United States Environmental Protection Agency Office of Research and Development Washington DC 20460 EPA/625/R-4/007 September 1994



## Guide to Cleaner Technologies

Alternative Metal Finishes



EP/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.

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#### SECTION ONE INTRODUCI'ION

What is a Cleaner Technology?	A cleaner technology is a sour eliminate or significantly reduce pollutant, or contaminant relear cleaner technologies is on pro Pollution prevention occurs throuvolume of wastes generated, and technology changes, or improved	rce reduction or recycle reduction or recycle reduction of any haz sed to the environment. weeks changes that can pugh source reduction, i.e. and source control (input d operating practices).	method applied to zardous substance, The emphasis of prevent pollution. , reductions in the material changes,
	Cleaner technologies include p environmental impact of wastes toxicity by transferring pollutant (e.g., from wastewater to sludge on not inherently cleaner and are not	rocess changes that redu or emissions. Processes s from one environmentation from air emissions to so t considered to be source	ce the toxicity or that reduce waste l media to another crubber wastes) are reduction.
	Cleaner technologies also includ considered only after source red implemented where technically techniques should take occur in	e recycle methods, but re uction alternatives have b feasible. Where they as an environmentally safe r	ecycling should be been evaluated and re used, recycling nanner.
Why Finish Metals?	Without metal finishing, products of their present life-span. Metal fi to enhance properties such as co conductivity, electrical resistance solderability, tarnish resistance, cl (vulcanizing), and a number of sterilizes stainless steel, for exar their manufacturing processes in	made from metals would finishing alters the surface prosion resistance, wear re- e, reflectivity, appearance hemical resistance, ability f other special properties nple). Industries that use iclude:	last only a fraction of metal products esistance, electrical , torque tolerance, to bond to rubber s (electropolishing metal finishing in
	► Automotive	► Electronics	► Aerospace
	<ul> <li>Telecommunications</li> </ul>	► Hardware	► Jewelry
	<ul> <li>Heavy Equipment</li> </ul>	<ul> <li>Appliances</li> </ul>	► Tires
	A wide variety of materials, proc and plate metallic and non-me workpieces undergo one or mo processes. Physical processes blasting. Chemical processes inc polishing, and electroless plating electropolishing, and anodizing.	cesses, and products are u etallic surfaces. Typicall re physical, chemical, ar include buffing, grindin lude degreasing, cleaning, . Electrochemical processo	sed to clean, etch, y, metal parts or id electrochemical ig, polishing, and pickling, etching, es include plating,

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.
	<ul> <li>Cyanide-based plating, especially zinc, copper, brass, bronze and silver plating.</li> </ul>
	<ul> <li>Chromium plating and conversion coatings based on hexavalent chromium compounds.</li> </ul>
	► 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?

 Would the process require Would new or different significantly different process pollution and health problems arise as a result of adopting it? controls? Would the product quality be Would the consumer accept the substitute? different from present? Would the process require Would production rates be significantly different procedures affected? for handling rejects? • Would production costs be • Would production personnel need to develop significantly increased? different skills? • 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.

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

**Organization of this** Guide

What difficulties would arise and need to be overcome or controlled if the alternate processes were used, including:

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 fishing. 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.

#### Section One

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

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

**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.

	Available Cleaner Technologies						Emerging Cleaner Technologies				
Benefits	Non- Cyanide Copper Plating	Non- Cyanide Metal Strippin g	Zinc/Zin c Alloy Electro- plating	Blackhole Technology	Ion Vapor Depositio n	Physical Vapor Depositio n	Chromiu m-Free Aluminum Surface Treatments	Metal Spray Coating	Nickel- Tungste n-Silicon Carbide	Nickel- Tungsten- Boron	In-Mold Plating
Pollution Prevention:											
Replaces cyanide	~	~					~				· <u>·</u> ·····
Replaces toxic metal			1	~	~			V	~	~	
Eliminates/reduces wastewater			V	v				~			~
Eliminates toxic organics			~			V					
Operational:											
Reduced process steps			~	~		~					~
Ability to automate	~	V	~		~		~		~	~	
Economic:											
Relatively low capital costs	~	~	~		~		~				
Relatively low operating costs		~				<i>.</i>	v				~
Relatively low skill level to operate	~	~	~	~	v	V	~	~			

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

#### 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** The metals finishing industry is concerned with pollution and wastes and Processes 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 cvanide-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  $Cd(CN)_4^{-2}$ . 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 ( $CrO_3$ ), 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<br/>Waste HandlingThe major pollutants of concern in the metal finishing industry are spent<br/>solutions containing heavy metals and other toxic and noxious chemicals.<br/>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** Alkaline non-cyanide copper plating solutions eliminate cyanide from rinse **Benefits** water and sludges generated during waste treatment of the rinsewater. Noncyanide 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 Cu++ state as compared to 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

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.

**Operational and Product Benefits** 

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.
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#### 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
- ceanorogy -	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.

