GUIDE TO
CLEAN TECHNOLOGY

ALTERNATIVE METAL FINISHES

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United States Environmental Protection Agency

NOTICE

This *Guide to Clean Technology: Alternative Metal Finishes* summarizes information collected from U.S. Environmental Protection Agency programs, peer-reviewed journals, industry experts, vendor data, and other sources. The original Quality Assurance/Quality Control (QA/QC) procedures for the reports and projects summarized in this guide range from detailed, reviewed Quality Assurance Project Plans to standard industrial practice. Publication of the guide 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 to provide guidance in identifying new approaches for pollution prevention in metal finishing operations. Final selection of a technology will be shop- and process-specific and, therefore, will be done by the individual users of metal finishing processes. Compliance with environmental and occupational safety and health laws is the responsibility of each individual business and is not addressed in this document.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the U.S. EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

Reducing the use of hazardous metals at the source or recycling the wastes on site will benefit industry by reducing disposal costs and lowering the liabilities associated with hazardous waste disposal.

Publications in the U.S. EPA series, *Guides to Pollution Prevention*, provide an overview of several industries and describe options to minimize waste in these industries. Their focus is on the full range of operations in existing facilities. Many of the pollution prevention techniques described are relatively easy to implement in current operations without major process changes.

This *Guide to Clean Technology: Alternative Metal Finishes* summarizes new commercially available and emerging technologies that prevent and/or reduce the production of hazardous materials during metal finishing processes. The technologies described in this document and in other documents in this series are generally "next generation" clean technologies that sometimes represent relatively major process changes, requirement for new training, and capital cost investments compared to the technologies described in the *Guides for Pollution Prevention*. The waste minimization techniques characterized in the *Guides for Pollution Prevention* should be considered and implemented first. They should be considered for retrofitting into current operations and for major plant expansions and new grass roots facilities.

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SECTION 1

OVERVIEW

What is Clean Technology?

A *clean technology* is a source reduction or recycling method applied to eliminate or significantly reduce hazardous waste generation. *Source reduction* includes product changes and source control. *Source control* can be characterized as input material changes, technology changes, or improved operating practices.

Pollution prevention should emphasize source reduction technologies over recycling but, if source reduction technologies are not available, recycling is a good approach to reducing waste generation. Recycling should be used where possible to minimize waste treatment requirements that remain after viable source reduction options have been evaluated and/or implemented.

The clean technology must reduce the quantity and/or toxicity of the waste produced. It is also essential that final product quality be reliably controlled to acceptable standards. In addition, the cost of applying the new technology relative to the cost of similar technologies should be considered.

Why Finish Metals?

Metal and surface finishing processes are applied in a variety of industries to improve product appearance, retard corrosion, provide hardness, protect sensitive components, control reflectivity, control friction, enable conductivity, or build up material for repair. Industries that apply metal finishes include:

- ♦ Automotive
- ♦ Electronic
- ♦ Aerospace
- ♦ Telecommunications
- ♦ Appliances

Types of finishes and processes that present pollution problems include:

- ♦ Cadmium coatings
- ♦ Cyanide-based solutions
- ♦ Chromium plating

Waste disposal regulations for waste generated from metal finishing operations are becoming more stringent. The amounts of metal allowed in wastewater discharges are approaching very low levels.

Overview

Some municipalities now require levels near zero. The metals can be removed and the other materials destroyed, but the resulting metal sludge (from typical hydroxide precipitation) is landfilled as a hazardous waste if not reclaimed.

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

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 numerous chemical baths that are followed by rinsing operations. The most common hazardous waste sources are rinse water effluent and spent process baths.

Although the most common hazardous waste stream is industrial waste treatment sludge, the industrial waste treatment process is not the source of this waste. The sources are the production activities that create the waste.

In selecting a metal finish, the process to be performed as well as the type of waste that might be generated are important considerations.

Pollution Problem

Metal coatings such as cadmium, lead, nickel, and chromium; solutions such as cyanides; and processes such as etching and electroplating these substances can generate waste streams requiring treatment. Some hazardous characteristics are shown in Table 1.

Cadmium is used in plating because it has properties that are superior to those of other coatings for some applications. It is used to plate fasteners to help ensure that the parts pass *torque-tolerance* tests. This simulates the action of a power wrench tightening a nut on a bolt. The nut should tighten quickly under the proper applied torque and hold securely thereafter. Cadmium is a soft metal and has natural lubricity; these properties give it good torque. It also has good corrosion resistance and meets salt-spray test requirements of the automotive industry. In the past, numerous military specifications have required the use of cadmium.

Table 1. Polluting Characteristics of Contaminating Metals

Substance	Toxicity Level	Contaminating Pathways
Cadmium (Cd)	High: • Poisoning from inhalation of fumes or dusts • Immediately dangerous to human health upon exposure to 1 mg/m^3 over an 8-h period (Chizikov, 1966) • Lethal in air concentrations of 6 mg/m^3	• Fumes formed at high temperatures industrial processes such as welding and brazing • Fumes released from incinerators that are unequipped with pollution control devices • Ingestion from cadmium-contaminated water and foods
Cyanide (Cn) and hydrogen cyanide (HCN)	High: Death can occur within seconds after inhalation or ingestion.	• HCN enters the human body by inhalation, skin absorption, or orally. It is described as having the odor of bitter almonds, but one of five people cannot sense this odor, causing it to be all the more dangerous to them. • Encountered as an industrial waste through the production of HCN and when other cyanide compounds are acidified.
Chromium (Cr)	High: The hexavalent form of chromium is a carcinogen.	• Inhalation of mist formed at plating bath. • Ingestion of chromium-contaminated water and food.

Overview

The major cadmium complex used in electroplating baths is cadmium cyanide, $Cd(CN)_4^{-2}$; other plating electrolytes include cadmium sulfate, sulfamate, chloride, fluoroborate, and pyrophosphate. Cadmium borates are used with a fluoroborate process for electrodeposition of cadmium on high-strength steels. Cadmium oxide is used in electroplating baths, dissolved in excess sodium cyanide.

Sodium cyanide is used in electroplating baths for copper, zinc, cadmium, gold, and silver. Potassium cyanide is also used in electroplating. Nickel cyanide is used as a brightener in plating of other metals, and silver cyanide and zinc cyanide are used, respectively, in silver and zinc plating. In the plating process, these metals form complex cyanides, such as ferrocyanide and ferricyanide complexes with iron. Although these complexes are less toxic, they are also resistant to removal by treatment processes, and are decomposed by ultraviolet light, so that there is a possibility of generating HCN in wastestreams containing cyanide complexes discharged by industry.

