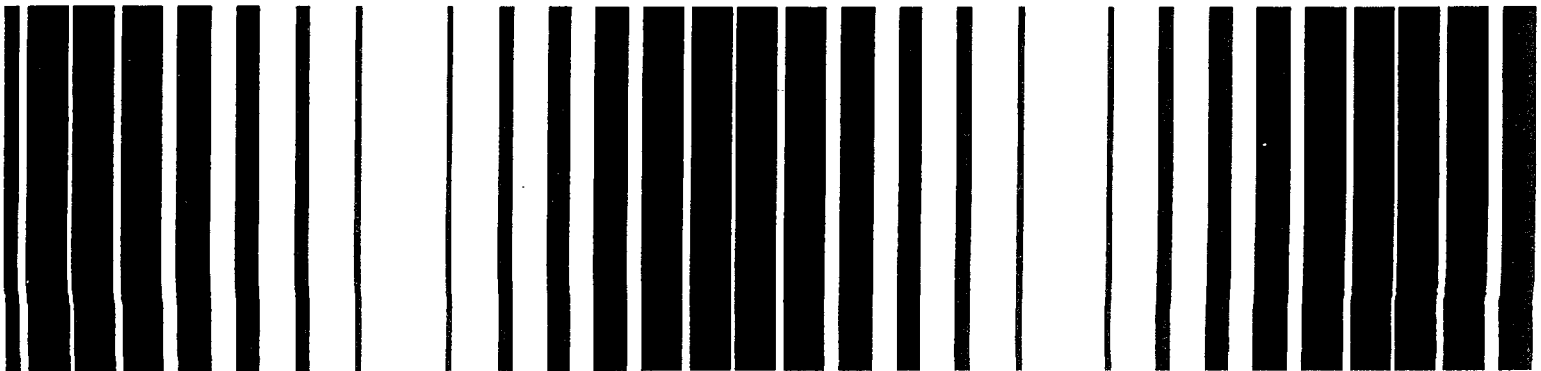




# Guide to Cleaner Technologies

## Alternative Metal Finishes



EPA/625/R-94/007  
September 1994

# **GUIDE TO CLEANER TECHNOLOGIES**

## **ALTERNATIVE METAL FINISHES**

Office of Research and Development  
United States Environmental Protection Agency  
Cincinnati, OH 45268

## **NOTICE**

This guide has been subjected to the U.S. Environmental Protection Agency's peer and administrative review and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. This document is intended as advisory guidance only to metal finishers in developing approaches for pollution prevention. Compliance with environmental and occupational safety and health laws is the responsibility of each individual business and is not the focus of this document.

Users are encouraged to duplicate portions of this publication as needed to implement a waste minimization plan.

## ACKNOWLEDGMENTS

This guide was prepared under the direction and coordination of Douglas Williams of the U.S. Environmental Protection Agency's (EPA's) Center for Environmental Research Information (CERI) and Paul Randall of the EPA Risk Reduction Engineering Laboratory (RREL), both located in Cincinnati, Ohio. Eastern Research Group, Inc. (ERG) of Lexington, Massachusetts, and Battelle of Columbus, Ohio, under contract to CERI, compiled and prepared the information used in this guide.

The following individuals participated in the development and review of this document. Their assistance is kindly appreciated.

Frank Altmayer  
Scientific Control Laboratories, Inc.  
3158 S. Kolin Avenue  
Chicago, IL 60623-4889

Theresa Harten  
Risk Reduction Engineering Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268

Jack W. Dini  
Lawrence Livermore National Laboratory  
University of California  
P.O. Box 808 L-332  
Livermore, CA 94557

William Sontag  
National Association of Metal Finishers  
1101 Connecticut Avenue NW, Suite 700  
Washington, DC 20036

# CONTENTS

	<u>Page</u>
<b>Section One</b> Introduction .....	1
<b>Section Two</b> Pollutants of Concern in the Metal Finishing Industry .....	9
<b>Section Three</b> Available Technologies .....	15
Non-Cyanide Copper Plating .....	15
Non-Cyanide Metal Stripping .....	19
Zinc-Alloy Electroplating .....	22
Blackhole Technology .....	28
Ion Vapor Deposition of Aluminum (IVD) .....	34
Physical Vapor Deposition (PVD) .....	39
Chromium-Free Surface Treatments for Aluminum and Zinc .....	42
Metal Spray Coating .....	44
<b>Section Four</b> Emerging Technologies .....	47
Nickel-Tungsten-Silicon Carbide Plating .....	47
Nickel-Tungsten-Boron Alloy Plating .....	49
In-Mold Plating .....	51
<b>Section Five</b> Pollution Prevention Strategies .....	53
<b>Section Six</b> Information Sources .....	57

---

**SECTION ONE  
INTRODUCTION**

---

**What is a Cleaner  
Technology?**

A *cleaner technology* is a source reduction or recycle method applied to eliminate or significantly reduce the amount of any hazardous substance, pollutant, or contaminant released to the environment. The emphasis of cleaner technologies is on process changes that can prevent pollution. Pollution prevention occurs through *source reduction*, i.e., reductions in the volume of wastes generated, and *source control* (input material changes, technology changes, or improved operating practices).

Cleaner technologies include process changes that reduce the toxicity or environmental impact of wastes or emissions. Processes that reduce waste toxicity by transferring pollutants from one environmental media to another (e.g., from wastewater to sludge or from air emissions to scrubber wastes) are not inherently cleaner and are not considered to be source reduction.

Cleaner technologies also include recycle methods, but recycling should be considered only after source reduction alternatives have been evaluated and implemented where technically feasible. Where they are used, recycling techniques should take occur in an environmentally safe manner.

**Why Finish Metals?**

Without metal finishing, products made from metals would last only a fraction of their present life-span. Metal finishing alters the surface of metal products to enhance properties such as corrosion resistance, wear resistance, electrical conductivity, electrical resistance, reflectivity, appearance, torque tolerance, solderability, tarnish resistance, chemical resistance, ability to bond to rubber (vulcanizing), and a number of other special properties (electropolishing sterilizes stainless steel, for example). Industries that use metal finishing in their manufacturing processes include:

- ▶ Automotive
- ▶ Electronics
- ▶ Aerospace
- ▶ Telecommunications
- ▶ Hardware
- ▶ Jewelry
- ▶ Heavy Equipment
- ▶ Appliances
- ▶ Tires

A wide variety of materials, processes, and products are used to clean, etch, and plate metallic and non-metallic surfaces. Typically, metal parts or workpieces undergo one or more physical, chemical, and electrochemical processes. Physical processes include buffing, grinding, polishing, and blasting. Chemical processes include degreasing, cleaning, pickling, etching, polishing, and electroless plating. Electrochemical processes include plating, electropolishing, and anodizing.

**Pollution Problem**

All metal finishing processes tend to create pollution problems and to generate wastes to varying degrees. Of particular importance are those processes that use highly toxic or carcinogenic ingredients that are difficult to destroy or stabilize and dispose of in an environmentally sound manner. Some of these processes are:

- ▶ Cadmium plating.
- ▶ Cyanide-based plating, especially zinc, copper, brass, bronze and silver plating.
- ▶ Chromium plating and conversion coatings based on hexavalent chromium compounds.
- ▶ Lead and lead-tin plating.
- ▶ Numerous other processes.

This guide presents information on process alternatives that can reduce or eliminate the generation of some of these wastes and emissions from metal finishing operations.

**Regulatory Environment**

The metal finishing industry is heavily regulated under numerous environmental statutes, including the Clean Water Act (CWA), Resource Conservation and Recovery Act (RCRA), Clean Air Act Amendments (CAAA), and additional state and local authorities. Emissions of cadmium, chromium, and cyanides are targeted for voluntary reduction under the U.S. EPA's 33/50 program, and emissions reporting for all three is required under the EPA's Toxic Release Inventory (TRI). These programs provide additional incentives to metal finishing facilities to reduce their waste generation and emissions.

In addition to RCRA requirements for a waste minimization program for all hazardous wastes, the Pollution Prevention Act of 1990 establishes a hierarchy that is to be used for addressing pollution problems. The Act emphasizes prevention of pollution at the source as the preferred alternative, with recycling and treatment and disposal identified as less desirable options. Many states have embraced the pollution prevention approach and now require certain categories of industrial facilities to prepare and submit pollution prevention plans detailing their efforts to reduce waste and prevent pollution.

As further regulations are passed or existing standards are revised the allowable concentrations of pollutants in emissions from metal finishing operations may continue to decrease, creating ongoing economic and compliance concerns for metal finishing industry.

**Follow-Up  
Investigation  
Procedures**

This guide covers several cleaner alternative metal finishing systems that are applicable under different sets of product and operating conditions. If one or more of these are sufficiently attractive for your operations, the next step would be to contact vendors or users of the technology to obtain detailed engineering data that will facilitate an in-depth evaluation of its potential for your facility. Section Five of this guide provides an extensive list of trade and technical associations that may be contacted for further information concerning one or more of these technologies, including vendor recommendations.

**Who Should Use this  
Guide?**

This guide should be valuable to metal finishing firms that apply all types of metal finishes to both metallic and non-metallic parts and components. Firms that apply cadmium and chromium finishes, as well as finishers that use cyanide-based baths or copper/formaldehyde solutions, will find information on alternative "cleaner" technology systems particularly useful.

The information contained in the guide can enable plant process and system design engineers to evaluate cleaner technology options for existing plants and proposed new metal finishing operations.

**What's in this Guide?**

This guide describes cleaner technologies that can be used to reduce waste and emissions from metal finishing operations. The objectives of the guide are:

- ▶ To identify potentially viable clean technologies that can reduce waste and emissions by modifying the metal finishing process.
- ▶ To provide resources for obtaining more detailed engineering and economic information about these technologies.

The following are the main pollution prevention issues discussed in the guide. In evaluating potential alternative processes and technologies, the reader is advised to explore these questions as thoroughly as possible:

- ▶ What alternate metal finishing processes are available or emerging that could significantly reduce or eliminate the pollution and/or health hazards associated with processes currently in use?
- ▶ What advantages would the alternate processes offer over those currently used?



- ▶ What difficulties would arise and need to be overcome or controlled if the alternate processes were used, including:
  - Would new or different pollution and health problems arise as a result of adopting it?
  - Would the process require significantly different process controls?
  - Would the product quality be different from present?
  - Would the consumer accept the substitute?
  - Would the process require significantly different procedures for handling rejects?
  - Would production rates be affected?
  - Would production personnel need to develop significantly different skills?
  - Would production costs be increased?
  - Would there be a need for significant capital investment?

This guide has been designed to provide sufficient information to users to help in selecting one or more candidate cleaner technologies for further analysis and in-plant testing. The guide does not recommend any single technology over any other, since site-specific and application-specific factors often can affect the relative attractiveness of alternatives.

The guide presents concise summaries of applications and operating information that can be used to support preliminary selection of clean technologies for testing in specific production settings. It is hoped that sufficient detail is provided to allow identification of possible technologies for immediate consideration in programs to eliminate or reduce waste production or toxicity.

**Organization of this Guide**

This guide is organized into five sections. Section One is an introduction to metal finishing and pollution prevention issues for the metal finishing industry. It identifies the principal metal finishing processes that give rise to environmental concerns. Section Two describes the environmental issues in further detail and serves as background to the discussions of cleaner technology alternatives addressed in Sections Three and Four. Section Three provides in-depth profiles of alternative cleaner technologies that partially or completely alleviate one or more of the environmental concerns discussed in Section Two. The technologies addressed in Section Three are considered to be "available", i.e., well-established and in use in a variety of metal finishing settings. Technologies discussed in Section Four, on the other hand, are more "emerging" in nature. They include techniques that, while not yet widespread

in use, are receiving increased attention for their pollution prevention potential. Section Five is a strategy section that provides an overview of the role of individual cleaner technologies in addressing specific environmental concerns of metal finishing facilities.

In reviewing the available and emerging technologies the reader should be aware that the need to reduce wastes and emissions has led to a considerable research effort into the development of cleaner technologies for metal finishing. Process alternatives developed from this research are in a constant state of refinement and evaluation. New developments in this area can be monitored in leading industry publications such as *Metal Finishing*, *Products Finishing*, and *Plating and Surface Finishing*. The trade associations listed in Section Six of this document are also an important source of additional information.

### Keyword List

The table on the next page presents keywords that enable the reader to scan the list of technologies and identify those that are generally available and those that are less widely used. Some but not all of the emerging technologies may still be in development or pilot stages.

The distinction between "available" and "emerging" technologies made in this guide is based upon the relative state of development of each group of technologies. It is not intended to reflect judgements concerning the ultimate potential for any one technology over any other.

**Table 1. Keyword list - cleaner technologies for metal finishing.**

General Keywords	Available Technologies	Technologies Under Development
Cleaner technology	Non-cyanide copper plating	Nickel-tungsten-silicon carbide substitute for chromium
Pollution prevention	Non-cyanide metal stripping	Nickel-tungsten-boron substitute for chromium
Source reduction	Zinc/zinc-alloy plating	In-mold plating
Source control	Blackhole Technology	
Recycling	Ion vapor deposition (IVD)	
	Physical vapor deposition (PVD)	
	Chromium-free substitutes for selected immersion processes	
	Metal spray coating	
	Trivalent chromium plating for decorative applications	

**Summary of Benefits**

The cleaner technologies described in this guide are categorized as either "available" or "emerging", depending on their level of development and extent of adoption of each technology within the industry. Available technologies include more commercially available processes that have been adopted by numerous metal finishers and are perhaps being used for more than one application. Emerging technologies are typically in a less developed state and may be currently in the advanced pilot plant stages.

