Regulatory Analysis of the Chromium Electroplating Industry and Technical Alternatives to Hexavalent Chromium Electroplating

Prepared by the
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Executive Summary

Electroplated hexavalent chromium has been used in a wide range of applications due to its exceptional protective properties and decorative appeal. Although hexavalent chromium offers many advantages, it is also potentially hazardous when released into the environment. For this reason, hexavalent chromium is strictly regulated under the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), and the Clean Air Act, as amended in 1990 (CAA). In addition, worker exposure to hexavalent chromium is regulated by the Occupational Health and Safety Administration (OSHA). These regulatory driving forces have pressured manufacturers to identify and implement acceptable alternatives for electroplated hexavalent chromium coatings.

At the request of the U.S. Army Armament Research Development and Engineering Center (ARDEC), a regulatory analysis and literature review was conducted to establish the "state of the market" of alternative materials and technologies for electroplated hexavalent chromium. The regulatory analysis provides an overview of the environmental, health, and safety regulations that negatively impact the use of chromium in the electroplating industry. Information obtained from the literature review was used to identify the following alternatives to electroplated hexavalent chromium: metallic and alloy electroplating, chemical vapor deposition (CVD), electroless plating, ion-based technologies, sputtering, surface (case) hardening, and thermal spraying. A description of each alternative is provided as well as a discussion of advantages and disadvantages, health and safety factors, and environmental issues associated with each material or technology. Relevant abstracts from the literature search are also included.

Statement of Activity

At the request of the U.S. Army Armament Research Development and Engineering Center (ARDEC), a “state of the market” assessment of alternatives to electroplated hexavalent chromium was conducted by the National Defense Center for Environmental Excellence (NDCEE). The study included a regulatory analysis of the chromium electroplating industry and a broad literature review to identify alternatives to electroplated hexavalent chromium. This report provides a general description of conventional hexavalent chromium electroplating, a discussion of the environmental, health, and safety regulations associated with the conventional process, and a brief description of the alternative materials and technologies identified in the literature review.

II. Hexavalent Chromium Electroplating

Hexavalent chromium electroplating is used extensively in a large range of applications since it provides desirable functional and aesthetic properties and offers high volume output at a relatively low cost. Two types of electroplated hexavalent chromium exist: decorative and hard chromium. Decorative chromium is a relatively thin deposit applied over other coatings to provide an appealing finish. Hard, or functional, chromium is a thick deposit (2 to 20 mils) that offers excellent wear and corrosion resistance and a low coefficient of friction.

Electroplating is not a single step "dip tank" process, but consists of several steps, each of which is critical to obtaining an acceptable coating. Generally, the process includes cleaning, pickling, activating, striking, plating, drying, and heat treating. The pickling and activating steps may be combined, and depending upon final product requirements, heat treating after plating may not be necessary. Rinsing between steps is critical to produce a suitable coating and to prolong the life of the processing solutions.

The actual plating process consists of placing the activated part (cathode) and anode in an aqueous solution containing chromic acid (Figure II-l). As direct current is passed between the anode and cathode, positively charged chromium ions move toward the negatively charged substrate. As the ions acquire electrons at the surface of the cathode, they are reduced to the neutral state of the metal and are deposited on the part. Introducing additives to the solution may change coating properties such as yield strength, ductility, hardness, microstructure, and internal stress. In addition, additives can be used to improve coating uniformity, brightness, and leveling.

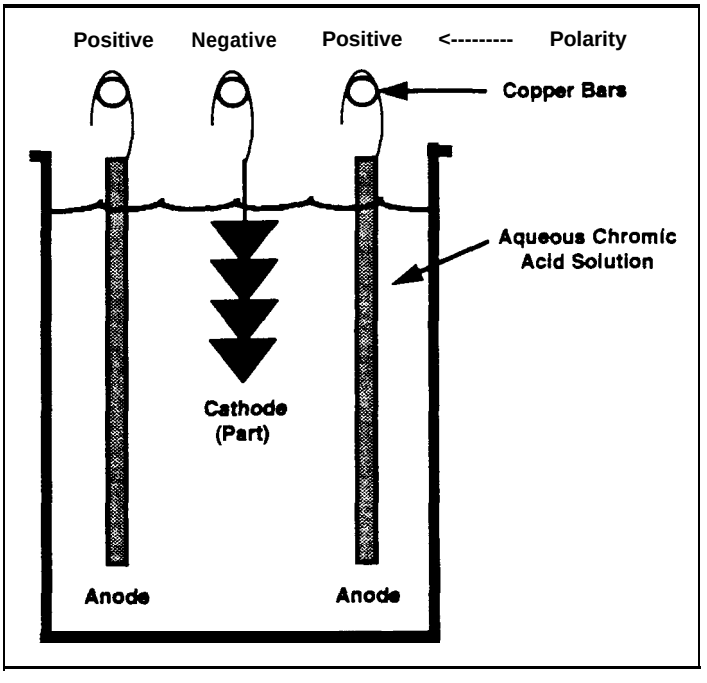

Figure II-l: Hexavalent Chromium Electroplating

III. Environmental, Health, and Safety Regulations Impacting the Chromium Electroplating Industry

Introduction

A number of existing environmental, health, and safety regulations currently affect the chromium electroplating industry. Many of these regulations have been increasing in scope of coverage and stringency over recent years and this trend is expected to continue in the future, particularly in the areas of wastewater discharges, air emissions, and worker exposure to hexavalent chromium.

This report focuses on the regulations affecting chromium electroplating operations that have been promulgated under the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), the Clean Air Act (CAA), and the Occupational Safety and Health Administration (OSHA). Where possible, anticipated future changes to the regulations have also been included.

2.0 Water Pollution Control under the Clean Water Act (CWA): The Impact of Current and Future Regulations on Electroplaters

Electroplating facilities are subject to a variety of pollution control requirements for wastewater under the federal Clean Water Act. The regulations that will apply to a particular facility will be based on a number of factors, including:

- Whether a facility discharges effluent directly to U.S. waters (e.g., to a stream, river, or other surface water) or to a sewage treatment plant;
- Whether a facility discharges directly to a waterbody that will require the application of water quality based standards to protect the *designated* uses (e.g., public water supply, fishing, navigation) for that waterbody;
- Whether a facility was in operation or under construction *before* the publication of applicable proposed regulations, or after;
- Whether a facility owns more than 50 percent (annual area basis) of the materials undergoing metal finishing (a “captive shop”) or 50 percent or less (a “job shop’*).

2.1 Current Regulations under the CWA

Electroplaters must be aware of the regulations in the U.S. *Code of Federal Regulations* (CFR) at 40 CFR 413 and 433 under the headings of the “Electroplating Point Source Category” (E) and the “Metal Finishing Point Source Category” (MF). These regulations establish effluent guidelines used to set permit limits for electroplaters.

Facilities discharging effluent directly into public waterways, as opposed to sewage treatment plants, fall under the authority of the National Pollutant Discharge Elimination System (NPDES) and are required to obtain an NPDES permit before making any discharges of pollutants. The effluent limits written into each permit are based on *technology-bused standards* (otherwise known as effluent limitations guidelines), which are found at 40 CFR 400 et seq. NPDES permits, which must be renewed at a minimum of every five years, also include facility monitoring and reporting requirements. The individual states usually administer the NPDES permit programs within the states, subject to oversight by the U.S. Environmental Protection Agency (EPA).

Facilities that discharge into sewage treatment plants (also referred to as publicly owned treatment works, or POWs) are not required to obtain an NPDES permit; however, the treatment plants they discharge into are required to obtain NPDES permits. The sewage treatment plants may then impose their own effluent limits and monitoring and reporting requirements. In addition, facilities subject to federal pretreatment standards must also meet those standards before any discharges can be made to the sewage treatment system.

Technology-based standards are used to establish numeric limits on the amounts of pollutants allowed for points of discharge. These standards establish a minimum level of performance required for dischargers and are applied regardless of the water quality of the receiving water-body. Technology-based standards are established for both existing and new facilities.

Technology-based standards are established based on the best water pollution control technology that has been developed or is capable of being developed for use by an entire industry segment. For existing facilities, effluent limits are based on Best Available Technology Economically Achievable (BAT) for toxic and nonconventional pollutants, and Best Conventional Technology (BCT) for conventional pollutants. Pretreatment Standards for Existing Sources (PSES), applicable to facilities that discharge wastewater into sewage treatment plants, are also based on BAT and BCT.

Because new facilities are expected to be in a better position to incorporate the latest pollution control technology in the design of their facility, EPA consequently considers it reasonable to hold new sources to more stringent standards. New facilities are controlled by either New Source Performance Standards (NSPS) or Pretreatment Standards for New Sources (PSNS); these two types of standards are established based on Best Available Demonstrated Control Technology (BADCT). These standards are to be achieved when the new facility begins operation.

Tables III-l and III-2 provide a brief summary of the regulations that are applicable to various categories of electroplaters.

Table III-l: FACILITIES THAT DISCHARGE DIRECTLY TO U.S. WATERS

EXISTING SOURCES	NEW SOURCES
Facilities must apply for an ***NPDES PERMIT.***	Facilities must apply for ***an NPDES PERMIT.***
Effluent limits in the permit will be set based on ***BAT*** and ***BCT*** in the ***MF EFFLUENT GUIDELINES***	***NEW SOURCE PERFORMANCE STANDARDS (NSPS)*** *in* the permit will be set based on ***BADCT*** and ***BCT. MF-EFFLUENT GUIDELINES*** apply.

TABLE III-2: FACILITIES THAT DISCHARGE TO SEWAGE TREATMENT PLANTS
(or "publicly owned treatment works-POTWs"

EXISTING SOURCES	NEW SOURCES
Applicable regulations are based on whether a facility is a job shop or captive shop. All shops ***MUST*** abide by ***PRETREATMENT LIMITS*** set by an agreement with the local POTW. ALL JOB SHOPS are subject to ***PRETREATMENT STANDARDS FOR EXISTING SOURCES (PSES)*** based on ***BAT*** and ***BCT. E EFFLUENT GUIDELINES*** apply. ALL CAPTIVE SHOPS are subject to ***PSES*** based on ***E EFFLUENT GUIDELINES FIRST,*** then the ***MF EFFLUENT GUIDELINES*** **are** applicable.	Facilities ***MUST*** abide by ***PRETREATMENT LIMITS*** set by an agreement with the local POTW. Facilities are subject to ***PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS)*** based on ***BADCT*** and ***BCT. MF EFFLUENT GUIDELINES*** apply.

Technology-based effluent limits establish a baseline level of treatment only. The permit-issuing authority has the power to impose more comprehensive or more stringent requirements provided that they conform to the purposes of the CWA. In addition to the technology-based standards, water quality based standards may also be used to set permit limits for dischargers. Established principally by the states, these standards go beyond the level of treatment required by technology-based standards to ensure that designated uses for specific waterbodies will be protected.

2.2 Future MF Effluent Guidelines

The EPA is proceeding with a study of the MF Category (40 CFR 433) and is in the process of reviewing MF Guidelines for potential revisions. This study is expected to be completed in November 1994. Electroplaters will need to carefully monitor any regulatory developments that might result from this study.

2.2.1 New Industry Category - Metal Products & Machinery (MP&M) Category To be Regulated by EPA

The EPA is in the process of developing regulations for the Metal Products & Machinery (MP&M) Category under the authority of the CWA. The MP&M Category is a new industry category intended to cover facilities that "manufacture, rebuild, and maintain finished metal parts, products, or machines." Electroplating is one of 47 unit operations to be affected by this new rulemaking which may potentially overlap, *and eventually supersede,* the regulations developed for the MF Category at 40 CFR 433.

TABLE III-IL: FACILITIES THAT DISCHARGE TO SEWAGE TREATMENT PLANTS
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The regulations for the MP&M Category will be developed in two phases. Phase I will cover the following industrial sector classifications: aerospace, aircraft, electronic equipment, hardware, mobile industrial equipment, ordnance, and stationary industrial equipment. Phase II will cover bus and truck, household equipment, instruments, motor vehicle, office machine, railroad, shipbuilding, and precious and nonprecious metals and instruments. EPA is required to propose effluent guideline regulations for Phase I by November 30, 1994 and promulgate a final rule by May 1996. The effluent guideline regulations for Phase II are expected to be promulgated three years after Phase I, in 1999. Under the 1994 Effluent Guidelines Plan issued on August 26, 1994, EPA announced plans to begin the development of Phase II (59 Fed. Reg. 44234, August 26, 1994).