Although electroplating is often assumed to be a major source of cyanide waste, the figures do not support such a view (Conner, 1990). According to the 1988 TRI Report (U.S.EPA, 1988), cyanide use in Plating and Polishing (SIC 3471) accounted for under 500,000 pounds, while Blast Furnaces and Steel Mills (SIC 3312), for example, accounted for over three times this amount.

Cyanide waste generated in metal finishing comes primarily from copper, zinc, cadmium, silver, and gold plating, where large amounts of sodium and potassium cyanides and smaller amounts of metal cyanides are used. A considerable volume of wastewater is produced in the finishing industry. This waste usually contains dilute cyanide (10-770 ppm) from rinsing operations.

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 the standard method for improving the hardness; smoothness; or resistance to wear, abrasion, galling, or high temperatures for a wide variety of substrates. 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 of chromium's traditional applications. Design engineers will be required to be more selective in specifying chromium plating by exploring alternative technologies.

Chromium coatings are electrolytically applied to substrates from an aqueous solution of chromic acid and sulfuric acid. The most common form of chromium in the plating baths is hexavalent chromic acid. Chromium metal is deposited on the substrate by a complex six-electron reduction. The reduction reaction is catalyzed by the sulfuric acid. Plating from a hexavalent bath reliably produces a bright chromium plating. However, the current efficiency, the quantity of chromium deposited per unit of electric energy used, the throwing power, and the ability to produce a uniform coating over a large area are low. Hydrogen produced by the plating operation can migrate into the metal substrate and embrittle it. The use of hexavalent chromium involves operator exposure to chromic acid – a toxic material – and requires treatment and disposal of chromium waste.

Solution

Clean technologies now exist or are being developed that would reduce or eliminate the use of cadmium, cyanide, and chromium for many metal finishing operations. There are two main focuses in describing clean technologies for metal finishing:

- **Alternative finishes** (e.g., aluminum, zinc or zinc alloys, and nickel-tungsten-silicon carbide) replace cadmium and chromium.
- **Process changes** (Blackhole™ Technology, ion vapor deposition, physical vapor deposition, in-mold plating, and metal spray) use different technologies for metal finishes. The capital costs may be greater for process changes, but the reduced cost of disposing of hazardous wastes often makes up for this.

Traditionally, most cadmium plating is done using cyanide because the baths exhibit excellent throwing power. Other plating solutions that do not contain cyanide and offer high cathode efficiency at high current density are being tried. These baths contain metallic salts such as neutral sulfates, acid sulfates, and acid fluoroborates. Non-cyanide baths are often preferred for cadmium plating of quenched and tempered high strength steels because less hydrogen is generated, thus lessening the danger of embrittlement. Ajax Metal Processing in Detroit plates a large number of parts using a proprietary non-cyanide method (Humphreys, 1989).

Incorporating process changes that do not use cyanide baths or increasing use of cyanide recovery systems will diminish cyanide pollution.

Sodium cyanide is considered to be a multipurpose ingredient in many plating operations, but is especially important when plating the more noble metals. However, many alternatives are now being investigated for pollution control. Some examples are acid fluoroborate in cadmium plating, copper pyrophosphate or copper sulfate in copper plating, gold sulfite in gold and gold alloy plating, silver succinimide and silver sulfite/thiosulfate in silver plating, and acid chloride and alkaline noncyanide zinc baths for zinc plating.

It may be possible to replace chromium plating with an alternative substrate that will provide sufficient hardness or corrosion resistance. For example, advanced ceramic and composite materials have been tested as replacements for metal parts in internal combustion engines. If an alternative substrate is not available, it may be possible to produce a coating with the necessary properties without plating from an aqueous bath. Hard coatings can be applied by physical vapor deposition (PVD). For example, titanium nitride is used as a coating to improve the wear resistance of cutting tools.

PVD coatings are applied in a heated vacuum chamber. A gas plasma or electric arc heats and vaporizes the metal that is to be plated onto the substrate. The vaporized metal ions are deposited onto the substrate as a thin, hard film (Gresham, 1991). PVD coatings are generally harder and thinner than electrolytically deposited coatings. The major research need is to develop PVD coatings that have the required adhesion, hardness and coating thickness, as well as other required performance characteristics, uniformly over a large complex part.

Aqueous electroplating with less hazardous metals is another approach to reducing use of chromium plating. The electroplating operation is conceptually the same as chromium plating but, of course, uses different bath composition and plating conditions such as voltage and current. Possible alternatives include nickel-tungsten-silicon carbide plating (Schiffelbein, 1991) and molybdenum plating (Groshart, 1989).

The major research need is to develop replacements for chromium that give the required hardness and coating thickness, as well as other required performance characteristics, at a reasonable cost. Given the generally low current efficiency, deposition rate, and throwing power of hexavalent chromium plating, it is likely that alternative plating systems will give similar or better production rates.

There is a continuing trend in the chromium plating industry toward replacing hexavalent chromium baths with trivalent chromium baths, although trivalent plating is used mainly for appearance coatings rather than for hard coatings. The chromium chemicals used in trivalent plating are more expensive than those used in hexavalent plating. Some of the higher cost can be offset by the higher current efficiency and better throwing power of the trivalent process, as well as by selection of additives and process optimization to reduce costs.

An impediment to wider acceptance of trivalent chromium was the color and finish achieved. Trivalent chromium gives a "gray" lustrous finish that is acceptable in many applications. While appearance should not be a major concern in most hardness and corrosion resistance applications, many customers prefer the "blue" finish typical of chromium plating from a hexavalent bath. Some trivalent baths are now said to provide a better color match.

Research is needed to optimize trivalent chromium plating and expand its range of application. The major area of concern is to develop trivalent chromium plating methods that produce a coating with similar thickness, hardness, and color to hexavalent chromium plating. Methods to optimize the trivalent plating bath composition and operation to reduce costs are needed.

Chromium plating is applied in some cases mainly to improve the appearance of the part. The plating solutions and procedures for appearance plating are similar to those for chromium plating. However, the operating conditions such as plating current and voltage are different.

Plated parts could be replaced by brushed aluminum or stainless alloy parts to eliminate the need for plating; a less hazardous metal could be applied to reduce the potential for pollution; or refractive plastics coatings could be used to eliminate metal plating. Because the appearance plating baths are similar in chemical composition to the chromium plating baths, optimization and the bath recovery and recycling approaches for functional chromium will also apply. Appearance chromium coatings have lower wear resistance and thermal resistance requirements, so additional options are available for chromium replacement in appearance applications.