Table 2 summarizes the pollution prevention, operational, and economic benefits of these metal finishing process alternatives. The reader may wish to scan this summary table to identify the cleaner technology options that best fit the operations and needs of his or her company. Detailed discussions of the benefits and operational aspects for each cleaner technology are provided in Sections Three and Four.

**Table 2. Summary of benefits - cleaner technologies for metal finishing.**

Benefits	Available Cleaner Technologies								Emerging Cleaner Technologies		
	Non-Cyanide Copper Plating	Non-Cyanide Metal Stripping	Zinc/Zinc Alloy Electroplating	Blackhole Technology	Ion Vapor Deposition	Physical Vapor Deposition	Chromium-Free Aluminum Surface Treatments	Metal Spray Coating	Nickel-Tungsten-Silicon Carbide	Nickel-Tungsten-Boron	In-Mold Plating
<b>Pollution Prevention:</b>											
Replaces cyanide	✓	✓					✓				
Replaces toxic metal			✓	✓	✓			✓	✓	✓	
Eliminates/reduces wastewater			✓	✓				✓			✓
Eliminates toxic organics			✓			✓					
<b>Operational:</b>											
Reduced process steps			✓	✓		✓					✓
Ability to automate	✓	✓	✓		✓		✓		✓	✓	
<b>Economic:</b>											
Relatively low capital costs	✓	✓	✓		✓		✓				
Relatively low operating costs		✓				✓	✓				✓
Relatively low skill level to operate	✓	✓	✓	✓	✓	✓	✓	✓			

---

**SECTION TWO  
POLLUTANTS OF CONCERN IN  
THE METAL FINISHING INDUSTRY**

---

**Introduction**

This section describes the major pollutants of concern in the metal finishing industry and the unit processes and operations that give rise to wastes and pollutants addressed by this cleaner technology guide.

**Hazardous Materials  
and Processes**

The metals finishing industry is concerned with pollution and wastes generated by all processes but especially those generated by the use of four specific materials in finishing processes: (1) the use of cadmium as a plating material, (2) the use of chromium as a plating material, (3) the use of cyanide-based electroplating solutions, and (4) the use of copper/formaldehyde-based electroless copper solutions. This section discusses the use, benefits, and hazards of each of these materials in further detail. The information presented provides background to the detailed profiles on individual pollution prevention technologies that are presented in Sections Three and Four. Most of these technologies address concerns related to cadmium and chromium plating and the use of copper/formaldehyde and cyanide-based plating solutions.

**Cadmium**

Cadmium is a common plating material that has properties superior to other metal coatings in some applications. Besides its excellent corrosion resistance, cadmium is valued for its natural lubricity. It is commonly used for plating fasteners to ensure that the fasteners pass torque-tolerance tests. These tests simulate the action of a power wrench tightening a nut on a bolt. The nut should tighten quickly under properly applied torque and hold securely thereafter. Cadmium is a soft metal with natural lubricity; these properties give cadmium good torque tolerance and bendability. Cadmium also exhibits good corrosion resistance, and meets the salt-spray test requirements of the automotive industry. It is a readily solderable metal and is toxic to fungus and mold growth. In the past, numerous military specifications have specified the use of cadmium.

The major cadmium complex used in electroplating baths is cadmium cyanide, or  $\text{Cd}(\text{CN})_4^{2-}$ . Other plating electrolytes include cadmium sulfate, sulfamate, chloride, fluoroborate, and pyrophosphate. Cadmium fluoborates are used with fluoroboric acid for electrodeposition of cadmium on high-strength steels. Cadmium oxide is dissolved in excess sodium cyanide to form the cadmium complex used in the bath most commonly used to plate cadmium.

### **Cyanide solutions**

Sodium and potassium cyanide are used in electroplating bath formulations for the deposition of copper, zinc, cadmium, silver, gold, and alloys such as brass, bronze, and alballoy (copper-tin-zinc). Electroplating baths may also utilize cyanide compounds of the metal being plated, such as copper cyanide, potassium gold cyanide, or silver cyanide. As the plating solution is consumed, complex cyanides are formed from the reaction between metals dissolved at the anode from dropped parts and the sodium or potassium cyanide (called "free" cyanide). In a well-designed wastewater treatment system, most cyanides can be destroyed (oxidized) to concentrations that comply with the CWA. Some of the complexed cyanides formed during plating, however, are resistant to conventional oxidation methods and become part of the solid waste stream (EPA Hazardous Waste Number F-006) generated by the system. Cyanides used in stripping solutions, especially those for stripping nickel, are similarly resistant to oxidation and typically must be disposed of in bulk at a high cost.

### **Copper/formaldehyde solutions**

Electroless copper deposits are frequently used to apply a conductive base to non-conductive substrates such as plastics. A thin copper deposit provides a base for an additional decorative or functional coating of copper, nickel, etc. One important application is in the coating of printed circuit boards.

Formaldehyde, a suspected carcinogen and water pollutant, is used as the reducing agent in electroless copper baths. Caustic mists resulting from hydrogen evolution and air sparging in the baths present an additional hazard.

### **Chromium**

Chromium plating falls into two basic categories depending on the service feature desired. When the goal is mainly a pleasing appearance and maintenance of appearance over time, the plating is considered "decorative". Decorative chromium plating is almost always applied over a bright nickel plated deposit, which in turn can be easily deposited on steel, aluminum, plastic, copper alloys, and zinc die castings. When chromium is applied for almost any other purpose, or when appearance is an incidental or lesser important feature, the deposit is commonly referred to as "hard chromium plating," or more appropriately, "functional chromium plating." Functional chromium plating is normally 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 plates/rolls, pistons for internal combustion engines, molds for plastic and fiberglass part manufacture, and cutting tools. Functional chromium is commonly specified for rebuilding worn parts such as rolls, molding dies, cylinder liners, and crankshafts.

Decorative chromium plating is most often less than 0.05 mils in thickness, and typically ranges from 0.005 mils to 0.01 mils. Decorative chromium plating can be found on numerous consumer items, including appliances, jewelry, plastic knobs, hardware, hand tools, and automotive trim.

**Hexavalent chromium**—Traditionally, chromium deposits are produced from an electrolyte containing hexavalent chromium ions. These deposits have a pleasing bluish-white appearance. Chemical compounds containing hexavalent chromium are used in several metal finishing operations, including plating, conversion coating, sealing of anodic coating, and enhanced adhesion of paint films on phosphated steel. Chromium plate is applied to a variety of substrates for abrasion resistance (hardness) and its resistance to household chemicals, as well as its ability to "hold" lubricants such as oils on the surface and the pleasing appearance (when plated over a bright nickel).

The main ingredient in all hexavalent chromium plating solutions is chromium trioxide ( $\text{CrO}_3$ ), a compound that contains approximately 25 percent hexavalent chromium. Other ingredients, typically present only at very low concentrations, are considered to be either catalysts or impurities. Hexavalent chromium has been linked to cancer in humans following prolonged inhalation, and is toxic to aquatic life at relatively low concentrations. Hexavalent chromium in rinsewater can be treated to very low concentrations using reducing agents such as bisulfites and sulfur dioxide.

Plating solutions based on hexavalent chromium are very low in current efficiency. As a result, much of the current (as much as 90 percent) goes towards decomposing water into oxygen and hydrogen gas. As the hydrogen and oxygen break the surface of the bath, they carry with them the bath constituents, including chromic acid, as a fine mist spray. The mist is exhausted through a ventilation system on the plating tank and captured in either a scrubber or mesh pad system. Hexavalent chromium emissions from decorative and functional chromium plating operations soon will be regulated under provisions of the Clean Air Act. These emissions are presently regulated on the local level throughout the U.S.

Hexavalent chromium plating solutions typically use lead anodes which decompose over time, forming lead chromates that must be treated and disposed of as hazardous wastes. These solutions also are frequently treated with barium compounds to control the sulfate concentration, which creates a barium sulfate that is typically soaked with chromium plating solution, and which must be disposed of as a hazardous waste.

Fugitive air emissions, water emissions from poorly treated rinsewater, and solid waste generated from hexavalent chromium plating processes can have a detrimental impact on the environment. This impact can be eliminated or reduced if a cleaner technology is used.

It is particularly difficult to substitute alternate materials for chromium because of chromium's hardness, bright appearance, resistance to commonly encountered corrosive environments, ease of application, and low cost.

Hexavalent chromium chemicals, such as chromic acid, are frequently used in metal plating applications to provide chromium coatings exhibiting hardness and aesthetic appeal. Chromium plating is used to provide a working surface for a part. It is also the standard method for improving hardness and smoothness for a wide variety of substrates, as well as the resistance to wear, abrasion, galling, or high temperatures. Typical applications are cylinder liners and pistons for internal combustion engines, and cylinders and rams for hydraulic pistons (Guffie, 1986). Chromium plating will continue to be needed for specific applications, but alternatives are available for many traditional uses. Because of environmental concerns, design engineers will be required to explore alternative technologies and be more selective in specifying chromium plating in the future.

**Trivalent chromium**—Decorative chromium plating is produced using aqueous solutions that contain either hexavalent or trivalent chromium compounds. The trivalent chromium process has been available for 20 years and is considered less toxic and more environmentally friendly because of the lower toxicity of trivalent chromium and the lower content of chromium in the plating solution. Over the last few years, several competitive plating processes based on trivalent chromium have been developed. Some of these processes yield a deposit that more closely resembles the plating produced by a hexavalent solution, albeit at a slightly higher cost and requiring more careful control of plating conditions. Functional chromium plating presently is available commercially only from the hexavalent formulation, although recent efforts to optimize trivalent chromium formulations and bath operation for hard plating show promise (Kudryavtsev and Schachameyer, 1994).

**Waste Generation and  
Waste Handling**

The major pollutants of concern in the metal finishing industry are spent solutions containing heavy metals and other toxic and noxious chemicals. Metal finishing operations typically treat these solutions in wastewater



pretreatment systems designed to meet CWA requirements. These systems in turn generate solid and liquid wastes that are regulated under the provisions of RCRA. The air emissions from many metal finishing processes must be controlled using scrubbing equipment. These can generate further wastes that must also be treated, disposed, or recycled. Some of the processing solutions used in metal finishing have a finite life, especially conversion coating solutions, acid dips, cleaners and electroless plating baths. These processes yield additional concentrated wastes that must be treated and disposed of.

Physical processes such as abrasive blasting, grinding, buffing, and polishing do not contribute as much to hazardous waste generation as chemical and electrochemical processes. The chemical and electrochemical processes are typically performed in chemical baths that are followed by rinsing operations. The most common hazardous waste sources are rinse water effluent and spent process baths.

It is important to recognize that wastes are created as a result of the production activities of the metal finishing facility, not the operation of wastewater pretreatment and air scrubbing systems. If the finishing processes were inherently "cleaner," significant progress could be made toward reducing environmental impacts.

**SECTION THREE  
AVAILABLE TECHNOLOGIES**

---

**Introduction**

This chapter describes cleaner technologies commercially available for the metal finishing industry that can reduce the finisher's reliance on one or more materials of environmental concern (e.g., cadmium, chromium, cyanide, copper/formaldehyde).

**NON-CYANIDE COPPER PLATING**

---

**Pollution Prevention  
Benefits**

Alkaline non-cyanide copper plating solutions eliminate cyanide from rinse water and sludges generated during waste treatment of the rinsewater. Non-cyanide baths contain one-half to one-quarter as much copper as full strength cyanide processes, resulting in lower sludge volume generation rates. The sludges from waste treatment of cyanide bearing rinsewater (EPA Hazardous Waste Number F-006) can be particularly difficult to dispose of because of residual cyanide content, which is regulated by RCRA to a maximum of 590 mg/kg of total cyanide and 30 mg/kg of cyanide amenable to chlorination. By eliminating cyanide from the rinsewater, compliance with cyanide regulations in wastewater discharges is ensured (in the absence of other cyanide bearing processes). Rinsewater from alkaline non-cyanide copper plating only requires pH adjustment to precipitate copper as the hydroxide. This eliminates the need for a two-stage chlorination system from the waste treatment system and avoids the use of chemicals such as chlorine and sodium hypochlorite.

**How Does it Work?**

Non-cyanide copper plating is an electrolytic process similar to its cyanide-based counterpart. Operating conditions and procedures are similar, and existing equipment usually will suffice when converting from a cyanide-based process to a non-cyanide process. Alkaline non-cyanide processes operate in a pH range of 8.8 to 9.8 compared to a pH of 13 to 14 for the cyanide processes. At least one proprietary process requires the addition of a purification/oxidation cell to the plating tank.

**Why Choose this  
Technology?**

**Applications**

Non-cyanide copper plating baths are commercially available for coating steel, brass, lead-tin alloy, zinc die cast metal, and zincated aluminum. The process can be used for rack or barrel plating. Other applications include fasteners, marine hardware, plumbing hardware, textile machinery, automotive and aerospace parts, masking applications, electro-magnetic interference (EMI) shielding, and heat treatment stop-off. Non-cyanide copper plating can be applied as a strike (thin deposit), or as a heavy plate.

### Operating Features

Non-cyanide copper plating has the following characteristics:

- ▶ Bath temperatures typically are elevated (110°F to 140°F). The pH is in the range of 8.8 to 9.8. Throwing power is as good as that of cyanide-based processes.
- ▶ Deposits have a matte appearance with a dense, fine-grained amorphous microstructure. Semi-bright to bright appearances can be obtained with the use of additives, .
- ▶ Copper ions are present in the  $\text{Cu}^{++}$  state as compared to  $\text{Cu}^{+}$  for cyanide-based baths, providing a faster plating speed at the same current density.
- ▶ Changing over to a non-cyanide process requires a lined tank and a purification compartment outside of the plating tank (for at least one commercial process). Good filtration and carbon treatment are also mandatory.