Although the development of the proposed rulemaking for the new MP&M Category is in its beginning stages, EPA currently anticipates that over 10,600 dischargers across the U.S. will be affected by this rulemaking. Of these, 85 percent are indirect dischargers and 15 percent are direct dischargers.

It is anticipated that pollution prevention technologies will be considered heavily by EPA in developing the proposed rulemaking for the MP&M Category. In the near term, EPA is expected to release a *Development Document* for the MP&M category. It is anticipated that the document will include a section on *Pollution Prevention* describing the pollution prevention technologies being considered by EPA in developing the proposed rule.

2.2.2 CWA Reauthorization

Efforts are also currently under way in Congress to reauthorize the CWA. Among the issues being considered for reauthorization are: greater control of toxic pollutants, increased emphasis on pollution prevention planning, and stricter enforcement. Reauthorization of the CWA had been expected to occur in late 1994, but with the recent adjournment of the 103rd Congress, reauthorization will not occur until 1995 at the earliest.

3.0 Regulations under the Resource Conservation and Recovery Act (RCRA)

Electroplating operations usually generate a number of wastewater streams. As mentioned earlier in this report, these wastewaters cannot be discharged to surface water or sewage treatment plants unless certain effluent limits are met. For this reason, many electroplating operations pretreat their wastewaters on-site. The resulting sludges from wastewater treatment processes may meet the definition of a hazardous waste. Other common wastes from the electroplating process that can meet the definition of hazardous waste include spent stripping, cleaning, and plating bath solutions and plating bath residues. RCRA regulations require generators to insure that such wastes are properly treated, stored and/or disposed.

3.1 General Hazardous Waste Definitions

For wastes to fall under the RCRA hazardous waste regulatory scheme, they must meet the definition of hazardous waste. To be hazardous, the waste must be:

1. A solid waste as defined by the statute and corresponding regulations: "... any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility or other discarded material ..." Discarded material is "... any material which is abandoned, recycled, or inherently waste-like ...," (42 U.S.C.A. §6903(27) and 40 CFR §261.2);

   and

2. it must also either:

   a. be a listed hazardous waste pursuant to the three lists of hazardous wastes established in the RCRA regulations at 40 CFR §261;

      or

   b. qualify as a characteristic hazardous waste (also see 40 CFR §261); the four characteristics satisfying this qualification are:

      –ignitability –reactivity –corrosivity –toxicity

3.2 Chromium Electroplating Wastes

A number of electroplating wastes are listed at 40 CFR §261.31 under the "Hazardous wastes from non-specific sources" heading. Wastes qualifying under these listings are automatically hazardous if they first meet the solid waste definition. Generators of these wastes must be careful to comply with all applicable RCRA hazardous waste regulations.

The following wastes, given with their EPA hazardous waste numbers, are listed under the "Hazardous waste from non-specific sources" heading:

F006 - Wastewater treatment sludges from electroplating operations except from the following processes: (1) Sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.

F007 - Spent cyanide plating bath solutions from electroplating operations.

F008 - Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process.

F009 - Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.

Facilities may file "delisting petitions" with EPA to remove certain wastes from coverage under RCRA. Delisting, however, is allowed only when a facility can demonstrate that the concentrations of hazardous materials in the listed waste are below the concentrations for which the waste was listed as hazardous and that the waste is not otherwise hazardous (40 CFR §260.22). For example, in Appendix VII to Part 261, cadmium, hexavalent chromium, nickel, and cyanide (complexed) are given as the hazardous constituents for which F006 sludges were listed. For a delisting petition to be successful, a facility must demonstrate to EPA that each of the constituents of concern are not present in their F006 wastewater sludge or are present in concentrations below specified regulatory levels.

Again, other electroplating process wastes that are not specifically listed may still be classified as hazardous if they have the characteristics of ignitability, reactivity, corrosivity, or toxicity (40 CFR §261.20 *et. seq.*). At 40 CFR §261.24 there is a table that assigns EPA hazardous waste numbers to a number of contaminants and that also provides the maximum concentration (regulatory level) of the contaminants for purposes of determining the toxicity characteristic. Wastes will be regarded as exhibiting the toxicity characteristic if they contain any of the listed contaminants at levels equal to, or exceeding, the given maximum concentration. For chromium, identified by EPA Hazardous Waste Number D007, the regulatory level is 5.0 milligrams per liter (mg/L).

3.3 General Requirements for Generators of Hazardous Wastes Under RCRA

Three classifications exist for hazardous waste generators: large quantity generators, small quantity generators, and conditionally exempt small quantity generators. These classifications are based on the amount of hazardous waste generated per month. Large quantity generators are those generating at least 1,000 kilograms per month, small quantity generators are defined as generating more than 100 kilograms but less than 1,000 kilograms per month, and the generation of less than 100 kilograms per month qualifies a facility as a conditionally exempt small quantity generator. The requirements for each of the three classifications vary somewhat under the federal regulations. It should be noted, however, that many states have EPA authorization to operate their own hazardous waste management programs under RCRA. These state programs can be more stringent than the federal program such that some states apply the same requirements to *all* generators, regardless of size. Furthermore, some states simply do not recognize the conditionally exempt small quantity generator classification.

In general, hazardous waste generators must obtain an EPA Identification Number and use only the services of hazardous waste transporters and treatment, storage, and disposal (TSD) facilities that also have EPA Identification Numbers. The centerpiece of the RCRA hazardous waste regulations is the manifesting system that allows for the tracking of hazardous wastes from the "cradle to grave." Generators are responsible for preparing the Uniform Hazardous Waste Manifest and for properly preparing hazardous wastes for off-site transport. If a final signed and dated copy of the Manifest is not returned to the generator by the ultimate TSD facility within 45 days of shipment, then the generator must file an "exception report" with EPA or the state program authority. Additionally, manifests must include a certification by the generator that the facility has a hazardous

waste minimization program in place. Generators also need to comply with all applicable recordkeeping and reporting requirements, such as the filing of biennial (sometimes annual) reports.

3.4 Reauthorization of RCRA

Congress has discussed the reauthorization of RCRA since 1989. The last time that there was a comprehensive reauthorization of RCRA was in 1984 with the Hazardous and Solid Waste Amendments (HSWA). Reauthorization of the Clean Water Act (CWA), the Superfund legislation (also referred to as CERCLA), and the Safe Drinking Water Act (SDWA) are three legislative efforts currently enjoying higher priority than RCRA reauthorization. Many in Congress expect that it will be at least 1997 before any serious efforts are undertaken to reauthorize RCRA.

EPA is currently working to revise the regulatory definitions of hazardous waste and hazardous waste recycling. These efforts could impact electroplating operations because EPA has stated that, once these changes are in place, the Agency intends to begin emphasizing hazardous waste recycling over treatment and disposal options. A continued focus on pollution prevention is also expected at EPA.

4.0 Regulations under the Clean Air Act, as Amended in 1990 (CAA)

The 1990 Amendments brought about many changes in the area of air pollution control. One of the major areas of focus has been on the regulation of emissions of air toxics, or hazardous air pollutants (HAP). In Title III of the Amendments, Congress included an initial list of 189 HAP and directed EPA to establish regulations controlling the emissions of these HAP. This list includes cadmium compounds, chromium compounds, cobalt compounds, cyanide compounds, lead compounds, and nickel compounds. 42 U.S.C.A. §7412(b).

The way in which HAP emissions are being regulated is through the establishment of control standards for various source categories emitting one or more HAP. Major sources, those sources emitting, or having the potential to emit, 10 tons per year or more of any one HAP or 25 tons per year or more of any combination of HAP, are generally being targeted first. For certain source categories, however, area sources (sources emitting below the major source threshold) have also been targeted. On its December 3, 1993 list of source categories to be regulated, EPA provided that final rules would be promulgated by November 15, 1994 for *both* major and area sources in the hard chromium electroplating, decorative chromium electroplating, and chromic acid anodizing source categories. 58 Fed. Reg. 63941.

4.1 Proposed Rules for Chromium Electroplating

In accordance with the above mentioned schedule, EPA proposed National Emission Standards for Hazardous Air Pollutants (NESHAP) to limit emissions of chromium compounds from new and existing hard and decorative chromium electroplating and chromium anodizing on December 16, 1993. 58 Fed. Reg. 65768. These standards, when finalized, would require both major and area sources to achieve an emissions level consistent with the installation and operation of maximum achievable control technology (MACT).

In the proposed rule, EPA states that this particular NESHAP developed out of a study begun in 1984 investigating chromium emissions, particularly hexavalent chromium,

from chromium electroplating operations. According to the Agency, this study was focused solely on chromium emissions from chromium electroplating and anodizing tanks and, as a result, other metal plating processes "such as nickel, copper, and cadmium plating" are not included in the December 16, 1993, proposed rule. The notice mentions, however, that various metal finishing processes producing acid mists do exist in a number of other source categories. When these source categories are regulated, the associated metal finishing processes may also be regulated (the miscellaneous metal parts and products surface coating source category, due to be regulated by November 15, 2000, may be an example of one).

Under the proposed NESHAP, the emission limit not to be exceeded for gases containing chromium from hard chromium electroplating tanks is proposed at 0.013 milligrams per dry standard cubic meter (mg/dscm) of ventilation air (5.7×10^{-6} grains per dry standard cubic foot [gr/dscf]) or 0.03 mg/dscm (1.3×10^{-5} gr/dscf) if the electroplating tank is an existing source and is located at a small hard chromium electroplating facility. Small hard chromium electroplating facilities are defined as facilities "that perform hard chromium electroplating and [have] a maximum cumulative potential rectifier capacity less than 60 million ampere-hours per year (Ah/yr)."

For decorative plating tanks using a chromic acid bath, the limit of chromium in the exhaust gas stream is proposed at 0.003 mg/dscm (1.3×10^{-6} gr/dscf) or a surface tension of the electroplating bath not to exceed 40 dynes per centimeter (dynes/cm) (2.7×10^{-3} pound-force per foot [lb_f/ft]) if fume suppressants are used in the plating bath. For decorative plating using a trivalent chromium bath, the exhaust gas stream limit is proposed at 0.048 mg/dscm (2.1×10^{-5} gr/dscf) or a surface tension of the electroplating bath not to exceed 55 dynes per centimeter (dynes/cm) (3.8×10^{-3} lb_f/ft) if fume suppressants are used in the plating bath.

For chromium anodizing tanks, the exhaust gas stream limit is proposed at 0.003 mg/dscm (1.3×10^{-6} gr/dscf) or a surface tension of the electroplating bath not to exceed 40 dynes per centimeter (dynes/cm) (2.7×10^{-3} lb_f/ft) if fume suppressants are used in the plating bath.

4.2 Other Electroplating Processes

A general source category for electroplating operations has not been included on the December 3, 1993 listing of source categories to be regulated. While the Agency will probably first focus on developing NESHAP for those source categories found on this list, the list is subject to change at any time and it could be revised to include a metals plating source category. Furthermore, electroplaters must be aware of the existing source categories under which their operations may fall. The development of any NESHAP for such source categories may include air emission limitations directly applicable to electroplating operations. For now, however, the only electroplating specific NESHAP is the proposed NESHAP for hard and decorative chromium electroplating and chromium anodizing.

5.0 EPA's 33/50 Program

EPA's 33/50 Program is a voluntary pollution prevention initiative to reduce national pollution releases to the air, water, and soil, and off-site transfers of 17 targeted toxic chemicals by 33 percent by the end of 1992 and by 50 percent by the end of 1995. In other words, the program attempts to reduce the releases and off-site transfers of these 17 chemicals from a national total of 1.4 billion pounds in 1988 to 700 million pounds by 1995.

The 33/50 Program bears mentioning in this report because chromium and chromium compounds are targeted on the "EPA 17" list. The 17 chemicals were targeted because of the large quantities released annually into the environment, because they are generally identified as toxic or hazardous pollutants and thus significant environmental and health benefits can potentially be realized by reducing their releases into the environment, and because of the potential to achieve reductions in the releases of these chemicals through pollution prevention practices.

When forecasting those substances likely to be more stringently regulated in the future, the "EPA 17" are likely candidates.

6.0 Worker Health and Safety Regulations

Worker health and safety regulations, particularly those aimed at limiting worker exposure to various air contaminants in the workplace, can limit the ability to use certain materials such as hexavalent chromium. To limit worker exposure to hazardous substances, OSHA has promulgated numerical standards called permissible exposure limits (PELs). These PELs are updated periodically.