Anodizing with chromic acid is a process for treating aluminum to give a highly corrosion-resistant coating that offers an excellent surface for bonding and painting. Anodizing uses electrochemical methods to form a thin aluminum oxide surface layer that contains chromium ions. Sodium dichromate as a sealant enhances fatigue properties after anodizing by depositing an oxydichromate compound into the anodized layers. Chromate solutions can be used to chemically deposit a thin hydrated chromium oxide film to prepare metal surfaces for subsequent painting (Evanoff, 1990).

What's In This Guide?

This application guide describes clean technologies that can be used to reduce waste in metal finishing operations. Its objectives are:

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

The following questions are addressed:

- What alternative metal finishing alternatives are available or emerging that could significantly reduce or eliminate pollution being generated from current operations?
- Under what circumstances might one or more of these alternatives be applicable to your operations?
- What pollution prevention, operating, and cost benefits could be realized by adapting the technology?

Other Questions Affecting Investment Decisions

These other considerations will affect the decision to explore one or more clean technologies for metal finishing:

- Might new pollution problems arise when implementing clean technologies?
- Will tighter, more complex process controls be needed?
- Will product quality and operating rates be affected?
- Will new operating or maintenance skills be needed?
- What are the overall capital and operating cost implications?

To the extent possible, these questions are answered in this guide. The clean technologies described in this guide are applicable under different sets of product and operating conditions. If one or more alternatives seem attractive for your operations, the next step is to contact vendors or users of the technology to obtain detailed engineering data in order to perform an in-depth evaluation of its potential for your plant.

Who Should Use This Guide?

This application guide has been prepared for plant process and system design engineers and for personnel responsible for process improvement. Process descriptions within this guide will help users evaluate options so that clean technologies can be considered for existing plants and factored into the design of new metal finishing operations.

This guide's purpose is to present sufficient information to enable users to select one or more candidate technologies for further analysis and in-plant testing. This guide does not recommend any one technology over any other. It presents concise summaries of applications and operating information to support preliminary selection of clean technology candidates for testing in specific processes. Sufficient detail is provided to allow identification of possible technologies for immediate application to eliminate or reduce waste production.

The keywords listed below will help you quickly scan the available and emerging technologies covered.

Keywords		
Clean Technology	Metal Finishing	Blackhole™ Technology
Pollution Prevention	Plating	Ion Vapor Deposition (IVD) of Aluminum
Source Reduction	Electroplating	Non-Cyanide Copper Plating
Source Control	Anodizing	Non-Cyanide Metal Stripping
Recycling	Metal Deposition	Zinc or Zinc/Nickel Alloy Electroplating
	Electroless Plating	Physical Vapor Deposition (PVD)
	Etching	Nickel-Tungsten-Silicon Carbide Plating
	Metal Stripping	Chromium-Free Aluminum Surface Treatment
	Ionization	In-Mold Plating
	Vapor Deposition	Metal Spray Coating
	Sputtering	
	Injection Molding	

Summary of Benefits

The clean technologies described in this guide are divided into two groups based on their maturity – commercially available technologies and emerging technologies in advanced pilot plant testing.

Table 2 summarizes the pollution prevention, operational, and economic benefits of these metal finishing process alternatives. You may wish to scan this summary table to select those clean technologies that best fit your operations and needs. Detailed discussions of the benefits and operational aspects for each clean technology are provided in Sections 2 and 3.

Table 2. Summary of Benefits of the Clean Technologies for Metal Finishing Alternatives

Benefits	Available Technologies					Emerging Technologies				
	Blackhole™ Technology	Ion Vapor Deposition (IVD) of Aluminum	Non-Cyanide Copper Plating	Non-Cyanide Metal Strip-ping	Zinc or Zinc/Nickel Alloy Electroplating	Physical Vapor Deposition (PVD)	Nickel-Tungsten-Silicon Carbide Plating	Chromium-Free Aluminum Surface Treatment	In-Mold Plating	Metal Spray Coatings
Pollution Prevention:										
Replaces cyanide			●	●						
Replaces toxic metal	●	●			●	●	●	●		
Eliminates/reduces wastewater	●	●				●			●	●
Eliminates toxic organics	●									
Operational:										
Reduced process steps	●					●			●	●
Batch process	●	●	●	●	●	●	●	●		●
High throughput	●*									
Economic:										
Relatively low capital costs	●		●	●	●			●		
Relatively low operating costs				●	●				●	●
Relatively low skill level to operate	●	●	●	●	●			●		●

*When using horizontal wet processing system.

SECTION 2

AVAILABLE TECHNOLOGIES

How to Use the Summary Tables

Five available clean technologies for metal finishing are evaluated in this section:

- Blackhole™ Technology (electroless copper alternative)
- Ion vapor deposition (IVD) of aluminum as an alternative for cadmium coatings
- Non-cyanide copper plating as an alternative to cyanide-based copper plating
- Non-cyanide metal stripper to replace cyanide-based strippers
- Zinc or zinc-nickel alloy electroplating as alternatives to cadmium electroplating

Tables 3 and 4 summarize descriptive and operational aspects of these technologies. They contain evaluations or annotations describing each available clean technology and give users a compact indication of the range of technologies covered to allow preliminary identification of those technologies that may be applicable to their specific situations. Readers are invited to refer to the summary tables throughout this discussion to compare and contrast technologies.

Descriptive Aspects

Table 3 describes each available clean technology. It lists the **Pollution Prevention Benefits**, **Reported Applications**, **Operational and Product Benefits**, and **Hazards and Limitations** of each available clean technology.

Operational Aspects

Table 4 shows key operating characteristics for the available technologies. The rankings are estimated from descriptions and data in the technical literature and are based on comparisons to typical technologies that the clean technologies would replace.

Process Complexity is qualitatively ranked as "high," "medium," or "low" based on such factors as the number of process steps involved and the number of material transfers needed. **Process Complexity** is an indication of how easily the technology can be integrated into existing plant operations. A large number of process steps or input materials or multiple operations with complex sequencing are examples of characteristics that would lead to a high complexity rating.

The **Required Skill Level** of equipment operators also is ranked as "high," "medium," or "low." **Required Skill Level** is an indication of the relative level of sophistication and training required by staff to operate the new technology. A technology that requires the operator to adjust critical parameters would be rated as having a high skill requirement. In some cases, the operator may be insulated from the process by complex control equipment. In such cases, the operator skill level is low but the maintenance skill level is high.

