process requires 1,200 BTUs per pound of water evaporated (Freeman 1995).

- ◆ **Multiple-effect evaporators:** A multiple-effect unit consists of a series of single-effect evaporators. Vapor from the first evaporator is used as the heat source to boil liquid in the second evaporator. Boiling is accomplished by operating the second evaporator at a lower temperature than the first. The process can continue through evaporators (effects). Depending on the number of effects, multiple units can require as little as 200 BTUs per pound of water evaporated (Freeman 1995).
- ◆ **Vapor recompression units:** The vapor recompression evaporator uses steam initially to boil the liquid. The vapor produced is compressed to a higher temperature. The compressed vapor then is directed to the jacketed side of the evaporator and used as a heat source to vaporize more liquid. These units require as little as 40 BTUs per pound of water evaporated (Freeman 1995).
- ◆ **Cold vaporization units:** A variation on standard vacuum evaporation technology is the cold vaporization process, which uses a similar evaporation separation principle but evaporates water at temperatures of 50 to 70 degrees Fahrenheit. This type of evaporation uses less energy than electrically heated systems because the system gets energy from the air around the unit. This equipment uses the heat generated from the vacuum system to provide heat needed for evaporation (Cushnie 1994).

### Applications and Restrictions

Metal finishers typically use vacuum evaporators in those applications in which atmospheric evaporators are not suitable. Operating expenses favor vacuum evaporators when feed rates are 190 to 265 liters per hour. These systems offer major advantages when configured to trap condensate for reuse in rinsing operations (EPA 1995). The primary advantages are:

- ◆ They operate at comparatively low temperatures. This protects temperature-

sensitive constituents in the plating solution.

- ◆ They are relatively safe for products that are sensitive to air oxidation because the process does not expose the solution to large volumes of air. For example, stannous tin might oxidize in an atmospheric evaporator, which could cause solubility problems in the system.
- ◆ These systems do not act as air scrubbers. Because these systems do not use air movement for evaporation, they do not scrub volatile components found in the air, minimizing potential air pollution problems (Veit 1989).

Capital costs for vacuum evaporators range from \$125,000 to \$175,000. Operating costs are lower than atmospheric evaporators, averaging \$0.05 to \$0.12 per gallon (EPA 1995).

## Membrane Technologies

### Overview of Membrane Filtration

Metal finishers use membrane filtration to remove suspended solids, oils, and other impurities from wastewater as well as to recover/recycle process solution. The membranes separate suspended or dissolved solids by applying pressure to one side of the membrane. Water and low molecular-weight compounds flow through the pores while larger molecules and suspended solids flow across the membrane and become part of the concentrate. In membrane filtration systems, wastewater flows parallel to the membrane surface. This cross flow allows high filtration rates to be maintained

continuously (RI DEM 1994). Membrane flow is illustrated in Figure 16. Platers moving toward zero discharge or total recycling should consider these systems as a means to achieve that goal.

Several different membrane filtration technologies are available including microfiltration, ultrafiltration, and nanofiltration. These technologies differ in the size of the membrane's pores and the amount of pressure that is applied to the wastestream. Table 22 presents the differences in the membrane processes.

Many industries use membrane technology for filtration. Membrane materials can be organic (e.g., polypropylene, polyethylene, polyester, polyacrylonitrile, and polysulfone) or inorganic (e.g., carbon fiber or ceramics). The choice of membrane depends upon pH, temperature, and specific application (Ieronimo 1995).

In recent years, membranes have become the preferred method of liquid/solid separation because of the consistent permeate (filtrate) quality achieved and lower pretreatment chemistry requirements. The membrane technologies used most commonly by metal finishing shops are microfiltration and ultrafiltration. However, platers use other membranes in specific applications (Ieronimo 1995).

### Where To Use Different Types Of Membrane Filtration

In general, microfiltration applications work best for metal finishing shops that have large amounts of oils in the wastestream. Ultrafiltration appli-

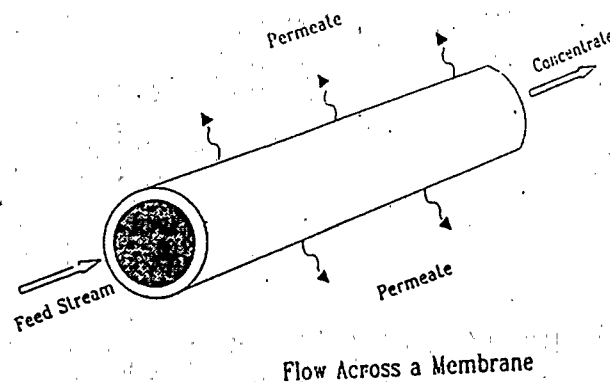


Figure 16. Illustration of Membrane Flow (RI DEM 1994)



Table 22. Overview of Membrane Processes (IAMS 1995)

Process	Pressure (psi)	Particle Size Ranges	Amount of Solid Captured
Microfiltration		0.10 micron or greater	Dissolved solids pass through
Ultrafiltration	10 - 125	.002 to 0.005 micron or molecular weight 1,000	Dissolved solids pass through
Nanofiltration	100 - 200	molecular weight 300 to 1,000	Blocks some dissolved solids, but allows some to pass through
Reverse Osmosis	200 - 800	molecular weight 100 to 1,000	Blocks almost all solids

cations are best for facilities with mixed wastes containing emulsified oils from aqueous cleaners. Metal finishers use other membranes in specific waste minimization activities including acid recycling (i.e., electrodialysis) or recycling wastewater (i.e., reverse osmosis).

Nanofiltration membranes are becoming popular for recycling systems as well and some membrane suppliers offer them for polishing treated water for recycling (IAMS 1995).

Platers should conduct a pilot test of any membrane system to avoid problems with flow (flux) rate deterioration or compatibility with trace constituents such as solvents or silicones. Manufacturers' warranties vary and many do not guarantee that effluent limits will be met (Ieronimo 1995).

### Maintenance and Equipment Cost

Depending upon the application, membrane systems require periodic flushing and cleaning. Some require little maintenance while other applications where a higher concentration of materials that could foul the membrane is present require additional maintenance. In all applications, the concentrate generated by the filtration system must be managed in one of three ways: (1) companies can use the solution in another application, (2) they can discharge the solution to the sewer, or (3) they can hire a licensed hauler to remove it (Ieronimo 1995).

The capital cost of a membrane system depends on the processing rate and the type of membrane material used. Cost can vary from \$4,000 for a

50 gallon-per-day system to more than \$100,000 for a 50,000 gallon-per-day system. Typical annual operating costs, which include maintenance, replacement membranes, and electricity, are 10 percent of the initial investment (EPA 1995).

### Microfiltration

Microfiltration is a relatively new technology for the removal of oil and grease from aqueous and semi-aqueous degreasing baths. Captive shops and non-plating facilities such as metal fabricators and painters currently use microfiltration. Microfiltration separates emulsified oils and suspended solids from cleaning solutions in the process bath, extending the life of the solution. Microfiltration also can remove cleaning solution dragout from rinsewater lines (Cushnie 1994).

To remove large particulates, platers typically filter the feed stream entering the microfiltration unit with conventional methods (e.g., cartridge filters). Facilities use various holding tank designs to trap or skim floating oils, allowing heavier solids to settle. Operators then pump fluid into the membrane compartment of the unit. The membrane separates the remaining oils and grease while water, solvent, and cleaning bath constituents pass through. Figure 17 illustrates a microfiltration system.

Two common configurations for microfiltration are dead-end filtration and cross-flow filtration. In dead-end filtration units, flows are similar to those in laboratory Buchner funnels, while in cross-flow filtration units, flows are tangential to

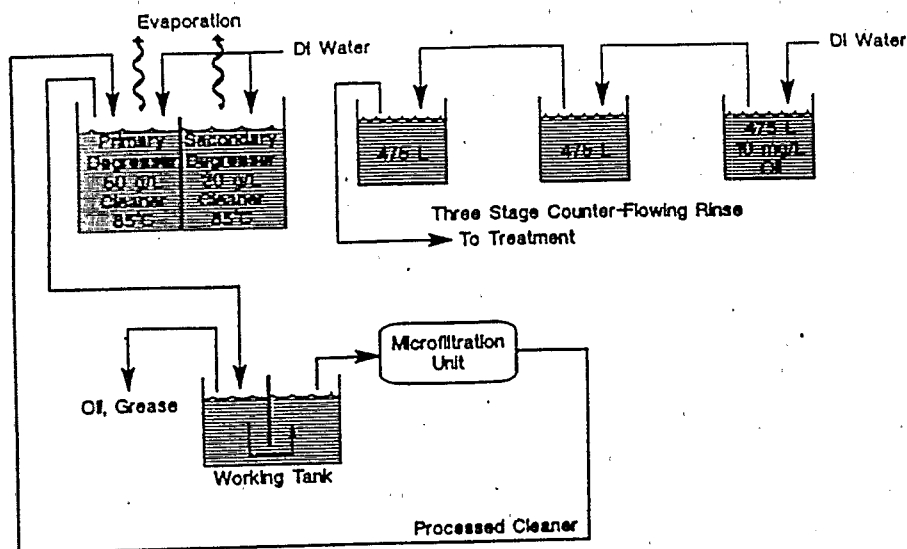


Figure 17. Example of Microfiltration Application (EPA 1995)

the filter surface. Filters used in these systems can be either membranes with pore sizes smaller than the diameter of the suspended solids or depth filters with pore sizes larger than the particle size, but that can still trap particles in interstices. Cross-flow filtration is used predominantly in metal finishing because of its self-cleaning ability, low pressure requirements, and high permeate fluxes. The membranes can be polymeric or ceramic materials. Polymeric membranes have service lives of 2 to 4 years while ceramic membranes can last 10 years. Despite a cost that is twice that of polymeric membranes, ceramic membranes are becoming more popular because of their high temperature and chemical resistance. All microfiltration systems require periodic cleaning to remove deposits on the surface and unplug membrane pores. Cleaning usually is accomplished by circulating acid (for inorganic scales), detergents (for colloids emulsions), alkali (for biological materials), or solvents (for organics) through the microfiltration membrane (Freeman 1995).

The equipment selected for microfiltration should have a simple mechanical configuration that is physically sturdy and compact. The unit should be constructed of materials that can withstand high alkalinity and temperatures and that can tolerate temperature fluctuations. It also should be impenetrable to soils and metal shavings. Selection of the membrane and

designation of pressure, retentate flow rate, and concentration of oil in the influent are the most important factors in determining the appropriate microfiltration system (Ieronimo 1995).

### Applications and Restrictions

Microfiltration is used in the recovery of caustic aqueous cleaners. As caustic cleaning solution is used, it accumulates dirt, grease, grime, free and emulsified oils, and metal particulates. With use, caustic cleaners lose their ability to remove contaminants. Rather than dumping the cleaning bath, it can be sent to a microfiltration unit for regeneration. Not all cleaners are good candidates for microfiltration and a facility might need to change its cleaning chemistry to use microfiltration. For example, high silicate cleaners that accumulate metal ions can foul membranes. Because these membranes do not remove dissolved ions such as aluminum or copper, bath life remains limited (EPA 1995). Microfiltration also can be used to polish wastewater after hydroxide precipitation (Freeman 1995).

### Costs

The cost of microfiltration systems varies depending on the size of the machine. Systems can range from \$15,000 to \$20,000 for a 1,000 liters-per-day unit to \$25,000 to \$35,000 for a 5,000 liters-per-day unit. Installation costs are usually 10 to 30 percent of the equipment cost.

Operating costs include membrane replacement, labor, and energy. The lifespan of a membrane depends upon the application. Some facilities might need to change the membrane every few years while other facilities can expect the membrane to function properly for more than 10 years. Companies can save money by reducing or eliminating replacement of spent cleaners and neutralization chemicals (EPA 1995).

## Ultrafiltration

Ultrafiltration (UF) membranes have smaller pores than microfiltration membranes with pore sizes of 0.0025 to 0.01 microns. The layout of a typical ultrafiltration recycling system is depicted in Figure 18. As shown, the operator pumps spent process water from a process tank to a holding/settling tank. If the spent process solution has a high solids content, the rinsewater first passes through a prefiltration unit (e.g., bag filter) before being pumped to a holding tank. From the holding tank, the ultrafiltration system recirculates and concentrates the process solution, providing a steady stream of clean fluid for reuse. The system then sends a stream of clean fluid to the holding tank for the operator to draw on as necessary. Typically, ultrafiltration systems use higher pressure than microfiltration systems (60 to 80 pounds per square inch) (RI DEM 1994).

Ultrafiltration membranes are tubular, hollow fiber, and spiral wound. Platers generally use tubular membranes in small flow, high-solids loading applications. The construction of tubular membranes allows easy cleaning, making them excellent applications where the operator expects severe fouling (RI DEM 1994).

The hollow fiber design consists of a membrane wound into a hollow cylinder. The expected solids loading governs the size of the cylinder that is needed for a specific application. Platers usually use spiral-wound membranes for high-volume applications. The spiral membrane consists of a rolled flat membrane that is netted together with specially designed spacer material. Spiral membranes cannot be mechanically cleaned and usually are reserved for applications where total suspended solids loading is low or has been reduced by prefiltration (RI DEM 1994).

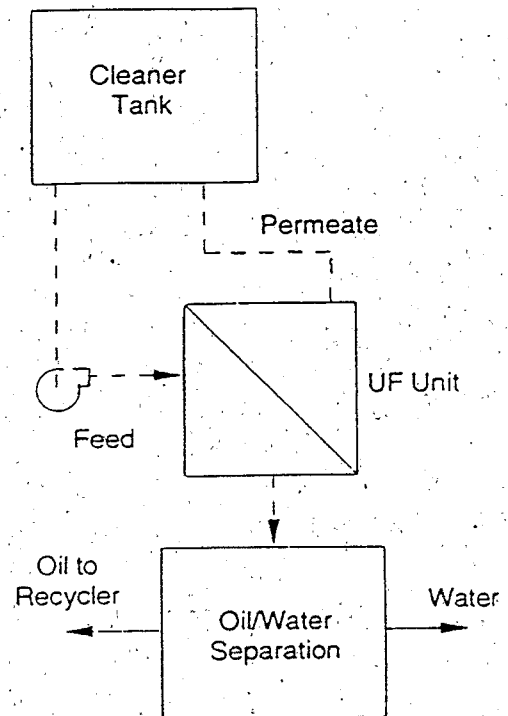


Figure 18. Example of Ultrafiltration (EPA 1995)

## Reverse Osmosis

Reverse osmosis (RO) is a pressure-driven membrane filtration process. In RO, a semi-permeable membrane permits the passage of purified water under pressure, but does not allow the passage of larger molecular-weight components. Water that passes through the membrane usually is recycled as rinsewater. Water that is rejected by the membrane (i.e., water containing dissolved solids) is returned directly to the process tank. Reverse osmosis is capable of removing up to 98 percent of dissolved solids, 99 percent of organics, and 99 percent of bacteria. Figure 19 illustrates a typical RO system. Reverse osmosis is a good component of a low- or zero-discharge configuration. The equipment, however, tends to be more expensive and less effective at recycling rinsewater than other technologies such as ion exchange (EPA 1995).

Reverse osmosis is especially suited for closing the loop on plating operations and sending concentrate back to the plating bath. Firms apply

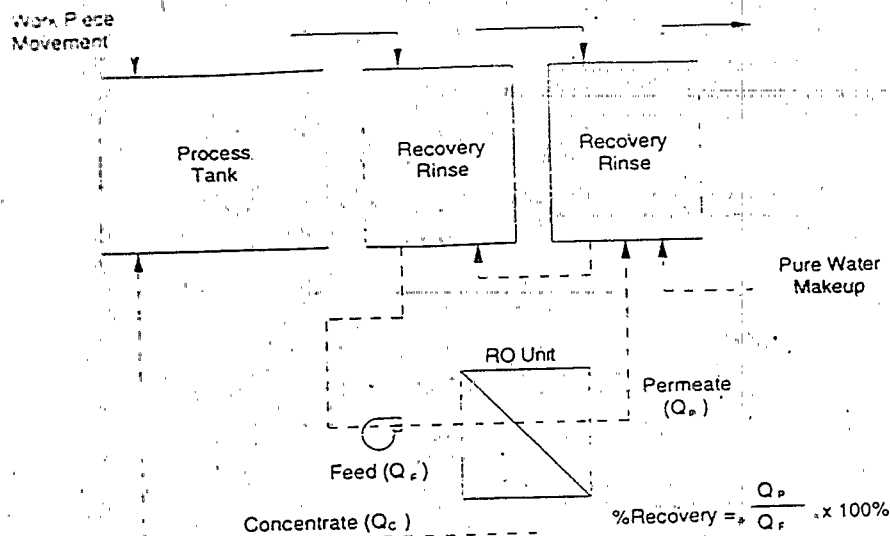


Figure 19. Example of Reverse Osmosis (EPA 1995)

RO to a variety of processes including brass cyanide, copper cyanide, copper sulfate, nickel, silver cyanide, non-cyanide alkaline zinc, and zinc cyanide plating. Recovery of dragout from acid nickel process bath rinses is the most common RO application. Reverse osmosis also is used to purify tap water, recover plating chemicals from rinsewater, and polish wastewater effluent. Although RO recovers a concentrated dragout solution, some materials (e.g., boric acid) cannot be fully recovered (Freeman 1995). Reverse osmosis generally is not suitable for applications that have a highly concentrated oxidative solution such as chromic acid, nitric acid, and peroxy-sulfuric etchant. Also, the membranes will not completely reject many non-ionized organic compounds. Therefore, activated carbon treatment typically is required before the rinsewater solution can be returned to the rinse system, which can be costly (Cushnie 1994).

Facilities must carefully consider the membrane used in RO. The membrane must be specifically matched with the process chemicals. For instance, polyamide membranes work best on zinc chloride and watts nickel baths, while polyetheramide membranes work best with chromic acid and acid copper solutions (EPA 1995).