Assuming 100 percent cathode efficiency, a non-cyanide bath requires twice as much current to plate a given weight of copper as a cyanide copper bath. The non-cyanide process, however, can operate at higher current densities, yielding plating speeds that are equivalent to or faster (in barrel plating) than the cyanide process.

### Required Skill Level

Non-cyanide copper plating requires more frequent bath analysis and adjustment than does cyanide-based plating. Cyanide-based copper plating baths are relatively forgiving to bath composition. Operating personnel should be capable of operating the non-cyanide process as easily as the cyanide-based process.

### Cost

Operating costs for the bath itself are substantially higher for the non-cyanide process than the cyanide process. Because replacing the cyanide-based bath with a non-cyanide bath eliminates the need for treatment of cyanide-containing solutions, however, the cost differential between the two processes is greatly reduced. Unless a facility faces substantial compliance costs for cyanide emissions, the higher operating costs of the non-cyanide process may not justify conversion on a cost comparison basis alone.

## Reported Applications

The use of non-cyanide copper plating baths is not widespread in industry. One industry consultant reports that the number of companies running non-cyanide plating trials is small but growing (Altmayer, 1994). Of the companies that have tried the process several have switched back due to the higher costs of the non-cyanide alternative.

One application for non-cyanide plating that could be attractive from a cost perspective alone 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, since hardness throughout could cause the part to become brittle. To achieve this selective hardening, a copper mask is applied to that portion of the part which is not targeted for hardening, and the part is then treated with carbon monoxide and other gases. In addition to eliminating the use of cyanide, non-cyanide copper baths can improve production efficiency of this masking process and produce a more dense carbon deposit.

## Availability

Non-cyanide processes are commercially available from several sources. These sources typically advertise in the following trade journals:

- ▶ *Metal Finishing*
- ▶ *Plating and Surface Finishing*
- ▶ *Products Finishing*
- ▶ *Industrial Finishing*

## Operational and Product Benefits

Non-cyanide copper plating has the following benefits:

- ▶ Greatly reduces safety risks to workers.
- ▶ Greatly reduces the costs and complexity of treating spent plating solutions.
- ▶ Drag-out to an acidic bath poses no risk of HCN evolution.
- ▶ Plating solution does not have to be treated for carbonates.

Replacement of cyanide-based plating baths greatly reduces safety risks to workers. Cyanide is extremely toxic and electroplaters are most at risk for exposure to hydrogen cyanide (HCN) through ingestion and inhalation. Skin contact with dissolved cyanide salts is somewhat less dangerous but will cause skin irritation and rashes. The most likely scenario for exposure to lethal doses of HCN is an accident involving the addition of an acid to a cyanide-containing electroplating bath or the mixing of cyanide wastes with acid-containing waste streams.

**Hazards and  
Limitations**

Cyanide-based baths remove impurities so that coatings are not compromised. Non-cyanide baths are less tolerant of poor surface cleaning, so thorough cleaning and activation of the surface to be coated is critical.

With one exception, alkaline non-cyanide processes are unable to deposit adherent copper on zinc die castings and zincated aluminum parts. The exception is a supplier that claims to be able to plate such parts using a proprietary process. Several facilities are currently testing this process on a pilot scale (Altmayer, 1994). Two facilities using the process reported that the application costs approximately two to three times as much as other processes, even when waste treatment and disposal costs are included. One of the facilities discontinued use of the process, while the other facility believed that the added safety and compliance insurance was worth the cost and has continued with the process.

**Summary of  
Unknowns/State of  
Development**

Non-cyanide copper plating baths typically are developed by manufacturers of bath solutions. Chemical compositions and their formulae are proprietary information and are outside the public domain. As a result, very little has been published on development activities. According to one manufacturer, product improvement will continue for some time, although no major developments are expected.

**REFERENCES**

- Altmayer, F. 1994. Personal communication between Frank Altmayer, Scientific Laboratories, Inc. and Jeff Cantin, Eastern Research Group, Inc. April, 1994.
- Altmayer, F. 1993. Comparing substitutes for Cr and Cu, to prevent pollution. *Plating and Surface Finishing*. February. pp. 40-43.
- Barnes, C. 1981. Non-cyanide copper plating solution based on a cuprous salt. *Annual Technical Conference - Institute of Metal Finishing*. Harrogate, England (May 5-9). London: Institute of Metal Finishing.
- Humphreys, P.G. 1989. New line plates non-cyanide cadmium. *Products Finishing*. May. pp. 80-90.
- Janikowski, S.K. et al. 1989. Noncyanide stripper placement program. Air Force Engineering & Services Center. ESL-TR-89-07. May.
- Kline, G.A. 1990. Cyanide-free copper plating process. U.S. Patent 4,933,051. June 12, 1990.
- Kline, G.A. and J.M. Szotek. 1990. Alkaline non-cyanide copper plating. *Asia Pacific Interfinish '90: Growth Opportunities in the 1990s*. Singapore (November 19-22). Victoria, Australia: Australasian Institute of Metal Finishing.

Krishnan, R.M. 1990. A noncyanide copper plating electrolyte for direct plating on mild steel. *Bulletin of Electrochemistry*. 6(11). November. pp. 870-872.

---

## NON-CYANIDE METAL STRIPPING

---

### **Pollution Prevention Benefits**

The use of cyanide-based metal strippers results in the generation of cyanide-contaminated solutions. These solutions require special treatment and disposal procedures. The use of a non-cyanide stripper eliminates cyanide from the spent stripper solution. In general, these non-cyanide strippers are less toxic than their cyanide-based counterparts and more susceptible to biological and chemical degradation, resulting in simpler and less expensive treatment and disposal of spent solutions.

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.

### **How Does it Work?**

Metal strippers are used to remove metallic coatings previously deposited on parts. Metal stripping is a common practice that might be required when defective coatings have been applied, or when reconditioning of parts and reapplication of worn coatings is required. Another common use of metal strippers is rack plating where it is employed to remove coatings that build up on part holders. Cyanide-based stripping solutions act by assisting in the oxidation of the coating metal. The oxidized metal complexes with the cyanide ligand and is subsequently solubilized.

Because non-cyanide stripping solutions are typically proprietary formulations, the detailed chemistry of coating removal is not known for most solutions. Stripping solutions are available for a wide variety of coating metal/base metal combinations. Some of the stripping processes are electrolytic; others are not. Processing temperatures, bath life, ease of disposal, and other operating characteristics vary widely.

### **Why Choose this Technology?**

#### **Applications**

Metal strippers can be purchased for a wide variety of coating and substrate metals. The U.S. Air Force has performed testing on a number of non-cyanide strippers, particularly nickel and silver non-cyanide strippers. Several of these strippers have been adopted at Kelly Air Force Base. Applications are not limited to aerospace, however, and industries such as railroads (locomotive crankshafts), automotive parts, and silverware all use stripping agents prior to refinishing. In addition, stripping is a normal step

in any production line using rack plating, as racking equipment will become encrusted with plate material and must be removed on a regular basis.

### **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 temperatures as high as 180°F. Stripping processes range from acidic to basic. In general, the same equipment used for cyanide-based stripping can be used for non-cyanide stripping. With acidic solutions, however, tank liners might be needed to prevent corrosion.

### **Required Skill Level**

Personnel trained in the use of cyanide-based strippers should also be able to use non-cyanide strippers. For example, the U.S. Air Force reported that higher skill levels were not required for the non-cyanide metal strippers implemented at Kelly Air Force Base.

### **Cost**

Non-cyanide strippers will have some impact on costs:

- ▶ Waste treatment costs will be reduced when switching to non-cyanide strippers. If cyanide-based solutions are not used elsewhere in the facility, the cyanide treatment system can be eliminated.
- ▶ A large capital outlay is not required when switching to a non-cyanide stripper because the equipment requirements are generally the same.
- ▶ The costs of the makeup solutions will increase slightly.

### **Reported Applications**

Non-cyanide strippers have been available for many years. Major drawbacks of this new technology include lack of speed, etching of some substrates, and the need for electric current. As the disposal costs of cyanide-based strippers continue to escalate, however, many companies have switched to non-cyanide stripping methods. Production cycles have been adjusted to account for the slower stripping speed.

---

### Availability

A partial list of companies that supply non-cyanide strippers is found below. This list does not constitute a recommendation.

---

Circuit Chemistry Corp.	Metalline Chemical Corp.
Electrochemical, Inc.	Metalx Inc.
Frederick Gumm Chemical Company	OMI International
Kiesow International	Patclin Chemical Company
MacDermid Inc.	Witco Corporation

---

### Operational and Product Benefits

Cyanide based strippers typically contain chelating agents and strong metal-cyanide complexes that make waste treatment of spent strippers and rinsewater extremely difficult. The use of non-cyanide based strippers improves waste treatment, making it easier and more efficient.

At least one proprietary non-cyanide stripping process can crystallize stripped nickel coatings. Crystallization extends the life of the stripping solution indefinitely and creates a product that is readily recycled by commercial firms.

Non-cyanide metal strippers have the following benefits:

- ▶ Significant potential for reducing waste treatment costs.
- ▶ Often easier to recover metals from spent solutions.
- ▶ Bath life is longer because higher metal concentrations can be tolerated.

One of the main incentives for eliminating the use of cyanide-based stripping processes is to reduce health hazards to personnel. Although cyanide in solution is itself very toxic, one of the main dangers for electroplaters is the accidental addition of acid into the cyanide bath, resulting in the formation of hydrogen cyanide gas, HCN. Dermal contact with dissolved cyanide salts is less dangerous than inhaling HCN or ingesting cyanide, but it nonetheless will still cause skin irritation and rashes.



### **Section Three**

---

Facilities that consider switching to non-cyanide strippers must consider the health and safety aspects of the substitute, such as higher operating temperatures, corrosivity, and so on.

#### **Hazards and Limitations**

Non-cyanide metal strippers have some disadvantages:

- ▶ For some strippers, the recommended process temperatures are high enough to cause safety problems. Operating at lower temperatures can slow down the stripping reaction and result in a loss of effectiveness.
- ▶ Stripping rates for certain coatings might be lower than for cyanide-based counterparts.
- ▶ Some strippers can produce undesirable effects on substrate metals, even if the stripper has been recommended by the manufacturer for the application in question.

#### **Summary of Unknowns/State of Development**

The removal of nickel coatings is a major use for non-cyanide strippers. Advances in non-cyanide alternatives for nickel have been spawned by the difficulty of treating nickel-cyanide waste streams. Opportunities for further improvement still remain, however, as non-cyanide processes are significantly slower than cyanide processes (8 hours versus 1 hour). Future development will focus on speeding up the process and adjusting the product to handle different metal coatings (e.g., silver) and substrates.

#### **REFERENCES**

Janikowski, S.K., et al. 1989. Noncyanide Stripper Placement Program. Air Force Engineering & Services Center. ESL-TR-89-07. May.

### **ZINC-ALLOY ELECTROPLATING**

---

#### **Pollution Prevention Benefits**

Alloys of zinc can be used to replace cadmium coatings in a variety of applications. Cadmium is a heavy metal that is toxic to humans. In addition, electroplated cadmium coating processes normally are performed in plating solutions containing cyanide. Cyanide is highly toxic to humans and animal life. The use of both cadmium and cyanide can be eliminated by substituting an acid or non-cyanide alkaline zinc-alloy coating process for a cyanide-based cadmium electroplating process.

#### **How Does it Work?**

Both zinc and zinc-alloy electroplating processes are very common and have a long history in the electroplating industry. Recently, however, these processes have been considered as possible replacements for cadmium coatings (Zaki, 1993). Viable replacements for cadmium should provide

equivalent properties, such as corrosion protection and lubricity, at an affordable cost. The ideal cadmium coating replacement is also a non-cyanide-based process, because this also eliminates cyanide waste and associated treatment costs.

Among the zinc and zinc-alloy processes evaluated as cadmium replacements, the most promising are the following:

- ▶ Zinc-nickel
- ▶ Zinc-cobalt

Zinc alone can provide corrosion protection equivalent to cadmium at plating thicknesses above 1 mil. For thinner deposits, however, cadmium will outperform zinc. Additionally, zinc coatings cannot match the other properties for which cadmium is valued, e.g., lubricity. For this reason, zinc is not considered to have wide potential for replacing cadmium (Brooman, 1993). Similarly, alloys such as zinc-iron may not qualify because they cannot match cadmium's appearance attributes. Tin-zinc is a potential substitute for cadmium (Blunden and Killmeyer, 1993) but will probably remain prohibitively expensive for most applications.

Table 3 compares relevant properties for several zinc alloys. The identification of zinc-nickel and zinc-cobalt as the alloys with the greatest potential for as a cadmium substitute is based on their properties and on the range of applications for which these alloys have already seen commercial use (see below).

### **Why Choose this Technology?**

#### **Reported Applications**

The ability of any alternative coating to replace cadmium depends on the properties required by the application in question. Some zinc alloys have as good and in some cases better resistance to corrosion, as measured in salt spray tests. Few match cadmium for natural lubricity in applications such as fasteners, however. In addition, where cadmium is selected for its low coefficient of friction or for its low electrical contact resistance, none of the candidates mentioned above may be suitable. Table 3 indicates that applications requiring heat treatment would eliminate zinc-cobalt alloys as a substitute.

#### **Operating Features**

Some of the operating features of the zinc-nickel and zinc-cobalt alloys are listed in Table 4. Both zinc-nickel and zinc-cobalt can be plated from acid or alkaline baths.