6.1 The 1989 PELs

A major revision lowering 212 PELs and establishing 164 new PELs was completed in 1989 (54 Fed. Reg. 2332, January 19, 1989). but that revision was overturned by the U.S. Court of Appeals for the Eleventh Circuit in 1992. *AFL-CIO v. OSHA*, *965* F.2d 962 (11th Cir., 1992). On June 30,1993, OSHA formally revoked the 1989 PELs and reinstated the limits that were in existence before 1989. 58 Fed. Reg. 35338, June 30, 1993.

This action affected all twenty-five states not operating under their own OSHA-approved state occupational safety and health program. Of the twenty-five states operating their own OSHA-approved occupational safety and health programs, however, only those states with program authorization mandating that their state standards be set parallel to the OSHA standards were affected. Electroplaters operating in states with their own OSHA-approved programs need to be sure that they understand the requirements under which they are operating.

Furthermore, the issue of the 1989 standards is far from over. Most recently, the Secretary of Labor, Robert Reich, and the Assistant Secretary of Occupational Safety and Health, Joe Dear, have both testified before Congress that the Administration is supportive of provisions to adopt the 1989 standards by legislative action in the OSHA Reform Bill currently under Congressional consideration. Even with this support,

however, the 103rd Congress failed to take action on the OSHA Reform Bill before recently adjourning.

6.2 PELs for Heavy-Metals

In addition to the wide ranging changes attempted in 1989, OSHA has taken steps to more stringently regulate exposure to heavy metals. Many of these heavy metals are commonly found in electroplating operations. For example, in 1979, OSHA promulgated new standards, which were phased in over a number of years, to reduce exposure to lead in the workplace. The standard that has been phased in is an 8-hour time weighted average (TWA) of 50 micrograms per cubic meter ug/m^3), which equals 0.05 milligrams per cubic meter (mg/m3) (29 CFR 1910.1025). In 1992, OSHA focused its efforts on cadmium, reducing the standards from 8-hour TWA's of 100 ug/m^3 (0.1 mg/m^3) for cadmium fume and 200 ug/m^3 (0.2 mg/m^3) for cadmium dust down to an 8-hour TWA PEL of 5 ug/m^3 (0.005 mg/m^3) for all cadmium compounds, including dust and fumes (57 Fed. Reg. 42102, September 14, 1992 and 29 CFR 1910.1027).

Hexavalent chromium appears to be next on the list to be regulated as a formal docket has already been opened. One source at OSHA has indicated that a proposed rule for chromium should be released in late 1994 or early 1995. This rulemaking process was initiated after a petition was received on July 19, 1993, from Public Citizen's Health Research Group and the Oil, Chemical, and Atomic Workers International Union (Petitioners). This petition focused on hexavalent chromium, but all forms of chromium are likely to be reviewed by OSHA for potential revision. Currently, there is no PEL specifically addressing hexavalent chromium, which is covered by the heading "chromic acid and chromates" at Table **Z-2** in 29 CFR 1910.1000. The current PEL is an 8-hour TWA of 100 ug/m^3 (0.1 mg/m^3). Citing concerns over the carcinogenic attributes of hexavalent chromium, the Petitioners have called on OSHA to issue an emergency temporary standard of 0.5 ug/m^3 (0.0005 mg/m^3). If adopted, such a standard would represent a 200-fold reduction from the current PEL.

While it is still uncertain what exact action will be taken on the hexavalent chromium PEL, it does appear that OSHA is slowly focusing its efforts on reducing the exposure limits for an increasing number of heavy metals found in the workplace. If the reduced PELs for lead and cadmium provide any indication, it is likely that a significant decrease in the hexavalent chromium PEL can be expected.

Table III-3 has been provided to illustrate the current PELs for chromium as well as the 1989 changes that were overturned but may still be implemented through legislative action. Where applicable, the Threshold Limit Values (TLVs) for chromium, established by the American Conference of Governmental Industrial Hygienists (ACGIH), are also provided. *See 1993-l994 ACGIH Threshold Limit Values for Chemical Substances and* ***Physical Agents and Biological Exposure Indices.***

The TLVs have been included due to OSHA's frequent reliance on the TLVs for setting its own PELs. When the first PELs were promulgated by OSHA in 1971, they were taken verbatim from the 1970 TLVs established by the ACGIH. OSHA again adopted the

ACGIH TLVs when it attempted to update the PELs in 1989. In this respect, the TLVs can give a good indication for where OSHA may go with its own standards.

Table III-3: Selected Worker Exposure Limits for Chromium

Air Contaminants	Current PEL	1989 PEL	ACGIH TLV
Chromic acid and chromates	0.1 mg/m³	no change	0.05 mg/m³
Chromium (II) compounds	0.5 mg/m³	n/a	0.5 mg/m³
Chromium (III) compounds	0.5 mg/m³	n/a	0.5 mg/m³
Chromium (VI) compounds, sol.	n/a	n/a	0.05 mg/m³
Chromium (VI) compounds, certain water insol.	n/a	n/a	* 0.05 mg/m³
Chromium, sol. chromic, chromous salts	n/a	0.5 mg/m³	n/a
Chromium metal and insol. salts	1 mg/m³	no change	0.5 mg/m³
*** ACGIH Intended Changes for 1993-1994**			**New TLV**
Chromium (VI), certain water insol.			0.01 mg/m³

IV. Technical Alternatives to Hexavalent Chromium Electroplating

1.0 Introduction

Electroplated hexavalent chromium has been used extensively to coat a wide variety of substrates in a large range of applications. Hexavalent chromium coatings offer excellent wear and corrosion resistance, a low coefficient of friction, a high degree of hardness, and decorative appeal. However, due to its toxic nature, hexavalent chromium is subject to regulation under the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), and the Clean Air Act, as amended in 1990 (CAA). In addition, worker exposure to hexavalent chromium is regulated by the Occupational Health and Safety Administration (OSHA). In response to these regulatory driving forces, alternatives for electroplated hexavalent chromium must be identified and implemented.

Although no single replacement for electroplated hexavalent chromium exists that can match its unique mechanical properties, several alternative materials and technologies are available for use in specific applications. These alternatives generate less pollution than hexavalent chromium, and typically have fewer associated health and safety risks. Identified alternatives for hexavalent chromium electroplating include the following:

- Metallic and Alloy Electroplating
- Chemical Vapor Deposition (CVD)

  Atmospheric CVD
  Low Pressure CVD
  Plasma Enhanced CVD

- Electroless Plating
- Ion-Based Technologies

  Ion Beam Assisted Deposition (IBAD)
  Ion Implantation
  Ion Plating

- sputtering

  Direct Current (DC) Sputtering
  Radio Frequency (RF) Sputtering
  Magnetron Enhanced Sputtering

- Surface (Case) Hardening
- Thermal Spraying

  Atmospheric Thermal Spraying (Flame Spraying)
  Electric (Wire) Arc Spraying
  Plasma Arc Spraying
  Detonation Gun (D-gun) Spraying
  High Velocity Oxygen-Fuel (HVOF) Spraying
  Vacuum/Plasma Arc Spraying

A description of each alternative and associated health, safety, and environmental concerns are presented in this document. Also included are relevant abstracts obtained from a brief and general literature search on several electronic databases. The initial search method consisted of finding references containing the terms “chromium and (replace? or alternative?)” in combination with each identified technology. The resulting number of matches was so large that only the first 25 abstracts were downloaded for each technology. Despite the many abstracts obtained, only a fraction of them were relevant to electroplated chromium alternatives. Therefore, a second literature search was done according to the strategy outlined in Table IV- 1.

Table IV-1 : Literature Search Strategy

Search Sequence	Search Term	Number of Matches
1	chromium	317,756
2	plat?	955,498
3	1 near 2	7,537
4	electroplat?	67,052
5	1 near 4	3,308
6	replac?	351,541
7	3 or 5 within ten words of 6	31
8	alternative?	366,496
9	3 or 5 within ten words of 8	27

The relevant abstracts from searches 7 and 9 as well as those from the initial search are included after the description of each alternative. In some cases, an abstract may appear in more than one section if applicable to several technologies.

2.0 Metallic and **Alloy Electroplating**

2.1 Description

Alternative metals and alloys may be used in the electroplating process simply by changing the plating bath composition and operating parameters such as voltage and current. A cathode (substrate to be plated) and anode (soluble metal to replace depleted ions or insoluble inert material) are placed in a plating bath containing the alternative metal or alloy (Figure IV-l). A current is passed between the cathode and anode to draw positively charged metal ions from the plating bath to the substrate surface where the ions acquire electrons. Ions are then reduced to the neutral state of the plating material, which results in a deposited layer of metal on the substrate. Additives may be placed in the plating solution to modify the surface properties of the coating.

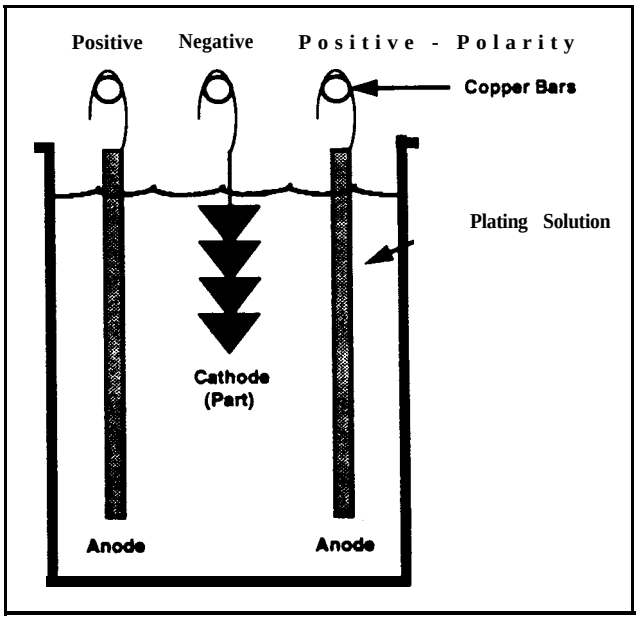

Figure IV-1 : Metallic and Alloy Electroplating

2.1.1 Metallic Electroplating

Alternative metals, such as trivalent chromium, magnesium, nickel, and zinc, may be used in the electroplating process to produce hard, protective coatings. Trivalent chromium is often used in decorative applications, but recent advances have shown that trivalent chromium may produce better physical properties, such as corrosion and wear resistance, than hexavalent chromium. Magnesium, nickel, and zinc may also be used as replacements to hard chromium or as undercoatings for subsequently applied protective layers.

2.1.2 Alloy Electroplating

Alloy electroplating utilizes a combination of two or more metals in the plating bath. Alloys can be designed to produce different properties than their alloying elements and, thus, may be used to replace hexavalent chromium in many applications. A variety of alloys may be electrochemically deposited, depending on the desired characteristics and end application of the substrate to be coated. Some alloys currently under consideration as replacements for hexavalent chromium include:

Nickel-boron	Nickel-tungsten-silicon carbide
Nickel-cobalt	Nickel-zinc
Nickel-tungsten	Tin-cobalt
Nickel-tungsten-boron	Zinc-tin

2.2 Advantages/Disadvantages

Environmental problems are significantly reduced by the elimination of hexavalent chromium from wastewater and air emissions. Equipment costs are reduced since less mist is generated during the plating process, decreasing the need for fume scrubbers and exhaust treatment. In addition, some processes offer reduced labor rate, increased energy efficiency, and improved throwing power.

2.3 Health and Safety

Worker protection including face masks, aprons, boots, and gloves may be required. Hazardous chemicals must be handled properly and adequate ventilation is required to reduce worker exposure to chemical vapors. In addition, plating tanks must be cleaned regularly to reduce hazardous gas formation and/or chemically induced fires.

2.4 Environmental

Scrubbing of some exhausts may be still be necessary (e.g., trivalent chromium plating). Rinsewater and used plating baths must be treated and disposed of properly along with the resulting solid sludges. Residual metal must be recovered by processes such as electrodialysis, evaporation, ion exchange, and reduced osmosis.

2.5 Relevant Abstracts

Advances in trivalent chrome plating.
Zaki, Nabil
Proceedings of the 80th AESF Annual Technical Conference, Anaheim, CA, USA. 1993. Publ by American Electroplaters & Surface Finishers Soc Inc, Orlando, FL, USA. pp 461-470

Abstract: Trivalent chrome plating technology is on the process of rapid transformation. The demand for improved performance and recognition prompted the scientists to conduct researches in this new technology. This safer alternative will make a coating that looks similar and protects the substrate the same, or better, than hexavalent chrome. A recent finding uses a sulfate or chloride based electrolyte, graphite anodes and pulse plating technique to significantly increase both efficiency and plating rate. Its exceptional feature is its ability to "self purify." As an alternative to hexavalent chrome, trivalent chrome plating improved plating rate, efficiency, color, and appearance modifications.