Although similar to other filtration technologies, RO is different in that:

- Only RO can concentrate dissolved salts.
- Reverse osmosis cannot tolerate large concentrations of suspended solids
- Reverse osmosis requires much higher operating pressures, mandating the use of heavy gauge stainless steel; other filtration technologies can use lightweight stainless steel or plastic (Cushnie 1994)

The membranes in RO are unable to withstand pH extremes and long-term pressures. Feed concentrations can reach saturation, precipitate on the membrane, and cause the membrane to fail. Precipitation of contaminants must be avoided or RO will fail. Feed stream concentrations must be kept low by adding a pre-filtering system to the RO unit, usually an ultrafiltration unit (Warheit 1988). Reverse osmosis membranes also can be damaged by some incoming materials (e.g., iron and manganese).

Another concern is the potential for a reject rate of more than 50 percent of incoming flow depending on the characteristics of the influent and membrane porosity. Such a high rejection rate can be difficult to handle in a metal finishing operation unless the firm is using RO to generate deionized water where the disposal of rejected flow is not expensive. In a waste application, platers must treat discharge of concentrate, increasing the cost of the system and limiting the use of RO to wastewater recycling applications.

## Reverse Osmosis

## Advantages

- ◆ Recovers process chemicals
- ◆ Recycles process water
- ◆ Achieves high separation rate
- ◆ Uses no chemicals
- ◆ Requires small floor space
- ◆ Low-energy process
- ◆ Less expensive than other recovery technologies for certain applications

## Disadvantages

- ◆ Problems with membrane durability
- ◆ Sensitive to hard water salts
- ◆ Fouls membranes because of feeds high in suspended solids
- ◆ Feed filtration is essential
- ◆ In some applications does not concentrate plating solution sufficiently for reuse
- ◆ Returns ionic impurities to plating bath
- ◆ Operates efficiently in a limited concentration range. (Ohio EPA 1994)

A typical application for process recovery using RO is nickel plating as shown in Figure 20. Because RO is such a delicate process, any change in bath chemistry can affect the operation of the RO unit.

While widely used in other industrial applications such as desalinization, RO is not used frequently as a recovery technology in metal finishing. The limited number of baths in which firms have successfully applied RO and the availability of competing technologies might be reasons. Other technologies that are available at much lower costs, such as atmospheric evaporation, often are more attractive options for metal finishers (Cushnie 1994).

## Costs

Since flux rates vary from application to application, and customization and special engineering can be necessary, cost estimates based simply on flow or flux rates are approximate. Reverse osmosis units can cost \$50,000 to \$75,000 for flow rates of 75 liters per minute with cost as high as \$300,000 for flow rates of 800 liters per minute. Operating costs include labor, energy, and membrane cleaning and replacement (EPA 1995).

## Reverse Osmosis in Specific Baths

Table 23 provides information on specific metals used with RO.

Table 23. Reverse Osmosis and Specific Metals (Nadeau 1986)

Metal	Use with Reverse Osmosis
<b>Nickel</b>	Most nickel plating lines with RO units use cellulose acetate membranes with recovery rates between 90 and 97 percent.
<b>Copper Sulfate</b>	Many of the copper sulfate RO units use hollow-fiber polyamide and cellulose triacetate membranes and spiral wound thin-film composite types, which offer a membrane life of approximately 3 years. Because of the low operating temperature of the plating bath, operators can return only a small portion of the concentrate back to the process bath.
<b>Brass Cyanide</b>	Platers have used both polyamide and cellulose triacetate membranes in brass cyanide applications. Average recovery rates are approximately 90 percent. Average membrane life in these systems is 3 to 4 years.

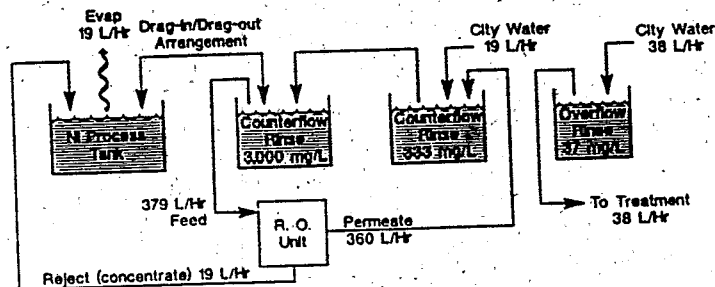


Figure 20. Typical Reverse Osmosis Configuration for Nickel Plating (EPA 1995)

## Ion Exchange

Many metal finishers are familiar with ion exchange technology. This versatile technology has been used for decades and can be a major component of a low- or zero-discharge configuration. The most common applications in plating include:

- ◆ Treatment of raw water to produce high-quality rinsewater
- ◆ Recovery of chemicals from rinsewater
- ◆ Treatment of plating baths to remove contaminants
- ◆ Primary end-of-pipe treatment
- ◆ End-of-pipe polishing for compliance with stringent effluent limits

The ion exchange process replaces some of the harmless ions located in a resin with ions of concern (i.e., plating chemicals). The system is a molecular process where metal ions in solution are removed by a chemical substitution reaction

with the ions in a resin bed. Resins are normally contained in vessels referred to as columns, rinsewater is passed through a series of resin beds that selectively remove both cations and anions. As rinsewater passes through the resin bed, the resin bed exchanges ions with organic compounds in the rinsewater. Figure 21 presents two typical configurations of ion exchange for bath maintenance.

Basically, ion exchange processes are either anionic or cationic. Anion resins exchange hydroxyl ions for negatively charged ions such as chromates, sulfates, and cyanides. Cation resins exchange hydrogen ions for positively charged ions such as nickel, copper, and sodium. An example of ion exchange is shown in Figure 22. Ion exchange systems typically operate in cycles consisting of the following four steps (Cushnie 1994):

- ◆ Service (exhaustion): Process effluent passes through the resin column or bed. Charged ions present in the wastestream are attracted to the resin and exchange with

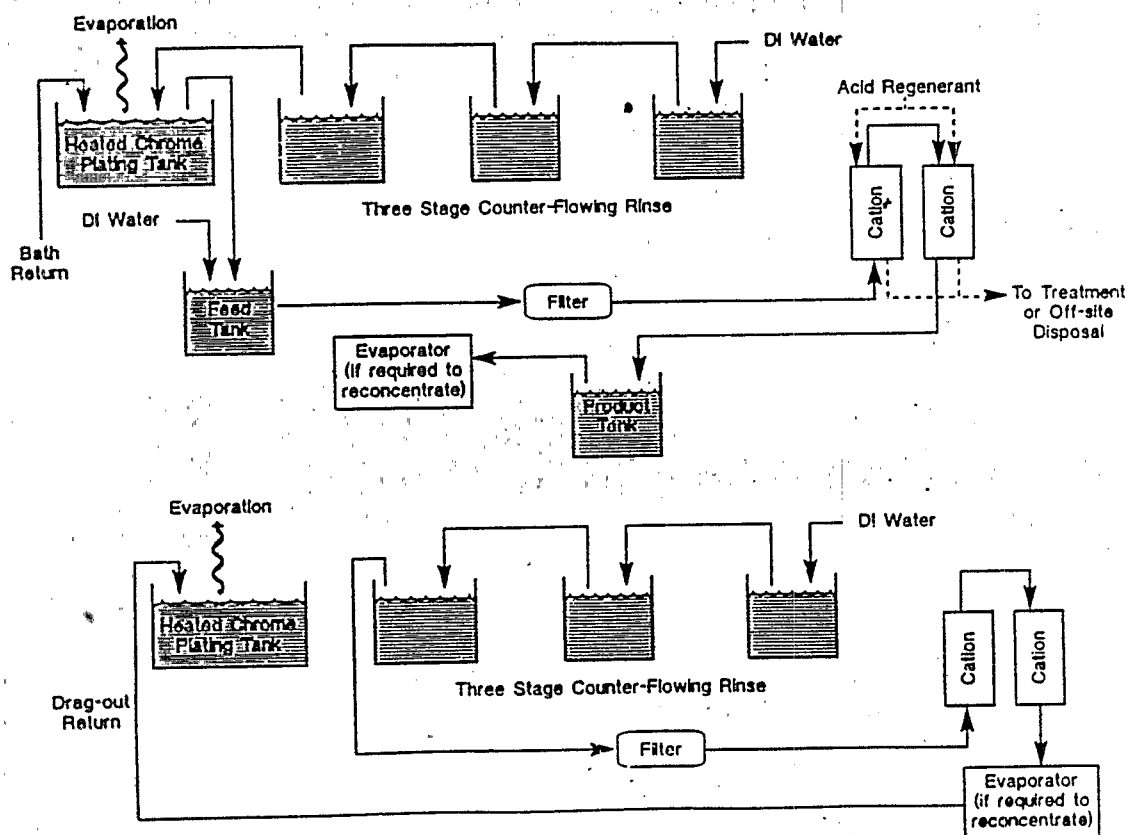


Figure 21. Two Common Configurations of Ion Exchange (EPA 1995)

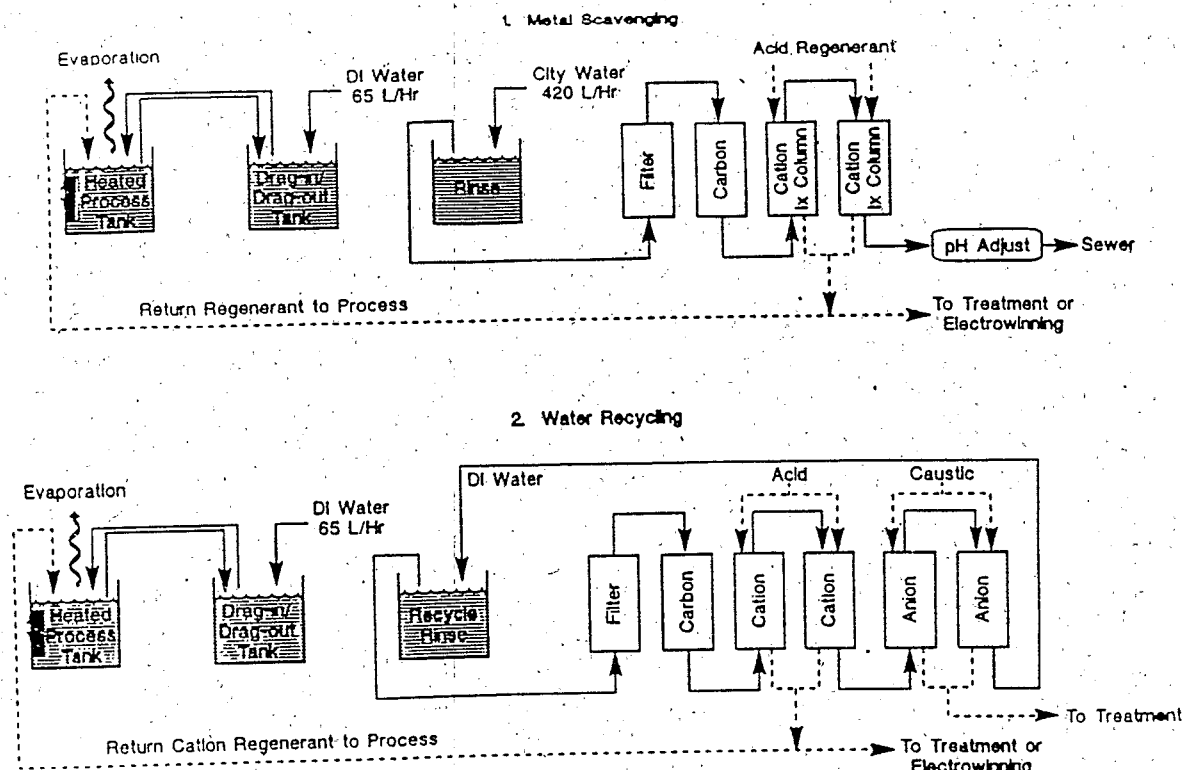


Figure 22. Example of Ion Exchange (EPA 1995)

similarly charged ions in the bed. After the majority of the exchange sites have been used up, the resin is considered exhausted. Although the resin could be discarded and replaced at this point, typically it is regenerated for reuse because of the high cost of resin.

- ◆ **Backwash:** Water is flushed through the resin bed in the reverse direction of the service cycle to redistribute the resin.
- ◆ **Regeneration:** The exchanger resin is regenerated by passing a concentrated solution of the original ion through the resin bed. Usually, the solution contains a strong mineral or acid.
- ◆ **Rinse:** Rinsing to remove excess regenerant is accomplished by circulating deionized water through the ion exchange column.

Metals held in the solution are recovered by cleaning the resin with an acid or alkaline solution. Operators can electrowin metals from the resin regeneration solution while the water treated by ion exchange can be returned to the

rinse system for reuse (Cushnie 1994). Figure 23 presents a typical ion exchange configuration for chemical recovery applications.

Ion exchange can selectively remove contaminants from a wastestream. In recycling applications, however, contaminants are not recovered along with the desired materials. Close control of the influent is important with low pHs reduce the capacity of the resin and high pHs tend to clog the resin with solids. One disadvantage of these systems is that no method exists to monitor the saturation of the resin. However, physical indicators such as reduced effluent quality can signify when the resin bed is saturated. Typically, facilities clean the cylinders on a time-based schedule (Freeman 1995). The recovery of chemicals from the resin columns generates significant volumes of regenerant and wash solutions, which can add to the wastewater treatment load (IAMS 1995).

Ion exchange should only be applied to relatively dilute streams and is best used in association with other conventional dragout recovery prac-

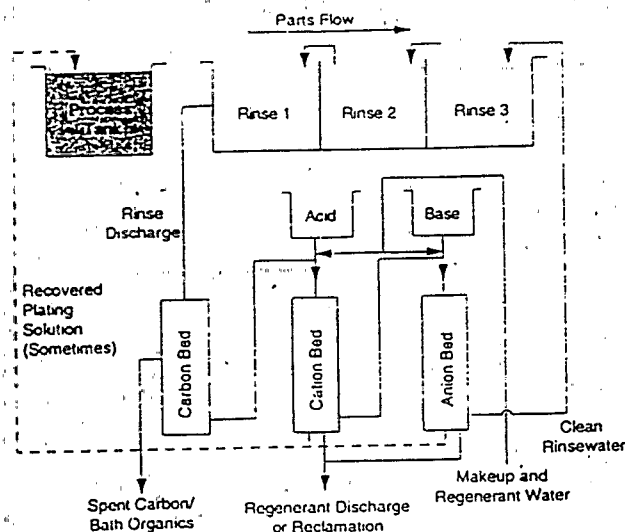


Figure 23. Common Ion Exchange Configurations for Chemical Recovery (EPA 1995)

### Recover of Zinc and Nickel Using Ion Exchange Case Study

Walbridge Coatings of Walbridge, Ohio, produces electrogalvanized zinc and zinc-nickel cold-rolled steel primarily for the automotive industry. In 1989, the company embarked on an aggressive metals recovery and reclamation program. After a year of engineering work, the firm decided that recovery of zinc and nickel was possible through ion exchange.

Initial tests indicated that a metals recovery rate of 90 percent was possible. The firm estimated that initial recovery efforts would result in approximately a 500 tons-per-year reduction in sludge generation. After installing the system on the zinc-nickel stream, the company found that the system could reduce sludge generation from zinc processes by an additional 350 tons per year.

During 1991 the project eliminated 515 tons of sludge. During 1992, with improved methods and the addition of the system to the zinc stream, more than 892 tons of sludge were eliminated, exceeding engineering expectations by 5 percent.

The total project costs were \$3.2 million with annual savings of \$2 million. The payback period, based solely on cost avoidance, was 1.5 years.

(Ohio EPA 1994)

Ion exchange systems are less delicate than RO systems, however, operators must filter the water to protect the resin, removing oil, grease, and dirt. In addition, certain other metals can foul the resin, requiring a special procedure to remove the foulant (Hunt 1988). In some applications, the solution generated from ion exchange (i.e., regenerant) is returned directly to the process tank. In most cases, however, regenerant is electrowinned or goes to traditional waste treatment systems (EPA 1995).

### Optimizing Ion Exchange System Performance

A properly designed system will operate at maximum efficiency. Conducting treatability testing of specific wastestreams to ensure proper resin selection and sizing of the system is critical to the overall success. Treatability testing also will ensure that the system is not undersized or oversized and that interferences are not present that will render the resin ineffective. Other items that facilities should consider include:

- ◆ Regeneration frequency and volume: A properly designed system will minimize regeneration frequency and the volume of waste regenerant solution generated. Various methods for regeneration are available including in-column or continuous and out-of-column batch techniques. From the operator's standpoint, in-column methods are



preferred. The batch in-column method (also known as the flooded vessel method) involves filling the column with regenerant solution, allowing it to sit for a specified time period, and then repeating this step or proceeding with deionized rinsing. The continuous in-column technique involves passing a specified amount of regenerant through the resin bed in a continuous flow (either up or down). Although operators might prefer the ease of the batch in-column method, the continuous flow method generally requires lower volumes of regenerant solution.

- ◆ **Determining breakthrough:** Breakthrough is defined as the point at which the resin has become spent or exhausted and must be regenerated. In some applications, the columns must be regenerated just prior to breakthrough in order to meet effluent quality standards. Various methods are available to determine breakthrough including timed-interval regeneration, on-line monitoring of ions and flow to identify regeneration intervals, and periodic off-line sampling to monitor effluent quality. Selection of the appropriate method depends on the effluent requirements of the facility.
- ◆ **Series versus parallel configuration:** Ion exchange systems can be designed in a series or a parallel configuration. Parallel configurations generally have higher flow rates. In applications where final effluent standards are high, the series configuration allows operators to observe breakthrough in the initial column(s) of the series prior to breakthrough in the last stage.
- ◆ **Charging and recharging vessels with resin:** Resins must be added or replaced in the vessels to prevent a premature loss in capacity because of flow restrictions or increased resin deterioration.
- ◆ **Storage of resin:** Resins should not dry out during storage. Re-wetting usually results in cracking and/or deterioration of the resin. Additionally, resin vessels should be backwashed prior to shutting down the system to prevent fouling or cementing of particulates in the resin bed. Prior to long-term shutdown, anion resins should be rinsed

with brine solution to ensure conversion to the more stable chloride form (versus the hydroxide form) (Wilk 1990).