**Table 3. Comparison of zinc alloy processes.**

	Bath Type				
	Alkaline Zinc	Alkaline Zinc-Nickel	Neutral Tin-Zinc	Alkaline Zinc-Iron	Acid Zinc-Cobalt
<b>Deposit properties</b>					
Appearance	Good	Good	Fair	Good	Excellent
Solderability	Fair	Fair	Excellent	Fair	Fair
Abrasion resistance	Fair	Good	Poor	Fair	Fair
Whisker	Fair	Good	Fair-Good	Fair	Fair
Ductility	Fair	Fair	Excellent	Fair	Fair
<b>Corrosion resistance</b>					
As plated					
To white rust	Fair	Excellent	Fair	Excellent	Fair
To red rust	Fair	Excellent	Excellent	Good	Good
Heat treated					
To white rust	Poor	Good	Poor	Poor	Poor
To red rust	Poor	Good	Fair	Poor	Poor
After bending					
To white rust	Fair	Good	Fair	Fair	Fair
To red rust	Fair	Good	Excellent	Fair	Fair
<b>Bath characteristics</b>					
Throwing power	Good	Excellent	Poor	Good	Poor
Plating speed	Fair	Poor	Good	Fair	Good
Covering power	Fair	Fair	Excellent	Fair	Fair
Bath control	Good	Fair	Fair	Fair	Fair
<b>Analysis &amp; measurement</b>					
Thickness					
X-ray fluorescence	Good	Good	Good	Good	Good
Coulometric	Good	Good	Good	Good	Good
Alloy ratio					
X-ray fluorescence	Good	Good	Good	Poor	Fair
Wet analysis	Good	Good	Good	Fair	Fair
<b>Anodes</b>	Separate	Zinc	Alloy	Zinc	Zinc

Source: Budman and Szelove (1993).

### Required Skill Level

Switching to a zinc or zinc-nickel coating process does not require any increase in operator skill level. These are conventional electroplating processes that require little or no retraining. Increased attention to bath monitoring and adjustment might be necessary because these processes are more sensitive to bath contaminants and variations in bath parameters than cyanide-based baths.

**Table 4. Bath parameters for zinc-nickel and zinc-cobalt plating.**

Properties	Plating bath				
	Acid Zinc-Nickel (rack plating)	Acid Zinc-Nickel (barrel plating)	Alkaline Zinc-Nickel	Acid Zinc-Cobalt	Alkaline Zinc-Cobalt
Bath contents	Zinc chloride, nickel chloride, potassium chloride	Zinc chloride, nickel chloride	Zinc metal, nickel metal, sodium hydroxide	Zinc metal, potassium chloride, ammonium chloride, cobalt (as metal), boric acid	Zinc, caustic soda, cobalt metal
pH	5.0-6.0	5.0-6.0	n/a	5.0-6.0	n/a
Temp °C	24-30	35-40	23-26	21-38	21-32
Cathode CD A/dm <sup>2</sup>	0.1-4.0	0.5-3.0	2-10	0.1-5.0	2.0-4.0
Anode CD A/dm <sup>2</sup>	n/a	n/a	5-7	n/a	n/a
Anodes	Zinc and nickel separately	Zinc and nickel separately	Pure zinc	Pure zinc	Steel

Source: Budman and Sizelove (1993).

Acid zinc-nickel delivers a higher nickel content than the alkaline bath (10 percent to 14 percent versus 6 percent to 9 percent). Corrosion protection increases with nickel content up to about 15 percent, thus favoring the acid bath. Acid solutions, however, tend to produce deposits with poorer thickness distribution and greater alloy variation between high and low current density areas. Alkaline baths produce a deposit featuring columnar

structures (which tend not to favor applications that require bendability), as opposed to the laminar structure deposited by the acid system. Alkaline baths are simpler to operate and are similar to conventional noncyanide zinc processes (Budman and Szelove, 1993).

Zinc-cobalt deposits contain approximately 1 percent cobalt with the remainder made up of zinc. The acid bath has a high cathode efficiency and high plating speed, with reduced hydrogen embrittlement compared to alkaline systems. Thickness distribution of the acid bath varies substantially with the current density.

#### **Cost**

Existing electroplating equipment can be used for any of these alternative processes. Therefore, a large capital expenditures would not be required to switch to an alternative process. Conversion to an acid bath, however, does require existing tanks to be relined. With older equipment, new tanks might possibly have to be installed to provide the necessary corrosion resistance.

The costs associated with cyanide waste treatment can be eliminated for any process line in which a cyanide-based cadmium process is replaced.

#### **Reported Applications**

Acid baths have been used for some time in zinc and zinc alloy plating. The desire to eliminate cyanide from the plating process has resulted in the development of non-cyanide alkaline baths and chloride-based baths for zinc coatings. The use of zinc-nickel alloys has gained ground because of their potential to replace cadmium, particularly in Japan and other countries where the use of cadmium coatings has been curtailed or prohibited for several years. Zinc-nickel alloys have been introduced in Japan and Germany in the automotive industry for fuel lines and rails, fasteners, air conditioning components, cooling system pumps, coils and couplings (Budman and Szelove, 1993). Improved warranty provisions from vehicle manufacturers such as Honda, Toyota and Mazda further boosted applications for zinc alloys. Chrysler followed with new specifications for zinc-nickel and zinc-cobalt in 1989, and Ford developed specs for alkaline zinc-nickel to replace cadmium in 1990 (Zaki, 1993). Additional applications include electrical power transmitting equipment, lock components, and the maritime, marine, and aerospace industries. Zinc-nickel coatings have also reportedly been substituted for cadmium on fasteners for electrical transmission structures and on television coaxial cable connectors (Brooman, 1993).

#### **Availability**

Zinc alloy plating systems are commercially available from numerous manufacturers. Suppliers can be identified through articles or

advertisements appearing in trade journals such as *Metal Finishing, Plating and Surface Finishing*, and *Products Finishing*.

**Operational and Product Benefits**

Replacing cyanide-based cadmium coating with one of the processes described eliminates workplace exposure to both cadmium and cyanide, and reduces environmental releases of both these chemicals.

Additional operational benefits may result depending on the properties of the alloy relative to the cadmium deposit being replaced:

- ▶ Corrosion resistance for zinc is as good as cadmium for many applications.
- ▶ Zinc-nickel alloys have better wear resistance than cadmium.
- ▶ Zinc-cobalt deposits show good resistance to atmospheres containing SO<sub>2</sub>.

As discussed, the desired properties for the application must be matched to the properties of the alloy.

**Hazards and Limitations**

Zinc and zinc-nickel alloy electroplating processes have the following disadvantages:

- ▶ Electrical contact resistance is higher for zinc than for cadmium.
- ▶ Zinc and zinc-nickel alloy coatings do not have the lubricity of cadmium coatings.
- ▶ Acid zinc coatings have comparatively poorer throwing power than cadmium, and deposits are not fully bright.
- ▶ In general, plating with non cyanide-based plating processes requires that parts be cleaner than for cyanide based processes.

**Summary of Unknowns/State of Development**

The processes outlined above are well-developed and are available from numerous vendors. These alternatives, however, have only recently been considered as replacements for cadmium coatings. Industry recognizes that the move away from cadmium plating is well underway and zinc alloys are expected to play an important role as substitute (Zaki, 1993). Nonetheless, more work needs to be done to compare these alternative coatings to cadmium for specific applications.

**REFERENCES**

- Blunden, S.J. and A.J. Killmeyer. 1993. Tin-zinc alloy plating: a non-cyanide alkaline deposition process. *1993 SUR/FIN*. pp. 1077-1081.
- Brooman, E. 1993. Alternatives to cadmium coatings for electrical/electronic applications. *Plating and Surface Finishing*. February. pp. 29-35
- Budman, E. and R. Sizelove. 1993. Zinc alloy plating. *1993 Products Finishing Directory*. pp. 290-294.
- Courter, E. 1990. Zinc-nickel alloy electroplating of components: corrosion resistance is selling point for autos. *American Metal Market*. May 17. p. 17.
- Dini, J.W. 1977. Electrodeposition of zinc-nickel alloy coatings. *Workshop on Alternatives for Cadmium Electroplating in Metal Finishing*. Gaithersburg, MD (October 4). Washington: U.S. Dept. of Energy. 38 pp.
- Hsu, G.F. 1984. Zinc-nickel alloy plating: an alternative to cadmium. *Plating and Surface Finishing*. April. pp. 52-55.
- Sharples, T.E. 1988. Zinc/zinc alloy plating. *Products Finishing*. April. pp. 50-56.
- Sizelove, R.R. 1991. Developments in alkaline zinc-nickel alloy plating. *Plating and Surface Finishing*. March. pp. 26-30.
- Wilcox, G.D. and D.R. Gabe. 1993. Electrodeposited zinc alloy coatings. *Corrosion Science*. 35(5-8). p. 1251-8.
- Zaki, N. 1993. Zinc alloy plating. *1993 Products Finishing Directory*. pp. 199-205

**BLACKHOLE TECHNOLOGY**

---

**Pollution Prevention Benefits**

The Blackhole Technology Process is an alternative to the electroless copper method used in printed wire board manufacturing. The following qualities make it environmentally attractive:

- ▶ Fewer process steps
- ▶ Reduced health and safety concerns
- ▶ Reduced waste treatment requirements
- ▶ Less water required
- ▶ Reduced air pollution

The chemistry in the Blackhole process avoids the use of metals (copper, palladium, tin) and formaldehyde used in electroless copper processes. The smaller number of process steps reduces the use of rinse water, decreasing waste treatment requirements.

**How Does it Work?**

The Blackhole Technology Process uses an aqueous carbon black dispersion (suspension) at room temperature for preparing through-holes in printed wire boards (PWBs) for subsequent copper electroplating. The carbon film that is obtained provides the conductivity needed for electroplating copper in the through-holes. The process steps are described in the following paragraphs and compared with the process steps used for the electroless copper method.

**Why Choose this Technology?**

**Applications**

The Blackhole Technology Process eliminates the need for electroless copper metalization of through-holes prior to electrolytic plating in the PWB industry. Formaldehyde, a suspected carcinogen and water pollutant, is an ingredient of the electroless copper plating process. The Blackhole process eliminates this waste stream and avoids costs and environmental/health risks associated with disposal or treatment of spent electroless copper plating solutions.

**Operating Features**

PWBs must be pretreated for desmear/etchback in both the Blackhole Technology and electroless copper processes. Permanganate is the preferred desmear process for Blackhole Technology because of its wide operating conditions and the resulting hole-wall topography.

**Process Comparison**

PWB manufacturers typically use the electroless copper process to plate through-holes. The electroless copper process consists of the following operational steps:



1. Acid cleaner	10. Rinse
2. Rinse	11. Electroless copper bath
3. Micro etch (sodium persulfate solution)	12. Rinse
4. Rinse	13. Sulfuric acid (10 percent) dip
5. Activator pre-dip	14. Rinse
6. Catalyst	15. Anti-tarnish dip
7. Rinse	16. Rinse
8. Rinse	17. Deionized water rinse
9. Accelerator	18. Forced air dry

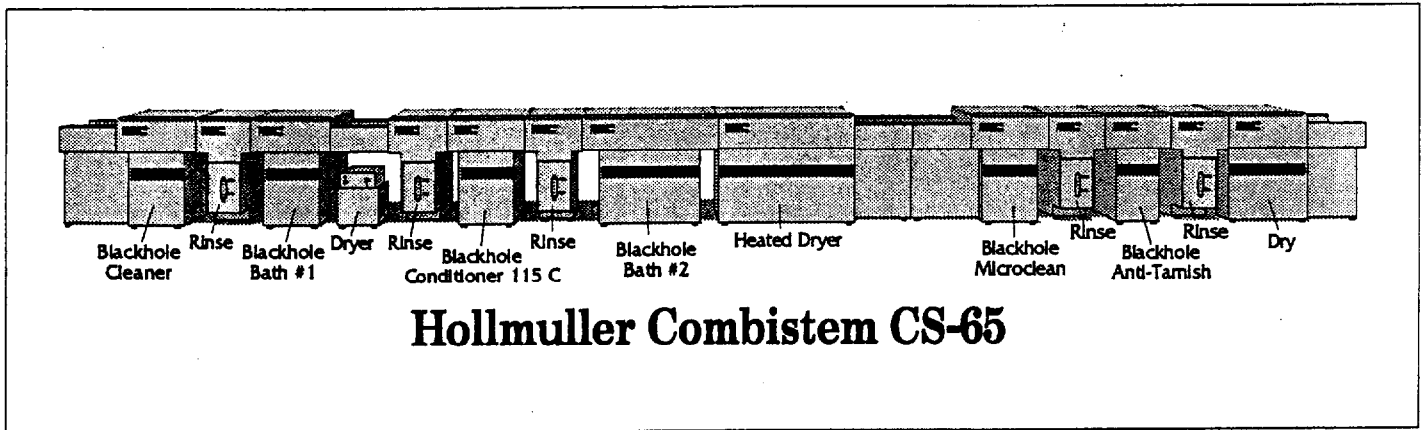
These steps are performed in order on a process line that uses an automated hoist to move racks of parts from tank to tank. All of the rinses are single use and generate large quantities of wastewater that contains copper. The rinses following the electroless copper bath (from Step 11 on) contain complexed copper, which is hard to treat using typical wastewater treatment technology, such as metal hydroxide precipitation.

The Blackhole Technology process replaces the electroless copper process for through-hole plating with a carbon black dispersion in water. The Blackhole Technology process consists of the following process steps:

1. Blackhole alkaline cleaner	7. Micro-etch
2. Rinse	8. Rinse
3. Blackhole alkaline conditioner	9. Anti-tarnish dip
4. Rinse	10. Rinse
5. Blackhole bath	11. Dry
6. Dry	

Steps 1 through 6 are performed, then repeated. Steps 7 through 11 complete the process. All process steps are performed automatically on either a horizontal conveyor system or using existing hoists and bath systems (see Figure 1).