Descriptors: Chromium plating; Electrolytes; Anodes; Electroplating solutions; Process control; Efficiency; Color; Purification; Impurities; Filtration

Identifiers: Trivalent chrome plating; Pulse plating technique; Hexavalent chrome; Metallic contamination; Plating rate; Graphite anodes; Sulfate

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Alternative for Tank Chromium Using (Brush) Plating.
Langan, John
SIFCO Selective Plat. Div., SIFCO Ind., Cleveland, OH, 44131, USA
Proc. AESF Annu. Tech. Conf. Date: 1992 Vol. 79 No. 2 pp 1137-50

Identifiers: Brush chromium electroplating alternative tank plating, Nickel chromium brush electroplating

Descriptors: Electrodeposits and electroplates brush; Chromium and nickel; Bend test on Electrodeposition and Electroplating; Brush of chromium; Alternative to tank chromium plating

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Atochem, Engelhard In Plating Venture.
Chem. Mark. Rep. Vol. 239 Issue 1 (paragraph) pp 4 Date: 1/7/91

Text: M&T Harshaw has been set up as a joint venture between Atochem N America Inc and Engelhard Corp. It combines the two companies' base metal plating businesses: M&T Chemicals from the Atochem group and Harshaw Metal Finishing from Engelhard. The venture will have sales of almost $ 200 M/y, placing particular emphasis on the HEEF 25 chromium plating processes, which is an alternative to chromic acid baths. The company also supplies an environment friendly trivalent chromium plating solution and a nonmetallic electrophoretic coating.

Descriptors: Metals industries; Industrie metallurgique; Industrie Metallerzeuegenden (MS-12)

Boeing's Evaluation of a Replacement for Chromium Plating: Nickel-Tungsten-Silicon Carbide.
Schiffelbein, Daniel V.

Boeing Commercial Airplane Group, Seattle, WA, 98124-2207, USA
Proc. AESF Annu. Tech. Conf. Date: 1992 Vol. 79th No. 2 pp 1125-36

Identifiers: Nickel tungsten silicon carbide electrodeposition

Descriptors: Electrodeposition and Electroplating with nickel-tungsten/silicon carbide composites, as replacement for hard chromium

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Case for Trivalent Chromium.
Snyder, Donald L.
Engelhard Corp, Beachwood, OH, USA
Products Finishing (Cincinnati) Vol. 53 No. 11 Aug 1989 pp 61-69

Abstract: Hexavalent chromium is the most common process for electroplating used currently in spite of the fact that it is very toxic and possibly carcinogenic. The reduction in a number of hexavalent chromium plating tanks by commercial alternatives is now possible. The substitute, trivalent chromium, eliminates most of the problems inherent to hexavalent chromium solutions.

Descriptors: Chromium plating-- Environmental Impact; Wastewater-Treatment; Water pollution--Control; Membranes--Ion Selective; Chromium compounds--Toxicity

Identifiers: Chromium electroplating; Anode solutions; Trivalent chromium; Hexavalent chromium

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Chloride Hard Chromium Plating Processes. Use of Pulsed Currents as a Future Alternative.
Setien, J.; Varona, J. M.; Gutierrez-Solana, F.; Fuentevilla, G.
ETSI Caminos, Univ. Cantabria, Spain,
Ing. Quim. (Madrid) Date: 1992 Vol. 24 No. 283 pp 97-104

Identifiers: Review hard chromium electroplating, Pulse plating hard chromium review

Descriptors: Electrodeposition and Electroplating, pulsed... with hard chromium

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Chromium Plating Using Acid-Free Electrolytes.
Die Verchromung Aus Chromsaeurefreien Elektrolyten.
Roubal, Jiri
Fabr fuer Galvanotech, Geislingen,
Galvanotechnik Vol. 69 No. 4 Apr 1978 pp 301-306

Abstract: The paper describes trivalent chromium plating solutions containing Cr-III salts as an alternative to the conventional hexavalent chromium. The advantages and disadvantages of these solutions are pointed out. In German.

Descriptors: Chromium Plating

Current Status of Galvanizing and Chromium Plating.
Stand Der Verzinkungs- Und Chromatierungsverfahren.
Knaak, Eberhard
Friedr. Blasberg & Co, Solingen
Galvanotechnik Vol. 66 No. 3 Mar 1975 pp 200-204

Abstract: The recent developments in galvanizing and chromium plating are characterized by replacement of cyanide electrolytes by alkaline cyanide-free processes, by improvement of high-cyanide electrolytes, and by introduction of weak-acid or neutral galvanizing processes. The various electrolytes, their fields of application, and their advantages and drawbacks are described. In German.

Descriptors: Galvanizing; Chromium Plating; Electrolytes

Electroplating: Where Its Going and Why.
Groshart, Earl C.
Boeing Co., Seattle, WA, 98124-2499, USA
Proc. AESF Annu. Tech. Conf. Date: 1988 Volume: 75th, Pages: L-6, 5 pp.

Identifiers: Review electroplating cadmium chromium, Nickel zinc alloy electroplate review, Plastic automobile airplane industry review

Descriptors: Plastics in automobiles and airplanes, as substitute for metals

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Enduro Industries Enhances Quality with New Chromium Plating Process.
Katz, Emanuel T.
M&T Chemicals Inc, Rahway, NJ, USA
Plating and Surface Finishing Vol. 76 No. 5 May 1989 pp 26-27

Abstract: Enduro Industries of Addison, Illinois, is a plating firm specializing in hard chromium plating of piston rods for hydraulic cylinders used in boom cranes, fork loaders and other heavy equipment. Recently, the company converted its plating chemistry to a new process. The process is specifically designed as a high-speed, etch-free, one-for-one replacement for conventional chromium plating baths, plating up to four times faster than conventional baths because of operation at higher current densities and greater efficiency.

Descriptors: Chromium Plating-- Efficiency; Machine Components-Electroplating; Hydraulic Machinery--Components; Electroplating--Energy Conservation

Identifiers: Hard Chromium Plating; Hydraulic Cylinder Piston Rods; High Current Density Plating; Energy-Efficient Electroplating

Reduced-Pollution Corrosion-Protection Systems.
Staebler, C. J., Jr.; Simpers, B. F.
Grumman Aerosp. Corp., Bethpage, NY, USA
117 pp, 1983

Abstract: Coating systems, designed to protect metallic components against corrosive attack using environmentally compatible materials and processes, were evaluated as potential alternatives for their higher polluting counterparts. Viable replacements were established for cyanide cadmium, cyanide copper, and hexavalent chromium electroplating. Alternatives to solvent-borne paints and phenolic-type paint strippers are available with slightly lower performance characteristics than their higher polluting counterparts. Performance characteristics were established for replacement systems of each type through comprehension testing. The performance, economic, and environmental aspects of the new coating systems were compared to those for a currently used control system.

Descriptors: Corrosion; Control systems; Economics; Metals

The Replacement of Chromium Plating by Cobalt--Tin Coatings.
Tranciatura Starnpaggio Vol. 17 No. 1 l/12 pp 81-82 Dec. 1980

Abstract: The replacement of Cr by Co--Sn coatings is considered. Advantages included better throwing power, easier application and less toxic effect. Two commercial Co--Sn processes are available: one based on SO, and one **on** Cl and F salts, giving a decorative deposit, approx. = 0.5 um thick, usually on a bright Ni substrate. Details are given of equipment and operational procedures for the two baths and of results obtained. The advantages and drawbacks of the two processes are compared.

Descriptors: Chromium plating; Cobalt-- Alloying elements; AlIoy plating; Tin base alloys-- Coatings
Alloy Index(Identifier): Sn-22Co-- SN

Study of the Feasibility of Replacing Cr(V1) Electrolytes by Cr(III) Solutions In the Production of Chromized Lacquered Tin Plate.
Larchenko, E. A.; Florianovich, G. M.; Filatova, N. G.; Litvinenko, V. A.; Paramonov, V. A.; Kolotyrkin, I. Ya.
L. Ya. Karpov Scientific-Research Physicochemical Inst.
Protection of Metals (English translation of Zaschita Metallov) Vol. 27 No. 3 Jan 1992 pp 367-371

Abstract: A method is developed for the application of a thin (0.02-0.05 um) porous layer of chromium on carbon steel from the solution Cr,(SO_3, plus (NH_3SO_4 plus $CO(NH_2)_2$, (pH2). The coating that is formed adheres well in relation to lacquer. The method is promising in connection with determining the feasibility of replacing toxic Cr(V1) in the production of chromized lacquered tin plate (CLTP) by nontoxic Cr(III). It

is established that with respect to corrosion resistance in the media employed in the canning industry, the method which is developed and is proposed in the present study is equal to the ecologically harmful method currently used.

Descriptors: Steel-- Protective Coatings; Chromium Plating; Chromium Compounds--Toxicity; Electrolytes; Tin Plate; Steel--Corrosion Resistance

Identifiers: Chromized Lacquered Tin Plate; Chromium Solutions; Tin Plate Replacements

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Technology Assessment of Selected Hazardous Waste Minimization Process Changes. (Final rept. 30 Sept 86-30 Apr 87)
Carpenter, C. J.
Air Force Engineering and Services Center, Tyndall AFB, FL. Engineering and Services Lab.
Report No.: AFESUESL-TR-87-45 Mar 88 66 pp

Abstract: The objective of this study was to technicalIy evaluate selected industrial process changes for applications to Air Logistics Centers for hazardous waste minimization. Those processes evaluated were as follows: (a) Ion vapor deposition of aluminum as a replacement for cadmium electroplating, (b) Noncyanide strippers to replace cyanide strippers, (c) Plasma spray of chromium to replace chromium electroplating, and (d) Nickel boron as a replacement for chromium electroplating. The study resulted in the recommendation to develop databases, test plans, pilot studies, and demonstrations of the effectiveness of processes a and b, above, in minimizing hazardous waste generation. Processes c and d showed minimum potential for hazardous waste minimization, and were not recommended for further study.

Descriptors: Air logistics support; Aluminum; Boron; Cadmium; Chromium; Data bases; Electroplating; Hazardous materials; Indoor air pollution; Industrial production; Ions; Nickel; Pilot studies; Planning; Plasma spraying; Pollution abatement; Test and evaluation; Vapor deposition; Wastes; Water pollution

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Theoretical and Practical Considerations on the Substitution of Nickel and Nickel-Chromium Protective Layers Using Zinc In Electroplating - A Contribution To Material Economy and Corrosion Protection.
Schulz, W. D.; Kassner, W.
Zentralstelle Korrosionsschutz, Dresden, E. Ger.
Technik Date: 1976 Vol. 31 No. 5 pp 297-8

Identifiers: Review zinc replacement nickel electroplating, Chromium electroplating zinc replacement review

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Tin-Based, Chromium-Like Finishes.
Hyner, Jacob
Whyco Chromium Co, Thomaston, Conn
Plating and Surface Finishing Vol. 64 No. 2 Feb 1977 pp 32,34,36

Abstract: An attempt by the Whyco Chromium Co. of Thomaston, Conn., to find a replacement for chromium plate has led to the development of a bright, tarnish-resistant and color-stable ternary alloy of about 40-90% tin, 10-50% cobalt and between one and 28% of a third metal of periodic groups II, III and VI. Typical third metals are zinc, cadmium, indium, antimony, and chromium. The company is now plating an alloy analyzed to be CoSn//2X, in which "X" is a percentage of one of the above-mentioned third metals. By weight, the alloy is one part cobalt to four parts tin, plus a fractional part of X. This CoSn//2S alloy, like tin-nickel, is tarnish-resistant because it rapidly passivates in the atmosphere. No post plating treatment is required.

Descriptors: Chromium Plating; Tin Cobalt Alloys--Electroplating

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Tin-Cobalt Alloy Plating From A Sulphate Electrolyte.
Hemsley, J. D. C.; Roper, M. E.
Oxy Met Ind Ltd, Woking, Surrey, Engl
Transactions of the Institute of Metal Finishing Vol. 57 Pt. 2 Summer 1979 pp 77-80

Abstract: This paper discusses bright tin-cobalt plating as an alternative to chromium plating, and as a coating with its own unique properties. Operational requirements are detailed, together with an outline of deposit and electrolyte properties. Reference is made to present and potential uses within the metal finishing field.