### Costs

Capital costs depend on the volume of flow and the level of automation. The components of an ion exchange system are relatively inexpensive and, depending on the application, can cost from \$100 to \$400 per cubic foot. Installation costs can be quite high. Platers can purchase and install small manual units, applied to flows of 20 liters per minute or less for \$15,000 or less. A fully automatic 75 liters-per-minute unit with an integrated electrowinning unit costs approximately \$75,000 installed (EPA 1995).

Operation and maintenance costs are generally low for ion exchange. A major expense is resin replacement. Resin should last 3 years or more, however, in certain applications (e.g., chrome) it can have a shorter lifespan. Resin costs from \$7 to \$22 per liter. Labor costs depend on the level of automation included with the unit and can cost from more than \$1 per 1,000 liters for manual or undersized installations to less than \$0.25 per 1,000 liters for fully automatic systems. Upstream components such as sand, polypropylene, and carbon filters also contribute to operating costs (EPA 1995).

### Electro/Diffusion Dialysis

Two types of membrane dialysis systems are electrodialysis and diffusion dialysis. These systems are becoming increasingly popular for chemical solution recovery especially because they are more efficient and less expensive than other recovery technologies for reclaiming acid. They also can remove metals and recycle water in plating or anodizing shops (EPA 1995).

### Electrodialysis

Platers commonly use electrodialysis to reclaim nickel and gold from plating rinsewaters. Figure 24 presents a flow schematic for a nickel plating line before and after installation of electrodialysis. This process uses both anion- and cation-charged selective membranes between a set of non-corrosive electrodes. As the plater recirculates contaminated rinsewaters between the charged surfaces, salts containing the metals are

## Cadmium and Chromium Recovery from Electroplating Rinsewaters Case Study

The Torrington Company based in Torrington, Connecticut, participated in a pilot study in conjunction with the Connecticut Hazardous Waste Management Service to test the feasibility of recovering cadmium and chromium with ion exchange. The objective of the study was to evaluate the effectiveness of ion exchange in cleaning rinsewater for reuse in the rinse tank, the pollution prevention potential of this technology, and the cost of ion exchange versus the cost of traditional control.

### Cadmium Line

Basically, the cadmium system has the following steps. Water from the first rinse tank passes through a filter to prevent suspended solids from contacting the resin in the ion exchange column. The anionic resin captures the cadmium cyanide complex and the second rinse tank receives the water. An emergency bypass valve allows this water to be discharged to the waste treatment system in case cadmium or cyanide levels are found to be too high. The company periodically regenerates the resin with a 15 to 20 percent sodium hydroxide solution and takes the regenerant to the electrolytic metal recovery unit where cadmium is recovered on the cathode and returned to the plating tank. Some cyanide is destroyed by decomposition during electrolytic metal recovery.

Laboratory analysis of the cadmium rinsewater samples found that ion exchange removed most of the cadmium cyanide, in some cases, to below detection levels. The pH of the rinsewater remained alkaline throughout testing. After ion exchange, the concentrations of cadmium, iron, and cyanide in the rinsewater decreased significantly. Ion exchange also reduced the overall dissolved solid levels, indicating a decline in dissolved mass levels. Conductivity did not show any significant change after ion exchange, indicating that the current-carrying capacity of the rinsewater did not change. The company added small amounts of fresh makeup water to the rinsewater loop from time to time to compensate for water lost to evaporation and dragout, and to assist in maintaining conductivity. In terms of pollutant reduction, the company was primarily concerned with cadmium and cyanide. Before ion exchange, cadmium remained in the wastewater that was sent to an on-site wastewater treatment plant for oxidization. The company treated the wastewater in a steel cyanide treatment tank using chlorine gas, sodium hypochlorite, calcium hypochlorite, and sodium hydroxide. Cadmium and other metals formed hydroxides that settled in the clarifier as sludge, which then was hauled off site for disposal. Under this system, the firm discharged treated water containing approximately 69 pounds of cadmium and 281 pounds of cyanide annually. Now because cadmium is recovered and reused, this pollutant has been virtually eliminated from the wastestream. Some cyanide also is destroyed in the cadmium recovery process.

The economic evaluation showed that the ion exchange unit was cost effective. The purchase cost of the cadmium ion exchange system was \$8,100. The price of the electrolytic metal recovery equipment price was \$4,125. Installation cost at the Torrington facility, including materials and labor, was approximately \$3,500. The company set aside \$5,000 for in-house testing. The payback period (with the cost of capital at 15 percent) was less than 1 year.

### Chromium Ion Exchange Unit

In order to remove hexavalent chrome, the company installed an ion exchange unit with an anionic configuration. The company regenerates the anionic resin with a 15 to 20 percent sodium hydroxide solution. The resulting solution (sodium chromate) is run through a secondary cationic exchange unit that is designed to convert the regenerant back to chromic acid and return it to the plating tank. In the future, Torrington plans to add a cationic resin to remove trivalent chrome that might be present in the rinsewater.

Total chromium and iron levels decreased significantly after ion exchange. The results of laboratory analysis of the chromium rinsewater samples showed that the rinsewater pH levels were slightly alkaline (9.31 to 9.45) because the hydroxide ions replaced chromate ions and any other contaminant anions. However, chromic acid residue on the parts neutralized the alkaline pH in the rinse tanks. The company uses a cartridge filter in conjunction with the ion exchange unit, which

significantly reduces the suspended solids. As in the cadmium test, the mass of dissolved solids decreased significantly, but conductivity (i.e., current-carrying strength) remained constant after ion exchange because the lighter hydroxide ions replaced heavier chromates in the rinsewater.

Without ion exchange, approximately 80 pounds of chromium were discharged annually. With ion exchange, most of the chromium was captured on the resin. To regenerate the resin, sodium hydroxide was passed through a cation exchange resin, converting sodium chromate to chromic acid. However, when this recovery was performed during the pilot test, the final regenerant liquid had a pH of 13.08. If sodium chromate had been converted to chromic acid, it would have a much lower pH. An excess use of regenerate and/or insufficient resin might have caused these results. The company plans to conduct further tests to determine the feasibility of the chromic acid recovery process.

The purchase price of the chromium exchange system was estimated at \$8,200. Installation costs were approximately \$3,500 including materials and labor. Additional capital is required for in-house testing.

(EPA 1995b)

retained and returned to the plating tank. Rinsewater is reused in the dirtiest rinse or dragout tank. Separation is accomplished by applying a direct current across a stack of selective membranes. The membranes are stacked in alternating cation/anion stacks. Each stack is separated by a spacer through which solutions are allowed to flow (Cushnie 1994).

When the solution passes through a cation-selective membrane, cations pass through and anions are trapped. As the solution continues to migrate, it will encounter an anion-selective membrane that will not allow the cations to pass. In this way, the wastestream is diluted of both anions and cations. The solution, which is returned to process tank, can be 10 times more concentrated than the feed stream, but usually is not as concentrated as the process bath (Cushnie 1994).

### *Applications and Restrictions*

For electrodialysis to offer any advantages over competing technologies, the process fluid must tolerate the direct return of the concentrate. Because the returned solution is usually less concentrated than the bath itself, and because of the evaporative nature of the process, only heated fluids are candidates for this process (EPA 1995). One advantage of electrodialysis is its ability to selectively retard the recovery of certain organic materials, especially nickel, that build up in some baths. In so doing, electrodialysis

### **Electrodialysis**

#### **Advantages**

- ◆ Energy efficient
- ◆ Returns minimal amount of unwanted inorganic material
- ◆ Recovers higher concentrations of ions than RO or ion exchange

#### **Disadvantages**

- ◆ Sensitive to clogging and ruptures, flow distribution, pH, and suspended solids
- ◆ Efficiency drops as purity increases
- ◆ Must filter feed
- ◆ Uses multi-cell stacks
- ◆ Uncertain membrane life

(Ohio EPA 1994)

can reduce the frequency of bath purification (Cushnie 1994). Most applications for electrodialysis are nickel-related although manufacturers have used this technology in copper cyanide, cadmium cyanide, and zinc phosphate applications (EPA 1995).

#### **Costs**

Capital costs are related to membrane surface area or to feed flow volume and characterization. Vendors customize most units for a particular application. In general, electrodialysis is more expensive than other recovery technologies. Units range in price from \$75,000 to several hundred thousand dollars depending on the capacity of the unit. Operating and maintenance costs include energy, labor, and membrane

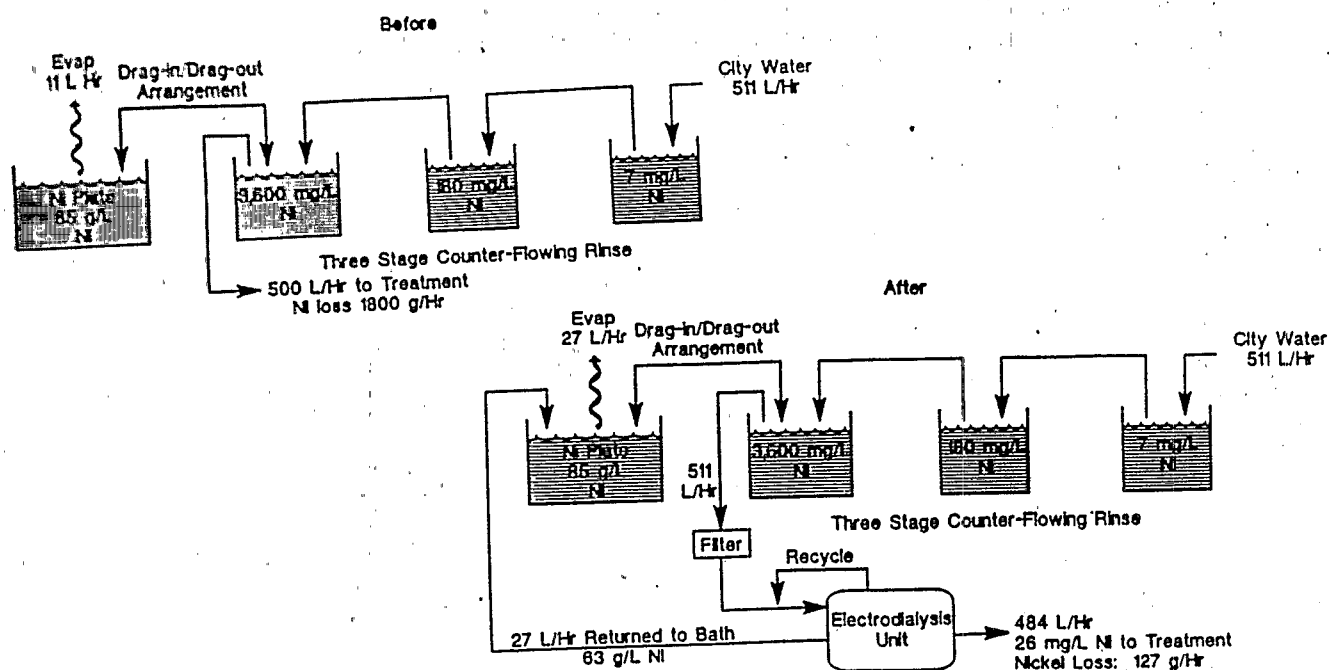


Figure 24. Example of Process Flow of a Nickel Plating Line Before and After Installation of Electrodialysis (EPA 1995)

### Nickel Recovery from Electroplating Rinsewater by Electrodialysis Case Study

Automatic Plating of Bridgeport (APB) in conjunction with the Connecticut Hazardous Waste Management Service tested the feasibility of using electrodialysis to recover nickel from spent rinsewater. APB has two nickel plating lines. Each line has its own plating bath and rinse tank. The two lines and the electrodialysis unit are operated for two shifts for a total of 10 to 16 hours per day. The recovery system is configured so that rinsewater overflow is sent to the dialysis feed tank by a level controller. After electrodialysis, the recycled water is stored in a rinse recycle tank and is sent back to the rinse tanks when needed. A small amount of sulfuric acid is added to the rinse tanks to remove flash rust after nickel plating. From the dialysis feed tank, water is circulated through the electrodialysis membrane stacks and to the feed tank. In the water loop, a carbon filter removes organics and a cartridge filter removes any carryover carbon particles.

The electrodialysis system provides a continuous supply of clean recycled water for the plating line. Nickel, a hazardous substance, is recovered and reused. Estimates indicate the system can recover 29,964 pounds of nickel and 1.07 million gallons of water from the waste treatment system. Capital costs for the system including installation were approximately \$110,000. Maintenance and energy costs are the primary operating costs, but reduced waste treatment costs and chemical purchased resulted in a payback of 1 year.

(EPA 1995b)

replacement (EPA 1995). One vendor estimated that operating costs are \$0.78 per gallon of acid feed. Primarily, these costs are incurred from operation and maintenance, labor, energy, deionized water, and membrane replacement (Cushnie 1994).

### Diffusion Dialysis

Diffusion dialysis is an ion exchange membrane technology used for the recovery of acids contaminated with metals from pickling, anodizing, stripping, etching, or passivation baths. This

technology is commonly used in finishing facilities in Europe and Japan, but not in the United States. Companies use diffusion dialysis to purify some acid baths that are contaminated by metals. This technology can separate mineral acids and metals such as copper, chrome, nickel, iron, and aluminum so that acid can be reused. Recovery rates in some instances are as high as 95 percent for acid solutions and 60 to 90 percent for metal contaminants (Cushnie 1994). Currently, this technology is popular with anodizers that generate large amounts of waste sulfuric acid (EPA 1995).

The efficiency of a membrane to concentrate dilute acids in solution depends on the surface area available and the type of acid. Diffusion dialysis separates acids from metal contaminants via an acid concentration gradient that is placed between two solution compartments. These compartments are divided by an anion exchange membrane. Water is metered through one side of an anionic membrane, causing the acid to migrate to one side and the metals to stay on the other. Purified acid is sent back to the process tank and contaminant-laden spent acid and metals are sent to the metal recovery or waste treatment system. This technology does not use pressure or charge to move material across the membrane as do other membrane technologies. Movement is caused by the different acid concentrations on either side of the membrane (Cushnie 1994).

Capital costs for diffusion dialysis systems start at \$18,000 for a 50 gallons-per-day system (EPA 1995).

### Diffusion Dialysis

#### Advantages

- ◆ Energy efficient
- ◆ Considerable reduction in acid consumption
- ◆ Fully automatic
- ◆ Low maintenance costs
- ◆ Long membrane life

#### Disadvantages

- ◆ Sensitive to clogging and ruptures, flow distribution, pH, and suspended solids
  - ◆ Efficiency drops as purity increases
- (Ohio EPA 1994)

### Acid Sorption

Acid sorption is an acid purification technology used on a variety of acid solutions including pickling or sulfuric acid anodizing baths. A bed of alkaline anion exchange resin separates the acid from the metal ions. The acid is taken up by the resin while the metal ions pass through the membrane. The acid is then desorbed from the resin by water. This technology is rarely used by the plating industry (Cushnie 1994).

Figure 25 shows the steps in the acid sorption process. First, spent acid is pumped upward through the resin bed. A metal-rich, mildly acidic solution passes through the resin bed and is collected at the top of the bed. Second, water is pumped downward through the bed and desorbs the acid from the resin. The purified acid solution is collected at the bottom of the bed (EPA 1995).

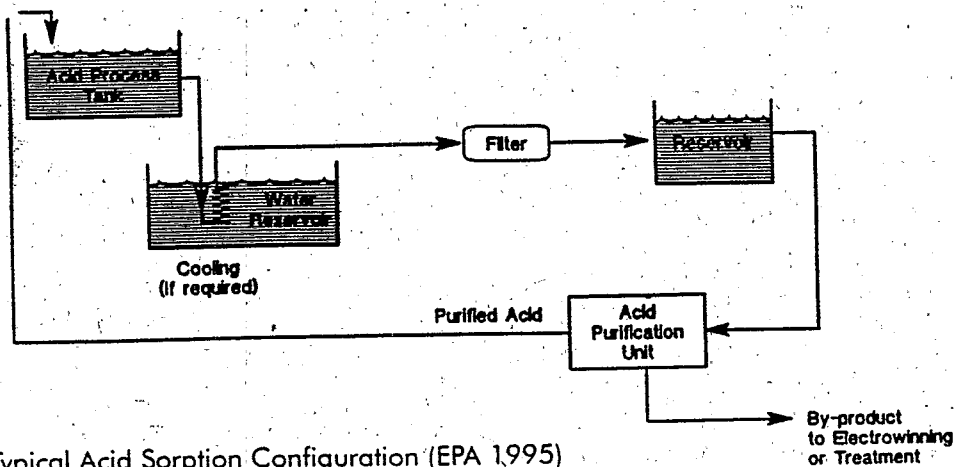


Figure 25. Typical Acid Sorption Configuration (EPA 1995)

This technology can recover approximately 80 percent of the free acid remaining in a spent solution. Facilities can purify the acid solutions in a batch mode, but using the technology in a continuous mode can produce a steady metal concentration in the concentrate. The capacity of a system is determined by the size of the resin bed and usually is expressed in terms of the mass of metal removed from the acid solution. Equipment capacities range from 100 grams per hour to several thousand per hour. Typically, vendors size a unit to remove metal near or above the rate at which metal is being introduced (EPA 1995).

### Applications and Restrictions

Many plating shops with acid solutions could use acid sorption technology. Heated solutions and those containing oxidizers have to be cooled and filtered respectively prior to purification. Platers generally send the process byproduct (i.e., metal-rich solution) to the treatment system, but some electrowin the solution for metals recovery. In addition to anodizing and pickling baths, companies can apply acid sorption to non-chromic acid copper, brass etch, bright dips, nitric acid strippers, aluminum bright dips, and cation ion exchange regenerant. Chromates, concentrated acids, and some hydrochloric acid processes are not good candidates for this technology (EPA 1995).

### Costs

Capital costs of acid sorption range from \$30,000 to \$40,000 for capacities under 200 grams per hour to more than \$100,000 for capacities of 1

kilogram per hour. Little data is available on operating costs (EPA 1995).

### Ion Transfer

Ion transfer generally is restricted to chromic acid plating baths, etches, and anodizing baths. As with the other chromic acid purification technologies, this technology selectively removes cations from chromic acid process fluids. Designs range from low-cost in-tank small porous pots to large multi-cell automated units with unified rectifiers and transfer pumps (EPA 1995).