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**<br/>**Product Benefits**Cyanide based strippers typically contain chelating agents and strong metal-<br/>cyanide complexes that make waste treatment of spent strippers and<br/>rinsewater extremely difficult. The use of non-cyanide based strippers<br/>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.

	Facilities that co health and saf temperatures, co	onsider switching to non-cyanide strippers must consider the ety aspects of the substitute, such as higher operating prrosivity, and so on.
Hazards and Limitations	Non-cyanide m	etal strippers have some disadvantages:
	Þ	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.
	۲	Stripping rates for certain coatings might be lower than for cyanide-based counterparts.
	۲	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 Advances in no difficulty of trea improvement significantly slo development v product to hand	Fnickel coatings is a major use for non-cyanide strippers. n-cyanide alternatives for nickel have been spawned by the ting nickel-cyanide waste streams. Opportunities for further still remain, however, as non-cyanide processes are wer than cyanide processes (8 hours versus 1 hour). Future vill focus on speeding up the process and adjusting the le different metal coatings (e.g., silver) and substrates.
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#### 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 eliminate 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).

#### **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.

Why Choose this Technology?

			Bath Type		
	Alkaline Zinc	Alkaline Zinc- Nickel	Neutral Tin-Zinc	Alkaline Zinc-Iron	Acid Zir Cobalt
Deposit properties					
Appearance	Good	Good	Fair	Good	Exceller
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
Corrosion resistance			As plated		
To white rust	Fair	Excellent	Fair	Excellent	Fair
To red rust	Fair	Excellent	Excellent	Good	Good
			Heat treated	<u> </u>	
To white rust	Poor	Good	Poor	Poor	Poor
To red rust	Poor	Good	Fair	Poor	Poor
			After bendin	2	
To white rust	Fair	Good	Fair	Fair	Fair
To red rust	Fair	Good	Excellent	Fair	Fair
Bath characteristics					
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
Analysis & measurement			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
Anodes	Separate	Zinc	Alloy	Zinc	Zinc

#### **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.

			Plating bath		
Properties	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
рН	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

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 Sizelove, 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 Sizelove, 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. Zincnickel coatings have also reportedly been substituted for cadmium on fasteners for electrical transmission structures and on television coaxial cable connecters (Brooman, 1993).

#### Availability

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

	advertisements a and Surface Fin	ppearing in trade journals such as Metal Finishing, Plating nishing, and Products Finishing.
Operational and Product Benefits	Replacing cya described elimir reduces environ	nide-based cadmium coating with one of the processes nates workplace exposure to both cadmium and cyanide, and mental releases of both these chemicals.
	Additional oper the alloy relativ	ational benefits may result depending on the properties of re 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,.
	As discussed, the properties of	ne desired properties for the application must be matched to f the alloy.
Hazards and Limitations	Zinc and zinc- disadvantages:	nickel alloy electroplating processes have the following
		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 numerous vend considered as re- the move away expected to play more work new cadmium for sp	outlined above are well-developed and are available from ors. These alternatives, however, have only recently been eplacements for cadmium coatings. Industry recognizes that from cadmium plating is well underway and zinc alloys are y an important role as substitute (Zaki, 1993). Nonetheless, eds to be done to compare these alternative coatings to pecific applications.

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BLACKHOLE TECHNOLOG	GY

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

- ۲
- ►
- 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	ll.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  $135^{\circ}$ 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 conveyorized 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	<b>Process Simplification-The</b> Blackhole technology requires fewer process steps as well as associated chemicals and rinses, greatly reducing waste streams from PWB plating.
	<i>Contamination</i> Reduction-Unlike the electroless copper process, the Blackhole Technology Process does not use formaldehyde.
	<i>Ease of Implementation</i> -Because the Blackhole process uses existing equipment in an electroless copper process line, it should be very easy to implement.
	Acceptable Product Qualify-Product quality should not be affected. The Blackhole Technology process is accepted under MIL-P-55110D.
	<i>Lower Operating Costs-The</i> 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.
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#### 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, <b>and</b> 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 Lantim). 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-lpsen Co. of Bensalem, Pennsylvania. Abar-lpsen 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.

**Operational and Product Benefits** 

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  $925^{\circ}$ F, as compared to  $450^{\circ}$ 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 dis	advantages of IVD coatings are:
	۲	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.
	۲	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.
	Þ	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 alumi commercially applications.	num coating process is a mature technology that has been available for a decade and is suitable for specialized

REFERENCES	Hinton, <b>B.R.W.</b> and W.J. Pollock. 1991. Ion vapour deposited aluminum coatings for the corrosion protection of high strength steel. Aeronautical Research Laboratories (Australia). <i>Government Research Announcements and Index.</i> April. 52 pp.
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PHYSICAL VAPOR DEP	POSITION (PVD)
Pollution Prevention	Hexavalent chromium is extremely toxic and is a known carcinogen. Health

Pollution Prevention 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 $900^{0}$ 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:
	<ul><li>Evaporation</li><li>Sputtering</li></ul>

► 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.
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#### 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 chromare 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  $205^{0}$ F or higher.