Descriptors: Tin Cobalt Alloys-- Plating; Electrolytes

Trivalent Chrome - A Real Alternative.
Anonymous
Finishing Vol. 7 No. 10 Oct 1983 pp 20-22

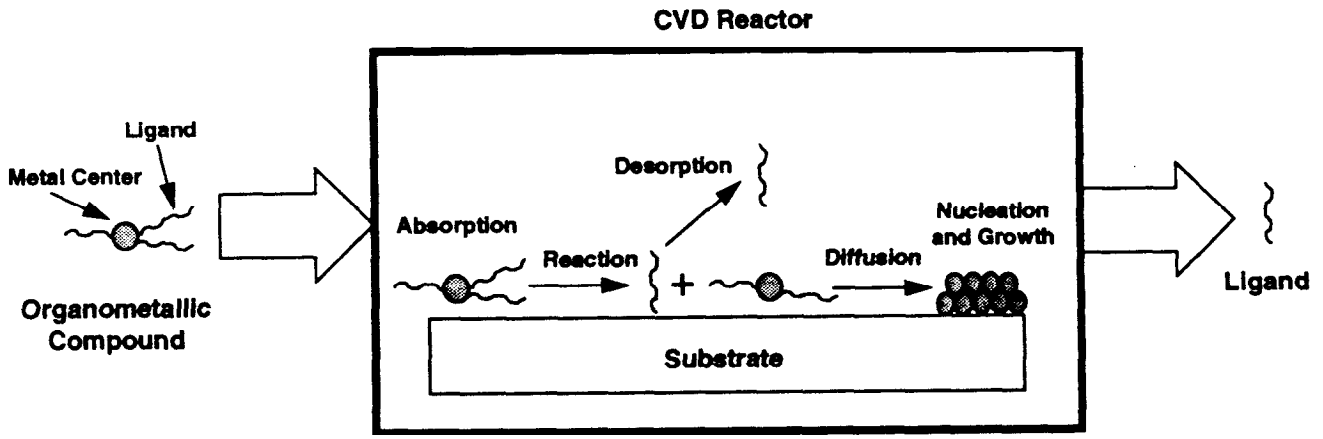
Abstract: The recent commercial launch of Envirochrome was preceded by five years of intensive search for a viable trivalent decorative chromium plating process that could replace the traditional but difficult and hazardous hexavalent process. The results of this work show that the new process produces deposits which commercially match the color of hexavalent chrome, plates work difficult or uneconomic with the traditional-process, gives better performance and removes the environmental and processing hazards. This report describes the Envirochrome process with emphasis on recently developed trivalent chromium solutions.

Descriptors: Chromium Plating-- Solutions

3.0 Chemical Vapor Deposition (CVD)

3.1 Description

Chemical vapor deposition (CVD) is a process in which a coating is delivered to a substrate by a reactive vapor, usually in the form of a metal halide, metal carbonyl, hydride, or organometallic compound. Energy is applied to the substrate to facilitate reaction of the coating material upon contact. As the metal species is deposited on the substrate, the ligand species is exhausted from the chamber (Figure IV-2). Most CVD reactions are endothermic and may be controlled by regulating the amount of energy input.



Chemical Vapor Deposition

3.1.1 Atmospheric CVD

Conventional CVD takes place at high temperature and atmospheric pressure and is referred to as atmospheric CVD. The vapor is reduced by hydrogen reduction or direct pyrolytic decomposition. The reduction causes released metal atoms to be deposited on the substrate. Disadvantages of this process include high reactant cost, low material utilization, and substrate distortion due to elevated temperatures.

3.12 Low Pressure CVD

Low pressure CVD is similar to atmospheric CVD, but it is conducted at **sub-** atmospheric pressures. A special pumping system is required to trapcorrosive compounds before they reach the vacuum pump and cause equipment damage. This process offers improved coating properties such as small grain size and uniform thickness and composition.

3.1.3 Plasma Enhanced CVD

Plasma enhanced CVD is a method used with substrates or reactions requiring lower temperatures. This method implements the kinetic energy of electrons from an electrical plasma instead of thermal energy to facilitate the chemical reaction.

3.2 Advantages/Disadvantages

Thick, dense, high-purity films are deposited by CVD. Since CVD is not a line-of-sight method, it may be used to coat complex shapes. However, high temperatures limit the use of CVD on some types of substrate materials.

3.3 Health and Safety

Ventilation is necessary to remove reacted and unreacted vapors. Protective equipment and clothing is also required. For plasma enhanced CVD, isolation of the power source is necessary to avoid the hazard of electrical shock.

3.4 Environmental

Waste effluents from the process must be appropriately managed, depending on the nature of the chemicals used. Corrosive materials must be rendered harmless, condensates must be collected, and flammable substances must be properly managed.

3.5 Relevant Abstracts

Application of a New Concept to Design Specific Materials for the Automotive Industry.
Wang, S. J.
Gentec
New and Alternative Materials for the Automotive Industries, Florence, Italy, l-5 June 1992
Automotive Automation Limited, 42 Lloyd Park Ave., Croydon CR0 5SB, UK, 1992
pp 275-280

Abstract: Coating the surface of a tough steel substrate with a thin, hard, wear-resistant film of a few pm thickness is described. Coatings of TiC and Cr_7C_3 improved service life of steels 20-360 fold. Coatings can be produced through PCVD, LTCVD, LCVD, and PVD. Automotive component coating experiments have been undertaken with valve tappets, roller bearings, and gears.

Descriptors: Conference Paper; Engine components-- Coating; Roller bearings-- Coating; Gears-- Coating; Vapor deposition coating; Physical vapor deposition; Chemical vapor deposition; Titanium carbide-- Coatings; Chromium carbide-- Coatings

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DLC by PCVD.
Durand, A. M.
Applicat Couches Minces SA, 9 Rue Gare/f-78640 Villiers Stfreder//France!
Vide-Couches Minces, 1991, Vol. 47, No. 259 (Nov-Dee), pp 327-334

Abstract: "Different ways are possible to deposit diamond-like carbon (DLC): Dual beam system, Magnetron system, Beam deposition or Plasma enhanced chemical vapor deposition. When the three first systems enable to deposit DLC only on flat surface (except if the sample is mounted on a rotating substrate holder), the fourth one permits the deposition in three dimensions. This matter opens a large panel of applications, for example in the mechanical area, where this kind of coating can replace the electrolytic hard chromium. Note that the PCVD deposition does not pollute, that is not the case for all electrolytic deposition. The other advantage is the low temperature of the deposition in regard with the TiN deposited by CVD. This deposition is done at around 450-^{0}C, that is too high for some applications (for example: the molds for plastic or the plastic itself). The hard carbon deposited by PCVD is also a very good protection against the corrosion, because of its thickness."

Vapor Phase Deposition Processes in the 1990s.
Johnson, P. C.
Vat-Tee Systems
Metal Finishing Vol. 89, No. 4, pp 61-64 Apr. 1991

Abstract: Based on a review on the applications and developments in vapor phase deposition in the 1980s, it becomes apparent that the use and application of plasma-assisted deposition would continue to enhance the quality of the growing film for the foreseeable future. The opportunities for new applications of vapor phase methods in the 1990s will fall into two categories: replacement of existing methods for economic/performance reasons and the development of applications based upon new capabilities (combining decorative and corrosion resistant finishes) and new materials (metal nitrides). The other growth is expected in the development of plasma-enhanced chemical vapor deposition with applications ranging from hard coatings, solar cells to semiconductors. Coating materials include Cr, Cu, Al, Ni and nitrides, carbide, oxides of titanium, tantalum, and tungsten.

Descriptors: Vapor deposition coating; Chromium-- Coatings; Copper-- Coatings; Aluminum-- Coatings; Nickel-- Coatings; Nitrides-- Coatings; Carbides-- Coatings; Oxides-- Coatings; Solar generators-- Coating; Stainless steels-- Coating; Electric equipment-- Coating

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4.0 Electroless Plating

4.1 Description

Electroless plating is a process in which metal ions in a dilute aqueous solution are deposited on a substrate by means of autocatalytic reduction (Figure IV-3). Autocatalytic reduction is a chemical reaction in which the substrate acts as a catalyst, causing ions to continuously deposit onto the substrate. Chemicals, such as hypophosphites, reduce metallic ions in the electroless plating solution to form a coating. Once a metal is reduced and deposited, the metal surface acts as a catalyst for further deposition in that location. Elements contained in the reducing agent (e.g., phosphorus in sodium hypophosphite) are also incorporated into the coating. By controlling the amount of these elements in the plating bath solution, various coating properties can be modified.

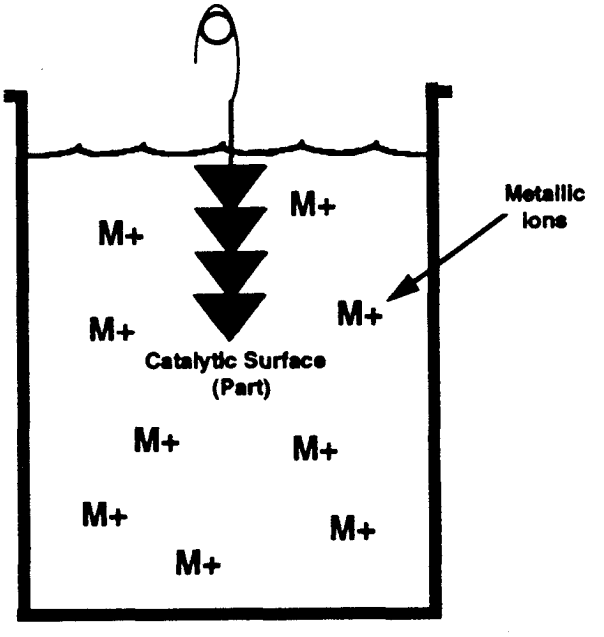

Figure IV-3: Electroless Plating

The most widely used material for electroless plating is nickel. Electroless nickel actually refers to a wide variety of alloys, typically of nickel with phosphorus or boron. Recently developed low-phosphorus formulations may be used for coating low heat tolerant substrates requiring high hardness. Electroless nickel coatings have excellent resistance to wear and corrosion and may be used in a wide range of applications. Electroless copper is the second most used process, often in the manufacturing of printed circuit boards.

4.2 Advantages/Disadvantages

Electroless plating offers many desirable properties, including uniform deposits with variable thickness, good corrosion and wear resistance, and effective coating of intricately shaped substrates.

4.3 Health and Safety

Hazardous vapors must be properly vented and corrosive chemicals must be handled appropriately. Worker protection such as boots, aprons, and eye protection is required.

4.4 Environmental

Rinsewater from this process must be neutralized and trace metals must be removed by ion exchange or other methods prior to discharging. Ion exchange techniques are more advanced than those used with chromium processes, allowing more complete recovery. Solid sludges must be recycled by smelting or disposed of properly.

4.5 Relevant Abstracts

Development of Low Cost Contacts to Silicon Solar Cells.
Final Report, 15 October 1978-30 April 1980
Tanner, D. P. ; Iles, P. **A.**
Optical Coating Lab., Inc., City of Industry, CA. Photoelectronics Div.
Sponsor: Department of Energy, Washington, DC.
1980 140 pp

Abstract: A summary of work done on the development of a copper based contact system for silicon solar cells is presented. The work has proceeded in three phases: (1) Development of a copper based contact system using plated Pd-Cr-Cu. Good cells were made but cells degraded under low temperature (300 exp 0 C) heat treatments. (2) The degradation in Phase I was identified as copper migration into the cells junction region. A paper study was conducted to find a proper barrier to the copper migration problem. Nickel was identified as the best candidate barrier and this was verified in a heat treatment study using evaporated metal layers. (3) An electroless nickel solution was substituted for the electroless chromium solution in the original process. Efforts were made to replace the palladium bath with an appropriate nickel layer, but these were unsuccessful. 150 cells using the Pd-Ni-Cu contact system were delivered to JPL. Also a cost study was made on the plating process to assess the chance of reaching 5 cents/watt. (ERA citation 05:037819)

Descriptors: Electric contacts; Silicon solar cells; Chromium; Copper; Diffusion; Economics; Electric conductivity; Electrical properties; Electroplating; Experimental data; Fabrication; Graphs; Heat treatments; Masking; Nickel; Palladium; Vacuum coating

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Developments and Industrial Applications of Electroless Coatings.
Celis, J. P.; Roos, J. R.; Bonte, M. De
KU Leuven
Conference: Surface Modification Technologies, Phoenix, Arizona, USA, 25-28 Jan. 1988
The Metallurgical Society/AIME, 420 Commonwealth Dr., Warrendale, Pennsylvania 15086, USA
1988 pp 215-235

Abstract: Electroless deposition of metals has received, over the last decade, full recognition as a valuable, industrially-applicable coating technology. Recent data on worldwide consumption of electroless plating baths seem to indicate that the amount of electroless Ni produced over the last few years is rather constant. Heat-treated electroless Ni--P is, for certain wear problems, a convenient alternative for electrolytic hard Cr. For electroless Cu plating, a still-growing market is expected, e.g. in the field of PCBs. It is expected that further development of the electroless plating technology will result in new coating materials with unique physical, chemical, and mechanical properties. Those aspects of electroless plating, which will be decisive for the further development of electroless plating, are discussed. These are: the development of on-line process control facilities, requirements concerning the chemicals to be used, and, last but not least, the insight into the trivalent relationships between production conditions, coating characteristics, and functionality of the coatings. These topics are illustrated by results from laboratory investigations and plant experience. Substrates can be ferrous and nonferrous alloys, special steels, and ceramics.