Figure 26 presents a typical ion transfer arrangement. Ion transfer units consist of one or several membrane compartments that separate the cathode from the anode of an electrolytic cell. The membrane is usually a porous ceramic pot that contains the cathode. The anode surrounds the pot. The membrane also can be constructed of a polyfluorocarbon material and the catholyte compartment can be reinforced with polyethylene. The anode is in direct contact with the process fluid while the cathode is separated from the process fluid by the membrane. Equipment can be in-tank or external. Small in-tank units often use a process rectifier and operate only while parts are being plated. Operators must remove these units when the rectifier is switched off because the membrane will leak cations back into the process tank. Automated ion transfer units include a system that replenishes the catholyte with fresh fluid at regular intervals (Cushnie 1994).

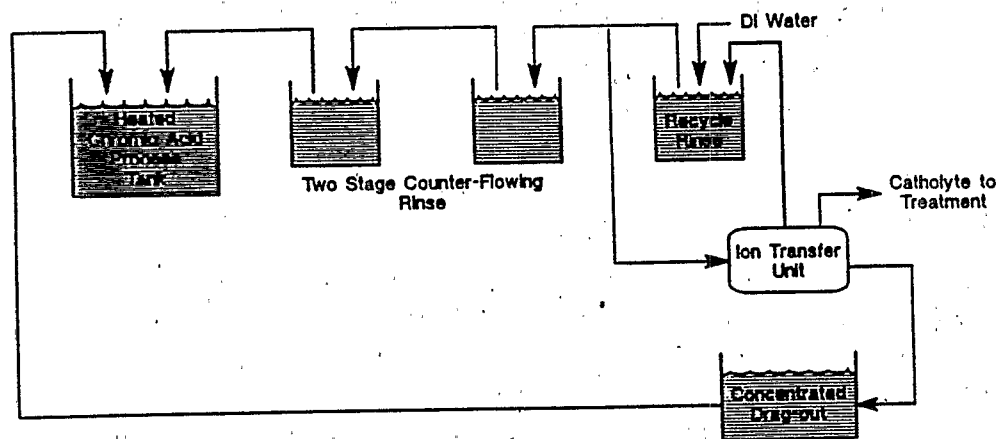


Figure 26. Typical Ion Transfer Configuration (EPA 1995)

Vendors determine the cation removal rates by the membrane area, the amperage applied to the cell, and the concentration of cations in the process fluid. Small units remove 10 to 50 cations per day while a multi-cell unit can remove up to 1,000 grams per day. Generally, removal rates fall sharply when the concentration of cations is below 3 grams per liter in the process fluid. Units usually are sized to remove cations at a rate near or somewhat faster than the introduction rate (EPA 1995).

### Applications and Restrictions

Because of relatively low cation removal rates, ion transfer is best suited to maintaining relatively clean baths rather than attempting to clean highly concentrated ones. Tramp metal concentrations of 4 grams per liter can be achieved with this technology. Achieving lower concentrations, if possible, will result in higher energy costs and an increase in the volume of waste catholyte. The waste catholyte can contain some chromium, which is lost during catholyte changes (EPA 1995).

Companies have applied ion transfer to aluminum and other cation removal operations such as chromic acid etch or anodizing solutions, although such applications are rare. In etch solutions, the introduction rate is quite high and a multi-cell external unit is required (EPA 1995).

### Costs

In-tank ceramic pot styles that operate with an off-the-tank rectifier can be purchased for less

than \$1,000. External units with 400 grams-per-liter removal capacities cost \$30,000 or more depending on automation and instrumentation. Operating expenses include labor, electricity, and membrane or pot replacement. Membranes can last for several years. However, the pots can be broken during cleaning and handling. Manual systems require frequent catholyte changes and operators generally clean the pot during these changes. Sludge buildup in the catholyte requires frequent cleaning. Extending the bath life, and thereby reducing chemical use and waste generation, can produce significant savings (EPA 1995).

### Membrane Electrolysis

Membrane electrolysis is one of the newer technologies for recovery in metal finishing. Membrane electrolysis units consist of a tank containing an anode and a cathode compartment separated by a selective membrane(s) and a power source. Similar to ion exchange, the resins in membrane electrolysis are ion specific. Depending upon the membrane, they allow the passage of only negative or positive ions. The use of ion-specific membranes rather than ceramic pots or polyfluorocarbon materials differentiates this technology from ion transfer or other non-ion permeable technologies (Cushnie 1994).

The primary function of membrane electrolysis, when applied as a bath maintenance technology, is to lower or maintain acceptable levels of contaminants in plating, anodizing, etching,

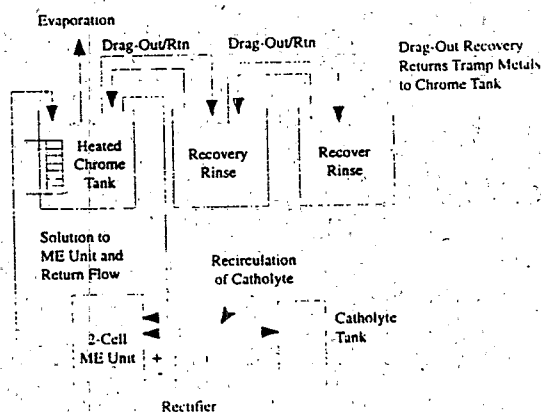


Figure 27. Configuration of Membrane Electrolysis Application for Bath Maintenance (Cushnie 1994)

stripping, and other metal finishing solutions. For the plating industry, membrane electrolysis is most applicable to the maintenance of chromic acid solutions including hard chromic and decorative chromium plating, chromic acid etching, chromic acid anodizing, and chromic acid stripping. Other potential applications include sulfuric and nitric acid and sodium hydroxide-based solutions (e.g., pickling, etching, stripping, and rust removal solutions), chromate conversion coating, and sodium dichromate deoxidizer (Cushnie 1994). Figure 27 illustrates a common configuration of membrane electrolysis.

### Costs

Costs for this technology are based on the removal of capacity of the unit and can range from \$10,000 to \$300,000. On average, however, the systems cost between \$25,000 and \$100,000. Installation costs are approximately 5 to 20 percent of the equipment costs. The main operating cost is labor. Other costs include electricity, cathodes, anodes, catholyte, and membranes.

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# 8 Alternative Methods of Metal Deposition

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Methods for depositing metal coatings such as chromium, nickel, cadmium, and copper in traditional electroplating processes have inherent pollution problems. Several alternative technologies exist to coat a substrate with metal without using electrolytic solutions or plating baths. These technologies do not eliminate the use of metal coatings, but they do eliminate the use of non-metal toxic components such as cyanide from the plating process. They also can reduce the amount of metal-contaminated wastewater and sludge that is generated from plating. These alternative technologies include thermal spray coating, vapor deposition, and chemical vapor deposition (EPA 1995).

In the future, these technologies might play a greater role in metal finishing operations. However, many of these alternative processes have high unit-plating costs and, therefore, are used only for special applications where the cost of coating is not a major consideration. Another drawback to alternative metal deposition methods is that metal overspray or tailings from remachining thick coatings from the alternative processes can actually increase waste generation (Davis 1994).

Alternative technologies for metal finishing have several features in common that distinguish them from conventional technologies. A general overview of each feature is presented below:

- ◆ **Energy:** Surface treatment energizes the surface of the workpiece so that the coating will adhere. Conventional surface finishing methods involve heating the entire part. The methods described in this section usually add energy and material onto the surface only, keeping the bulk of the object relatively cool and unchanged. In so doing, surface properties are modified with minimal change to the underlying structure of the substrate.
- ◆ **Plasmas:** The alternate technologies described in this chapter (with the exception of thermal spraying) use plasmas (e.g., clouds of electrons and ions from which particles can be extracted). Plasmas are used to reduce process temperatures by adding kinetic energy to the surface rather than thermal energy.
- ◆ **Vacuum:** Advanced surface treatments require the use of vacuum chambers to ensure proper cleanliness and control. Vacuum processes are generally more expensive and difficult to use than liquid or air processes. Facilities can expect less complicated vacuum systems to appear in the future.

Table 24 presents a summary of the various alternative coating technologies and their applications and limitations. Table 25 compares these alternatives to their conventional counterparts and presents information on the status of the technology; the surface preparation required; the relative capital and operating costs; and the relative environmental, health, and safety (EHS) risks (EPA 1995).

## Thermal Spray Coatings

The basic steps involved in any thermal coating process are:

- ◆ **Substrate preparation:** This usually involves oil/grease removal and surface roughening. Surface roughening is necessary for most of the thermal spray processes to ensure adequate bonding of the coating to the workpiece. The most common method used to perform this task is grit blasting with alumina.
- ◆ **Masking and fixturing:** Masking the part reduces the amount of overspray that an operator must strip after deposition.

Table 24. Overview of Alternative Methods for Metal Deposition (Freeman 1995)

Technology	Applications	Limitations
<b>Thermal Spray Coating:</b> <ul style="list-style-type: none"> <li>◆ Combustion torch</li> <li>◆ Electric arc</li> <li>◆ Plasma sprays</li> </ul>	Primarily repair operations although some firms now incorporate thermal spray coatings into original manufacturing processes	Technologies in varying states of development; commercial availability might be limited in certain cases
<b>Vapor Deposition:</b> <ul style="list-style-type: none"> <li>◆ Ion plating</li> <li>◆ Ion implantation</li> <li>◆ Sputtering and sputter deposition</li> <li>◆ Laser surface alloying</li> </ul>	Primarily high technology applications that can bear additional costs; expected to improve product quality and increase lifespan	Cost often limits application to expensive parts; might require improved process controls, employee training, and automation
<b>Chemical Vapor Deposition</b>	Used primarily for corrosion and wear resistance in electronics	Startup costs are high

Table 25. Comparison of Alternative Deposition Methods with Conventional Plating (Freeman 1995)

Replacement Technology	Conventional Technology	Status	Surface Prep	Operation Ease	Relative Capital Cost	Relative Operating Cost	EHS Risk
<b>Plasma and Thermal Spray</b>	Plating (electrolytic)	P	Less	Same	Higher	Same	Lower
	Plating (electroless)	P	Less	Same	Higher	Same	Lower
	Cladding	P	More	Same	Higher	Same	Lower
<b>Ion Beam Techniques</b>	Plating (electrolytic)	P	Same	Better	Higher	Higher	Lower
	Plating (electroless)	P	Same	Better	Higher	Higher	Lower
	Cladding	R	More	Better	Higher	Higher	Lower
	Case hardening	C	More	Better	Higher	Higher	Lower
	Dip/galvanizing	R	More	Better	Higher	Higher	Lower
<b>Chemical Vapor Deposition</b>	Plating (electrolytic)	P	Same	Better	Higher	Same	Lower
	Plating (electroless)	P	Same	Better	Higher	Same	Lower
	Cladding	P	More	Better	Higher	Higher	Same
	Anodizing	R	Same	Better	Higher	Same	Lower

C=Commercial, P=Pilot plant, R=Research; EHS=Environmental, health, and safety

- ◆ **Coating application:** Coatings can be sprayed from rod or wire stock or from powder material. Operators feed materials to a flame that melts it. The molten stock then is stripped from the end of the wire and atomized by a high-velocity stream of compressed air or other gases, coating the materials onto the workpiece. Depending on the substrate, bonding occurs because of mechanical interlock with a roughened surface and/or because of Van der Waals forces (i.e., mutual attraction and cohesion between two surfaces).
- ◆ **Stripping:** Stripping can be performed with acids or bases or electrolytically. If none of these techniques are possible, operators can use a grinding process, but these can be time-consuming.
- ◆ **Finishing:** The final step is finishing the workpiece. Most often it is accomplished by grinding and lapping the workpiece.

The basic parameters that affect the deposition of metals in thermal spray applications include the particle's temperature, velocity, angle of impact, and amount of reaction with gases during the deposition process. As with traditional electroplating, part geometry also influences how the surface coating is deposited. Several industries use thermal spray coatings as a substitute for plating. They include:

- ◆ Tungsten carbide replacement of chrome plating on oil field piston rods: Prior to the adoption of thermal spraying, there were considerable problems with chrome flaking. The flakes would work themselves into the cylinders, causing additional wear on the piston and cylinder. The tungsten carbide substitute has shown excellent wear characteristics and does not require recoating as the chrome finish did (except when damaged externally, resulting in longer operational life).
- ◆ Replacement of chrome-plated water rolls in the printing industry: Ceramic coatings applied by thermal spraying have replaced chrome-plated water rolls. Ceramic rolls are used because of their excellent wetting action. Chrome-plated rolls required acid etching and the use of volatile isopropyl alcohol to increase wetting action. The use of the ceramic rolls has reduced or, in some cases, eliminated the need for wetting agents. Since the rolls do not flake, they do not contaminate the water or ink (Gansert 1989).

Three basic categories of thermal spray technologies are combustion torch (e.g., flamespray, high-velocity oxy fuel, and detonation gun), electric (wire) arc, and plasma arc.

### Combustion Torch/Flame Spraying

Flame spraying involves feeding gas and oxygen through a combustion flame spray torch. A coating material in powder or wire form is fed into the flame. The coating is heated to near or above its melting point and accelerated by the combustion of the coating material. The molten droplets flow together on the surface of the workpiece to form the coating. Platers can use this technique to deposit ferrous-, nickel-, as well as cobalt-based alloys and ceramics. Companies

use combustion torches to repair machine-bearing or seal areas and to provide corrosion and wear resistance for boilers and structures (EPA 1995).

Combustion torch deposits are noted for their relatively high porosity, low resistance to impact or point loading, and limited thickness (0.5 to 3.5 millimeters). Advantages include low capital costs, simplicity of use, and relative ease of operator training. In addition, the technique uses materials efficiently and has low maintenance requirements (EPA 1995).

### Combustion Torch/High-Velocity Oxy Fuel

With high-velocity oxy fuel (HVOF) systems, the coating is heated to near or above its melting point and is deposited by a high-velocity combustion gas stream. Continuous combustion of fuels typically occurs in a combustion chamber, enabling higher gas velocities. Typical fuels include propane, propylene, or hydrogen. This technique might be an effective substitute for hard chromium plating for certain jet engine components. Typical applications include worn parts reclamation and machine buildup, abrasion-resistant seals, and ceramic hard facings (EPA 1995).

This technique has high-velocity impact. Coatings applied with HVOF exhibit little or no porosity. Deposition rates are relatively high, and the coatings have acceptable bond strength. Coating thicknesses range from 0.00013 millimeters to 3 millimeters. Some oxidation of metallics or reduction of oxides can occur, altering coating properties (EPA 1995).

### Combustion Torch/Detonation Gun

Combustion torches and detonation guns mix oxygen and acetylene with a pulse of powder containing carbides, metal binders, and oxides. This mix is introduced into a water-cooled barrel about 1 meter in length and 25 millimeters in diameter. A spark initiates detonation, resulting in expanding gas that heats and accelerates the powder materials so that they are converted into a plastic-like state at temperatures ranging from 1,100 degrees Celsius to 19,000 degrees Celsius. A complete coating is built up through repeated, controlled detonations (EPA 1995).

This technique produces some of the densest thermal coatings. Platers can use almost any metallic, ceramic, or cement materials that melt without decomposing to coat parts. Typical coating thicknesses range from 0.05 millimeters to 0.5 millimeters, but both thinner and thicker coatings can be achieved. Because of the high velocities in this application, the properties of the coatings are much less sensitive to the angle of deposition than most other spray coatings (EPA 1995).

This technology is used with a narrow range of coating materials and substrates. Oxides and carbides commonly are deposited. Because of the high-velocity impact of depositing materials such as tungsten carbide and chromium carbide, combustion torches and detonation guns can be used only on metal substrates (EPA 1995).

### Electric Arc Spraying

During electric arc spraying, an electric arc forms between the ends of two wires that are made of coating material. The arc continuously melts the ends of the wire while a jet of gas (e.g., air or nitrogen) blows the molten droplets toward the substrate. Platers can use electric arc spraying for simple metallic coatings such as copper and zinc and for some ferrous alloys. Coating deposits can be applied thinly or thickly depending on the end use. Electric arc spray coatings have high porosity and low bond strength. Industrial applications include coating paper, plastics, and other heat-sensitive materials. It is also used in the production of electromagnetic shielding devices and molds (EPA 1995).

### Plasma Spraying

Plasma spraying involves the introduction of a flow of gas (usually argon-based) between a water-cooled copper anode and a tungsten cathode. A direct current arc passes through and is ionized to form a plasma. The plasma heats the powder coating to a molten state. Compressed gas propels the material to the workpiece at high speeds. Materials suitable for plasma spraying include zinc, aluminum, copper alloys, tin, molybdenum, some steels, and numerous ceramic materials. Platers can use plasma spraying to achieve thicknesses from 0.3 to 6 millimeters depending on the coating and substrate materials.

With proper process controls, this technique can produce coatings with a wide range of selected physical properties including coatings with a wide range of porosities (EPA 1995).

Companies can use plasma spraying to deposit molybdenum and chromium on piston rings, cobalt alloy on jet engine combustion chambers, tungsten carbide on the blades of electric knives, and wear coatings on computer parts (Kirk-Othmer 1987).

## Vapor Deposition Technologies

Vapor deposition technologies include processes that put materials into a vapor state via condensation, chemical reaction, or conversion. Manufacturers use these processes to alter the mechanical, electrical, thermal, optical, corrosion resistance, and wear properties of substrates. They also use vapor deposition technologies to form freestanding bodies, films, and fibers and to infiltrate fabric-forming composite materials (EPA 1995).

This section describes physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD, the workpiece is subjected to plasma bombardment. In CVD, thermal energy heats gases in a coating chamber, driving the deposition reaction. Vapor deposition processes usually take place within a vacuum chamber (EPA 1995).

### Physical Vapor Deposition

Physical vapor deposition involves dry vacuum deposition methods in which a coating is deposited over the entire object rather than in certain areas. All reactive PVD hard coating processes combine:

- ◆ A method for depositing the metal
- ◆ An active gas such as nitrogen, oxygen, or methane
- ◆ Plasma bombardment of the substrate to ensure a dense, hard coating

The primary PVD methods are ion plating, ion implantation, sputtering, and laser surface

alloying. The production of metals and plasma differs in each of these methods (EPA 1995).