Table 4 also lists the **Waste Products and Emissions** from the available clean technologies. It indicates tradeoffs in potential pollutants, the waste reduction potential of each, and compatibility with existing waste recycling or treatment operations at the plant.

The **Capital Cost** column provides a preliminary measure of process economics. It is a qualitative estimate of the initial cost impact of the engineering, procurement, and installation of the process and support equipment. Due to the diversity of data and the wide variation in plant needs and conditions, costs will vary for each facility. Cost analyses must be plant-specific to adequately address factors such as the type and age of existing equipment, space availability, production volume, product type, customer specifications, and cost of capital.

The **Energy Use** column provides data on energy conversion equipment required for a specific process. In addition, some general information on energy requirements is provided.

The last column in Table 4 lists **References** to publications that will provide further information for each available technology. These references are given in full in Section 4.

The text further describes pollution prevention benefits, reported applications, operational and product benefits, hazards and limitations, tradeoffs, unknowns, and the current state of development for each available technology. Technologies in earlier stages of development are summarized to the extent possible in Section 3, Emerging Technologies.

Table 3. Available Clean Technologies for Metal Finishing: Descriptive Aspects

Available Technology Type	Pollution Prevention Benefits	Reported Applications	Operational and Product Benefits	Hazards and Limitations
Blackhole™ Technology	• Avoids copper • Avoids formaldehyde • Reduces water use	• Replaces electroless copper metalization of through-holes prior to electrolytic plating for PWBs	• Uses carbon black suspension to provide a thin conductive coating • Fewer process steps • Simple process • Less water used • Meets military standards	• Process not accepted by all PWB users • May increase solids loading to wastewater treatment
Ion Vapor Deposition (IVD) of Aluminum	• Alternative for cadmium • Avoids aqueous waste streams	• U.S. DoD Contractors • Incorporated into several military and industrial specifications	• Two process steps for cleaning and plating, no rinsing • Permits thicker coatings • Can be used at higher temperatures (925°F) as compared to 450°F for cadmium	• Cannot apply aluminum to deep recesses • Coating tends to be porous • Chromate conversion coating, or equivalent, required as with cadmium or zinc coatings for maximum corrosion protection
Non-Cyanide Copper Plating	• Avoids cyanide	• Widespread industrial use	• Better throwing power • Reduced safety risks • Reduces treatment costs • No carbonate problems	• Parts need to be cleaner before plating • Less able to provide levelling
Non-Cyanide Metal Stripping	• Avoids cyanide	• Kelly Air Force Base • Increasing industrial use	• Reduces waste treatment costs • Reduced safety risks • Increased bath life • No carbonate problems	• High operating temperature may be required • Slower stripping rates typical • Stripper may cause undesirable substrate effects
Zinc or Zinc-Nickel Alloy Electroplating	• Replacement for cadmium	• Many industrial applications	• Uses equipment similar to that used in cadmium plating • Comparable corrosion resistance • Better wear resistance (Ni-Zn) • Better ductility (Ni-Zn)	• Higher contact resistance • Lower lubricity • Acid zinc coatings have comparatively poor throwing power

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Table 4. Technologies for Metal Finishing: Operational Aspects

Available Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Capital Cost	Energy Use	Operations Needed After Application	References
Blackhole™ Technology	Low	Low	• Rinsewater containing carbon powder and complexing agents • Used solution	• Low • Solution cost medium	Low	• Treat wastewater generated • Electrolytic copper plating (same as for electroless copper)	Bracht and Piano, 1990 Olin Hunt, undated Polakovic, 1988
Ion Vapor Deposition (IVD) of Aluminum	Medium	High	• No waste product	• High	High	• May need lubricant for lubricity requirements • Chromate conversion coating or equivalent	Ahmed, undated Carpenter, 1988 Hinton, 1987 Holmes, 1989
Non-Cyanide Copper Plating	Low	Low	• Rinsewater • Used solution	• Low: Use existing tanks • Solution cost medium	Low	• None	Electrochemical Products, Inc., undated Kline, 1990 Krishnan, 1990 Udylite, undated
Non-Cyanide Metal Stripping	Low	Low	• Rinsewater • Used solution	• Low: Use existing tanks • Solution cost medium	Low	• None	Electrochemicals, Inc., undated Frederick Gumm Chemical Company, undated Janikowski et al., 1989
Zinc or Zinc-Nickel Alloy Electroplating	Low	Low to medium	• Rinsewater • Used solution	• Use existing tanks • Solution low to medium	Low	• Chromate conversion coating	Hanna and Noguchi, 1988 Ko et al., 1991 Sharples, 1988 Sizelove, 1991

BLACKHOLE™ TECHNOLOGY

Pollution Prevention Benefits

The Blackhole™ Technology Process is an alternative to the electroless copper method. It claims the following qualities that make it environmentally attractive:

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

The chemicals used in the low number of process steps avoids the use of metals and formaldehyde. The small number of process steps also results in less rinse water used, reducing waste treatment requirements.

How Does It Work?

The Blackhole™ Technology Process uses an aqueous carbon black dispersion (suspension) operating at room temperature to prepare through-holes in printed wire boards (PWBs) for subsequent copper electroplating. The carbon film obtained provides the conductivity needed to electroplate copper in the through-holes. The process steps are listed 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.

Operating Features

PWBs must be pretreated in the same way as those for electroless copper for desmear/etchback. Permanganate is the preferred desmear process for Blackhole™ Technology due to its wide operating conditions and resultant hole-wall topography.

Basic Function. Conventional plating tanks and horizontal conveyorized systems can be used for the Blackhole™ Technology Process. The process steps are explained in the following paragraphs.

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

The conditioner also is a slightly alkaline solution containing a weak complexing agent, which operates at room temperature. The conditioner is used to neutralize the negative charge on the dielectric surfaces which helps increase the absorption of the carbon in the next step.

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

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

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

These steps are typically done in the above sequence in a process line that uses an automated hoist to move racks of parts from tank to tank. All the rinses are single use and generate large quantities of wastewater containing copper. The rinses following the electroless copper bath (Step 11) contain complexed copper, which is hard to treat by typical wastewater treatment technology, namely metal hydroxide precipitation.

The Blackhole™ Technology process replaces the electroless copper used 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
2. Rinse
3. Blackhole™ alkaline conditioner
4. Rinse
5. Blackhole™ bath
6. Dry
7. Micro-etch
8. Rinse
9. Anti-tarnish dip
10. Rinse
11. Dry

Steps one through six are performed, then repeated. Steps seven through twelve are performed. All process steps are done automatically in a horizontal conveyor system or can be done using existing hoists and bath systems.