**Stage** Three-Treat in a proprietary permanganate solution at 135 to 145  $^{0}$ 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. he 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<sup>0</sup>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 (199 1).

**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.

Wear resistance	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.	
Dimensional Restoration	Coatings can be applied up to 0.100 inch thick to restore worn dimensions and mismachined surfaces.	
Corrosion Resistance	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.	
Thermal Barriers	Zirconia $(ZrO_2)$ coatings are applied to insulate base metals from the high-temperature oxidation, thermal transients, and adhesion by molten metals.	
Abrasion	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.	
Dielectrics	Alumina $(Al_2O_3)$ is generally used to resist electrical conductivity. These coatings have a dielectric strength of 250 V/mil of coating thickness.	
Conduction	Materials are selected for their intrinsic thermal or electrical conductivity. Copper, aluminum. and silver are frequently used for this application.	
RFI/EMI Shielding	These conductive coatings are designed to shield electronic components against radio frequency or electromagnetic interference. Aluminum and zinc are often selected.	
Medical Implants	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. <i>Advanced Materials &amp;</i> Processes. October. pp. 63-68.
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#### SECTION FOUR EMERGING TECHNOLOGIES

Introduction	Three emerging this section:	clean process changes for metal finishing are presented in
	•	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 EfJiciencies-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 NiSO <sub>4</sub> 6H2 <sub>0</sub>	30-40g/l
Sodium tungstate Na <sub>2</sub> WO <sub>4</sub> 2H <sub>2</sub> O	55 - 75 g/l
Ammonium citrate NH4HC6H5O7	70-110 g/l
Silicon carbide (0.8 - 1.5 urn particles)	10 - 50 <b>g/l</b>
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-silcon 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 pH2 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 ben 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/RFl 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.
	<b>Process substitutions-(e.g.,</b> 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:
	<ul> <li>Ability to cover complex shapes somewhat uniformly (high throwing power).</li> <li>High tolerance to impurities.</li> <li>High tolerance to improperly cleaned surfaces.</li> <li>Ability to obtain a porous deposit that allows for hydrogen embrittlement relief.</li> <li>Ability to obtain a ductile deposit at high thicknesses.</li> <li>High adhesion to substrates.</li> </ul>
	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-A significant effort is being made in the aerospace industry to evaluate Silicon Carbide and chromium substitutes produced from alternate aqueous electroplating processes. The main focus of these efforts is the application of an alloy of Nickel-Tungsten-**Boron Alloy Plating** nickel and tungsten containing finely dispersed particles of silicon carbide, molybdenum plating, and an aboy of nickel-tungsten-boron. The nickel tungsten aboy 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 that 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 that 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 unfunctional 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 ahoy, 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 fishing 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

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

American Institute of Chemical Engineers (AIChE) 345 E. 47th St.. New York, NY 10017 212/705-7338 2121752-3297 FAX

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

American Zinc Association 1112-16th St., N.W, Ste. 240 Washington, DC 20036 202/835-0164 202/835-0155 FAX Aluminum Anodizers Council 1000 N. Rand Rd., Ste. 214 Wauconda, IL 60084 708/526-2010 708/526-3993 FAX

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

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

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

ASM International Materials Park, OH 44073 216/338-5151 216/338-4634 FAX Aluminum Association 900 19th St., N. W, Washington, DC 20005 202/862-5100 202/862-5164 FAX

American Galvanizers Association 12200 E. Iliff Ave., Ste. 204 Aurora, CO 80014-1252 303/750-2900 303/750-2909 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 of Electroplated Plastics (ASEP) 1101 14th St., N.W, Ste. 1100 Washington, DC 20005 202/371-1 323 202/371-1090 FAX

Associacio Brasileira De Tratmentos De Superficie (ABTS) Av. Paulista, 1313,9<sup>0</sup> Andar Conj. 913 Cep01311 Sao Paulo, SP Brazil 55 11 289 75 01 55 11 251 25 88 FAX Association Francaise Des Ingenieurs Et Techniciens De L'Electrolyse Et Des Traitements De Surface 5 me Le Bua Paris 75020 France 14 030 06 80

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

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

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

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

International Copper Association Ltd. 260 Madison Ave. New York, NY 10016 212/251-7240 212/251-7245 FAX Australasian Institute of Metal Finishing Clunies Ross House 191 Royal Parade Parkville, Victoria 3052 Australia 613 347 2299 613 347 9162 FAX

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

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

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

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

International Hard Anodizing Association 14300 Meyers Rd. Detroit, Ml 48227 313/834-5000 3131834-5422 FAX Bumper Recycling Association of North America (BRANA) 1730 N. Lynn St., Ste. 502 Arlington, VA 22209 703/525-1191 703/276-8196 FAX

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

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

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

Institute of Metal Finishing (IMF) Exeter House 48 Holloway Head, Birmingham B1 INQ England 44 21622 73 87 44 21666 63 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 703/821-1 824 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 Manufacturers (NAAMM) 6005. Federal St., Ste. 400 Chicago, IL 60605 312/922-6222 3121922-2734 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 B 18 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 7131492-8254 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 O2903 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 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