### **Ion Plating/Plasma-Based**

Plasma-based plating is the most common form of ion plating. In plasma-based plating, the substrate is placed in close proximity to a plasma. Ions then are accelerated from the plasma by a negative bias onto the substrate. The accelerated ions and high-energy neutrons from the charge-exchange processes in the plasma deposit the coating on the surface substrate with a spectrum of energies (EPA 1995).

This technique produces coatings that typically range from 0.008 millimeters to 0.025 millimeters. Advantages of ion plating include the excellent surface covering ability, good adhesion, flexibility in tailoring film properties (e.g., morphology, density, and residual film stress), and in-situ cleaning of the substrate prior to film deposition. Disadvantages include tightly controlled processing parameters, potential contamination activated in the plasma, and potential contamination of bombarded gas species into the substrate and coating (EPA 1995).

Ion plating can deposit a wide variety of metals including alloys of titanium, aluminum, copper, gold, and palladium. Manufacturers use plasma-based ion plating in the production of X-ray tubes, piping threads used in chemical environments, aircraft engine turbine blades, steel drill bits, gear teeth, high-tolerance injection molds, aluminum vacuum-sealing flanges, and decorative coatings and for corrosion protection in nuclear reactors. In addition, ion plating is widely used as an alternative to cadmium for applying corrosion-resistant aluminum coatings. Compared to other deposition processes, ion plating is relatively inexpensive (EPA 1995). Capital costs are high for ion plating, creating a significant barrier to its use. Ion plating is used mainly in value-added equipment such as expensive injection molds rather than inexpensive drill bits (EPA 1995).

### **Ion Implantation**

Ion implantation does not produce a discrete coating; rather, the process alters the elemental

chemical composition of the surface of the substrate by forming an alloy with energetic ions. A beam of charged ions of the desired element is formed by feeding a gas into the ion source where electrons, emitted from a hot filament, ionize the gas and form a plasma. An electrically biased extraction electrode focuses the ions into a beam. If the energy is high enough, ions alloy with the substrate instead of onto the surface, changing the surface composition. Three variations of ion implantation have been developed: beam implementation, direct ion implantation, and plasma source implementation (EPA 1995).

Cleaning is critical to the success of this technology. Platers must pretreat (e.g., degrease, rinse, and ultrasonically clean) the substrate to remove any surface contaminants prior to implantation. The process is performed at room temperature. Deposition time depends on the temperature resistance of the workpiece and the required dose (EPA 1995).

Platers can use ion implantation for any element that can be vaporized and ionized in a vacuum chamber. The benefits of this process include high reliability and reproducibility, elimination of post-treatment, an easily controlled process, and minimal waste generation. Ion implantation does not produce a stable finish if the coating is exposed to high temperatures. When this happens, implanted ions diffuse from the surface because of limited depth of penetration. Commercial availability of this technology is limited by a lack of familiarity, scarcity of equipment, and the need for strict quality control. Manufacturers commonly use nitrogen to increase the wear resistance of metals because nitrogen easily produces ion beams (EPA 1995).

Implantation is used primarily as an anti-wear treatment for components of high value such as biomedical devices (e.g., prostheses), tools (e.g., molds, dies, punches, cutting tools, and inserts), and gears and balls used in the aerospace industry. Other industrial applications include depositing gold, ceramics, and other materials into plastic, ceramic, and silicon and gallium arsenide substrates for the semiconductor industry (EPA 1995).

The initial capital cost of ion implantation is relatively high although large-scale systems have proven cost effective. An analysis of six systems manufactured by three companies found that coating costs range from \$0.04 to \$0.28 per square centimeter. Depending on throughput, capital costs range from \$400,000 to \$1.4 million and operating costs range from \$125,000 to \$250,000 (EPA 1995).

### Sputtering and Sputter Deposition

Sputtering is an etching process that alters the physical properties of a surface. In this process, a gas plasma discharge is set up between two electrodes: a cathode plating material and an anode substrate. Positively charged gas ions are attracted to and accelerated into the cathode. The impact knocks atoms off the cathode, which impact the anode and plate the substrate (Davis 1994). A film forms as atoms adhere to the substrate. The deposits are thin, ranging from 0.00005 millimeters to 0.01 millimeters. The most commonly applied materials are chromium, titanium, aluminum, copper, molybdenum, tungsten, gold, and silver. Three techniques for sputtering are available: diode plasmas, RF diodes, and magnetron-enhanced sputtering (EPA 1995).

Sputter deposition provides a versatile process for depositing metals, alloys, compounds, and dielectrics on surfaces. Manufacturers have used this technology to apply both hard and protective industrial coatings. Areas requiring future research and development include better methods for in-situ process control, stripping, and understanding of process controls that affect coating properties (EPA 1995).

Sputter-deposited films are used routinely in decorative applications such as watchbands, eyeglasses, and jewelry. The electronics industry relies on heavily sputtered coatings and films (e.g., thin film wiring on chips and recording heads as well as magnetic and magneto-optic recording media). Companies also use sputter deposition to produce reflective films for large pieces of architectural glass and decorative films for plastic used in the automotive industry. The food packaging industry uses sputtering to produce thin plastic films for packaging. Com-

pared to other deposition processes, sputter deposition is relatively inexpensive (EPA 1995).

### Laser Surface Alloying/Laser Cladding

Increasingly, lasers are being used for surface modification. Surface alloying is one of the many kinds of alteration processes that use lasers. This technology is similar to surface melting, but it promotes alloying by injecting another material into the melt pool that alloys into the melt layer. Surface characteristics of this technology include high-temperature performance, wear resistance, improved corrosion resistance, better mechanical properties, and enhanced appearance (EPA 1995).

One of many methods of laser surface alloying is laser cladding. The overall goal of laser cladding is to selectively coat a defined area. In laser cladding, a thin layer of metal (or powder metal) is bonded with a base metal via a combination of heat and pressure. Specifically, ceramic or metal powder is fed into a carbon dioxide laser beam above the surface of a substrate, melted in the beam, and transferred to the substrate. The beam welds the material directly into the surface region, providing a strong metallurgical bond. Powder feeding is performed using a carrier gas in a manner similar to that used for thermal spray systems. Large areas are covered by moving the substrate under the beam and overlapping deposition tracks. Pretreatment is not vital to the successful application of laser cladding coatings although the surface might require roughening prior to deposition. Grinding and polishing generally are required after the coating is applied (EPA 1995).

This technique can apply most of the same materials as thermal spraying technologies. Materials that are easily oxidized are difficult to deposit without using inert gas streams and envelopes. Deposition rates depend on laser power, power feed rates, and traverse speed. Coating thicknesses can range from several hundred microns to several millimeters. If the density is too high, however, cracking and delamination can occur as is the case with aluminum and some steels. This technology also is unable to coat areas that are out of the line of sight. Although laser processing technologies



have been in existence for many years, industrial applications are limited, partly because of high capital costs (EPA 1995).

## Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a subset of PVD as described above. Over time, the distinction between PVD and CVD has blurred as new technologies have been developed. Chemical vapor deposition includes sputtering, ion plating, plasma-enhanced CVD, low-pressure CVD, laser-enhanced CVD, active reactive evaporation, ion beam, laser evaporation, and other variations. The variations are distinguished by the way that the precursor gases are converted into the reactive gas mixtures (EPA 1995).

In CVD processes, a reactant gas mixture comes in contact with the substrate. Gas precursors are heated to form the reactive gas mixture. The coating is delivered by another precursor material, known as a reactive vapor, that can be dispensed in either a gas, liquid, or solid form. Gases are fed to the chamber under normal pressures and temperatures while solids and liquids require high temperatures and/or low pressures. Once in the chamber, energy is applied to the substrate to facilitate the coatings reaction with the carrier gas. The basic steps in the CVD processes are:

- ◆ Formation of the reactive gas mixture
- ◆ Mass transport of the reactant gas through a boundary layer to the substrate
- ◆ Adsorption of the reactants on the substrate
- ◆ Reaction of the adsorbents to form the deposit

Substrate pretreatment is important in vapor deposition, particularly in CVD. Pretreatment involves using mechanical and chemical means to minimize pretreatment before placing the substrate in the deposition reactor. Substrates must be cleaned prior to deposition and the deposition reactor chamber must be clean, leak-tight, and free of dust and moisture. Cleaning is usually performed using ultrasonic cleaning and/or vapor degreasing. To improve adhesion, vapor honing might follow. During the coating

process, operators must maintain surface cleanliness to prevent particulates from accumulating in the deposit. Manufacturers use mild acids or gases to remove oxide layers formed during heat-up. Post-treatment can include heat treatment to facilitate diffusion of the coating material (EPA 1995).

Companies use CVD mainly for corrosion and wear resistance. CVD usually is applied to obtain specific properties that are difficult to obtain with other processes. CVD's ability to control the microstructure and/or chemistry of the deposited material makes it important for some applications. The microstructure of CVD deposits depend on the chemical makeup and energy of atoms, ions, or molecular fragments; chemical composition and surface properties of the substrate; substrate temperature; and presence or absence of a substrate bias voltage. The most commonly used metals in CVD coatings are nickel, tungsten, chromium, and titanium carbide (EPA 1995).

Companies also use CVD to deposit coatings and to form foils, powders, composite materials, free-standing bodies, spherical particles, filaments, and whiskers. The majority of applications are in electronics production including structural applications, optical, opto-electrical, photovoltaic, and chemical industries. Startup costs are high (EPA 1995).

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# 9

## Design of a Modern Metal Finishing Facility

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Rarely do technical assistance providers have the opportunity to assist a facility in designing or redesigning their shop. However, if this opportunity does arise, some key points should be incorporated in the layout and design of the facility. The following section provides information on designing the overall facility and key items to consider in tank design.

The first step in designing a modern shop is containing chemicals so that the likelihood of spills and property contamination is minimized. Achieving this involves the following general requirements:

- ◆ Process islands
- ◆ Proper rinse tank design
- ◆ Bath makeup transfer systems
- ◆ Rinse-to-rinse transfer systems
- ◆ Enclosed waste lines
- ◆ Secondary containment
- ◆ Shop design
- ◆ Facility maintenance

Each of these characteristics is described in the following sections.

### Process Islands

In the past, metal finishers generally designed their shops with the cleaning line in one area, the acid room in another, and the plating process in a third. Operators carried work dripping wet from one area to another with wastewater consequently tracked around the facility. In designing a facility, work should ideally enter the process line dry, stay on a single wet-processing island, and dry before leaving that island and entering the next process. Each processing line must be independent and self-sufficient with its own cleaning, pickling, plating, and post-treatment tanks (Mooney 1994).

### Rinse Tank Design

Rinse tanks used in the process islands also should be properly designed. Proper rinse tank design is a basic component of a water conservation program. If the tanks cannot provide adequate rinsing, conservation techniques will be ineffective. Good rinse tank design is based upon the following concepts:

- ◆ Agitate rinse tanks using an oil-free, low-pressure regenerative blower. Good mixing ensures efficient equilibrium of rinse water and part design.
- ◆ Add water to the final rinse tank at the bottom of the rinse tank. The water feed should be protected by a syphon breaker and should be equipped with a flow restrictor. Individual water meters also might be incorporated.
- ◆ Eliminate accidental tank overflow by using automatic level controls.
- ◆ Design process lines with segregated spill controls.
- ◆ Minimize external piping and pumps. (Hunt 1988)

### Bath Makeup Transfers

The methods for handling the transfer of liquids among tanks and making up of fresh water varies across facilities. The most primitive method is the use of buckets and hoses. Unless operators are conscientious, this method easily can result in overflows. If tanks are filled to less than adequate levels, the rinse will not be able to clean workpieces. Proper piping and valves to handle these problems are inexpensive and should be considered standard equipment (Hunt 1988).

The best method to transfer bath makeup, either from a rinse tank or other tanks, is to incorporate a small pump that is activated by a "dead-man's" switch. As long as the switch is depressed, transfer occurs. If the operator leaves, the transfer is shut off automatically. The best pumps are magnetically driven and seamless to preclude leaks. These systems are generally available in the range of \$200 to \$300; the switch is approximately \$50. The complete system including piping and wiring should cost approximately \$500 (Hunt 1988).

In countercurrent rinsing, rinsewater makeup comes from the final rinse tank. The simplest way to maintain proper water levels for these systems is to have a local float control valve in the first rinse. This valve is similar to a toilet float valve but is designed to control the water level in the rinse tanks with the discharge side of the valve piped to the last rinse. The flow to the final rinse should be no higher than actually required. A small fixed valve or discharge pipe can limit the flow. Facilities also can use an orifice in the line to the valve. Putting a hand valve on the inlet side of the water control valve for shutoff during non-operating hours is a cost-effective solution. Systems to automatically control makeup water are inexpensive to buy and easy to install. The float valve should cost \$50 to \$100; the entire system costs approximately \$300 including connections and labor (Hunt 1988).

## Rinse-to-Rinse Transfers

The optimum equipment system for transfers among rinse tanks is a weir box and baffle arrangement. In this system, the rinse level is controlled by diverting overflow water into a weir box that contains a baffle system. This box is piped to the bottom of the next rinse tank. The baffle height in each tank should decrease about 1 inch from the preceding tank. When parts are immersed in a tank and the level rises, rinsewater cannot flow into the cleaner rinse tank and flow can enter the box area only. The same result can be achieved by installing baffling between the compartments of rinse tanks. A facility also can use a single baffle overflow, but this method is not normally adequate because the liquid from the surface of one tank simply goes to the surface

of the next. A more effective technique is a double baffle. Liquid overflows the first baffle, which controls tank level, then flows down a slot that is created by a second baffle to the bottom of the next tank. Baffles should be placed  $\frac{1}{2}$  to 1 inch apart. The second baffle must be higher than the liquid level and should stop short of the bottom of the next tank to allow liquid entrance (Hunt 1988).

An important feature of a well-designed baffle system is that liquid proceeds from the top of one tank to the bottom of the next to avoid stratification of water layers. Also, each successive tank level (going toward the process bath) must be lower by at least the maximum increase in water level that is anticipated when parts are immersed in the tank. In cases where only separate tanks are available, the solution is simple: assuming liner damage is not an issue, the plater can simply drill a hole at the top and bottom on the same side of each tank and install soft-sealed, screw-in bulkhead fittings (Viton seals are available for highly corrosive situations). The final rinse tank normally does not need a bottom fitting. The first tank does not need a top fitting unless it is to control water levels by overflow. Once holes are drilled and bulkhead fittings installed, install pipes from the top of one rinse to the bottom of the next, using in most cases  $1\frac{1}{2}$ - or 2-inch fittings unless the counterflow is small (Hunt 1988).

## Enclosed Waste Lines

Traditionally, plating shops often had trenches into which wastewater and waste solutions flow. This setup allowed toxic materials to seep into floor coatings and then leach into the ground. Most floor coatings go unmaintained for years or decades and, because the coating is on the floor with no observable dry space, operators are not able to detect leaks before damage is done. Allowing wastewater to flow into open trenches almost guarantees that the ground below will eventually become contaminated. Conveying waste in enclosed pipes is preferred. The pipes should be elevated off the floor, creating a space between the bottom of the pipe and the floor that can be checked for leaks. While few plating shops use double containment piping, design of any shop should allow enough space in the

trenches for double contained piping to be installed in the future (Mooney 1994).

## Secondary Containment

Valves and piping occasionally fail and tanks get overfilled. For this reason, as well as compliance with local sewer codes and OSHA safety rules, secondary containment is becoming increasingly necessary. Some platers believe that a curbed and coated floor is a good secondary containment device, however, plastic containment pans are often a better approach for two reasons. First, a leak in a containment pan elevated off the floor is visible and can be corrected before contamination of the ground occurs while a breach in a floor coating is almost undetectable. Second, employees must understand that the floor must be dry. Installing a floor that is designed to be wet appears to encourage operator sloppiness. Alarm horns also should be installed to detect liquids in floor sumps or containment pans (Mooney 1994).

## Shop Design

### Materials

The use of the right materials is key to a modern shop. Steel tanks and catwalks can be essentially unmaintainable. Extensive rust and corrosion can be costly, condemn housekeeping programs to failure, and demand impossibly high maintenance levels. Even worse than steel is aluminum and aluminized or galvanized materials because they corrode. In some environments, these types of products have a relatively impervious skin, but in a humid and acidic plating shop, aluminum and zinc accelerate corrosion. Steel bolts, nuts, and washers should not be used in a plating tank. Where a facility cannot easily use plastic, stainless steel hardware should be a minimum requirement.

More appropriate for use in a finishing facility is polyvinylchloride (PVC), polypropylene, and proper grades of fiberglass. These materials will last indefinitely in most plating environments without significant maintenance. Metal electrical conduits, pipes, pipe support clamps, and patent channels can be impossible to maintain in

a plating environment. When made of plastic, these items can be installed and forgotten and, with occasional cleaning, will perform like new for many years.

Depending on the process chemistry, nickel plating the anode and cathode rods and saddles is usually advantageous and results in improved appearance, corrosion resistance, and durability over copper. The copper in bus runs can be lacquered to prevent corrosion and to enhance cleanability (Mooney 1994).

### Lighting

Trying to save energy at the cost of inadequate lighting is inefficient in a metal finishing facility. The energy requirements for lighting a plating shop are minimal compared to rectification and tank heating. Inadequate lighting often can result in increased reject rates. Appropriate lighting actually saves energy. In many areas, electric utilities help pay for energy-efficient lighting fixtures (Mooney 1994).

High-pressure sodium is adequate for outdoor lighting at night, but for most operations, lighting should be white, not orange. Fluorescent lighting is adequate, but metal halide lights are even better. These lights can be mounted in the rafters so that their exposure to corrosive tank fumes is lessened, reducing the need for constant cleaning and maintenance. Another option facilities should consider is natural lighting (Mooney 1994).

### Color

Bright paint in varied colors can imply a sense of organization and purpose. Acid tanks could be painted bright red while acid rinses could be painted bright pink. Electrical panels should be blue enamel, moving parts OSHA orange, and aisles yellow. Ceilings and walls probably should be brilliant white not only for a clean appearance, but also for reflectivity (Mooney 1994).

## Facility Maintenance

A plating shop that is spotless will have far less trouble with the regulators and the public.