**Figure 1**  
**Blackhole Technology Plating Line**



Source: MacDermid Inc.

The Blackhole Technology Process first uses a slightly alkaline cleaning solution containing a weak complexing agent. The solution is operated at 135°F (57°C) to remove drilling debris from the hole-wall, to clean the copper surfaces, and to prepare the hole-wall surface for the subsequent conditioning step.

A second alkaline solution containing a weak complexing agent serves as the conditioner. This solution is applied at room temperature. The conditioner neutralizes the negative charge on the dielectric surfaces, which helps to increase the absorption of the carbon in the next step.

The Blackhole Technology step uses a slightly alkaline, aqueous carbon black-based suspension operating at room temperature. The viscosity of the solution is very close to water. The carbon particles have a diameter of 150 to 250 nanometers (1500 Angstroms to 2500 Angstroms).

Conventional plating tanks and horizontal conveyerized systems can be used for the Blackhole Technology Process.

#### **Material and Energy Requirements.**

Compared to electroless copper, the Blackhole Technology Process uses fewer individual process steps. Some process steps are repeated, which reduces the floor space needed for the process baths. The number of chemicals used also is reduced. The energy requirements should be about the same, because both processes use a drier and several heated solutions.

#### **Required Skill Level**

The skill level required of system operators running the Blackhole process is the same as or less than that for electroless copper processing.

#### **Cost**

If existing process equipment is used, the only installation cost is the disposal of the electroless copper solutions, cleaning of the tanks, and replacement with the Blackhole Technology process solutions.

#### **Reported Applications**

The Blackhole Technology process has been available commercially since 1989. The technology is currently used by PWB manufacturers but is gaining acceptance. Military Standard MIL-P-55110D now permits through-hole plating technologies other than electroless copper.

### Availability

The Blackhole Technology process is sold by Mac Dermid (formerly Olin Hunt).

### Operational and Product Benefits

*Process Simplification*—The Blackhole technology requires fewer process steps as well as associated chemicals and rinses, greatly reducing waste streams from PWB plating.

*Contamination Reduction*—Unlike the electroless copper process, the Blackhole Technology Process does not use formaldehyde.

*Ease of Implementation*—Because the Blackhole process uses existing equipment in an electroless copper process line, it should be very easy to implement.

*Acceptable Product Quality*—Product quality should not be affected. The Blackhole Technology process is accepted under MIL-P-5511OD.

*Lower Operating Costs*—The Blackhole process results in reduced costs for chemicals, water, and wastewater treatment.

### Hazards and Limitations

By using a carbon black suspension, the Blackhole process avoids the use of metals (copper, palladium, and tin) and formaldehyde. The process solutions used in the Blackhole process are mildly alkaline and pose a small skin/eye irritation hazard. Overall health risks would be significantly reduced if the electroless copper process was replaced by the Blackhole Technology Process.

### State of Development

The Blackhole Technology is commercially available.

### REFERENCES

Battisti, A.J. 1986. Blackhole: beyond electroless copper. In *Proceedings, National Electronic Packaging and Production Conference*. Anaheim, CA: February 25-27. Vol. 2. pp. 271-37.

Olin Hunt. Undated. Blackhole Technology. Olin Hunt, 5 Garret Mountain Plaza, West Paterson, NJ 07424. Product literature.

Plakovic, F. 1988. Blackhole - a description and evaluation. Presented at IPC Fall Meeting. Anaheim, CA: October 24-28. IPC-TP-754.

*Printed Circuit Fabrication*. 1990. Blackhole update. 13(5). May. pp. 36-42.

## **ION VAPOR DEPOSITION OF ALUMINUM (IVD)**

---

### **Pollution Prevention Benefits**

Electroplated cadmium coating processes normally use plating solutions that contain cyanide. Cadmium is a heavy metal that is toxic to humans. In addition, cyanide is highly toxic to humans and animal life. Aluminum coatings deposited through ion vapor deposition (IVD) can replace cadmium coatings in some applications, eliminating the use of both cadmium and cyanide. Aluminum is considered nontoxic, and IVD does not employ or create any hazardous materials.

### **How Does it Work?**

In IVD, the coating metal is evaporated and partially ionized before being deposited on the substrate. A typical IVD system consists of a steel vacuum chamber (measuring 6 feet in diameter by 12 feet in length), a pumping system, a parts holder, an evaporation source, and a high-voltage power supply.

Parts to be coated must be clean to ensure good adhesion of the coating. To minimize surface contamination, parts are treated frequently with a dry blasting process using pure aluminum oxide mesh (150-220 mesh). Parts then are loaded into the chamber on racks, or suspended on hooks from the ceiling. The chamber may hold as few as 2 large parts to as many as 1,000 small parts.

Once loaded, a vacuum is drawn on the chamber to remove trace gases and vapors from the parts, racks, and chamber shields. The chamber is then backfilled with argon to 10 microns, and a large negative potential is applied between the evaporation source and the parts to be coated. The argon ions created by the potential difference bombard the part surfaces, dislodging substrate atoms and removing surface contamination (sputtering). As this occurs, the parts typically emit a glow of light. This gas cleaning cycle lasts approximately 10 to 20 minutes.

The evaporation apparatus consists of a series of concave ceramic "boats" through which a thin strand of aluminum wire is continuously fed. These boats can move back and forth between the parts to ensure even coverage. A high current supplied to the boat melts and vaporizes the aluminum. Once evaporated, the aluminum atoms collide with high-energy electrons in the chamber and become ionized. The positively aluminum charged ions accelerate toward the negatively charged substrate, condensing to form a protective metal coating.

The coating process itself can take between 1 hour and 2.5 hours, depending on the configuration of the parts and the desired coating thickness.

**Why Choose this Technology?**

**Applications**

IVD aluminum coatings can be applied to a wide variety of metallic substrates, including aluminum alloys, and most recently, to plastic/composite substrates. To date, IVD has been mainly used on high-strength steels in the aerospace industry and for some marine applications. According to Nevill (1993), IVD and paint currently are specified as the prime coatings on three leading Department of Defense missile contracts (Patriot, Amraam, and Lantirn). IVD has replaced anodize on fatigue-critical structures such as wing sections and bulkheads on both military and commercial aircrafts. Lansky (1993) reports that approximately 80 percent of aircraft parts currently coated with cadmium can be coated with IVD aluminum with no change in corrosion control or performance.

IVD aluminum coatings tend to be porous when applied. Burnishing with glass media often is used to reduce porosity and improve the durability of the finish. Thin coatings of IVD aluminum (0.001 inches) may exhibit low corrosion resistance. Such parts are often chromated after the coating is applied to improve corrosion resistance.

IVD coatings tend to be brittle on fatigue-prone substrates and are applied most often to parts that are not subject to fatigue in service. A common application is steel fasteners on aluminum parts, which must be coated to avoid galvanic corrosion in service. IVD aluminum is ideal since identical metal provides for zero galvanic corrosion potential, and the steel core provides much higher strength than solid aluminum fasteners.

Advantages of IVD aluminum coatings are the uniformity of thickness and the excellent "throwing power" that results from the scattering of metal ions. Deposition is not limited strictly to "line of sight" applications, and parts with complex shapes, such as fasteners, can be coated successfully. The process is limited, however, in its ability to deposit coating into deep holes and recesses. In configurations where hole depth exceeds the diameter, for example, thickness distribution can drop off substantially. The reduced thickness in these areas may not be significant since the relevant military specification (MIL-C-83488C) requires coating of recessed areas without specifying the required thickness of the deposit.

**Operating Features**

IVD has the following operating features:

- ▶ Large and/or complex parts can be plated.
- ▶ Somewhat limited to "line of sight" applications.
- ▶ There is no buildup of the coating on sharp edges, such as can occur in electroplating.

### **Required Skill Level**

Although equipment for IVD is entirely different that used in electroplating, operators who have performed cadmium electroplating have sufficient skills and education to be retrained to perform IVD. Maintenance of the equipment would require significant retraining. Although the equipment requires less routine maintenance overall, proper maintenance of vacuum pumps, in particular, is critical to the operation.

### **Cost**

Capital costs and operating costs for aluminum IVD equipment are significantly higher than electroplating, but are partially offset by reduced waste treatment and disposal costs. IVD does not generate hazardous waste, and it requires less maintenance than tank electroplating. IVD also does not require handling of hazardous chemicals, ventilation systems, plating solutions, and rinse tanks.

A typical IVD system can cost in excess of \$500,000 with another \$500,000 for installation. Electroplating equipment and wastewater treatment for producing the same amount of plated work would be approximately 1/4 to 1/6 that amount (Altmayer, 1994). The costs of the aluminum IVD process are higher than those for cadmium physical vapor deposition (PVD), but lower than those for either the low-embrittlement or diffused nickel-cadmium processes. Costs for cadmium electroplating are likely to keep rising because of ever-increasing hazardous waste disposal costs. In contrast, more widespread use of IVD aluminum will probably lead to cost reductions.

### **Reported Applications**

The aluminum IVD process is used by a large number of U.S. Department of Defense contractors, and is incorporated into several military and industrial specifications as an option for cadmium plating. Applications include pneumatic line fittings, steel fasteners and rivets, electrical bonding, EMI and RFI shielding, and coatings for plastic/composite materials (Nevill, 1993). Non-military applications include the coating of steel houses for trolling motors used on fishing vessels and for exhaust manifold headers on high-performance speed boats.

### **Availability**

The aluminum IVD process was developed in large part by the McDonnell Aircraft Company (a subsidiary of McDonnell-Douglas) of St. Louis, Missouri. The trade name of the process equipment developed by McDonnell is the Ivadizer. In 1987, McDonnell sold the rights to the process to the Abar-Ipsen Co. of Bensalem, Pennsylvania. Abar-Ipsen

**Operational and  
Product Benefits**

currently manufactures the equipment. Other companies have licenses to use the technology.

Health and safety risks can be greatly reduced when IVD is used in place of cadmium electroplating. Cadmium is a significant health hazard, as is the cyanide bath often used in cadmium electroplating.

For many applications, a chromate conversion coating is used on top of both cadmium and aluminum IVD coatings to improve corrosion resistance and adherence of subsequent organic coatings. The use of chromate conversion coatings generates some hazardous waste. Switching to an aluminum IVD process, however, should not increase the use of these coatings.

The greatest advantage of aluminum IVD is that the process significantly reduces the generation of hazardous wastes, and potentially eliminates the need for special pollution control systems. Some waste is generated in alkaline cleaning and stripping although these wastes can be neutralized and disposed of as special (i.e., non-hazardous) wastes. Other potential advantages of aluminum IVD coatings are listed below (Nevill, 1993):

- ▶ Outperforms cadmium coatings in preventing corrosion in acidic environments.
- ▶ Can be used at temperatures up to 925°F, as compared to 450°F for cadmium coatings.
- ▶ Can be used to coat high-strength steels without danger of hydrogen embrittlement. Unlike cadmium electroplating, the aluminum IVD process does not expose the substrate to hydrogen gas.
- ▶ Can be used in contact with titanium without causing solid metal conversion problems.
- ▶ Can be used in contact with fuels.
- ▶ Superior to the vacuum-applied cadmium process in resisting particle impact (e.g., can withstand burnishing pressures up to 90 psi as compared to 40 psi for vacuum-applied cadmium coatings).
- ▶ Permits coatings of several mils compared to about 1 mil for electroplated and vacuum-applied cadmium coatings, increasing corrosion resistance.



- ▶ Provides better uniformity of coatings on the edges of parts than does electroplating.

**Hazards and Limitations**

Some of the disadvantages of IVD coatings are:

- ▶ It is difficult to coat the interiors of blind holes or cavities that have a depth greater than their diameter.
- ▶ Compared to cadmium, aluminum IVD coatings have a higher electrodeposit coefficient of friction as well as inadequate lubricity. Application of a lubricant is sometimes required for proper torque-tension of fasteners. When lubricants cannot be used, inadequate lubrication might be a significant limitation.
- ▶ Unlike cadmium, aluminum IVD cannot be combined with nickel to provide an erosion-resistant surface.
- ▶ Unlike electroplating, there is no simple way to repair damaged aluminum IVD coatings.
- ▶ Aluminum IVD is slower than cadmium electroplating (above a certain level of plating throughput) due to capacity limits of the IVD system. For high-strength parts, however, reduced speed is not an issue because these parts would have to undergo hydrogen embrittlement relief after cadmium electroplating.
- ▶ Parts coated by aluminum IVD do not require time-consuming heat treatment for hydrogen embrittlement (hydrogen stress cracking) relief, thus compensating for the slower application speed.
- ▶ Because IVD aluminum coatings have a columnar structure and tend to be porous, parts might need to be peened with glass beads to improve fatigue and corrosion resistance. Peening can add to production costs and slow productivity. Cadmium electroplating has neither of these disadvantages.

**State of Development**

The IVD aluminum coating process is a mature technology that has been commercially available for a decade and is suitable for specialized applications.

---

**REFERENCES**

Hinton, B.R.W. and W.J. Pollock. 1991. Ion vapour deposited aluminum coatings for the corrosion protection of high strength steel. Aeronautical Research Laboratories (Australia). *Government Research Announcements and Index*. April. 52 pp.

Hinton, B.R.W. et al. 1987. Ion vapor deposited aluminum coatings for corrosion protection of steel. *Corrosion Australasia*. June. pp. 15-20.