Descriptors: Electroless plating; Ferrous alloys-- Coating; Nonferrous alloys-- Coating; Ceramics-- Coating; End uses; Nickel plating; Chromium plating

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Electroless Nickel: Alternative To Chromium Coatings.
Duncan, Ronald N.
Met Prog Vol. 127 No. 7 Jun 1985 pp 31-36

Abstract: Electroless Ni is a metallic glass containing approx. 10.5% phosphorus dissolved in Ni and < 0.05% other impurities, normally used for functional rather than decorative applications. The internal stress of electroless Ni deposits is very low on most substrates. Coating thickness is the same on any area of the part exposed to fresh plating solution and coating thickness can be controlled to suit the application. It has high strength, limited ductility, and relatively low conductivity. As deposited, electroless Ni is complete nonmagnetic. It can be easily soldered, brazed, and bonded. One of the most important properties for many industrial applications is its hardness and wear resistance. The adhesion of these coatings to steels and to Al, Cu. and their alloys normally exceeds the shear strength of the substrate. Because of their homogeneity and freedom from defects, electroless Ni coatings provide a true barrier to corrosion. They do not offer any pathways to the substrate. The metallic bonds they form with the substrate also prevent underdeposit attack.

Descriptors: Electroless nickel plating; Wear resistance; Corrosion resistance; Thermal expansion; Electroless coatings-- Physical properties

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Electroless Nickel as a Replacement for Hard Chromium: The Phosphorus Content Makes the Difference.
Durkin, Brad; Crotty, David
Proc. AESF Annu. Tech. Conf.
Date: 1992 Vol. 79 No. 2 pp 1151-71

Identifiers: Nickel phosphorus coating, Chromium replacement

Descriptors: Coating materials...nickel-phosphorus, Properties of electroless, as replacement for hard chromium

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Electroless Nickel Plating Used For Corrosion & Wear Resistance.
Surface Modification Technology News July, 1992 Vol. 2 No. 7
Publisher: Business Communications Company, Inc.

Full Text: Topping the list of reasons why electroless nickel plating is so widely accepted in so many industries is its resistance to wear and corrosion. EN coatings have long been specified in the chemical process industries to protect components against corrosive chemicals. Their uses range from nuts and bolts to large valves and, in some cases, tank car linings.

The industries that use EN include food processing, aerospace, electronics, batteries, oil and gas, and automotive. The uniform coverage of EN, on even the most complex, irregular **surfaces,** is a key **advantage.** EN features inherent lubricity. It is easy to solder and braze and has excellent hardness.

There are ongoing technological developments and refinements in EN that assure the best use of it for a particular environment. A good example is the newest generation low-phosphorus EN formulations. They have been developed for applications where high hardness was a requirement - from 58 to 60 on the Rockwell C scale - and having low tolerance to heat treatment. The success of EN in these types of applications has helped it become widely used as a replacement for chromium plating.

The use of EN to protect automotive components that are in direct contact with new alternative fuel systems is another recent development. An example of alternative fuel systems are gasoline/methanol blends. High-phosphorus electroless nickel coated steel and aluminum have been tested with excellent results, especially in the area of protection against corrosion.

For applications from the most basic to the sophisticated, EN offers an alternative to more traditional finishes and materials of construction.

Identifiers: Electroless nickel plating, phosphorus compounds, corrosion and wear resistance

Kirk-Othmer Online.
(c) 1993 John Wiley & Sons Inc.
Chapter: Electroless Plating
Section Heading: Plating on Metals

Text: The first large-scale process was the Kanigen electroless nickel process from General American Transportation Co. This hot nickel process uses a hypophosphite reducing agent. Properties of electroless nickel deposits vary greatly depending on the reducing agent used. Hydrazine gives a practically pure nickel, and the organoboron reducing agents give very hard nickel-boron alloys. The most widely used hypophosphite baths deposit a range of nickel-phosphorus (l-15 wt % P) alloys with unique properties. Acidic baths (pH 4.0-5.5) are preferred, but alkaline baths (pH 8-10) are also used. Operating temperatures are 70-95 ^{0}C. Table 1 shows some typical formulations. A large number of commercial baths are available with properties tailored to suit specific applications.

The engineering properties of electroless nickel have been summarized. The Ni-P alloy has good corrosion resistance, lubricity, and especially hardness. It can be heat-treated to a hardness equivalent to electrolytic hard chromium (Fig. l), and its lubricity is comparable. Thus it is not surprising that the main applications for electroless nickel are in replacement of hard chromium.

The advantages over hard chromium include safety of use, ease of waste treatment, plating rates of as much as 40 um/h, low porosity films, and the ability to uniformly coat any geometric shape without burning or use of special anodes. The uniformity of coating thickness can also minimize expensive machining after plating, and can be used to salvage parts that have been overmachined. Electroless nickel has superior corrosion and erosion resistance as compared to electrolytic nickel. It is used extensively on molds, pistons, pump parts. oil field equipment, dies, compressors, tanks, and piping.

The market size for electroless nickel solutions is not known with any certainty. The best guesses are based on hypophosphite production, as virtually all is used for electroless nickels. An estimate for 1977 usage is 900 metric tons of nickel, of which 85% may be for plating on metals and 15% for plating on nonconductors. However, in terms of plated area, plating of nonconductors is at least ten times as great owing to the much lower thicknesses used.

Electroless nickel can be used to plate aluminum. The adhesion is often poor unless the aluminum is etched to remove oxides. The best method is to use an intermediate zincate deposit. Adhesion can vary widely depending on the aluminum alloy used.

Electroless nickel or nickel-lead alloys can improve the solderability and braisability of aluminum even when a continuous film is not present. Electroless nickel systems based

on dimethylamineborane reducing agents are used to coat aluminum contacts and semiconductors in the electronics industry (see Electrical connectors).

Preparation of the Substrate: All parts must be cleaned thoroughly before plating. Any traces of dirt or oxide will either prevent deposition or lead to adhesion loss. Nickel can be spontaneously deposited from hot electroless solutions on most common metals, including mild steel, beryllium-copper, aluminum, stainless steel, and titanium. Generally, special etchants are used for difficult materials such as titanium and some stainless steels. Lead and a few other materials cannot be plated directly because they poison the electroless reaction. A thin electrolytic layer may be used to mask such surfaces to make them platable. Where initiation is slow or difficult, such as with copper substrates, it can be started by briefly contacting the inactive part with one that is actively plating, by giving it a brief cathodic pulse of current, by contact with a dissimilar metal, such as iron, or by prior immersion in a dilute solution of a precious metal such as platinum or palladium.

The parts are allowed to plate until the desired thickness is reached. This point can be monitored by knowledge of the bath operating rate, or by direct thickness or weight measurement of standard test parts.

Chapter: Electroplating
Section Heading: Nonelectrolytic Plating Processes

Text: There are many other ways than electroplating to deposit a coating of a metal on a substrate (see Film deposition techniques). Hot dipping, vacuum evaporation, chemical vapor deposition, and various aqueous processes not requiring current are some of the best developed. These last processes are sufficiently related to electroplating to be included in a discussion of the technology. Nonelectrolytic aqueous deposition includes immersion plating and chemical, autocatalytic, or what has come to be known as electroless plating.

Immersion Plating: When the substrate metal is less noble than the plating metal, or can be made so by appropriate complexing agents in the solution, an immersion deposit may be formed, the prototype of which is the familiar $Fe + Cu^{2+} \text{----> } Cu + Fe^{2+}$. Many such immersion deposits are of no value because they are powdery or nonadherent, and in fact are to be avoided. On the other hand, some immersion processes have commercial use. Tin can be deposited on copper and its alloys from solutions containing a tin salt and a complexing agent for copper such as cyanide or thiourea. Two formulas are given in Table 28 and proprietary methods are available.

Tin is deposited on aluminum alloy pistons by immersion in alkaline stannate solutions. This process is practiced on a large scale by all the major automotive manufacturers. Copper-tin alloys are applied to steel wire (liquor finish) as a drawing lubricant and for color in such items as paper clips and hair pins.

Gold and some of the other precious metals are also frequently applied by immersion techniques.

In general, immersion deposits cannot be built up to thicknesses comparable to those obtainable by electrolytic methods, for as soon as the substrate is completely covered the reaction ceases. Nevertheless, some such deposits have appreciable thickness, entirely sufficient for the intended application. Immersion processes have the advantages of practically unlimited throwing power (limited only by access and renewal of the solution to the surface) and low capital cost, since they require no source of DC power.

Autocatalytic Plating: Electroless plating, as autocatalytic plating is better known, is defined as deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited. The term electroless plating has been carelessly applied to all processes that do not require an outside source of current, but the distinction between truly chemical reduction methods (electroless plating) and electrochemical replacement (immersion plating) is a valuable one and should be maintained. The most widely used of the truly electroless processes is electroless nickel, in which nickel ions in the solution are reduced to the metal by a reductant. The deposition process is catalyzed by certain metallic surfaces, including the deposited metal itself; thus once initiated the deposition is autocatalytic. Fortunately, under proper control the reaction takes place only at the catalytic surface and not on the walls of the containing vessel or in the bulk of the solution.

The process has several advantages over electroplating: virtually unlimited throwing power, little or no excess deposit on high points, deposits of excellent chemical and physical properties, and the ability to coat surfaces such as those on the inside of tank cars which would be difficult or impossible to do with conventional electrolytic techniques. The principal disadvantage is high cost. The reducing agent, sodium hypophosphite, which is expensive, is consumed in substantial quantities, and the setup is often complicated, requiring exacting control. If ordinary electrolytic techniques will do the job, they are preferred, but electroless methods enlarge the range of possibilities.

Typical formulations contain nickel chloride, sodium hypophosphite, and one or more hydroxy acids such as lactic or glycolic. Operating temperatures range from 65 to 100 ^{0}C. Several proprietary processes are available.

When sodium hypophosphite is used as the reductant, electroless nickel is not pure nickel but a nickel-phosphorus alloy containing 5-15% phosphorus.

Although sodium hypophosphite is the most widely used chemical reductant solutions using sodium borohydride or amine boranes [especially dimethylaminoborane (DMAB)] are also employed, yielding deposits containing ca 0.3- 10% boron, according to the bath used and the operating conditions.

Electroless nickel alloys have been tested against hard chromium for wear resistance on crank-shafts and found to be somewhat superior. Hardness and wear resistance were reported as well as the effect on corrosion resistance of the complexing agents used in the

bath. Ternary and quatemary nickel alloys produced autocatalytically have been reported.

Next in importance to electroless nickel is electroless copper. This has been particularly useful in plating on nonmetallics and in printed circuitry. Typical baths contain copper sulfate, Rochelle salts, sodium hydroxide, formaldehyde as reducing agent, and other additives to increase plating rate and minimize spontaneous decomposition. As usual, many proprietaries are available. Electroless copper, widely used in printed circuitry competes with electroless nickel in plating in plastics.

Electroless processes have been reported for gold, rhodium, palladium, cobalt, and silver.

New Electroless Nickel Technology as an Alternative to Hard Chromium Plating.
Bleecks, T.; Shawhan, G
Enthone
Met. Finish. Vol. 87 No. 10 pp 21-27 Oct. 1989

Abstract: in the metal finishing area where functional coatings are required to solve problems of wear and corrosion at a competitive cost, two principal processes are considered, namely hard Cr and electroless Ni. Because of the concerns with Cr waste, many hard Cr platers are considering electroless Ni as an in-house plating alternative. Advances in electroless Ni technology, principally with the introduction of high hardness, LP electroless Ni, have narrowed the performance difference between electroless Ni and hard Cr plating. The corrosion resistance of electroless Ni is excellent in many process environments and is normally far superior to hard Cr.