Material and Energy Requirements. 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 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 and is gaining acceptance. Military Standard MIL-P-55110D now permits through-hole plating technologies other than electroless copper.

Availability

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

Operational and Product Benefits

- Process Simplification. The technology reduces the number of different process steps and their associated chemicals and rinses. This greatly reduces waste streams.
- Contamination Reduction. Avoids formaldehyde in the electroless copper solution.
- Ease of Throughput. The operation using existing equipment from an electroless copper process line would be about the same. The use and installation of a horizontal process line would ease operation, especially if the electroless copper line was hand-operated.
- Acceptable Product Quality. The product quality should not be affected. The Blackhole™ Technology process is accepted under MIL-P-55110D.
- Lower Operating Costs. Costs for chemicals, water, and wastewater treatment are reduced.

Hazards and Limitations

- Potential Health Risk. By using a carbon black suspension, this technology avoids the use of metals (copper, palladium, and tin) and formaldehyde. The process solutions contain some chemicals that are irritants. The overall health risk would be reduced by using the technology.

- Potential Peripheral Costs. None.

Tradeoffs

Due to current limited use of this technology, it may not be widely accepted by all PWB users.

State of Development

The Blackhole™ Technology is commercially available.

ION VAPOR DEPOSITION (IVD) OF ALUMINUM

Pollution Prevention Benefits

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

How Does It Work?

Ion vapor deposition (IVD) is a coating method whereby the coating metal is evaporated and partially ionized before being deposited on the substrate. A typical IVD system consists of a steel vacuum chamber, a pumping system, a parts holder, an evaporation source, and a high-voltage power supply. A vacuum is drawn on the chamber, which is then backfilled with argon. A large negative potential is then applied between the evaporation source and the parts to be coated. The argon ions created by the potential difference help clean the substrate surface.

Then the coating metal typically is heated resistively in a crucible and exposed to the ionized argon. The ionized gas molecules collide with the metal vapors and ionize some of the metal molecules. The metal molecules are accelerated toward the substrate, which results in good adhesion of the coating.

Why Choose This Technology?

Applications

IVD aluminum coatings can be applied to a wide variety of metallic substrates, including aluminum alloys. Because deposition is not limited to "line of sight" applications, parts with complex shapes, such as fasteners, can be coated. However, coating inside blind holes, tubes, or deep recesses is difficult.

Operating Features

IVD has the following operating features:

- Large and/or complex parts can be plated.
- The technology is not limited to "line of sight" applications.
- There is no buildup of the coating on sharp edges, such as can occur in electroplating.
- Thicker coatings can be applied than when cadmium is used.

Required Skill Level

With some training, operators who have performed cadmium electroplating operations can perform aluminum IVD. Aluminum IVD involves more decision-making than does cadmium electroplating, but this difference should not require replacement of operators.

Cost

Capital costs for aluminum IVD equipment are higher than those for cadmium electroplating equipment. However, the aluminum IVD process requires no pollution control equipment. If pollution control equipment costs are included in the comparison, the costs for aluminum IVD are competitive. In comparing costs to other cadmium coating processes, costs for the aluminum IVD process are higher than those for the cadmium physical vapor deposition process, but are lower than those for either the low-embrittlement or diffused nickel-cadmium processes. Costs for cadmium electroplating are likely to keep rising due to ever-increasing hazardous waste disposal costs. In contrast, expanding use of IVD aluminum probably will 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.

Availability

The aluminum IVD process was developed in large part by the McDonnell Aircraft Company (a subsidiary of McDonnell-Douglas), St. Louis, Missouri. The equipment developed by McDonnell is called the Ivadizer^{R}. In 1987, McDonnell sold the rights to the process to the Abar-Ipsen Co. of Bensalem, Pennsylvania. Abar-Ipsen currently manufactures the equipment. Other companies have licenses to use the technology.

Operational and Product Benefits

Health and safety risks are greatly reduced when this technology is used in place of cadmium electroplating. Cadmium is a significant health hazard. as is the cyanide bath often used in cadmium electroplating.

For many applications, a chromate conversion coating is used on 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 should not require increased use of these coatings.

The greatest advantage of aluminum IVD is that the process generates no hazardous waste. Therefore, no pollution-control systems are required. Other potential advantages of aluminum IVD coatings are listed below:

- Outperforms cadmium coatings in preventing corrosion in acidic environments.
- Can be used at temperatures up to 925°F, as compared to 450°F for cadmium.
- Can be used to coat high-strength steels without danger of hydrogen embrittlement because, 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).
- Permits thicker coatings of several mils compared to about 1 mil for electroplated and vacuum-applied cadmium, thus increasing the corrosion resistance of the coating.
- Provides better coating uniformity on edges of parts than does electroplating.

Hazards and Limitations

Some of the disadvantages of IVD coatings are listed below:

- It is difficult to coat the interiors of blind holes of cavities that have a depth greater than their diameter.
- Aluminum IVD coatings have higher coefficients of friction than cadmium coatings. This changes the torque tension relationships for fasteners. This problem is manageable with use of lubricants.
- Unlike cadmium, aluminum IVD cannot be combined with nickel to provide a more erosion-resistant surface.
- The is no simple way to repair damaged aluminum IVD coatings.
- Aluminum IVD is slower than cadmium electroplating. However, for high-strength parts, 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 this time-consuming treatment, thus compensating for the slower application speed.

- Aluminum IVD coatings often take on columnar structures with porosities high enough to allow access to the base metal. Coatings can be peened with glass beads to make the coating more dense and minimize this problem, or the coatings can be sealed.

State of Development

The IVD coating for aluminum is commercially available. Aluminum IVD is a mature technology. New technologies or techniques could affect the process, but no significant changes are expected in the aluminum IVD process in the near future.

NON-CYANIDE COPPER PLATING

Pollution Prevention Benefits

The main benefit of using a non-cyanide copper plating process is that it eliminates use of cyanide. Spent cyanide plating solutions require extensive treatment before they can be disposed of. In contrast, treatment of spent non-cyanide copper plating solution is simple and straightforward. It requires only treatment with lime or other calcium-containing compounds prior to disposal.

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 to a non-cyanide process.

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. It can be used on fasteners, marine hardware, plumbing hardware, textile machinery, automotive and aerospace parts, masking applications, electro-magnetic interference (EMI) shielding, and heat treatment stop-off. It can be used as a complete coating or as a strike bath only.