Holmes, V.L., D.E. Muehlberger, and J.J. Reilly. 1989. The substitution of IVD aluminum for cadmium. Final report. EG&G Idaho. Report No. AD-A215 633/9/XAB. 201 pp.

Lansky, D. 1993. IVD: eliminating tank electroplating solutions for cadmium. *Plating and Surface Finishing*. January 1993. pp. 20-21.

Legge, G. 1992. High volume automotive-type aluminum coatings by ion vapor deposition. *SUR/FIN '92*. Vol 1. Atlanta, GA (June 22-25). Orlando, FL: American Electroplaters and Surface Finishers Society, Inc.

Nevill, B.T. 1993a. An alternative to cadmium: ion vapor deposition of aluminum. *Plating and Surface Finishing*. January 1993. pp. 14-19.

Nevill, B.T. 1993b. Diverse applications of IVD aluminum. *Proceedings of the 36th Annual Technical Conference*, Dallas, TX. Albuquerque, NM: Society of Vacuum Coaters. pp. 379-384.

Nevill, B.T. 1992. Ion vapor deposition of aluminum. Atlanta, GA (June 22-25). Orlando, FL: American Electroplaters and Surface Finishers Society, Inc.

Ressl, R. and J. Spessard. Evaluation of ion vapor deposition as a replacement for cadmium electroplating at Anniston Army Depot. Final Report. IT Environmental Programs. *Government Research Announcements and Index*. May. 128. pp.

---

**PHYSICAL VAPOR DEPOSITION (PVD)**

**Pollution Prevention  
Benefits**

Hexavalent chromium is extremely toxic and is a known carcinogen. Health and safety considerations as well as rising disposal costs have prompted the plating industry to consider alternatives for coating processes that involve hexavalent chromium. Physical vapor deposition (PVD) of alternative materials is one candidate for replacing chromium electroplating.

**How Does it Work?**

PVD encompasses several deposition processes in which atoms are removed by physical means from a source and deposited on a substrate. Thermal energy and ion bombardment are the methods used to convert the source material into a vapor.

**Operating Features**

The thoroughly cleaned workpiece is placed in a vacuum chamber, and a very high vacuum is drawn. The chamber is heated to between 400 and 900°F, depending on the specific process. A plasma is created from an inert gas such as argon. The workpiece is first plasma-etched to further clean the surface. The coating metal is then forced into the gas phase by one of the three methods described below:

- ▶ Evaporation
- ▶ Sputtering
- ▶ Ion plating

**Evaporation**

High-current electron beams or resistive heaters are used to evaporate material from a crucible. The evaporated material forms a cloud which fills the deposition chamber and then condenses onto the substrate to produce the desired film. Atoms take on a relatively low energy state (0.2 to 0.6 eV) and the deposited films, as a result, are not excessively adherent or dense. Deposition of a uniform coating may require complex rotation of the substrate since the vapor flux is localized and directional. Despite this, evaporation is probably the most widely used PVD process.

**Sputtering**

The surface of the source material is bombarded with energetic ions, usually an ionized inert gas environment such as argon. The physical erosion of atoms from the coating material that results from this bombardment is known as sputtering. The substrate is placed to intercept the flux of displaced or sputtered atoms from the target. Sputtering deposits atoms with energies in the range of 4.0 to 10.0 eV onto the substrate. Although sputtering is more controllable than evaporation it is an inefficient way to produce vapor. Energy costs are typically 3 to 10 times that of evaporation.

**Ion plating**

Ion plating produces superior coatings adhesion by bombarding the substrate with energy before and during deposition. Particles accelerate towards the substrate and arrive with energy levels up to the hundreds of eV range. These atoms sputter off some of the substrate material resulting in a cleaner, more adherent deposit. This cleaning continues as the substrate is coated. The film grows as over time because the sputtering or cleaning rate

is slower than the deposition rate. High gas pressure results in greater scattering of the vapor and a more uniform deposit on the substrate.

An important variation on these process involve the introduction of a gas such as oxygen or nitrogen into the chamber to form oxide or nitride deposits, respectively. These reactive deposition processes are used to deposit films of material such as titanium nitride, silicon dioxide, and aluminum oxide.

PVD coatings are typically thin coatings between 2 and 5 microns.

Titanium nitride is a prime candidate for replacing chromium coatings using PVD. Titanium nitride is much harder than chromium but can be cost effectively applied in much thinner coatings. Because of the thin, hard nature of the coating, titanium nitride is inferior to chromium as a coating in highpoint or line-load applications. Titanium nitride coatings also do not provide as much corrosion protection as do thicker, crack-free chromium coatings.

Substrates coated with titanium nitride and other PVD coatings are not subject to hydrogen embrittlement. PVD results in a thin, uniform coating that is much less likely to require machining after application. However, PVD is a line-of-sight coating process, and parts with complex shapes are difficult to coat.

#### Reported Applications

Titanium nitride coatings have already gained wide acceptance in the cutting tool industry. They are now being examined by a variety of industries, including the aerospace industry.

#### REFERENCES

- Comello, Vic. 1992. Tough Coatings Are a Cinch with New PVD Method. *R&D Magazine*. January pp.59-60.
- Dini, J.W. 1993b. Ion plating can improve coating adhesion. *Metal Finishing*. September 1993. pp. 15-20.
- Dini, J.W. 1993a. An electroplater's view of PVD processing. *Plating and Surface Finishing*. January, 1993. pp. 26-29.
- Johnson, P. 1989. Physical vapor deposition of thin films. *Plating and Surface Finishing*. 76(6)30-33. June 1989.
- Konig, W. and D. Kammermeier. 1992. New ways toward better exploitation of physical vapour deposition coatings. *19th International Conference on Metallurgical Coatings and Thin Films*, II. San Diego, CA (April 6-10). pp. 470-475.

Podob, M. and J.H. Richter. 1992. CVD and PVD hardcoatings for extending the life of tools used in the stamping industry. Proceedings: *Manufacturing Solutions*, v. 2. Nashville, TN (Feb. 23-26). Richmond Hts, OH: Precision Metalforming Association.

Russell, T.W.F., B.N. Baron, S.C. Jackson, and R.E. Rocheleau. 1989. Physical vapor deposition reactors. *Advances in Chemistry Series*. Washington, DC: ACS, Books and Journals Division. pp. 171-198.

Vagle, M.C. and A.S. Gates. 1990. PVD coatings on carbide cutting tools. *High Speed Machining: Solutions for Productivity*. San Diego, CA (Nov. 13-15). Materials Park, OH: ASM International.

Zega, B. 1989. Hard decorative coatings by reactive physical vapor deposition - 12 years of development. *16th International Conference on Metallurgical Coatings (ICMC)*, Part 2, San Diego, CA (April 17-21). In: *Surface and Coatings Technol.* 39(40):507-520.

---

## **CHROMIUM-FREE SURFACE TREATMENTS FOR ALUMINUM AND ZINC**

---

### **Description**

One of the many uses of chromium in the metal finishing industry is for conversion coatings, which are used to treat nonferrous metal surfaces (mainly magnesium, aluminum, zinc, and cadmium) for corrosion protection or to improve adhesion of subsequent organic coatings. Unfortunately, chromates, the form of chromium used for treatment, are carcinogenic and highly toxic. Small amounts of chromic acid or potassium dichromate will cause kidney failure, liver damage, blood disorders and eventually death. Prolonged skin exposure can cause rashes, blisters, and other dermatological problems. Chromate mists entering the lungs may eventually cause lung cancer.

These health and safety considerations and the increasing cost of disposal of chromium-containing finishing wastes have prompted users to look at alternatives to treatment of aluminum, zinc, and other substrates with chromates. Although a number of alternative treatments have been examined, very few provide even close to the corrosion protection afforded by chromate conversion coatings. Even fewer have been developed to the point where their commercial viability can be assessed.

Sulfuric acid anodizing can substitute for some chromium conversion coatings, although the coatings are more brittle and significantly thicker than chromate films.

One of the few commercially proven, non-chromate surface treatments for aluminum is an inorganic conversion coating based on zirconium oxide.

This treatment 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 a zirconium oxide. These coatings have been used on aluminum cans for some time, but they have not been tested in the kind of environments in which chromate conversion coatings are typically used. Wider application of this coating must await this type of testing.

Another process showing promise is the SANCHEM-CC chromium-free aluminum pretreatment system developed by Dr. John Bibber of Sanchem, Inc. This process can be summarized as follows:

*Stage One*—Use of boiling deionized water or steam to form a hydrated aluminum oxide film.

*Stage Two*—Treat in proprietary aluminum salt solution for at least 1 minute at 205 °F or higher.

*Stage Three*—Treat in a proprietary permanganate solution at 135 to 145 °F for at least one minute.

A fourth stage of the process exists for cases where maximum corrosion resistance is required for certain aluminum alloys. The developers claim that the film produced by this process closely matches the performance of a chromate conversion process.

A recent chrome-free post-rinse process has been developed for use on phosphated steel, zinc, and aluminum surfaces prior to painting. The new rinse, known as Gardolene VP 4683, contains neither hexavalent or trivalent chrome. It contains only inorganic metallic compounds as the active ingredient. The rinse is applied at temperatures ranging to 100 °F and at a slightly acidic pH. The manufacturer describes tests showing corrosion protection and paint adhesion equal to that of hexavalent chrome (Finishers' Management, 1990).

Some of the other possible alternatives to chromate conversion coatings that have been examined are molybdate conversion coatings, rare earth metal salts, silanes, titanates, thioglycollates, and alkoxides. These alternatives are discussed in detail in Hinton (1991).

## REFERENCES

*Finishers' Management*, 1990. Chrome free passivating post-rinse for phosphate coatings reduces toxicity. May, 1990. pp. 51-52.

Hinton, 1991. Corrosion prevention and chromates: the end of an era? *Metal Finishing*. Part I, September. pp. 55-61. Part II, October. pp. 15-20.

## METAL SPRAY COATING

---

### Description

Metal spray coating refers to a group of related techniques in which molten metal is atomized and directed toward a substrate with sufficient velocity to form a dense and adherent coating. Metal spray coating has been used in a wide variety of applications, as shown in Table 5. The technique avoids use of plating solutions and associated rinses, thereby reducing wastes. However, the parts to be sprayed still need to be cleaned prior to spraying.

The individual techniques vary mainly in how the coating is melted and in the form of the coating prior to melting. The three basic means for melting the metal are as follows:

*Molten Metal*—The metal is heated by some suitable means (either resistance heating or a burner) and then supplied to the atomizing source in molten form.

*Fuel/Oxidant*—Oxygen/acetylene flames are typically used. The metal melts as it is continuously fed to the flame in the form of a wire or powder. The flame itself is not the atomizing source. Instead, the flame is surrounded by a jet of compressed air or inert gas that is used to propel the molten metal toward the substrate.

*Electric arc*—In this method an electric arc is maintained between two wires that are continuously fed as they melt at the arc. Compressed air atomizes the molten metal at the arc and propels it toward the substrate. DC plasma arc spraying and vacuum plasma spraying are variations of this technique in which an inert gas (usually argon) is used to create a plasma between the electrodes.

The technologies for thermal spraying of metals are well developed, but they tend to have their own market niche and are not typically thought of as a replacement for electroplating. As the costs of hazardous waste treatment and disposal rises, however, this family of techniques may become cost-effective replacements for coating applications currently performed by electroplating. The coatings can be applied to a wide range of substrates, including paper, plastic, glass, metals, and ceramics with choice of suitable materials and control of the coating parameter.

**Table 5. Applications of thermal spray.**

<b>Wear resistance</b>	Metals, carbides, ceramics, and plastics are used to resist abrasion, erosion, cavitation, friction, and fretting. Coating hardness range from < 20 to > 70 Rc are attainable on practically any substrate.
<b>Dimensional Restoration</b>	Coatings can be applied up to 0.100 inch thick to restore worn dimensions and mismachined surfaces.
<b>Corrosion Resistance</b>	Ceramics, metals, and plastics resist acids and atmospheric corrosion either by the inert nature of the coating or by galvanic protection. Nonporous coatings must be applied.
<b>Thermal Barriers</b>	Zirconia ( $ZrO_2$ ) coatings are applied to insulate base metals from the high-temperature oxidation, thermal transients, and adhesion by molten metals.
<b>Abrasion</b>	Softer coatings such as aluminum, polyester, graphite, or combinations are used for clearance control, allowing rotating parts to "machine in" their own tolerance during operation.
<b>Dielectrics</b>	Alumina ( $Al_2O_3$ ) is generally used to resist electrical conductivity. These coatings have a dielectric strength of 250 V/mil of coating thickness.
<b>Conduction</b>	Materials are selected for their intrinsic thermal or electrical conductivity. Copper, aluminum, and silver are frequently used for this application.
<b>RFI/EMI Shielding</b>	These conductive coatings are designed to shield electronic components against radio frequency or electromagnetic interference. Aluminum and zinc are often selected.
<b>Medical Implants</b>	Relatively new porous coatings of cobalt-base, titanium-base, or ceramic materials are applied to dental or orthopedic devices to provide excellent adhesive bases or surfaces for bone ingrowth.

Source: Kutner (1988).



**REFERENCES**

Kutner, Gerald. 1988. Thermal spray by design. *Advanced Materials & Processes*. October. pp. 63-68.

Thorpe, Merle L. 1988. Thermal spray applications grow. *Advanced Materials & Processes*. October. pp. 69-70.

Herman, Herbert. 1990. Advances in thermal spray technology. *Advanced Materials & Processes*. April. pp. 41-45.