Descriptors: Electroless nickel plating; Chromium plating; Surface pretreatments; Plating baths; Wear resistance-- Coating effects; Corrosion resistance-- Coating effects

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Recent Developments in Surface Finishing Technology.
Rajagopalan, S R
National Aeronautical Laboratory (India)
Journal of the Electrochemical Society of India Vol. 39 No. 1 pp 54-55 Jan 1990

Abstract: Advantages offered by new surface finishing techniques to the aircraft, automotive and electronics industries are considered. Electroless Ni (EN) thereby plays an important role and so does Ni-coated graphite. Other new features mentioned are: the use of Pd, Pd--Ni electroless Ni--B to replace Au in electrical contacts. Then; to overcome electromagnetic radiation, there are the developments of plastic housings with conductive coatings.

Descriptors: Aircraft components-- Coating; Automotive components-- Coating; Electronic devices-- Coating; Electroless nickel plating; Electroless coatings-- Mechanical properties; Hardness; Corrosion resistance; Wear resistance; Electroplating; Chromium plating; Nickel plating; Palladium base alloys-- Coatings; Tin base alloys-- Coatings

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Reinforced Electroless Nickel Coatings for the Substitution of Hard Chromium Platings.
Boose, C A
TNO Metals Research Institute
Conference: European Research on Materials Substitution, Brussels, Belgium, 9-11 Dec. 1986
Elsevier Applied Science Publishers, Crown House, Linton Road, Barking, Essex IG11 8JU, UK
1988 pp 253-258

Abstract: In some applications electroless Ni--P coatings can replace hard Cr coatings. In this study, the electroless Ni--P coatings are compared to hard Cr coatings in two aspects: wear resistance and corrosion resistance. The investigated electroless coatings are produced under different circumstances, allowing the determination of the effects of (a) alloying constituents, (b) a second phase like codeposition of particles, (c) pulsed currents and (d) heat treatment procedures. Wear tests included use of Tabar Abraser and pin-disc equipment. Corrosion tests have been carried out according to the standard neutral salt spray test ASTM B 117 with outdoor exposures as reference.

Descriptors: Chromium plating; Electroplate-- Materials substitution; Electroless coatings-- Materials substitution; Electroless nickel plating; Abrasion resistance; Corrosion resistance

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Why Use Electroless Nickel With a Hard Chrome Overlay? (Pamphlet).
Brockman, D A
Electroless Nickel Conference II, Cincinnati, Ohio, 17-18 Mar. 1981
Publ: Products Finishing Magazine, 600 Main St., Cincinnati, Ohio 45202
1981 9pp

Abstract: In many areas hard Cr can be replaced by electroless Ni. Compared to most coatings electroless Ni and hard Cr are functional, hard and wear resistant. In specific applications, one or the other may be superior, because of its unique characteristics and properties. When combining electroless Ni with hard Cr overlay one has many of the advantages of hard Cr with those of electroless Ni supporting it. Corrosion resistance, complete and uniform coverage and an economical deposit on complex shapes and metals are achieved. This can be seen when comparing some of the properties and characteristics of each deposit. Applications include aircraft pistons and brakes, rams and shafts used in steel mills and ball valves and shafts used in oil field machinery.

Descriptors: Aircraft components-- Coating; Pistons-- Coating; Brakes (for arresting motion)-- Coating; Shafts (power)-- Coating; Electroless nickel plating; Chromium plating; Corrosion resistance

5.0 Ion-Based Technologies

5.1 Description

Ion-based technologies utilize positive ions or neutral atoms to bombard a substrate and deposit the coating material. An electrostatic field accelerates ions from the source to the substrate (Figure IV-4). These processes are very versatile in that any element or alloy capable of being vaporized, evaporated, or sputtered may be deposited by one of the ion-based techniques.

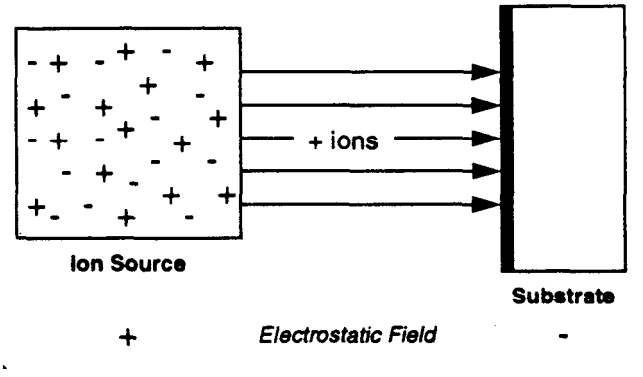

Figure IV-4: Ion-Based Technologies

5.1 .1 **Ion Beam** Assisted Deposition (IBAD)

Ion beam assisted deposition incorporates physical vapor deposition and simultaneous ion bombardment. Low energy ions bombard the substrate surface to provide nucleation sites for the deposited coating. Concurrently, neutral species of coating material are delivered to substrate via evaporation or sputtering and impinge on the surface to form islands of deposited material. These islands overlap to form a film of the desired coating. This method offers improved adhesion, increased density, reduced porosity, and increased control of coating properties such as composition, internal stress, and morphology.

5.12 Ion Implantation

The ion implantation process does not produce a discrete coating, but alters the near surface region of the substrate. A beam of charged ions of the desired element is formed and accelerated by an electrostatic field toward the-substrate. Once embedded in the surface, ions become atoms surrounded by atoms of the original surface material. This process enables creation of unique alloys from species that are normally immiscible or have low solubility. Properties of the surface depend on the element(s) implanted, but penetration depth may be inadequate for some applications. This coating method offers low temperatures, ease of control, and no changes in bulk properties or substrate dimensions.

5.1.3 Ion Plating

Ion plating is a vacuum coating process used to deposit elements or alloys on a negatively-biased substrate in the presence of a reactive gas. The substrate is placed in an evacuated chamber that is then backfilled with an inert and/or reactive gas. A high negative potential is applied to the substrate (or conductive screen in the case of non-conductive substrate) to ionize the gas. Then, the coating material is vaporized into the glow discharge of the ionized gas. Ions of the coating material are accelerated by the electrostatic field to the negatively charged substrate where they bombard the surface and adhere to form a coating. Film properties may be improved by ion bombardment during deposition.

5.2 Advantages/Disadvantages

Ion-based technologies offer improved adhesion and film structure. However, equipment costs are typically high.

5.3 Health and Safety

Precautions must be taken against high voltages and toxic chemicals must be handled appropriately.

5.4 Environmental

These processes are essentially environmentally benign. Only minor amounts of residue are produced from vacuum systems.

5.5 Relevant Abstracts

Composition Depth Profiles and the Effects of Annealing for Ion-Implanted Alloys. (Rept. of investigations)
Campbell, III, A. B. ; Saxtwell, B. D. ; Needham, Jr, P. B.
Bureau of Mines, Avondale, MD. Avondale Metallurgy Research Center.
Report No.: BUMINES-RI-8387 1979 31 pp

Abstract: The Bureau of Mines is developing alloys using ion implantation as an alternative to bulk alloys that consume large quantities of strategic materials such as chromium and nickel. These alloys are formed at the outer layer of relatively common materials. To more fully understand the corrosion characteristics and physical properties of this outer layer, it was necessary to determine the alloy concentration as a function of depth into the substrate material. Also, since many of the ion-implanted alloys would be utilized at elevated temperatures, it was necessary to determine the diffusion behavior of the implanted element. Proton-induced X-ray emission and inert gas ion sputtering have been utilized to generate composition depth profiles for Fe-Cr, Fe-Ni, and Fe-AI ion implanted alloys fabricated by implanting 25-kev Cr(+), Ni(+), or AI(+) into iron substrates. The data were fitted (utilizing a computer program) with symmetrical Gaussian profiles yielding values for the range and range straggle of the ions. These

parameters were then compared with those calculated from theory. Changes in the profiles due to annealing were investigated and values for the diffusion coefficient were obtained assuming diffusion according to Fick's Law. For the Cr(+) and Ni(+) implantation, the profiles as-implanted agree reasonably well with theory and exhibit 'normal' diffusion characteristics at 500 ^{0}C. For the Al+ implantation, the profile as-implanted is much broader than predicted and exhibits substantial enhanced diffusion at temperatures up to 500 ^{0}C.

Descriptors: Iron alloys; Implantation; Chromium; Nickel; Aluminum; Annealing

Identifiers: Ion implantation

Development and Testing of Multilayer Physically Vapor-Deposited Coatings for Piston Rings.
Lyubimov, V.V.; Voevodin, A.A.; Yerokhin, A.L.; Timofeev, Y.S.; Arkhipov, I.K.
Tula Polytech Inst., Dept. Prod Machines & Apparatus, 92 Lenin Ave/Tula 300600//USSR/; Tula Polytech Inst. Electrophys & Electrochem Treatment Lab/Tula 300600//USSR/; Tula Machinebldg Plant, Electrochem Treatment Grp/Tula 300002//USSR/; Tula Polytech Inst, Dept High Math/Tula 300600//USSR
Surface & Coatings Technology, 1992, Vol. 52, No. 2 (April 30), pp 145-151

Abstract: The development of multilayer coatings prepared by physical vapour deposition (PVD) for piston rings of internal combustion engines to decrease the wear of both ring and cylinder is discussed. Theoretical considerations on the wear and composition of the PVD coatings for piston rings are presented. An optimization of the combination, thickness and deposition conditions of the coating layers is proposed. It was found that the coating must have layers for different purposes: running in, wear resistance, compliance, adhesion. Wear tests of piston pairs with cast iron rings having ion-assisted arc-evaporated PVD coatings consisting of TiN and titanium layers and chromium-electroplated coatings and of piston pairs without coatings were carried out. Application of the developed PVD coating resulted in a ring wear of 30% compared with uncoated rings and 60% compared with rings having chromium-electroplated coatings, the wear of cylinders against coated rings being 70% compared with the wear against uncoated rings. A conclusion concerning the advantage of replacing chromium-electroplated coatings with multilayer PVD coatings is drawn.

Industrial Development of Ion Nitriding.
Pourprix, Y
Trait. Therm. Vol. 141 pp 25-28 Jan. 1980

Abstract: The mechanical properties of ionic nitrided layers were examined in fatigue tests on annealed XC32,42C2,30CD12,3OCAD6-12,30CDV12 steels and cast iron, and in binding tests using an Amsler machine. Rolling tests were also carried out on 100C6, 30CAD6-12,30CDV12 and 16C4 steels. The advantages, disadvantages and price comparison of ionic nitriding with other techniques indicate the advantageous

replacement of salt bath treatment, electrolytic chromium plating, cementation and carbonitriding and the resolution of many friction problems.

Descriptors: Ion nitriding; Carbon steels-- Heat treatment; Chromium steels-- Heat treatment; Chromium molybdenum steels-- Heat treatment; Fatigue strength-- Heating effects; Alloy Index

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Ternary Coatings Family Available
Technical Insights 1991

Full Text: Talk to Germany's Leybold Technologies about a new family of sputter-ion plated wear and corrosion coatings and the deposition equipment to apply them on three-dimensional parts. The new coatings have been optimized for cutting tools (drill and milling bits), forming tools (drawing and stamping dies), and components subject to intense wear (bearings, shafts, pistons).

The coatings are produced by Leybold's TriTec large-volume sputter-ion plating system, which uses plasma amplifiers to intensify plasma density and volume and to improve the technique's cost-effectiveness. A key feature of the new apparatus is that users can deposit ternary and quaternary alloys with compositions virtually identical to the starting source materials. Seybold offers TriTec systems capable of 400 mm dia x 600 mm tall coating volume and 600 mm dia x 1000 mm tall.

The system can produce four types of coatings: monolayer TiNAl for cutting tools; multilayer TiNAI for high-wear tools; CrN to replace electroplated hard-chromium; and a multilayer metal-impregnated amorphous carbon film that combines hardness up to 2000 I-IV with coefftcients of friction below 0.1.

The amorphous carbon, MeC 2000, is made by embedding tungsten, titanium, or tantalum into largely amorphous carbon. It can be deposited as a conductor or insulator, and is self-healing, forming graphite films to cover local rupture. Potential uses are automotive engine components and tools to machine low-strength materials. The coating ranges in hardness from 1500 HV to 2000 HV, and is highly abrasion-resistant. It can be deposited at 150 ^{0}C to 200 ^{O}C, lower than for other PVD and CVD methods. The resulting films have low internal stress, and are virtually resistant to changes in humidity.