Operating Features

Non-cyanide copper plating has the following characteristics:

- Bath temperatures are typically elevated (110 to 140°F)
- The pH is in the range of 8.8 to 9.8.
- Its throwing power is as good as that of cyanide-based processes.
- Deposits are matte in appearance with a dense, fine-grained amorphous microstructure.
- With additives, semi-bright to bright appearances can be obtained.
- Copper ions are in the Cu^{++} state as compared to Cu^{+} for the cyanide-based bath.

Assuming 100% cathode efficiencies, a non-cyanide bath requires twice the current to plate a given amount of copper as does a cyanide bath. However, the current density can be increased to levels such that plating speed is equivalent to cyanide-based baths.

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. The same operating personnel should be capable of operating the non-cyanide process.

Cost

Operating costs for the bath itself are substantially higher for the non-cyanide process. However, because replacing the cyanide-based bath with a non-cyanide bath eliminates the need for treatment of cyanide-containing solutions, the cost differential between the two processes is greatly reduced if not eliminated.

Reported Applications

Use of non-cyanide copper plating baths is not widespread in industry.

Availability

The process is available commercially from several sources. These sources typically advertise in the following trade journals:

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

Operational and Product Benefits

Non-cyanide copper plating has the following benefits:

- Greatly reduces safety risks to workers.
- Greatly reduces costs of treating spent plating solutions.
- Dragout to an acidic bath provides 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. Electroplaters are most at risk through ingestion and inhalation of hydrogen cyanide (HCN). 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 addition of an acid to a cyanide-containing electroplating bath or mixing cyanide waste with acid-containing waste streams.

Hazards and Limitations

Without cyanide in the bath, thorough cleaning and activation of the surface to be coated become more critical. Cyanide-based baths remove impurities so that the coating is not compromised.

Summary of Unknowns/State of Development

Non-cyanide copper plating baths typically are developed by manufacturers of the bath solutions. Chemical compositions are outside the public domain, and their formulae are proprietary. 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.

NON-CYANIDE METAL STRIPPING

Pollution Prevention Benefits

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

In addition, use of a non-cyanide stripper can simplify removal of metals from the spent solution. Because of the strong complex they form with the cyanide ligand, these metals are difficult to remove.

How Does It Work?

Metal strippers are used to remove previously deposited metallic coatings from parts. Cyanide-based stripping solutions act by enabling or assisting oxidation of the coating metal, after which the metal complexes with the cyanide ligand and is subsequently solubilized.

Because the 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 processes are electrolytic; others are not. Processing temperatures, bath life, ease of disposal and other operating characteristics all vary widely.

Why Choose This Technology?

Applications

Metal strippers can be purchased commercially for a wide variety of coating and substrate metals. The U.S. Air Force has performed testing on a number of non-cyanide strippers. The Air Force was particularly interested in nickel and silver non-cyanide strippers. Several of these have been implemented at Kelly Air Force Base.

Operating Features

The wide variety of non-cyanide strippers makes it difficult to generalize about operating features. Some are designed to operate at ambient bath temperatures, whereas others are recommended for temperatures as high as 180°F. Processes range from acidic to basic. In general, the same equipment was used for cyanide-based stripping can be used for non-cyanide stripping. However, with acidic solutions, tank liners may be needed to prevent corrosion.

Required Skill Level

Personnel who use cyanide-based strippers should be able to use non-cyanide strippers. For example, the U.S. Air Force reported that, for the non-cyanide metal strippers implemented at Kelly Air Force Base, no higher skill level was required.

Cost

Non-cyanide strippers will have the following impacts on cost:

- ♦ Waste treatment costs will be reduced. If cyanide-based solutions are not used elsewhere in the facility, the cyanide treatment system can be eliminated as a result of a switch to non-cyanide strippers.
- ♦ No large capital outlay is required to switch to a non-cyanide stripper because the equipment requirements are generally the same.
- ♦ There is a slight increase in the costs of the makeup solutions.

Reported Applications

Manufacturers have only a limited use history on their non-cyanide products. This indicates that use is not yet widespread. However, use of the product has been growing at a rate of 20 to 30% per year, according to one manufacturer.

Availability

A partial list of companies from which non-cyanide strippers are available is listed below in alphabetical order. This listing does not constitute a recommendation.

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

Operational and Product Benefits

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 can be longer because higher metal concentrations can be tolerated
- No problems with carbonation of the solutions.

One of the main incentives of eliminating cyanide-based stripping processes is to reduce health hazards to personnel. Cyanide is an extremely toxic substance. While cyanide in solution is itself very toxic, one of the main dangers for electroplaters is an accidental addition of an acid into the cyanide bath, which results in the formation of hydrogen cyanide gas, HCN. Skin contact with dissolved cyanide salts is less dangerous than inhaling HCN or ingesting cyanide, but it will cause skin irritation and rashes.

Facilities considering a switch to a non-cyanide stripper must, of course, look at the health and safety aspects of the substitute, such as high operating temperature, corrosivity, and so on.

Hazards and Limitations

Non-cyanide metal strippers have some disadvantages:

- For some strippers, recommended process temperatures are high enough to cause safety problems. Operating at lower temperatures can result in a loss of effectiveness.
- Stripping rates for certain coatings may be lower than for cyanide-based counterparts.
- The stripper may cause undesirable effects on the substrate metal, even if the manufacturer has recommended it for the application in question.

Summary of Unknowns/State of Development

A major market for non-cyanide strippers is for removing nickel coatings. Non-cyanide nickel strippers are largely a mature product. Future development will be oriented toward adjusting the product to handle different metal coatings (e.g., silver) and substrates.

ZINC OR ZINC-NICKEL ALLOY ELECTROPLATING

Pollution Prevention Benefits

In certain cases, zinc or zinc alloy electroplating can replace cadmium coatings. Cadmium is a heavy metal that is toxic to humans. In addition, electroplated cadmium coating processes are normally performed in plating solutions containing cyanide. Cyanide is highly toxic to humans and animal life. If an acid or non-cyanide alkaline zinc or zinc-nickel coating process can be used in place of a cyanide-based cadmium electroplating process, then use of both cadmium and cyanide is eliminated.

How Does It Work?

Zinc and zinc-nickel alloy electroplating processes are very common and have a long history in the electroplating industry. Recently, however, they have been examined specifically as a possible replacement for cadmium coatings. The ideal cadmium coating replacement would be a non-cyanide-based process, because this would also eliminate cyanide waste treatment costs.

Three alternative zinc and zinc-nickel processes have shown promise as replacements for cadmium coatings:

- Acid zinc
- Chloride-based zinc or zinc-nickel alloy
- Alkaline, non-cyanide zinc or zinc-nickel alloy

Why Choose This Technology?