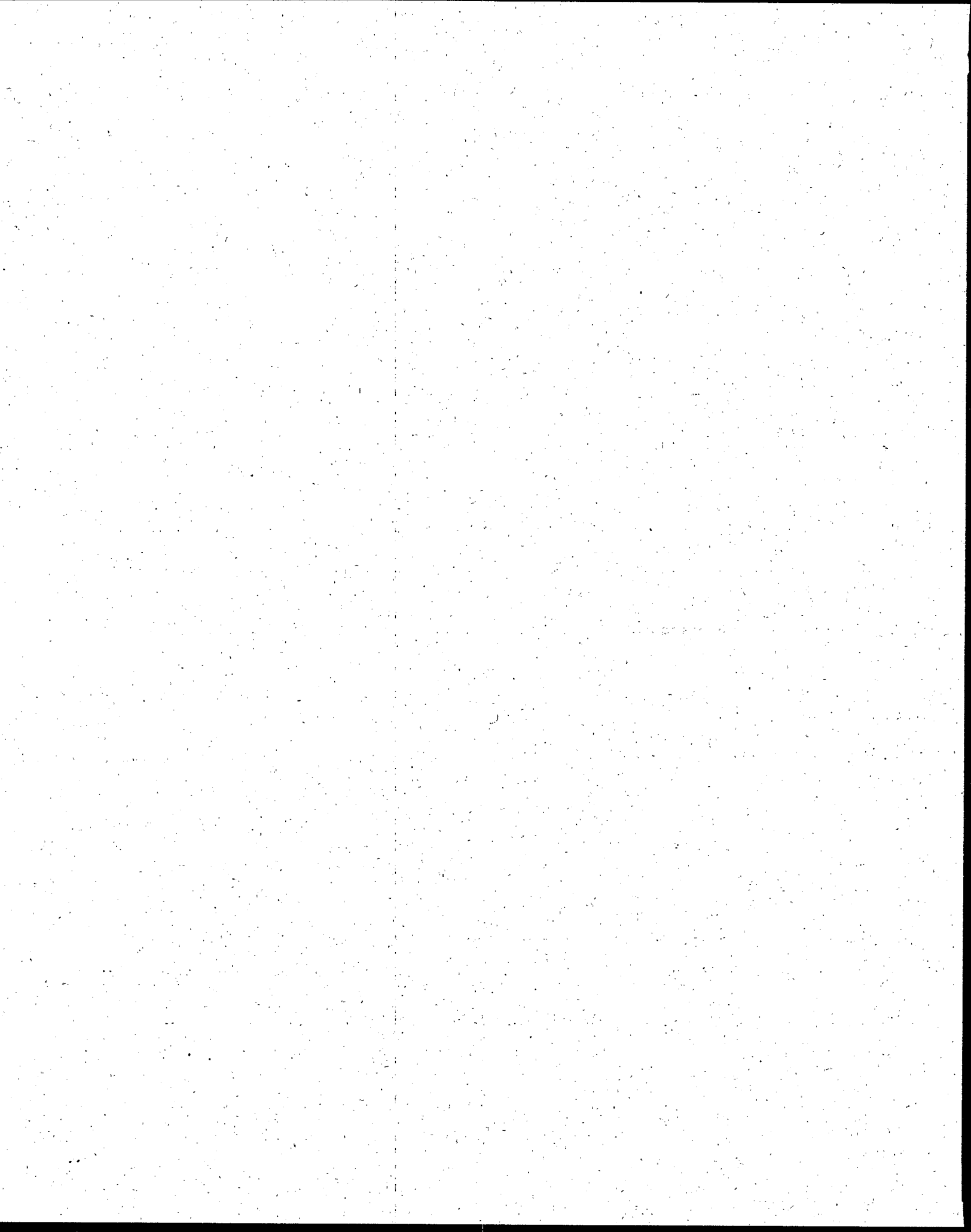
While enforcing a program of regular cleaning is important, the shop also should be designed so that cleaning is easy and practical:

Mooney, Ted E. 1994. *Plating Shops for the '90s and Beyond*. Plating and Surface Finishing. January. pp. 35-37.

- ◆ Design the process islands for easy access to all areas of the equipment. When one side or end of a tank line is inaccessible because it is against a wall, cleaning and maintaining can be impossible or dangerous. Platers should maintain aisles between walls and the process lines.
- ◆ Elevate tanks to a minimum of 12 inches off the floor so that the underside of the tanks can be readily inspected and maintained and all areas can be swept and mopped. If maintenance staff have to climb ladders or install temporary scaffolding to gain access to an area, that area probably will not be cleaned and maintained properly. Permanent access platforms can be the solution.
- ◆ Shape the contour of the floor and design of the walkways so that the amount of structure to clean, coat, and maintain is minimized. Strive for an integrated design where each piece of structure serves multiple purposes rather than tacking on this and that.
- ◆ New shops should be planned with high headroom. Exhaust ventilation is necessary for safety reasons as well as to maintain cleanliness. Designing a draft-free environment when high air-flow rates are used in a shop with low headroom can be impossible. Additionally, a high headroom shop reduces corrosion of the ceiling panels and roof supports, keeping the work environment cleaner and easier to maintain and providing better lighting and cleaner air for employees (Mooney 1994).

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# Appendix A

## Glossary

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**abrasive blasting** = A method to remove brittle materials such as millscale oxide, remains of paint etc. More generally referred to as grit blasting.

**acid** = Chemical substance whose water solutions exhibit a pH less than 7.

**acid descaling** = An alternative name for "pickling" a process using acid to dissolve oxide and scale

**activation** = Process of removing last trace of oxide on a metal surface and a thin layer of the metal itself to ensure that the metal surface to be plated is electrochemically active. (see "etching")

**addition agent** = Material used to modify the character of the deposit, usually used only in small amounts.

**alkaline descaling** = A chemical process for removing scale. A typical descaling solution uses caustic soda with additives such as detergents and chelating agents.

**alloying** = The addition of one metal to another metal or non-metal or combinations of metals. For instance, steel is an alloy of carbon and iron. Other metals are added to steels to impart specific characteristics like strength or corrosion resistance.

**"Alochrom"** = A proprietary process applied to aluminum and its alloys to improve corrosion resistance or to prepare surfaces for painting. Treatment produces an adherent aluminum oxide with some absorbed chromate.

**amalgamating** = Process in which alloys are formed with mercury such as gold, silver, iron, copper and aluminum. Due to the toxicity of mercury, use of the technique is declining

**amorphous** = Structure that is non-crystalline or without a regular structure.

**ampere** = The current that will deposit silver at the rate of 0.0011180 grams per second. Current flowing at the rate of one coulomb.

**annealing** = A heat treatment process which may be applied to all metals to soften them.

**anode** = The positive electrode in electrolysis, at which negative and positive ions are discharged, positive ions are formed, or other oxidizing reactions occur.

**anodic coating** = A protective, decorative, or functional coating formed by conversion of the surface of a metal in an electrolytic oxidation process.

**anodic etching** = A form of electrolytic etching where the workpiece is being etched is anodic in the electrolytic circuit (in electroplating, the workpiece is the cathode).

**anodizing** = A process generally applied to aluminum and its alloys to produce an adherent oxide film to impart corrosion resistance or surface hardness.

**anolyte** = The portion of an electrolyte in the vicinity of the anode. In a divided cell, the portion of the electrolyte that is on the anode side of the diaphragm.

**aquablast** = A surface cleaning process which can be applied to any material where an abrasive material is suspended in water. The resulting slurry is pressurized and ejected through a nozzle. Since higher pressures can be used in this process than in other types of blasting, surface metal can be quickly removed and leaving a good surface finish.

**barrel plating (or cleaning)** = Plating or cleaning in which the work is processed in bulk in a rotating container.

**base metal** = A metal that readily oxidizes or dissolves to form ions. The opposite of a base metal.

**basis metal** = Material upon which coatings are deposited.

**blasting** = See listing by specific medium (e.g., abrasive, dry, grit, shot, aqua)

**borax treatment** = A method of coating steel with a thin film of dry lubricant. After surface cleaning or acid pickling, the material is placed in a hot borax solution, allowed to come to solution temperature and removed and dried. The resulting alkaline coating imparts lubrication for subsequent drawing operations and provides minor corrosion protection.

**boriding** = A high temperature process used for surface hardening of mild low carbon steels.

**bright chrome plating** = Decorative chromium plate deposited directly on a nickel plate substrate.

**bright dip** = A solution used to produce a bright surface on a metal.

**bright plating** = A process that produces an electrodeposit that is luminous.

**bright throwing power** = The measure of the ability of a plating solution or a specified set of plating conditions to uniformly deposit bright electroplate upon an irregularly shaped cathode; in particular, those areas that are recessed and have a low current density area.

**brightener** = An addition agent that increases the brightness of the deposit.

**bronzing** = A chemical process generally applied to steel to impart the appearance of bronze (antimony chloride in hydrochloric acid followed by ammonium chloride in dilute acetic acid). The resulting "bronze" film does not have the corrosion resistance of true bronze.

**brush plating** = A method of plating that is applied to the metal with a brush or pad within an anode that is moved over the cathode to be plated.

**buffing** = A specific type of mechanical polishing using a high speed disc made from layers of cloth, leather, or plastic impregnated with an abrasive. The workpiece is pressed against the disc for buffing.

**building up** = Electroplating for the purpose of increasing the dimensions of an article.

**burnishing** = A form of metal finishing where the surface is treated mechanically so that no appreciable metal is removed but the surface is smoothed.

**burnt deposit** = A rough or otherwise unsatisfactory deposit produced by the application of an excessive current density and usually containing oxides or other inclusions.

**carbonitriding** = A surface hardening technique for steel in which a hydrocarbon (e.g., butane or propane) and ammonia are injected into a furnace (750 - 800 degrees Celsius) containing the workpiece. The resulting atomic carbon and nitrogen react with the surface iron to form iron carbides and iron nitrides.

**carburizing** = A process used for certain types of ductile steel which increase surface hardness from two to six times. It generally is conducted in a heat resistant box containing an atmosphere of carbon monoxide, carbon dioxide, water vapor, methane, hydrogen, and butane in correct ratios and heated to 900 degrees Celsius.

**case hardening** = A family of surface hardening processes generally applied only to steels (see specific listings for carbonitriding, carburizing, chromium plating, cyanide hardening, electroless nickel plating, and nitriding).

**casting** = A general term covering a production technique where any metal is heated until it is molten and then poured into a mold, allowed to cool and solidify.

**catalyst** = An element or ion that promotes or assists in a reaction without affecting or changing the element.

**cathode** = The negative electrode in electrolysis at which positive ions are discharged, negative ions are formed, or other reducing actions occur.

**cathodic etching** = A technique applied to steel workpieces where the workpiece is made the cathode in an electrolytic cell with sulfuric acid as the electrolyte. The anode will generally be lead or stainless steel. When a current is applied, hydrogen will be evolved at the cathode and the surface metal oxide will be reduced. The technique is usually applied immediately prior to electroplating.

**cathodic protection** = A technique applied to steel where metals anodic to iron (e.g., zinc, aluminum, magnesium) are applied to the surface on the steel workpiece to provide a corrosion resistant surface. The process relies on the fact that where a cell exists between two metals with an electrolyte, one of the metals will corrode and in the process of corroding protect the other metal.

**cation** = A positively charged ion.

**chemical polishing** = A process carried out on mild- and low-alloy steel, stainless steel, aluminum. Special solutions are used to attack the surfaces of these metals in such a manner that the peaks or corners are affected in preference to the concave surfaces. The result is a general smoothing of the surface.

**chromate coating (chromating)** = A corrosion protection technique which has many variations and can be applied to steel, aluminum, magnesium, and zinc. It results in the formation of metal oxide on the surface of the workpiece which reacts to form metallic chromates. Chromating of aluminum and magnesium improves corrosion resistance considerably. With steel it is much less permanent.

**chromium plating** = This electrodeposition of chromium is generally applied to steel in all its forms. It is usually done for decorative purposes

(bright chromium) or to provide a hard surface for engineering purposes (hard chromium). Chromium plate is nearly always deposited on top of a nickel deposit. The nickel deposit supplies corrosion resistance.

**chromizing** = A treatment applied to mild- and low-alloy steel only. It is a surface diffusion process in which chromium is alloyed with iron to create a chromium-rich surface layer. Thoroughly cleaned workpieces are placed in a heat resistant box with a proprietary powder of an unstable chromium compound. When the box is heated to over 1,000 degrees Celsius, the chromium decomposes into an active state which reacts with the iron to produce an alloy. The longer the workpiece is retained in the heated box the deeper the chromium alloy penetrates.

**cold galvanizing** = A term sometimes used to differentiate between electroplating zinc on steel from the hot dipping of steel in molten zinc. It can also refer to a form of painting with specialized paints which result in a film of up to 90 % powdered zinc. The purpose of all these processes is to provide corrosion resistance.

**coloring** = The production of desired colors onto a the workpiece using chemical or electrochemical action.

**color anodizing** = A process used only on aluminum and its alloys using dyes to color the anodic film. The anodic process produces a porous film which when fresh will absorb dyes. The anodizing is carried out using the sulfuric acid process. After completion of the anodizing the workpieces are rinsed in cold water and placed in a dye solution. After dyeing, the workpieces are again rinsed in cold water followed by immersion in nearly boiling water. The heat seals the anodic film and the surface remains permanently colored.

**complex ion** = An ion composed of two or more ions or radicals, both of which are capable of independent existence, that imparts the property of solubility necessary for electroplating.

**complexing agent** = A compound that will combine with metallic ions to form soluble ions. See *complex ion*.

**concentration polarization** = The increase in solution concentration at a membrane surface because of solution retentation.

**contact plating** = Deposition of a metal with the use of an internal source of current by immersion of the work in solution in contact with another metal.

**contact tin plating** = A form of electroless plating commonly used in the printed circuit board and general electronics industries to improve solderability of workpieces. The workpieces are immersed in a hot chemical solution containing unstable tin compounds. The tin reduces on the surface of the workpieces.

**conversion coating** = A coating produced by chemical or electro-chemical treatment of a metallic surface that provides a superficial layer containing a compound of the metal; for example, chromate coatings on zinc and cadmium or oxide coatings on steel.

**copper plating** = Copper is electrodeposited for conductivity in the printed circuit and electrical industries and for decorative purposes. There are four basic types of copper plating solutions; copper sulfate, copper cyanide, copper pyrophosphate, and copper fluoroborate.

**corrosion** = Corrosion occurs in all metals at some time and can be divided into four basic forms. Room temperature oxidation, the most common form, is most obvious in mild and low-alloy steels. The process is accelerated dramatically by comparatively small amounts of contaminants like chloride, sulfate, and fluoride. When exposed to high temperatures, metals will almost invariably result in oxidation of metal surfaces. Chemical corrosion is the result of attack by acids or alkaline compounds which dissolve the metal surface. Electrolytic corrosion occurs when two metals in contact with each other have different electrode potentials. It is a major contributor to most of the corrosion found in steels.

**covering power** = The ability of a plating solution, under a specified set of plating conditions, to deposit metal on the surfaces of recesses

or deep holes (to be distinguished from throwing power).

**cromodizing** = A name given to the chromating of steel where a film of iron chromate is formed on the surface. The corrosion protection provided by this treatment is of a very low order. "Phosphating" and oiling will probably provide superior resistance without the use of chromium.

**current density (cd)** = Current per unit area; usually expressed in amperes per square foot or amperes per square decimeter.

**cyanide hardening** = A surface hardening technique which uses molten cyanide salts to give workpieces a case containing carbon and nitrogen. Temperatures of 650 degrees to 800 degrees Celsius must be maintained for 20 - 30 minutes to be effective. The high toxicity of the cyanide makes this an expensive process due to high treatment costs.

**DC (Direct Current)** = A flow of electricity from a positively charged terminal to a negatively charged terminal.

**degreasing** = A form of cleaning which generally uses chlorinated solvents. In the most common form, a liquid solvent is heated in an open topped container. As it boils a hot vapor rises above the liquid. The vapor is held within the container by means of a cooling coil which runs around the inside of the container a short distance below the rim. This cold zone causes the vapor to condense and return to the sump for reboiling continuously distilling itself.

When any cold component is placed in the container, the vapor immediately condenses on the surface. The solvent dissolves any grease on the surface and as more solvent condenses it runs off the workpiece carrying the soluble soils into the sump.

**deposit** = Refers to the metal coating deposited on the workpiece.

**descaling** = This term describes a process that can be applied to all materials to remove scale. Scale is generally produced during manufacture

or storage. Sometimes it is easily seen in the form of rust or millscale, in other instances it is inconspicuous. Various methods are used for this process including blasting, pickling, acid or alkaline sodium hydride treatments, and polishing.

**die-casting** = A method of casting in which molten metal is poured, sometimes under pressure, into a mold or die. The die is made of metal and immediately after solidification of the casting the die opens and the casting is ejected.

**diffusion coating** = An alloy coating produced by applying heat to one or more metal coatings deposited on a metal.

**distribution** = Refers to the uniformity of the metal deposited from a plating process.

**dragin** = The water or solution that adheres to workpieces introduced into a bath.

**dragout** = The solution that adheres to a workpiece removed from a bath.

**dry blasting** = A general name given to any form of blasting where the abrasive agent is not carried in water.

**dry-form lubrication** = A form of painting applied to steel surfaces of workpieces subject to light wear or abrasion. It generally uses colloidal or molybdenum disulfide carried in a phenolic resin.

**ductility** = Refers to the flexibility of an electroplated deposit; this parameter is critical when bending and forming operations occur after plating.

**dummy (dummy cathode)** = A cathode in a plating solution that is not to be used after plating; often used for removal or decomposition of impurities.

**effluent** = Any gas or liquid emerging from a pipe or similar outlet; usually refers to waste products from chemical or industrial plants as stack gases or liquid mixtures.

**electrocleaning** = An electrochemical cleaning process by which a workpiece is first made the cathode in an electrolytic cell. When current is applied, the generation of hydrogen gas from the electrolysis of water at the surface of the workpiece results in a highly efficient scrubbing action. Following initial treatment as a cathode the circuit is reversed so that the workpiece is the anode. Oxygen gas, which is generated at the surface produces a final cleaning action.