---

## SECTION FOUR EMERGING TECHNOLOGIES

---

### Introduction

Three emerging clean process changes for metal finishing are presented in this section:

- ▶ Nickel-tungsten-silicon carbide plating to replace chromium coatings
- ▶ Nickel-tungsten-boron plating to replace chromium coatings
- ▶ In-mold plating to replace electroless plating followed by electrolytic plating.

---

## NICKEL-TUNGSTEN-SILICON CARBIDE PLATING

---

### Description

The nickel-tungsten-silicon carbide (Ni-W-SiC) composite electroplating process is a patented process (Takada, 1990) that can be used to replace functional (hard) chromium coatings in some applications. 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.

The composition and operating conditions for the Ni-W-SiC plating bath are given in Table 6.

Chromium electroplating processes generate toxic mists and wastewater containing hexavalent chromium. Hexavalent chromium has a number of toxic effects including lung cancer and irritation of the upper respiratory tract, skin irritation and ulcers. These toxic emissions are coming under increasingly stringent regulations and are difficult to treat and dispose of. In addition to hazardous waste reduction, the Ni-W-SiC process has the following benefits:

*Higher Plating Rates*—The Ni-W-SiC process exhibits much higher plating rates than for chromium. Plating rates ranged from 1.7 to 3.3 mils/hr at 300 ASF, compared to the typical hard chromium plating rate of less than 1 mil/hr.

*Higher Cathode Current Efficiencies*—Current efficiencies are approximately double those for chromium plating. Current effi-

ciencies range from 24 percent to 35 percent, whereas typical chromium plating current efficiencies range from 12 percent to 15 percent.

**Table 6. Composition and operating conditions for Ni-W-SiC composite plating**

Composition	Operating conditions
Nickel sulfate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30 - 40 g/l
Sodium tungstate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	55 - 75 g/l
Ammonium citrate $\text{NH}_4\text{HC}_6\text{H}_5\text{O}_7$	70 - 110 g/l
Silicon carbide (0.8 - 1.5 $\mu\text{m}$ particles)	10 - 50 g/l
pH (adjust with ammonium hydroxide or citric acid)	6.0 - 8.0
Bath temperature	150 - 175°F
Cathode current density	100 - 300 ASF

**Better Throwing Power**—Cathode current efficiencies for the Ni-W-SiC process decrease with increasing current density. This results in much better throwing power than for chromium plating. In chromium plating baths, current efficiency increases with current density, which results in poor throwing power.

**Better Wear Resistance**—Precipitation-hardened and relief-baked Ni-W-SiC composite coatings all showed better wear resistance than a chromium coating in tests using a Taber Abraser.

The main disadvantage of Ni-W-SiC process uncovered so far is that the plating bath is more susceptible to metallic and biological contamination. As a result, many questions remain to be answered before widespread use will occur. Some of the unknowns include:

- ▶ Susceptibility of coated parts to hydrogen embrittlement
- ▶ Fatigue life of coated parts
- ▶ Corrosion resistance of coated parts
- ▶ Maximum thickness of coating before cracking or flaking occurs
- ▶ Effect of coating parameters on internal stresses in deposit

- ▶ Lubricity of coated parts
- ▶ Maximum service temperature for coating
- ▶ Stripping techniques for coated parts
- ▶ Processing techniques for promoting adhesion to various surfaces
- ▶ Grinding characteristics
- ▶ Ability to plate complex shapes
- ▶ Repair of damaged coatings
- ▶ Facility requirements.

## REFERENCES

Takada, 1990. Method of nickel-tungsten-silicon carbide composite plating. U.S. Patent 4,892,627. January.

Takada, K. 1991. Alternative to hard chrome plating. SAE (Soc. Automotive Engineers). 100:24-27.

## NICKEL-TUNGSTEN-BORON ALLOY PLATING

---

### Description

Following several years of development, a new chromium alternative based on an alloy of nickel, tungsten, and boron has been recently introduced (Scruggs et al., 1993). A family of these alloys is patented under the trade name AMPLATE. Properties for one specific alloy, known as AMPLATE "U" have been reported by the developers in the literature. This alloy consists of approximately 59.5 percent nickel, 39.5 percent tungsten, and 1 percent boron.

Unlike most metals which exhibit a crystalline structure at ambient temperatures, the AMPLATE alloys are structureless. Metals of this type are often described as "amorphous" and have "glasslike" properties that render substrate surfaces smooth and free of the defects that are exhibited by lattice-structured metals. Because of the smoothness and hardness of their surfaces, amorphous metals have excellent corrosion and abrasion resistance properties.

### Properties

The properties of this alloy and its advantages as a coating are summarized as follows (Scruggs et al., 1993):

*Appearance*—The alloy is reflective and has an appearance of bright metal similar to chromium, bright silver, or bright nickel. Being amorphous, it adopts the surface characteristics of the substrate being coated (e.g., etching, patterning, or irregularities on the substrate surface will show through the coating).

*Hardness*—When deposited, the Ni-W-B alloy has a hardness of about 600 Vickers. Heat treatment for 4 hours at 60°F will raise the hardness to about HV1000. Other properties are unaffected.

*Abrasion/Wear Resistance*—The alloy compares comparably to chromium and electroless nickel. In one test, rollers were plated with chromium and the AMPLATE U alloy and rotated at 600 and 700 RPM with a load of 102 Newtons. The chromium coating failed within 60 to 100 minutes while at the end of 1300 minutes the alloy showed little oxidative wear.

*Corrosion*—The alloy exhibits corrosion resistance properties far superior to those of chromium. In testing, pieces coated with chromium were immersed in a 5 percent NaCl brine acidified with acetic acid to pH 2 and saturated with hydrogen sulfide. Following seven days of immersion, the chromium was completely stripped and the substrate had been heavily attacked. A similar coating of the U alloy showed no signs of corrosion.

*Ductility*—The coating exhibits surprising ductility. In one test, a foil of the coating was obtained by dissolving the substrate. The foil could be tied in a loose knot and bent 18 degrees on itself. Plated items were successfully bent 9 degrees over a quarter-inch mandrel with no separation of the plating material.

*Heat Resistance*—The structure of the amorphous coating is unaffected by heat to at least 1200°F. The finish remains bright upon short exposure to temperatures of 400°F. Treatment in air can lead to yellowing due to oxidation of the tungsten. This coloration can be removed by polishing or avoided by heat treating in an inert gas environment.

### **Operating Conditions**

The plating system is operated at temperature range of 115°F to 125°F and a pH of 8.2 to 8.6. Optimum concentrations of Ni, W, and B are maintained by adding liquid concentrates containing dissolved salts of the three metals.

### **Deposition Characteristics**

Two versions of the alloy solution are available (UA and UA-B), the difference in the "B" formulation being the addition of a brightener and a lower metal concentration. This results in a deposition rate approximately half that of UA. The UA solution is recommended for heavier applications where the surface will be subsequently dimensioned by grinding and polishing. The UA-B solution will produce a fully bright coating of ten mils thick or more and can be used for both decorative and engineering purposes. Thinner deposits of 1-2 mils over bright nickel have the appearance of chromium but with superior corrosion resistance.

### **Equipment Requirements**

Standard plating equipment is suitable for plating with the Ni-W-B alloy. Automated chemical feed equipment is recommended for optimizing concentrations of ammonia and the metals.

### **Surface Preparation**

Extra attention is needed to ensure that parts to be plated are absolutely clear of contaminants. When plating with amorphous coatings, even minute defects can become stress inducing points or pore generating sites.

### **Cost and Efficiency**

Coating efficiency is around 38 percent or three times that of chromium. This reduces energy and plating costs. Savings are also generated due to reduced need to "grind back" chromium to obtain suitable surfaces and sizes.

### **Environmental**

The plating solution is only slightly alkaline and is operated at relatively low temperature. There are virtually no hazardous or carcinogenic emissions associated with the process. Mild ammonia odors can be controlled through proper ventilation.

Because the UA-B deposit remains bright and smooth at thicknesses up to ten mils or more, the need for grinding and polishing is greatly reduced. In addition to reducing costs, this also minimizes atmospheric contamination.

### **REFERENCES**

Scruggs, D., J. Croopnick, and J. Donaldson. 1993. An electroplated nickel/tungsten/boron alloy replacement for chromium. 1993 AESF Symposium on the Search for Environmentally Safer Deposition Processes for Electronics.

## **IN-MOLD PLATING**

---

### **Description**

In-mold plating is the name given to a process developed and patented by Battelle, Columbus, Ohio. This process combines high-speed plating and injection molding to apply metal coatings to plastics in the following manner. First, the mold is cleaned and prepared, then a plating fixture is placed on top and a metal, such as copper or zinc, is applied by a high-speed plating technique. When the required thickness has been reached, the mold cavity is emptied, the deposit is rinsed and dried in situ, and the coated mold is transferred to the injection molding machine. A plastic is then injected, the mold cooled and a metal-coated plastic part ejected. The plastic typically is a thermosetting resin, but it may be filled with particles or fibers to improve stability or toughness. Similarly, a foamed plastic can be used

because the coated mold surface defines the surface of the finished part, not the plastic material. Besides injection molding, the process can be adapted for compression molding. The process has several advantages:

- ▶ It has fewer process steps than conventional techniques for plating plastics.
- ▶ It does not generate any waste etching or sensitizing solutions that contain organics, heavy metals, or precious metals.
- ▶ It avoids the use of electroless copper to initially metalize the surface.
- ▶ It deposits only the amounts of metal required and only in the areas that require coating; thus it conserves materials and energy.
- ▶ It provides a very broad range of metal coating and plastic combinations that can be processed.

While potentially reducing and minimizing some waste streams, the process itself only replaces the need for etching and sanitizing the plastic part prior to plating. It still utilizes a plating process to plate the mold (and therefore will generate wastewater and wastes to dispose of). Skillful fixturing is required to deposit an adequate plate or sequence of plates into the mold. Improper cleaning and preparation can cause the metal to stay on the mold, requiring chemical stripping (generates waste) and possibly a need for polishing.

The appearance of the final product is directly related to the surface condition of the mold itself, since the plating replicates the surface. The appearance therefore will not match the luster of bright nickel plated plastic parts that are processed conventionally. Also, the process is labor intensive and very difficult and expensive to automate. It has only specialized applications.

Although in-mold plating is not available commercially, several companies are exploring its use in such applications as decorative finishes, plumbing and architectural hardware, and EMI/RFI protection for electronic components.

#### REFERENCES

PF. 1983. New way to plate on plastics. *Products Finishing*. March. pp. 75-76.

AMM. 1986. Battelle adopts technology for in-mold plating. *American Metal Market*. December 1. p. 8.

---

**SECTION FIVE**  
**POLLUTION PREVENTION STRATEGIES**

---

**Introduction**

Alternate technologies are presently available, and others are under development, for the reduction or elimination of use of cadmium, cyanide, chromium, and copper/formaldehyde in specific metal finishing applications. These alternate technologies tend to fall into two main categories:

*Alternate finishes*—(e.g., aluminum, zinc or zinc alloys, and nickel-tungsten-silicon carbide) replace traditional cadmium and chromium finishes.

*Process substitutions*—(e.g., Blackhole Technology, ion vapor deposition, physical vapor deposition, in-mold plating, and metal spray) use different technologies for metal finishes.

Both types of changes have the potential to reduce costs (through reduction in waste volumes or toxicity and associated savings in disposal costs) and improve environmental health and safety. Barriers to acceptance of these alternate processes often include high capital cost, higher maintenance costs, high levels of required skill, difficulty in automation or bulk processing of large volumes of parts, and inferior properties of the alternate process coating.

**Cadmium plating**

The vast majority of cadmium plating is performed using cyanide-based chemistry for a number of reasons, including:

- ▶ Ability to cover complex shapes somewhat uniformly (high throwing power).
- ▶ High tolerance to impurities.
- ▶ High tolerance to improperly cleaned surfaces.
- ▶ Ability to obtain a porous deposit that allows for hydrogen embrittlement relief.
- ▶ Ability to obtain a ductile deposit at high thicknesses.
- ▶ High adhesion to substrates.

A growing number of platers have successfully substituted non-cyanide cadmium plating solutions based on proprietary chemistries substituting sulfate and/or chloride salts and organic additives for the cyanide.

**Cyanide-based plating solutions**

Alternates to cyanide processes for other plating solutions are also available and in the developmental stage. For example, significant progress has been made in developing mildly alkaline, non-cyanide copper plating processes for application in both rack and barrel plating on ferrous parts, on zinc die castings, and on zincated aluminum die castings. These proprietary



processes are available from at least four commercial suppliers (Lea-Renal, Harshaw-Atotech, Enthone-OMI, and Electrochemical Products). In addition to the cyanide free alkaline copper and the acid cadmium processes, non cyanide formulations for plating gold and silver have been available for many years. Additional progress in process control and lowering of operating costs is required to allow these substitutes to more readily compete with the cyanide based formulations.

### **Chromium plating**

To find a suitable substitute for chromium, an alternate coating must be found that offers the combination of benefits provided: wear, corrosion protection, ability to hold oil/lubricants in microcracks, high temperature wear resistance, low coefficient of friction, ability to produce very thick deposits (10 mils and more), ease of solution maintenance, ease of embrittlement relief (due to micro-cracked structure), ease of stripping rejects, and high tolerance of impurities.

There is no single other metallic coating that offers the above combination of beneficial properties and processing advantages. However, alternative coatings presently in the research and pilot plant stage, show promise in providing some of the noted properties, and can be used as substitutes in selected applications. For example, advanced ceramic and composite materials have been tested as replacements for chromium plated parts in internal combustion engines. Hard coatings such as titanium nitride have been applied using sophisticated (expensive) equipment that produces the coating by condensing vaporized metals inside a vacuum chamber.