Applications

The ability of an alternative coating to replace cadmium depends on the properties required for the application in question. In some cases, none of the replacement coatings identified above may serve. For example, if the cadmium coating is being used for its low coefficient of friction or for its low electrical contact resistance, none of the candidates mentioned above may be suitable. On the other hand, with suitable chromate conversion coatings, alternative coatings can have as good and in some cases better resistance to corrosion as measured in salt spray tests.

Operating Features

Some of the operating features of the three alternative processes mentioned above are listed in Table 5.

Table 5. Operating Parameters of Selected Alternatives to Cadmium Coatings

Coating	Relative pH	Temperature, °C	Predominant
Acid zinc	acidic	15-30°	sulfate
Chloride-based zinc-nickel alloy	slightly acidic	30-35°	chloride
Alkaline non-cyanide zinc-nickel alloy	alkaline	23-30°	hydroxyl

Required Skill Level

No increase in skill level is expected as a result of switching to a zinc or zinc-nickel coating process. These processes are conventional electroplating processes that would require little or no retraining. Increased attention to bath monitoring and adjustment may be necessary because these processes are less forgiving than are cyanide baths.

Cost

Existing electroplating equipment could be employed for any of these processes. Therefore, no large capital expenditures would be required to switch. However, a switch to an acid bath would require tank linings to existing tanks or possibly new tanks to provide the necessary resistance to corrosion.

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

Reported Applications

Acid zinc baths have been used for a long time in zinc plating. Non-cyanide alkaline baths and chloride-based baths for zinc coatings are newer developments driven mainly by the desire to eliminate cyanide from the plating process. Use of zinc-nickel alloys has gained interest because of their potential to replace cadmium, particularly in Japan and other countries, where use of cadmium coatings has been outlawed.

Availability

Acid zinc, chloride zinc or zinc-nickel, and alkaline non-cyanide zinc or zinc-nickel plating systems are commercially available from manufacturers.

Operational and Product Benefits

Replacing a cyanide-based cadmium coating with one of the processes outlined above would benefit electroplating workers by eliminating exposure to both cadmium and cyanide.

Among other benefits are the following:

- Corrosion resistance is as good as cadmium for many applications.
- Zinc-nickel alloys have better wear resistance than cadmium.
- Zinc coatings have better ductility than cadmium.

Hazards and Limitations

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

- Electrical contact resistance is higher than for cadmium.
- Zinc and zinc-nickel alloy coatings do not have the lubricity that cadmium coatings have.
- Acid zinc coatings have comparatively poor throwing power, and deposits are not fully bright.

Summary of Unknowns/State of Development

The processes outlined above are well-developed, commercially available processes. Only recently, however, have these processes been considered as replacements for cadmium coatings. More work needs to be done in the area of directly comparing these coatings to cadmium coatings for given applications.

SECTION 3

EMERGING TECHNOLOGIES

How to Use the Summary Tables

Five emerging clean process changes for metal finishing are evaluated in this section:

- Physical vapor deposition (PVD) of materials to replace chromium plating
- Nickel-tungsten-silicon carbide platings to replace chromium coatings
- Chromium-free, aluminum surface treatments to replace chromium-based surface treatments
- In-mold plating to replace electroless plating followed by electrolytic plating
- Metal spray coating to replace electroplating

Tables 6 and 7 summarize descriptive and operational aspects of these technologies. They contain evaluations or annotations describing each emerging technology and give a compact indication of the range of technologies covered to allow preliminary identification of those that may be applicable to specific situations. Readers are invited to refer to the summary tables throughout this discussion to compare and contrast technologies.

Descriptive Aspects

Table 6 describes each emerging clean technology. It lists the **Pollution Prevention Benefits**, **Reported Applications**, **Operational and Product Benefits**, and **Hazards and Limitations** of each.

Operational Aspects

Table 7 shows key operating characteristics for the emerging technologies. The rankings are estimated from descriptions and data in the technical literature.

Process Complexity is qualitatively ranked as "high," "medium," or "low" based on such factors as the number of process steps involved and the number of material transfers needed. **Process Complexity** is an indication of how easily the technology can be integrated into existing plant operations. A large number of process steps or input chemicals or multiple operations with complex sequencing are examples of characteristics that would lead to a high complexity rating.

Table 6. Emerging Clean Technologies for Metal Finishing: Descriptive Aspects

Emerging Technology Type	Pollution Prevention Benefits	Reported Applications	Operational and Product Benefits	Hazards and Limitations
Physical Vapor Deposition	• Avoids plating solutions • Eliminates rinsing	• Titanium nitride	• Reduces process steps • Avoids hydrogen embrittlement	• Applies thin coatings • High vacuum required
Nickel-Tungsten-Silicon Carbide Plating	• Chromium alternative	• Undergoing testing	• Higher current efficiencies than chromium plating • Better throwing power • Better wear resistance	• Corrosion resistance • Internal stresses • Complex shapes
Chromium-Free Aluminum Surface Treatments	• Eliminates chromium	• Industry – aluminum cans; aircraft components	• Limited operation data available	• Corrosion resistance
In-Mold Plating	• Eliminates etching, sensitizing solutions, and electroless plating	• Undergoing development	• Reduces process steps • Reduces number of waste streams	• Complex shapes • Limited data available
Metal Spray Coating	• Avoids plating solutions • Eliminates rinsing	• Industry	• Reduces process steps • Avoids hydrogen embrittlement	• High cost • Limited applications

Table 7. Emerging Clean Technologies for Metal Finishing: Operational Aspects

Emerging Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	References
Physical Vapor Deposition (PVD)	Medium	Medium	None from deposition	Comello, 1992 Gresham, 1991 Hermanek, 1987 Johnson, 1989 Key, 1991 Weiner, 1992
Nickel-Tungsten-Silicon Carbide Plating	Medium	Medium	Avoids chromium use	Schiffelbein, 1991
Chromium-Free Aluminum Surface Treatments	Low to Medium	Low	Avoids chromium use	Bibber, 1991 Hinton, 1991
In-Mold Plating	Medium	Medium	Avoids etching, sensitizing solutions, and electroless copper	E. Brooman, Battelle personal communication, 1992
Metal Spray Coatings	Medium	Medium	None from deposition	Hermanek, 1987 Key, 1991 Weiner, 1992

The **Required Skill Level** of equipment operators also is ranked as "high," "medium," or "low." **Required Skill Level** is an indication of the level of sophistication and training required by staff to operate the new technology. A technology that requires the operator to adjust critical parameters would be rated as having a high skill requirement. In some cases, the operator may be insulated from the process by complex control equipment. In such cases, the operator skill level is low but the maintenance skill level is high.