**electrode** = A conductor through which current enters or leaves an electrolytic cell at which there is a change from conduction by electrons to conduction by charged particles of matter or vice versa.

**electrode potential** = The difference in potential between an electrode and the immediately adjacent electrolyte.

**electroforming** = A specific form of electroplating used where intricate shapes and relatively thin metal deposits are required. Molds of plastic, wax, or sometimes metals are made conductive by application of carbon or metallic powder and are plated by conventional methods. Nickel, copper, or precious metals are generally selected for this form of plating. The mold is generally removed at the completion of the plating process by one of a number of methods depending on the material from which the mold is constructed.

**electrogalvanizing** = Electrodeposition of zinc coatings.

**electroless plating** = The process of depositing metal from a water-based solution using chemical catalysts for the metal cation reduction process. In this process no external potential (electrical current) is applied.

**electrolyte** = A conducting medium in which the flow of current is accompanied by movement of matter; most often an aqueous solution of acids, bases, or salts, but includes many other media such as fused salts, ionized gases, and some solids.

**electrolysis** = Production of chemical changes by the passage of current through an electrolyte.

**electrolytic etch** = A technique generally applied to steels which attack the surface to produce a clean, oxide free material. It is often used prior to electroplating, especially chromium plating. Since it preferentially attacks edges it will open up small cracks in the surface of the workpiece. Due to this, this process can be used to inspect finishes for flaws.

**electrolytic polishing** = An electrochemical process usually applied to steels, aluminum, and aluminum alloys. This process produces a surface that is bright and highly reflective. In most instances this is used for decorative purposes and is often used in conjunction with some other form of metal finishing such as anodizing, plating, or lacquering.

**electroplating** = The process of depositing metal from an aqueous solution using an external potential (electrical current) for the metal cation reduction process; usually, the potential applied is DC, but can approach controlled AC with some sophisticated switching devices (pulsed electroplating).

**electro-osmosis** = See "reverse osmosis"

**electrorefining** = The process of anodically dissolving a metal from an impure anode and depositing it cathodically in a purer form.

**electrowinning** = The production of metals by electrolysis with insoluble anodes in solutions derived from ores or other materials.

**emulsion cleaning** = A cleaning technique which acts by emulsifying contaminants. Emulsions are mixtures of two liquids, with one liquid holding the other in a suspension similar to colloidal suspension. The liquids will typically have different polarities and will dissolve different types of materials. One of the liquids is usually water and the other will have non-polar properties. They can therefore be used to dissolve non-polar contaminants like oil and grease from metal surfaces.

**etching** = Etching is sometimes used a surface preparation technique prior to electroplating or for removal of metal such as in the printed circuit

industry where material not required on the finished product is removed by a chemical solution. It can also be used as an inspection technique due to its ability to accentuate surface cracks and defects.

**"ferrostan" process** = A method of continuous electrolytic tin plating of steel strip in which cold reduced strip is continuously fed through the cleaning, etching, plating, and rinsing processes. The solution is generally acid sulfate which produces a matte finish.

**filtration** = A means of separation where constituents are separated usually by physical methods.

**fire gilt process** = A process used exclusively in the jewelry trade in which gold dissolved in mercury (gold amalgam) is wiped on surfaces to be plated. When the article is heated the mercury is driven off leaving a gold film. The process represents a considerable health hazard due to the emission of the mercury vapor.

**flocculation** = The combination or aggregation of suspended colloidal particles in such a way that they form small clumps; usually used in conjunction with additive chemicals (flocculants) to treat wastewater.

**fluxing** = A process used in the heating of metals which may be intended to reduce or eliminate oxidation, confine the products of oxidation, reduce their melting point, and improve fluidity of surface metal layers. Fluxing is generally used in casting, welding, and soldering.

**foam blanket** = An additive that forms a layer on the surface of electroplating baths that have poor anode/cathode efficiency, to prevent any mist or spray from escaping.

**fouling** = Deposition of materials on a membrane surface or within the pores because of solubility limits (at the surface) or pore size and/or shape.

**free cyanide** = (1) *Calculated* - the concentration of cyanide or alkali cyanide present in solution in excess of that calculated as necessary to form a specified complex ion with a metal or metals present in solution. (2) *Analytical* - the free



cyanide content of a solution as determined by a specified analytical method.

**frosting** = A type of metal finishing where a fine matte finish is produced by using techniques such as acid-etching, blasting, scratch brushing or barreling.

**galvanic cell** = An electrolytic cell capable of producing electrical energy by electrochemical action.

**galvanic protection** = A general term used in the corrosion protection of steel. Technically, it refers to a metal used to protect a metal higher than itself in electrode potential. In practice, it refers to the use of zinc to protect steel.

**galvanizing** = A corrosion protection technique applied only to mild steel, cast iron, and steel alloys in which workpieces are immersed in liquid zinc at 500 degrees Celsius. A zinc/iron alloy is formed at the surface of the workpiece giving it an adherent coating of zinc. Prior to galvanizing, the metal surface must be in a state of moderate cleanliness. This is generally accomplished by light acid pickling or blasting. Galvanized coatings are generally about 0.005 inches thick and can give protection for 10 to 20 years.

**gilding** = A process in which gold is coated on the surface of another base metal. Gold leaf, a layer beaten so thin it is porous to light, is glued or beaten onto the article to be gilded. A similar method applies a fine gold powder mixed with a flammable liquid solvent applied to the article like a paint. The solvent is allowed to evaporate or in some cases may be ignited.

**gold plating** = gold has two specific properties which make it valuable in industrial and commercial uses, it resists oxidation and corrosion to a very high degree and it retains its attractive color. The main advantage of gold plating over other methods of applying gold to surfaces, is that electroplated coatings do not have pores as gilded coatings do. This provides significantly longer lifespans and corrosion resistance.

**grit blasting** = A technique of abrasive cleaning or surface preparation using sharp particles (e.g.,

cast iron shot, aluminum oxide). It covers such processes as removal of scale, corrosion, paint and other surface films. Use of free silica presents a health threat and should be avoided.

**hard chromium** = Chromium plate for engineering rather than decorative applications; not necessarily harder than the latter, but generally thicker or heavier. See "chromium plating"

**hard facing** = A term referring to processes used to harden metal surfaces and impart wear resistance by a variety of heat treatments. See "metal spraying".

**HCD (High Current Density)** = High amperes per surface area.

**hot dip coating** = See "galvanizing"

**hydrogen embrittlement** = A defect which occurs during the electroplating process. Atomic hydrogen is produced at the cathode of the workpiece being plated. This atomic hydrogen is extremely reactive and has the capability of entering the interstices of the metal. Being unstable in the atomic state, the hydrogen will combine as rapidly as possible with other atoms to form molecular hydrogen. This molecular hydrogen, having a higher unit volume than atomic hydrogen results in internal pressure in the plated metal.

**immersion plating** = A plating technique similar to electroless plating where a more electropositive metal is dissolved in an electrolyte and is plated onto the surface of a less electronegative metal workpiece. The term immersion plating is used where a deposit is obtained and the plating process then stops. This is distinguished from electroless plating where the deposition of the metal being plated continues to deposit as long as the workpiece remains in the solution.

**inchrom process** = see "Chromizing"

**indicator (pH)** = A substance that changes color when the pH of the medium is changed; in the case of most useful indicators, the pH range within which the color changes is narrow.

**indium plating** = Indium is a metal not unlike lead but with friction and corrosion resistance properties that are unique. In fact, the sole purpose of indium plating is improving the friction characteristics of very high-rated bearings.

**ion** = An electrified portion of matter of atomic or molecular dimensions.

**ion exchange** = A reversible process by which ions are interchanged between a solid and a liquid with no substantial structural changes in the solid.

**"kanigen plating"** = First proprietary process for electroless nickel plating.

**LCD (Low Current Density)** = Low amperes per surface area.

**lead plating** = lead plating does not have many common uses except in the production of electrodes for lead acid batteries. Steel which has been plated with lead is much stronger mechanically and lighter than the same thickness of pure lead. It is also used as a base layer for indium plating. Lead plating solutions contain approximately 100 grams of lead per liter and 40 grams per liter of fluoroboric acid.

**leveling** = Electrodeposited materials tend to be concentrated at sharp corners, peaks, and ridges, due to the fact that current distributed on a surface will tend to concentrate at these irregularities more than in concave surfaces such as recesses. Therefore, when a workpiece with a rough surface is electroplated, the rate of deposition will be faster on convex irregularities resulting in an accentuation of the item's original roughness. To counteract this effect, additives are added to the electrolyte solution to produce a polarization effect concentrated at the peaks and ridges. This polarization effect lowers the current density at the peaks and reduces deposition rates. The net result is to smooth or "level" the surface of the workpiece.

**mandrel** = A form used as a cathode in electroforming; a mold or matrix.

**mechanical plating** = The application of an adherent metallic coating by mechanical means involving the compacting of finely divided particles of such metal to form coherent coatings.

**membrane** = A microporous structure that acts as a highly efficient filter that allows passage of water, but rejects suspended solids and colloids; depending on membrane type, ions and small molecules might or might not be rejected.

**metal spraying** = The general term is applied to the spraying of one of several metals onto a metal substrate. In general, it is intended to produce three effects. The first, corrosion protection, usually involves the spraying of zinc or aluminum on structural steel components. It is also used on high tensile workpieces, such as those used in the aerospace industry, that can not be electroplated due to hydrogen embrittlement. The second purpose is "hard facing". Materials used in hard facing are tungsten bearing or tungsten carbide materials, cobalt, and nickel with small amounts of chromium, and high manganese chrome materials. These materials provide significant wear resistance. The third application is for salvage purposes. When engineering components are found to exhibit wear while in service, technical and economic considerations may make metal spraying to replace the wear a better alternative to replacement.

The most common method of metal spraying is "flame impingement". The technique uses powdered metal continuously fed into a high velocity flame. The flame atomizes the metal powder into a molten state and the particles are projected by the energy of the flame onto a prepared metal surface. Plasma coating is a similar method which uses radio frequency-induced plasmas at temperatures up to 30,000 degrees Celsius. This method's use is limited to high integrity components where excellent adhesion or sophisticated materials are required.

**"Micro-chem"** = A proprietary electrocleaning process used for "brightening" and "passivating" stainless steel. It is a form of electropolishing which gives a considerably smoother and shinier finish.

**micro-throwing power** = The ability of a plating solution or a specified set of plating conditions to deposit metal in tiny pores or scratches.

**mil** = One thousandth of an inch.

**nickel plating** = A very common form of electrolytic deposition that is generally used as an undercoating for subsequent deposits. There are three common solution for nickel plating: Watt's solution, Sulfuric acid, and electroless plating.

**nitriding** = A surface hardening process that is applied only to certain types of steel. This process creates a finish that is the hardest surface attainable using heat treatment processes. The process consists of maintaining a workpiece in a 500 degree Celsius ammonia atmosphere for up to 100 hours. Under these conditions atomic nitrogen combines with surface iron to form iron nitride. The nitrogen slowly diffuses away from the surface as long as the proper temperature is maintained. The resulting case thickness is therefore dependent on length of heat treatment.

**noble metal** = A metal that does not readily tend to furnish ions and, therefore, does not readily dissolve nor easily enter into such reactions as oxidations; the opposite of a base metal.

**nodule** = A rounded projection formed on a cathode during electrodeposition.

**passivation** = The cleaning of stainless steel with nitric acid to remove carbon and other impurities.

**pH adjustment** = The act of changing the pH of an aqueous solution by adding acid or caustic.

**phosphating** = A process that converts the surface of a steel workpiece to iron phosphate usually prior to painting. Before phosphating, the surface of the workpiece must be free of rust and scale. This is usually accomplished with acid pickling, mechanical wire brushing, or blasting. Phosphating is a relatively short process, usually 5 to 20 minutes. Workpieces are generally painted or chromated within 24 hours

of treatment since the phosphating provides little corrosion resistance.

**pickling** = A chemical treatment which removes oxide or scale from the surface of a metal. It most often refers to the use of sulfuric or hydrochloric acid to remove scale formed on mild and low-alloy steel during hot forming operations. Treatment of stainless steel or high nickel alloys is done with hydrofluoric acid, a particularly hazardous material that must be handled with extreme care.

**plating** = An electroplating or electroless plating process.

**plating range** = The current density range over which a satisfactory electroplate can be deposited.

**pulse plating** = A method of plating that uses a power source capable of producing square-wave current pulses.

**rack plating** = A frame for suspending and carrying current to articles during plating and related operations.

**reducing agent** = A compound that causes reduction thereby itself becoming oxidized.

**reflowing** = A technique used in the printed circuit board industry in which a component is heated in order to melt solder deposits and causing them to flow. It produces a bright, attractive looking material but its main purpose is for quality control. With reflowing, any defect on the substrate will not wet, clearly indicating areas where solder is missing.

**rustproofing** = A general term that refers to processes applied to steel. It can include painting or galvanizing, but most often refers to phosphating and similar low duty rust preventatives.

**sacrificial protection** = A corrosion protection technique that uses a metal of lower electrode potential to protect a metal of higher electrode potential. This is possible because in the presence of an electrolyte an electrochemical cell is

established in which the lower potential metal acts as an anode and the metal that is being protected acts as the cathode. The anode corrodes and deposits onto the surface of the cathode. In practice, zinc and aluminum are the two metals most commonly used for this process.

**sealing or anodic coating** = A term commonly applied to any metal process having a subsequent treatment capable of affecting a previous process coating in order to reduce staining and corrosion of the workpiece or to improve the durability of color of the coating.

**sensitizing** = A relatively non-specific term used to cover a range of metal finishing processes that improve the treatability of a workpiece for subsequent processes. It often refers specifically to a part of electroless plating procedure on plastics or non-metal surfaces. After the surface has been etched it is reacted with solution that deposits a very thin film of a metal or metallic compound. The surface is then referred to as sensitized.

**silver plating** = Silver, the easiest metal to plate, is deposited for decorative purposes on household and jewelry items. Sometimes it is used by the electrical industry where it is plated over copper to improve corrosion resistance.

**solder plating** = The term covers deposition of an alloy of 60% tin and 40% lead that is widely used in the electrical and electronics industries. It provides two valuable features, corrosion resistance and "solderability".

**stop-off** = Method of protecting portions of a workpiece from chemical processes. Waxes, lacquers, or special tapes are applied to areas to prevent chemical attack or deposition.

**strike** = (1) A thin film of metal to be followed by other coatings. (2) To plate for a short time, usually at a high initial current density.

**substrate** = Surface material or electroplate upon which a subsequent electrodeposit or finish is made. *See basis metal.*

**surface hardening** = A general term referring to methods for making the surface of steel

workpieces mechanically harder than their inner portions. Also see: "nitriding", "carburizing", "cyanide hardening", "carbonitriding".

**throwing power** = The ability to effect satisfactory coverage in recessed or blind (hole) areas of a part being plated.

**total cyanide** = The total content of cyanide expressed as the radical CN or as alkali cyanide, whether present as simple or complex ions; the sum of both the combined and free cyanide content of a solution.

**ultrafiltration** = The process that uses membranes to achieve separation of various constituents; a typical ultrafiltration membrane allows water, ions, and small molecules to pass through while rejecting large molecules and suspended solids.

**vacuum deposition** = A process in which certain pure metals are deposited on a substrate. The technique relies on the fact that, in a vacuum, pure metals can be vaporized at a low temperature in a closed container. The metal vapor will condense evenly on all surfaces to produce a metallic coating. Aluminum is the most successfully deposited material, producing a highly reflective finish.

**vapor deposition** = (1) *Chemical* - process for producing a deposit by chemical reaction, induced by heat or gaseous reduction of a vapor condensing on the substrate. (2) *Physical* - a process for depositing a coating by evaporating and subsequently condensing an element or compound, usually in a high vacuum.

**wetting agent** = A substance that reduces the surface tension of a liquid, causing it to spread more readily on a solid surface without it beading up.

**workpiece** = The part that is being electroplated or electroless plated.

**zinc coating** = See "galvanizing"

**zinc phosphating** = A process applied to freshly zinc plated workpieces that are immersed in a zinc phosphate solution acidified with

phosphoric acid. The zinc surface deposit is converted to zinc phosphate. The workpieces are then immersed in a dilute chromic acid solution to seal the zinc phosphate deposits and prevent rust formation of unsightly zinc oxide.

**zinc plating** = Common form of plating used to provide corrosion resistance for steels.

**zincate treatment** = A treatment necessary for aluminum and its alloys before electroplating. After cleaning, etching in chromic or phosphoric acid to remove oxide and dipping in nitric acid to activate the surface, workpieces are immersed in a sodium zincate solution. Metallic zinc is deposited on the surface of the workpiece. It is then rinsed and immediately brought to the final plating operation.



# Appendix B

## Resource List

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The following pages provide further sources of information on pollution prevention in metal finishing. Information is provided on regional information clearinghouses where assistance providers can locate specific documents on metal finishing. A list of technical assistance programs with experience in metal finishing also is provided. Other federally funded organizations working on metal finishing, as well as, metal finishing trade associations also are listed. A list of publications and periodicals and web sites on the industry also is provided.