The deposits obtained from these alternatives are normally very thin and can exceed chromium in hardness, but do not match up to chromium electroplate in economy, ability to produce thick coatings, corrosion resistance, ease of stripping reject parts, or ability to deposit into deep recesses.

### **Nickel-Tungsten-Silicon Carbide and Nickel-Tungsten-Boron Alloy Plating**

A significant effort is being made in the aerospace industry to evaluate chromium substitutes produced from alternate aqueous electroplating processes. The main focus of these efforts is the application of an alloy of nickel and tungsten containing finely dispersed particles of silicon carbide, molybdenum plating, and an alloy of nickel-tungsten-boron. The nickel tungsten alloy electrodeposits offer better wear resistance and coefficient of friction than chromium plate. The plating solution is approximately 50 percent to 100 percent faster in plating speed than typical functional chromium plating solutions (although one supplier of proprietary chromium plating chemicals has developed a process that would be 20 percent faster than the nickel tungsten alloy solution).

A primary concern of the nickel-tungsten substitutes is that they contain ingredients that have similar health/environmental concerns as hexavalent chromium. Additionally, these substitutes utilize a plating solution that produces a wastewater that requires treatment, the solutions themselves are

subject to biological decomposition and offer current efficiencies that are only marginally more efficient than functional chromium plating formulations. The tungsten compound used in the process (sodium tungstate) is very expensive and not readily available. Parts that have been plated with nickel-tungsten alloys are typically very difficult to strip, if a defective deposit is placed, and the plating solution is more sensitive to impurities. At least one of these processes (Ni-W-B) uses platinized titanium anodes encased in a membrane cell. This is expensive and the membrane is subject to fouling, and expensive to replace. Considerable process control problems can be encountered when attempting to deposit an alloy, especially one with three alloying elements (Ni-W-B).

Trivalent chromium solutions require much greater care in operation to minimize contamination by metallic impurities than hexavalent solutions. These metallic impurities can affect the color of the deposit, and if not controlled to a steady state, the deposit will vary in color (darkness) from week to week. When carefully controlled, these solutions are capable of producing thin chromium deposits for decorative parts that are equivalent in color, corrosion resistance, and abrasion resistance to thin deposits from hexavalent chromium plating solutions.

Since decorative applications of chromium may be optional for some parts, those parts can also be engineered/designed to be functional in the absence of the chromium deposit. If the parts are molded from plastic, or formed/cast from stainless steel, they may not need plating at all to function and be "decorative". The surface of the molded plastic part would be much softer than a chromium plated part. The stainless steel part would also be softer and would be far more expensive to produce than a part made from zinc and nickel-chromium plated.

Most other metals commonly used for consumer items (zinc, aluminum, carbon steel) require some form of protective coating, since those metals corrode to an unpleasant and possibly un-functional condition upon exposure to humidity, salt, water, and household chemical products. Alternative finishes need to provide a pleasing appearance along with high corrosion resistance and (sometimes) high abrasion resistance in order to adequately replace a nickel-chromium electroplate.

#### **Hexavalent chromium**

Hexavalent chromium compounds are also utilized in conversion coatings produced on aluminum, zinc, cadmium, magnesium, copper, copper alloy, silver, and tin surfaces. There are a number of other metal finishing operations that utilize solutions containing hexavalent chromium compounds, including phosphating and passivation of certain stainless steel alloys.

#### **Other solutions**

The surface of aluminum parts can be converted to an oxide coating in a number of solutions, by making the part anodic (positively charged, direct

current). When fatigue failure and corrosion by trapped anodizing solution in crevices and faying surfaces is of concern, the anodizing solution is formulated from chromic acid, a hexavalent chromium compound.

Some anodic coatings are further processed through a sealing operation consisting of an aqueous solution of sodium dichromate. The sealing operation further enhances fatigue resistance and "seals" the pores in the coating to enhance the corrosion resistance.

---

**SECTION SIX**  
**INFORMATION SOURCES**


---

**Trade Associations**

The following is a list of trade, professional, and standard-setting organizations that provide technical and other types of support to various segments of the metals finishing industry. Readers are invited to contact these trade associations and request their assistance in identifying one or more companies that could provide the desired technological capabilities.

**Abrasive Engineering Society**  
 108 Elliot Dr.  
 Butler, PA 16001  
 412/282-6210

**Aluminum Anodizers Council**  
 1000 N. Rand Rd., Ste. 214  
 Wauconda, IL 60084  
 708/526-2010  
 708/526-3993 FAX

**Aluminum Association**  
 900 19th St., N.W.,  
 Washington, DC 20005  
 202/862-5100  
 202 862-5164 FAX

**American Chemical Society  
 (ACS)**  
 11-55 16th St., N.W.  
 Washington, DC 20036  
 202/872-4600  
 202/872-6067 FAX

**American Electroplaters' and  
 Surface Finishers' Society  
 (AESF)**  
 12644 Research Pkwy.  
 Orlando, FL 32826  
 407/281-6441  
 407/281-6446 FAX

**American Galvanizers  
 Association**  
 12200 E. Iliff Ave., Ste. 204  
 Aurora, CO 80014-1252  
 303/750-2900  
 303/750-2909 FAX

**American Institute of Chemical  
 Engineers (AIChE)**  
 345 E. 47th St.  
 New York, NY 10017  
 212/705-7338  
 212/752-3297 FAX

**American National Standards  
 Institute (ANSI)**  
 11 West 42nd St., 13th Floor  
 New York, NY 10036  
 212/642-4900  
 212/398-0023 FAX

**American Society for  
 Nondestructive Testing (ASNT)**  
 1711 Arlington Lane  
 P.O. Box 28518  
 Columbus, OH 43228-0518  
 614/274-6003  
 800/222-2768  
 614/274-6899 FAX

**American Society for Quality  
 Control (ASQC)**  
 310 W. Wisconsin Ave.  
 Milwaukee, WI 53203  
 414/272-8575  
 414/272-1734 FAX

**American Society for Testing  
 Materials (ASTM)**  
 1916 Race St.  
 Philadelphia, PA 19103-1187  
 215/299-5400  
 215/977-9679 FAX

**American Society of  
 Electroplated Plastics (ASEP)**  
 1101 14th St., N.W., Ste. 1100  
 Washington, DC 20005  
 202/371-1323  
 202/371-1090 FAX

**American Zinc Association**  
 1112-16th St., N.W., Ste. 240  
 Washington, DC 20036  
 202/835-0164  
 202/835-0155 FAX

**ASM International**  
 Materials Park, OH 44073  
 216/338-5151  
 216/338-4634 FAX

**Associação Brasileira De  
 Tratamentos De Superfície  
 (ABTS)**  
 Av. Paulista, 1313, 9º Andar  
 Conj. 913 Cep 01311  
 Sao Paulo, SP Brazil  
 55 11 289 75 01  
 55 11 251 25 88 FAX

*Section Six*

---

Association Francaise Des  
Ingenieurs Et Techniciens De  
L'Electrolyse Et Des  
Traitements De Surface  
5 rue Le Bua  
Paris 75020 France  
14 030 06 80

Australasian Institute of Metal  
Finishing  
Clunies Ross House  
191 Royal Parade  
Parkville, Victoria 3052  
Australia  
613 347 2299  
613 347 9162 FAX

Bumper Recycling Association  
of North America (BRANA)  
1730 N. Lynn St., Ste. 502  
Arlington, VA 22209  
703/525-1191  
703/276-8196 FAX

Cadmium Council Inc.  
12110 Sunset Hills Rd., Ste. 110  
Reston, VA 22090  
703/709-1400  
703/709-1402 FAX

Canadian Association of Metal  
Finishers  
14 Vintage Ln.  
Thornhill, Ontario  
L3T 1X6 Canada  
416/731-4458  
416/731-5884 FAX

Chemical Coaters Association  
International (CCAI)  
P.O. Box 54316  
Cincinnati, OH 45254  
513/624-6767  
513/624-0601 FAX

Coated Abrasives  
Manufacturers' Institute  
1300 Sumner Ave.  
Cleveland, OH 44115-2851  
216/241-7333  
216/241-0105 FAX

Copper Development  
Association Inc.  
260 Madison Ave., 16th Fl.  
New York, NY 10016  
212/251-7200  
212/251-7234 FAX

Deutsche Gesellschaft fur  
Galvano und Oberflach-  
entechnik e.V. (DGO)  
Horionplalz 6, D-4000  
Dusseldorf, Germany  
211 13 23 81

Electrochemical Society (ECS)  
10 S. Main St.  
Pennington, NJ 08534  
609/737-1902  
609/737-2743 FAX

Gas Research Institute  
8600 W. Bryn Mawr Ave.  
Chicago, IL 60631  
313/399-8100  
312/399-8170 FAX

Gold Institute  
1112 16th St., N.W., Ste. 240  
Washington, DC 20036  
202/835-0185  
202/835-0155 FAX

Halogenated Solvents Industry  
Alliance  
2001 L St., N.W., Ste. 506  
Washington, DC 20036  
202/775-2790  
202/223-7225 FAX

Institute for Interconnecting &  
Packaging Electronic Circuits  
(IPC)  
7380 N. Lincoln Ave.,  
Lincolnwood, IL 60646  
708/677-2850  
708/677-9570 FAX

Institute of Metal Finishing  
(IMF)  
Exeter House  
48 Holloway Head, Birmingham  
B1 1NQ England  
44 21622 73 87  
44 21666 63 FAX

International Copper  
Association Ltd.  
260 Madison Ave.  
New York, NY 10016  
212/251-7240  
212/251-7245 FAX

International Hard Anodizing  
Association  
14300 Meyers Rd.  
Detroit, MI 48227  
313/834-5000  
313/834-5422 FAX

International Lead Zinc  
Research (ILZR)  
2525 Meridian Parkway  
Research Triangle Park, NC  
27709  
919/361-4647  
919/361-1957 FAX

International Magnesium  
Association  
1303 Vincent Pl., Ste. 1  
McLean, VA 22101  
703/442-8888  
703/821-1824 FAX

International Thermal Spray  
Association  
12 Thompson Rd.  
East Windsor, CT 06088  
203/623-9901  
203/623-4657 FAX

Mass Finishing Job Shops  
Association  
1859 Onion Cneek Rd.  
Colville, WA 99114-9623  
509/732-6191  
509/732-6191 FAX

National Association of  
Architectural Metal Manu-  
facturers (NAAMM)  
600 5. Federal St., Ste. 400  
Chicago, IL 60605  
312/922-6222  
312/922-2734 FAX

Nickel Development Institute  
214 King St W, Ste. 510  
Toronto, Ontario  
M5H 356 Canada  
416/591-7999  
416/591-7987 FAX

Society of Automotive  
Engineers (SAE)  
400 Commonwealth Dr.  
Warrendale, PA 15096  
412/772-7129  
412/776-2103 FAX

International Precious Metals  
Institute (IPMI)  
4905 Tilghman St.  
Allentown, PA 18104  
215/395-9700  
215/395-5855 FAX

Lead Industries Association Inc.  
295 Madison Ave.  
New York, NY 10017  
212/578-4750  
212/684-7714 FAX

Metal Finishing Association  
Federation House  
10 Vyse St.  
Birmingham B18 6LT England  
44 21 236 26 57  
44 21236 39 21 FAX

National Association of  
Corrosion Engineers (NACE)  
1440 S. Creek Dr.  
Houston, TX 77084-4906  
713/492-0535  
713/492-8254 FAX

Porcelain Enamel Institute  
1101 Connecticut Ave. N.W.,  
Ste. 700  
Washington, DC 20036  
202/857-1134  
202/223-4579 FAX

Society of Manufacturing  
Engineers (SME)  
One SME Dr., P.O. Box 930  
Dearborn, MI 48121  
313/271-1500  
313/271-2861 FAX

International Society for Hybrid  
Microelectronics (ISHM)  
P.O. Box 2698  
Reston, VA 22090-2698  
703/471-0066  
800/232-4746  
703/471-1937 FAX

Manufacturers Jewelers &  
Silversmiths of America  
100 India Street  
Providence, RI 02903  
401/2743840  
401/274-0265 FAX

Metal Finishing Suppliers'  
Association (MFSA)  
801 N. Cass Ave.  
Westmont, IL 60559  
708/887-0797  
708/887-0799 FAX

National Association of Metal  
Finishers (NAMF)  
401 N. Michigan Ave.  
Chicago, IL 606114267  
312/644-6610  
312/321-6869 FAX

Society for the Advancement of  
Material and Process  
Engineering (SAMPE)  
1611 Parkins Dr.  
Covina, CA 91724  
818/331-0616  
818/332-8929 FAX

Society of Plastics Engineers  
(SPE)  
14 Fairfield Dr.  
Brookfield, CT 06804-0403  
203/775-0471  
203/775-8490 FAX

*Section Six*

---

Society of Vacuum Coaters  
(SVC)  
440 Live Oak Loop  
Albuquerque, NM 87122  
505/298-7624  
505/298-7942 FAX

Tin Information Center  
1353 Perry St.  
Columbus, OH 43201  
614/424/6200  
614/424-6924 FAX

Titanium Development  
Association  
4141 Arapahoe Ave., Ste. 100  
Boulder, CO 80303  
303/443-7515  
303/443-4406 FAX

United States  
Environmental Protection Agency  
Center for Environmental Research Information  
Cincinnati, OH 45268

Official Business  
Penalty for Private Use  
\$300

EPA/625/R-94/007

Please make all necessary changes on the below label,  
detach or copy, and return to the address in the upper  
left-hand corner.

If you do not wish to receive these reports CHECK HERE :  
detach, or copy this cover, and return to the address in the  
upper left-hand corner.

BUL . . .  
POSTAGE & FEES  
EPA  
PERMIT No. G-35