Table 7 also lists the **Waste Products and Emissions** from the emerging clean technologies. It indicates tradeoffs in potential pollutants, the waste reduction potential of each, and compatibility with existing waste recycling or treatment operations at the plant.

The last column in Table 7 lists **References** to publications that will provide further information for each emerging technology. These references are given in full in Section 4.

The text further describes operating characteristics, reported applications, operational and product benefits, and known and potential hazards and limitations. Technologies in later stages of development are discussed in Section 2, Available Technologies.

PHYSICAL VAPOR DEPOSITION (PVD)

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.

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

- ♦ Evaporation – high-current electron beams or resistive heaters are used to evaporate material from a crucible.
- ♦ Sputtering – surface of the source material is bombarded with energetic ions, usually an ionized inert gas such as argon.
- ♦ Vacuum Arc – the source material is significantly ionized, typically by a cathodic arc plasma.

The process often involves introduction of a gas such as oxygen or nitrogen into the chamber to form oxide or nitride deposits, respectively. PVD coatings are typically thin coatings between 2 and 5 microns.

Chromium and a variety of other metals have been successfully used as coatings with PVD. 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 high-point or line-load applications. Titanium nitride coatings also do not provide as much corrosion protection as do thicker, crack-free chromium coatings. They are also highly colored and do not look metallic.

Titanium nitride coatings, along with other PVD coatings, do not subject the substrate to hydrogen embrittlement. In addition, the throwing power of chromium electroplating baths is poor. 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 cast.

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.

NICKEL-TUNGSTEN-SILICON CARBIDE PLATING

The nickel-tungsten-silicon carbide (Ni-W-SiC) composite electroplating process is a patented process (Takada, 1990) that can be used to replace chromium coatings. 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 8.

Table 8. Composition and Operating Conditions for Ni-W-SiC Composite Plating

Composition	Operating Conditions
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	30 – 40 g/l
Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$	55 – 75 g/l
Ammonium citrate, $NH_4HC_6H_5O_7$	70 – 110 g/l
Silicon Carbide (0.8 – 1.5 μm particles)	10 – 50 g/l
pH (adjust with ammonium hydroxide or citric acid)	6.0 – 8.0
Bath temperature	150 – 175°F
Cathode current density	100 – 300 ASF

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 chromium plating rate of less than 1 mil/hr.

- Higher Cathode Current Efficiencies – Current efficiencies are approximately double those for chromium plating. Current efficiencies range from 24 to 35%, whereas typical chromium plating current efficiencies range from 12 to 15%.
- Better Throwing Power – Cathode current efficiencies for the Ni-W-SiC process increase with decreasing 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. This technology is in a very early stage of development. As a result, many questions remain to be answered before widespread use will occur. Some of the unknowns include:

- Effect of the coating process on hydrogen embrittlement of parts
- Effect of coating on fatigue life of part
- 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.

CHROMIUM-FREE ALUMINUM SURFACE TREATMENTS

One of the many uses of chromium in the metal finishing industry is to treat metal surfaces 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 with chromates. Although a number of alternative treatments have been examined, very few are 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.

One of the few commercially proven, non-chromate surface treatments for aluminum is an inorganic conversion coating based on zirconium oxide. This treatment usually involves immersion of the substrate in an aqueous solution containing a polymeric material and a zirconium salt. The zirconium deposits on the surface in the form of a zirconium oxide. These coatings have been used on aluminum cans for some time, but they have not been tested in the kind of environments in which chromate conversion coatings are typically used. Wider application of this coating must await this type of testing.

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

- Stage One – Use of boiling deionized water or steam to form a hydrated aluminum oxide film.
- Stage Two – Treat in proprietary aluminum salt solution for at least 1 minute at 205°F or higher.
- Stage Three – Treat in a proprietary permanganate solution at 135 to 145°F for at least one minute.

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

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

IN-MOLD PLATING

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.

The system can be totally contained and integrated, such that waste materials are minimized. For example, rinse waters containing metal ions can be evaporated and returned to the plating bath, provided that cations such as sodium, calcium, and magnesium do not build up to unacceptable levels.

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

* A variation of this technique makes it possible to plate circuit patterns in the mold cavity. These patterns can then be incorporated into molded components.

METAL SPRAY COATING

Metal spray coating is a group of related techniques whereby 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 9. 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.

Table 9. Applications of Metal Spray Coating

Application	Materials Applied
Wear Resistance	Metals, carbides, ceramics, and plastics are used to resist abrasion, erosion, cavitation, friction, and fretting. Coating hardness range from < 20 to > 70 R_c 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.

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.

SECTION 4

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Trade Associations

Table 10 shows the trade associations and the technology areas they cover. 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.

Table 10. Trade Associations and Technology Areas

Trade Association	Technology Areas Covered	Contact
American Electroplaters' and Surface Finishers' Society	Metal and surface finishing	12644 Research Parkway Orlando, FL 32826 tel. (407) 281-6441
American Society of Electroplated Plastics	Plating on plastics	1104 14th St. NW, Suite 1100 Washington, DC 20005 tel. (202) 371-1323 fax (202) 371-1090
Association for Finishing Processes of the Society of Manufacturing Engineers	Industrial finishing operations	P.O. Box 930 One SME Drive Dearborn, MI 48121 tel. (313) 271-1500
Federated Societies for Coating Technology	Decorative and protective (organic) coatings	492 Norristown Road Bluebell, PA 19422 tel. (215) 940-0777
Institute for Interconnecting and Packaging Electronic Circuits	Plating (printed circuit board fabrication)	7380 North Lincoln Avenue Lincolnwood, IL 60646-1705 tel. (708) 677-2850 fax (708) 677-9570
Institute of Metal Finishing	Metals finishing	Exeter House Holloway Head Birmingham B1 1VQ England tel. (021) 622-7388
Metal Finishing Suppliers Association	Metal finishing supplies	801 N. Cass Ave. Westmount, IL 60559 tel. (708) 887-0797 fax (708) 887-0799)
National Association of Metal Finishers	Metal finishing operations	111 E. Wacker Drive Chicago, IL 60601 tel. (312) 644-6610
Society of Vacuum Coaters	Vacuum coating	440 Live Oak Loop, NE Albuquerque, NM 87112-1407 tel. (505) 298-7624 fax (505) 298-7942