### Clearinghouses

EPA's Pollution Prevention Information Clearinghouse  
401 M Street, SW MC 7409  
Washington, DC 20460  
(202) 260-1023

Waste Management and Research Center Library and Clearinghouse  
One East Hazelwood Drive  
Champaign, Illinois 61820  
(217) 333-8940

The Northeast Waste Management Officials' Association (NEWMOA) Clearinghouse  
129 Portland Street, 6th Floor  
Boston, MA 02114  
(617) 367-8558

Toxics Use Reduction Institute  
University of Massachusetts-Lowell  
One University Avenue  
Lowell, MA 01854  
(508) 934-3275

Waste Reduction Resource Center  
3825 Barrett Drive, Suite 300  
PO Box 27687  
Raleigh, NC 27611-7687  
(919) 715-6500

### Technical Assistance Programs with Expertise in Metal Finishing

Arizona Department of Environmental Quality - Pollution Prevention Program  
3033 North Central Avenue  
Phoenix, AZ 85012  
(602) 207-4210

ConnTAP  
50 Columbus Blvd., 4th floor  
Hartford, CT 06106  
Contact: Bob Brown (860) 241-0777

Delaware Pollution Prevention Program  
DNREC  
PO Box 1401, 89 Kings Highway  
Dover, DE 19903  
(302) 739-3822

Illinois Waste Management and Research Center  
One East Hazelwood Drive  
Champaign, Illinois 61820  
(217) 333-8940

Indiana Pollution Prevention and Site Materials Institute  
Purdue University  
1291 Cumberland Avenue  
Suite C-1  
West Lafayette, IN 47906-1385  
Contact: Shayla Barrett (317) 494-6450

Maine Metal Products Association  
190 Riverside Street  
Portland, ME 04103-1073  
(207) 871-8254

Massachusetts Office of Technical Assistance  
100 Cambridge Street, Room 2019  
Boston, MA 02202  
(617) 727-3260

MnTAP  
1315 5th Street SE, #207  
Minneapolis, MN 55414  
(612) 627-4556

NIST Great Lakes Manufacturing Technology  
Center  
Environmental Services Program  
Prospect Park Building  
4600 Prospect Avenue  
Cleveland, OH 44103-4314  
(216) 432-5300

North Carolina Division of Pollution Prevention  
and Environmental Assistance  
PO Box 29569  
Raleigh, NC 27626-9569  
(919) 715-6500

Pacific Northwest Pollution Prevention Research  
Center  
1326 Fifth Avenue, Suite 650  
Seattle, Washington 98101  
(206) 223-1151

Great Lakes Pollution Prevention Centre  
265 N. Front St., Suite 112  
Sarnia, ON N7T 7X1 CANADA  
Tel: (519) 337-3423

Rhode Island Pollution Prevention Program  
83 Park Street  
Providence, RI 02903  
(401) 277-3434

Solid and Hazardous Waste Education Center  
University of Wisconsin - Madison  
610 Langdon Street  
Madison, WI 53703  
(608) 262-0385

## Other Information Centers

Battelle-Pacific Northwest Laboratory  
The Pacific Northwest Laboratory (PNL) is a

public/private partnership between the federal government and Battelle Memorial Institute, and includes almost 2 million square feet of consolidated laboratory space. PNL can provide assistance to metal platers in the following areas:

- ◆ Development of waste acid distillation and recovery systems used in reclaiming spent plating and etching solutions
- ◆ Development of supercritical CO<sub>2</sub> cleaning to eliminate solvent use in fine-surface preparation prior to plating
- ◆ Development of biometric surface coatings and other advanced materials technologies that will eventually meet customer's needs for surface modification and protection without the need for chromium, cadmium, or other regulated materials

These technologies can be developed further with platers through a variety of technology development and transfer mechanisms, depending on plater's specific needs. For more information, contact Scott Butner at Battelle Seattle Research Center: (206) 528-3290.

### Canadian Pollution Prevention Resource Centre for the Metal Finishing Industry

This resource offers easy access to technical and information resources for the metal finishing industry. Linkages with international information resources provide a comprehensive range of expertise to companies seeking pollution prevention solutions. For more information, call: (800) 667-9790.

### The Energy and Manufacturing Technology Assess Project

The Energy and Manufacturing (EEM) project is a 2 year cooperative agreement between government and industry that will help manufacturers access energy, environmental, and manufacturing improvement technologies. The EEM project has produced an integrated EEM self-assessment and benchmark tool that has been used by more than 100 metal finishers to benchmark their EEM performance. A series of pilot tests are currently underway at metal finishing shops that will test a number of technologies, including a reduction of



hexavalent chrome emissions. For more information, contact Ken Sauter: (313) 769-4234.

### **National Defense Center for Environmental Excellence - Control Technologies Corporation**

The National Defense Center for Environmental Excellence (NDCEE) is a technical assistance organization that helps to integrate clean technologies into defense and private industrial facilities. NDCEE's assistance includes access to a demonstration factory that has 28 clean technologies that can be evaluated off-line, using a company's own parts. In many cases, NDCEE demonstrates the technology, trains personnel, assists in startup, and researches additional applications to achieve maximum performance. Specific technology available through NDCEE for research or testing that might be of interest to a metal finishing facility include:

- ◆ Inorganic finishing technologies such as advanced electroplating, ion plating, ion beam assisted deposition, ion implantation, plasma spray, and high velocity-oxy fuel
- ◆ Advanced cleaning technology including power washer, rotary basket, dual-use ultrasonic, advanced immersion, supercritical carbon dioxide, and honeycomb cleaning
- ◆ Water reuse/recycling technologies such as diffusion dialysis, membrane electrolysis, electrowinning, ion exchange, cross-flow microfiltration, reverse osmosis, and vacuum evaporation

The NDCEE's main demonstration facilities are located in Johnstown, Pennsylvania.

### **Research Triangle Institute**

The federal government, through the Environmental Protection Agency and Departments of Defense, Energy, and Commerce, has funded numerous pollution prevention projects related to metal finishing. Research Triangle Institute in North Carolina developed a document called the *Summary of Federal Research on Pollution Prevention in Electroplating and Surface Finishing*, which provides a project name, contact, and

brief description for 36 projects funded with federal dollars.

## **Web Sites**

### **Department of Defense (DOD) P2 Tech Library**

**Access:** [http://clean.rti.org/larry/nav\\_in.html](http://clean.rti.org/larry/nav_in.html)

This site is actually part of EnviroSenSe. It contains a variety of P2 information including data sheets on electroplating and finishing, hazardous materials/hazardous management, ozone depleting substances, painting/depainting, petroleum, oils, lubricants, and more.

### **EnviroSenSe**

**Access:** <http://es.inel.gov/>

EnviroSenSe, funded by the US EPA and the Strategic Environmental Research and Development Program (SERDP—a joint effort of DOD, DOE, and EPA) is one of the largest and most inclusive sites for pollution prevention information. Its features include: a pollution prevention forum for all levels of government, researchers, industry, and public interest groups; Solvent Umbrella, a solvent alternative information guide; ASK EPA, an interactive forum for P2 questions; a directory of federal, state, and local P2 programs; international resources; technical/research and development information; and compliance and enforcement information. Industry content guides for the commercial printing and graphic arts, electronics assembly and manufacturing, iron and steel foundries and metal finishing sectors have recently been developed.

### **Finishing.com, The Home Page of the Finishing Industry**

**Access:** <http://www.finishing.com/>

This site provides information about surface finishing, from anodizing to powder coating.

### **Metal Finishing - The On-Line Finishers Resource**

**Access:** <http://www.Metal-Finishing.com>

Metal Finishing is a resource for suppliers, metal finishers, engineers, end-users, specifiers and other professionals that need metal finishing information. This site contains searchable databases for company and product data along

with related information for the metal finishing industry. New features include web pages for on-line catalogs, new products, announcements for developments in technology, classifieds for used equipment, chemicals, and metals, and much more.

#### **The National Metal Finishing Resource Center**

**Access:** <http://www.ncms.org/nmfrc/>

The National Metal Finishing Resource Center was created to serve the needs of the metal finishing industry and their technical assistance providers. The Center offers pollution prevention and compliance assistance information, and creates a forum for information exchange.

#### **Products Finishing - The Gardner Web**

**Access:** <http://www.gardnerweb.com>

Gardner web was launched in 1995 to provide metalworking and finishing specifiers the information they need. Information on this site includes supplier information, industry event listings, and technical resources.

#### **The Society of Vacuum Coaters**

**Access:** <http://www.svc.org/>

The Society of Vacuum Coaters, a non-profit professional, trade and educational organization, is dedicated to the development of equipment and processes for high-volume production of coatings using vacuum-based processes. Its unique industrial focus targets the processing engineer and technician, end-user, equipment manufacturer, and the materials supplier. SVC seeks to disseminate knowledge, experience, and techniques to the vacuum coating industry through a variety of forums.

#### **European Journal of Cleaner Production**

**Access:** <http://telebonn.gmd.de/chemsoft/coatings>

#### **IAMS Industry Sector**

**Access:** <http://www.iams.org/p2irisde/p2iris.htm>

#### **Thomas Register**

**Access:** <http://www.thomasregister.com>

## **Trade Associations**

The American Electroplaters and Surface Finishers Society, Inc. (AESF)

12644 Research Parkway  
Orlando, FL 32826-3298  
(407) 281-6441

National Association of Metal Finishers (NAMF)

401 N. Michigan Avenue  
Chicago, IL 60611-4267  
(312) 644-6610 ext. 3479

Metal Finishers Suppliers Association

801 N. Cass Avenue, Suite 300  
Westmont, IL 60559  
(708) 887-0957

## **Publications**

#### **Guide to Cleaner Technologies: Alternative Metal Finishes**

This publication discusses alternative processes in metal plating including cleaning, material substitutes, and alternative deposition processes.

#### **Industrial Pollution Prevention Handbook**

This is a general reference book for people working on environmental projects. It contains information on 53 subjects such as pollution prevention planning, agile manufacturing, and pollution prevention in specific industrial sectors. The handbook is available from McGraw-Hill, Inc. for \$94.50. To order, call (800) 262-4729 and reference ISBN #0-07-022148-0.

#### **Metal Finishing Industry Pollution Prevention Project: Second Progress Report**

The report presents 10 site-specific pollution prevention case studies from Canada. Information is provided on plant projects, target chemicals, objectives, project descriptions, cost savings and expected reductions. For a free copy, please call the Great Lakes Pollution Prevention Centre at (800) 667-9790.

#### **Metal Finishing Pollution Prevention Guide**

This manual provides guidance to metal finishers for incorporating pollution prevention planning into their everyday business activities. Stepwise directions will help a P2 team in identifying,

prioritizing, and implementing solutions to pollution problems. Available for \$25 (Canadian) by calling (800) 667-9790.

#### **Pollution Prevention and Control Technology for Plating Operations**

This publication is the result of a survey conducted with hundreds of electroplating companies of all sizes to determine the actual track record of currently available pollution prevention techniques and pollution control equipment. A 400-page report describes the available options and summarizes the survey results. The report and associated database enables users to match their requirements and capabilities with the experience of survey respondents. The report costs \$43; the report and database cost \$48.50. To order contact CAI Engineering, 3433 Valewood Drive, Oakton, VA 22124, or call George Cushnie: (710) 264-0039.

#### **The Product Side of Pollution Prevention: Evaluating the Potential Safe Substitutes**

This publication evaluates substitutes for a variety of processes in metal plating, including cleaning, plating, and coating.

#### **Profile of the Metal Finishing Industry**

The report written by the Waste Reduction Institute for Training and Applications Research (WRITAR) provides an overview and analysis of the competitive, process, and environmental issues shaping the metal finishing industry. Energy, environment, and manufacturing technologies are described in the plating and coating areas. The report can be ordered from WRITAR for \$50 by calling (612) 379-5995.

#### **Waste Minimization for Metal Finishing Facilities**

This publication provides a detailed description of waste issues, alternative processes, and policy implications for metal finishing. To order, call EPA's Pollution Prevention Information Clearinghouse (202) 260-1023

## **Periodicals**

#### **Metal Finishing**

Metal finishing is a technical journal with information on practical and technical issues for

finishing metal and plastic products, including waste treatment and pollution control. For information on subscribing, contact Elsevier Science/Metal Finishing: (212) 633-3950.

#### **Plating and Surface Finishing**

This journal focuses on a wide variety of information related to finishing including plating, painting and cleaning. For information on subscribing contact AESF International Headquarters (407) 281-6441.

#### **Pollution Prevention Review**

This journal focuses on a wide variety of pollution prevention related topics including technical case studies, environmental management, and regulatory issues. The journal is published quarterly. For subscription inquiries, call: (212) 850-6479.

#### **Product Finishing**

Product Finishing is published on a monthly basis and provides technical information on electroplating, painting, and other finishing operations. For subscription information contact (513) 527-8800.

## **Videos**

*Rinsing Process Modifications for Metal Finishers.* 32 minutes (VHS with audio script). \$25. Available from WRITAR: (612) 379-5995.

*Pollution Prevention in Metal Finishing* Available from the North Carolina Office of Waste Reduction: (919) 715-6500.

The following videos are available from AESF. For prices and/or to place an order call: (800) 334-2052.

*The History of Electroplating with Al Weisberg.*

*The Basics of Wastewater Treatment*  
*The Role of Microfiltration in Waste Treatment*

*Avoiding Metal Finishing Disasters*

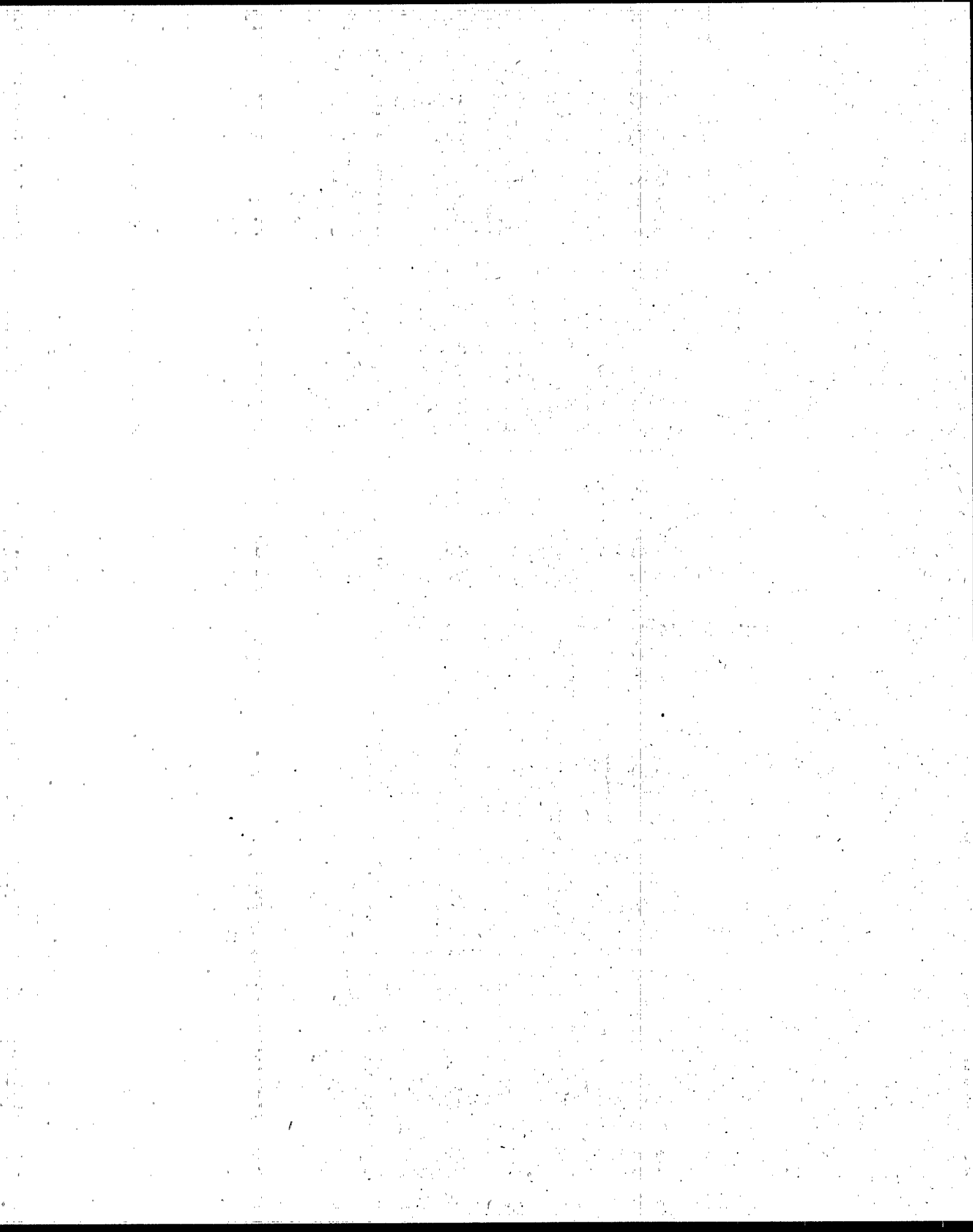
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*Making Surface Tension Measurements*

*Control of Chromium Emissions*

*Safety in Metal Finishing*

*Introduction to Electroplating and Surface Finishing*



# Reader Response Survey

## Pollution Prevention for the Metal Finishing Manual - Reader Response Survey

This manual has been published as a pilot project to develop a comprehensive pollution prevention manual for technical assistance programs for the metal finishing sector. In order to determine the utility and make improvements in future editions, we would like to hear from you. Your comments will enable us to increase the value of this document. Please take a few moments to answer some questions. When completed, simply fold in half, staple and mail the survey back. We appreciate your comments and suggestions.

Where did you learn about this report?

NEWMOA newsletter

EPA Pollution Prevention Information Clearinghouse (PPIC)

Colleague

E-mail announcement

Internet site (please name) \_\_\_\_\_

Other \_\_\_\_\_

**For the following questions, please circle the number that best describes your level of agreement with each statement.**

1. The overall quality (organization, content) of the manual was high?

5                      4                      3                      2                      1

2. The manual provided a comprehensive overview of pollution prevention techniques for metal finishing.

5                      4                      3                      2                      1

If you felt the manual was not comprehensive what information was lacking:

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Was there any information that was unnecessary or inaccurate?

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3. Information was easily located in the Manual.

5                      4                      3                      2                      1

4. Additional comments regarding the Manual

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5. What type of organization do you work for?

- Federal State Local pollution prevention assistance program
- Federal State Local environmental regulatory program
- Other government (federal, state, or local) assistance program
- Environmental consultant
- Metal finishing facility
- University-affiliated researcher
- Privately-employed researcher
- Environmental organization
- Student
- Other \_\_\_\_\_

6. Would you like to receive updated/revised copies of the metal finishing manual.

Yes

No

7. If you would like receive NEWMOA's quarterly newsletter, please complete the information below.

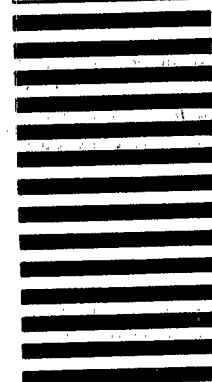
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