Contact: Leybold A. G., Industrial Coating, Wilhelm-Rohn-Str. 25, P.O. Box 1555, D-6460 Hanau 1, Germany.

6.0 Sputtering

6.1 Description

Sputtering is a vacuum coating process in which positive gas ions are formed and accelerated to high speeds to strike a negatively charged metal source (target). The energy is transferred to the metal atoms of the target in the form of momentum, causing them to be ejected from the surface or “sputter" (Figure IV-5). The substrate to be coated is placed in the direct path of the ejected neutral atoms and a film is formed as they strike the surface.

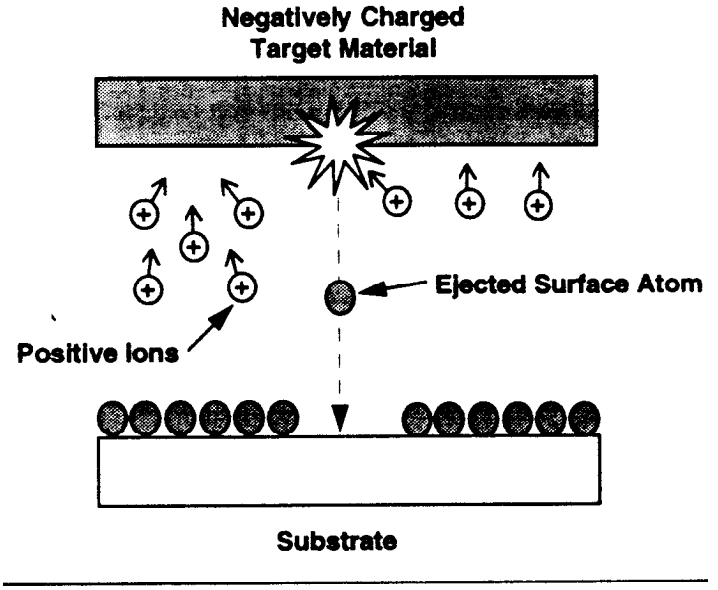

Figure IV-5: Sputtering

6.1.1 Direct Current (DC) Sputtering

Direct current sputtering is used for coating conductive substrates. The coating material (target) is the cathode and substrate is the anode. Plasma is formed by applying a negative potential across the electrodes and ionizing an inert or reactive gas. Positive ions are attracted to the target and eject atoms as they strike the surface. The neutral metal atoms are then deposited on the substrate.

6.1.2 Radio Frequency (RF) Sputtering

Radio frequency sputtering is utilized when sputtering non-conductive-substrates. An RF potential is applied to a metal cathode located behind the target. Electrons emitted from the cathode collide with gas atoms with sufficient energy to ionize them. The ions strike the surface of the target and eject metal atoms that travel to the substrate to produce a coating.

6.1.3 Magnetron Enhanced Sputtering

Magnetron enhanced sputtering incorporates the use of a magnet with an RF or DC sputtering unit. A magnetic field in conjunction with an electric field induces electrons to be confined to an area in front of the target, increasing ionization efficiency and sputtering rates.

6.2 Advantages/Disadvantages

This process produces high quality coatings with good adhesion and uniformity. It is limited by high cost, the thickness of coatings that may be applied, and line-of-sight restrictions for coating complex shapes.

6.3 Health and Safety

Protective clothing and shielding of electromagnetic interference is required.

6.4 Environmental

Depending on the **composition** of the coating material, wastes and effluents must be managed appropriately.

6.5 Relevant Abstracts

Alternatives To Conventional Chromium Plated Plastics.
Lindsey, David M.
GM, Warren, Mich
Products Finishing (Cincinnati) Vol. 43 No. 10 Jul 1979 pp 34-43

Abstract: The first part of this article discussed vacuum metallizing and directly electroplateable plastics as probable future alternatives for conventional chromium plated plastics at Chevrolet. Part II picks up with the background of Chevrolet Engineering's exterior vacuum metallizing program. General Motors Corp.'s current metallizing program is outlined, and more sputtering and directly electroplated plastic trim are forecast for future Chevrolet automobiles.

Descriptors: Automobile Materials-- Metallizing; Plastics--Metalllizing; Chromium Plating--Applications; Metallizing--Vacuum Application

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Materia Innovation and Its Impact on the Development of Components for Reciprocating Engines.
Parker, D. A.
AE Developments Ltd, Rugby, Engl
Int J Mater Prod Technol Vol. 1 No. 1 Jul 1986 pp 23-49

Abstract: An account is given of the special techniques used to develop engine components and of their use to solve the problems arising from a hostile operating environment. It is concluded, however, that the development of special surface and substrate materials provides the most universal contribution. Recent applications to pistons include the use of alumina fiber reinforcement to prevent thermal cracking, and the development of insulating crowns. The range of piston ring coatings to reduce overall wear has recently been extended to include nitrocarburizing, which offers a cost-effective alternative to chromium plate. Valve train applications include chill cast camshafts with locally enhanced hardness and sintered valve seat inserts with solid lubricant to replace the lead in fuel. In the bearing area, developments of the aluminum silicon range of alloys have combined high strength with enhanced seizure resistance. Current developments are illustrated from the application of sputtered coatings and of ceramics.

Descriptors: Automobile Engines-- Pistons; Aluminum And AlIoys--Fiber Reinforcement; Protective Coatings--Sputtering; Automobile MaterialS--Light Metals

Identifiers: Engine Component Design; Materials Innovation; Vehicle Design; Reciprocating Engines

7.0 Surface (Case) Hardening

7.1 Description

Surface hardening, or case hardening, is a thermochemical treatment in which a steel substrate is heated to its lower transformation temperature at which a gaseous or liquid medium absorbs and diffuses into the substrate surface (Figure IV-6). Elements commonly diffused are carbon, nitrogen, or a mixture of both. These case hardening processes are referred to as carburizing, nitriding, and carbonitriding, respectively. Surface properties may be controlled by regulating the post-process cooling rate.

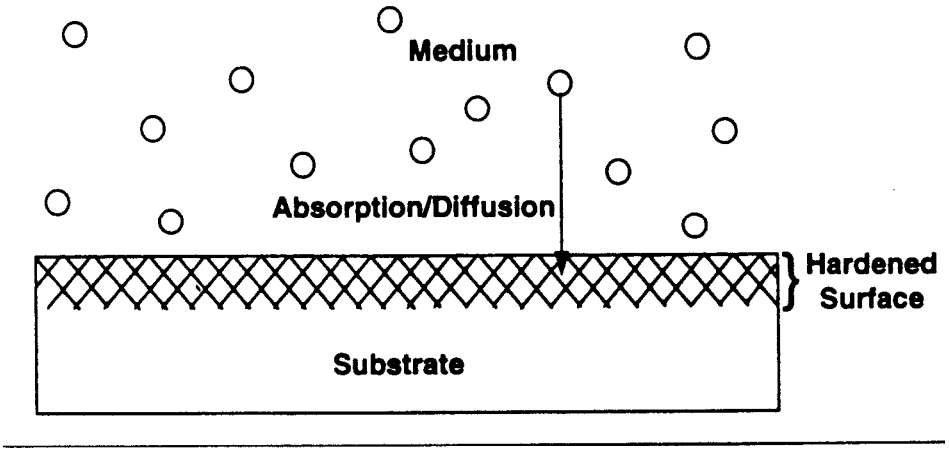

Figure IV-6: Surface (Case) Hardening

7.2 Advantages/Disadvantages

Surface hardened substrates typically have high hardness and fatigue strength and good wear resistance.

7.3 Health and Safety

If the bath contains cyanide, care must be taken since cyanide salts are highly poisonous. Baths should be hooded to contain odors.

7.4 Evironmental

Some baths contain cyanides, which require controls and permits.

7.5 Relevant Abstracts

Material Innovation and Its Impact on the Development of Components for Reciprocating Engines.
Parker, D. A.
AE Developments Ltd. Rugby, Engl
Int J Mater Prod Technol Vol. 1 No. 1 Jul 1986 pp 23-49

Abstract: An account is given of the special techniques used to develop engine components and of their use to solve the problems arising from a hostile operating environment. It is concluded, however, that the development of special surface and substrate materials provides the most universal contribution. Recent applications to pistons include the use of alumina fiber reinforcement to prevent thermal cracking, and the development of insulating crowns. The range of piston ring coatings to reduce overall wear has recently been extended to include nitrocarburizing, which offers a cost-effective alternative to chromium plate. Valve train applications include chill cast camshafts with locally enhanced hardness and sintered valve seat inserts with solid lubricant to replace the lead in fuel. In the bearing area, developments of the aluminum silicon range of alloys have combined high strength with enhanced seizure resistance. Current developments are illustrated from the application of sputtered coatings and of ceramics.

Descriptors: Automobile Engines-- Pistons; Aluminum And Alloys--Fiber Reinforcement; Protective Coatings--Sputtering; Automobile Materials--Light Metals

Identifiers: Engine Component Design; Materials Innovation; Vehicle Design; Reciprocating Engines

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NIOX - ein modifiziertes Nitrocarburierverfahren zur Verbesserung des Widerstandes gegen VerschIeiss und Korrosion sowie der Dauerbelastbarkeit von Bauteilen aus Eisenwerkstoffen.

(NIOX - A Modified Nitrocarburising Process For Improving The Resistance To Wear And Corrosion And The Load Capacity Of Components Made Of Steel)

Pakrasi

Volkswagenwerk A. G., Wolfsburg (Germany, F.R.).

Abt. Forschung und Entwicklung. 19 Jun 86 30 pp

In German, Volkswagenwerk AG. Forschungsbericht, No. FZL 8402 Vol. 5.

Abstract: The state achieved by conventional nitrocarburising of steel components is described. There is **a** report on the effects of the further development of one of these processes at Volkswagen (using a nitrocarburising temperature of 590 ^{0}C < T < 700 ^{0}**C)** on the formation of the surface layer of components made of steel, if oxidation in steam at temperatures up to 570 ^{0}C follow the nitrocarburising (NIOX treatment). The effect of temperature and duration during the nitrocarburising and subsequent oxidation on the formation of the surface layer, the permanent load capacity of components treated by NIOX and their resistance to corrosion and wear are examined. Applications are derived for this process and examples are described. It is shown that NIOX treatment can be an alternative to galvanic coating processes such as chromium plating, nickel plating, zinc plating and cadmium plating and that by applying this process, a contribution can be made to saving expensive and rare metals and to environmental protection. (TIB: RN 6902 (8402).)

Descriptors: Carburizing; Wear resistance; Corrosion resistance; Steels; Surface properties; Heat treatment; Austenitizing; Gamma iron; Coating processes: Nitrogen

Identifiers: Foreign technology

Salt Bath Treating as an Alternative for Chromium Plating.
Wood, W. G.
Conference: Technical Aspects of Critical MateriaIs Use by the Steel Industry. Vol. II-B, Nashville, Tenn., U.S.A., 4-7 Oct. 1982
Publ: National Bureau of Standards, U.S. Dept. of Commerce, Washington, D.C. 20234, U.S.A., 1983 15 pp

Abstract: The oxygen-diffused nitriding process has the capability of producing a surface comparable or superior to Cr plating with respect to wear resistance and corrosion resistance in numerous industrial applications. Unlike Cr plating, there is no requirement for the utilization of strategic materials. Also, unlike electroplating processes, there is no water or air pollution problems involved when the oxidized liquid nitriding process is practiced. The materials required to produce both of the fused salts involved in the process are readily available common chemicals and none of the compounds present in the effluent rinse waters are categorized on a restricted discharge basis. Unit costs of any process are usually suspect after a very short period of time because of rapidly changing economic conditions but, on a comparative basis, the total costs involved in Cr plating and the O-diffused nitriding process are quite similar and are likely to be that way even with future changes in the cost of living index.

Descriptors: Nitriding; Carbon steels-- Heat treatment; Alloy steels-- Heat treatment; Wear resistance; Corrosion resistance; Chromium plating-- MateriaIs substitution

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8.0 Thermal Spraying

8.1 Description

Thermal spraying is a particle impact method in which the coating material is melted, and then particles are projected with compressed air or gas toward the surface to be coated. Particles are flattened as they impact the surface, adhering to the substrate and each other to produce a coating (Figure IV-7). Stresses that may occur due to excess shrinkage of molten material upon solidification may be relieved by applying heat treatment after the coating process.

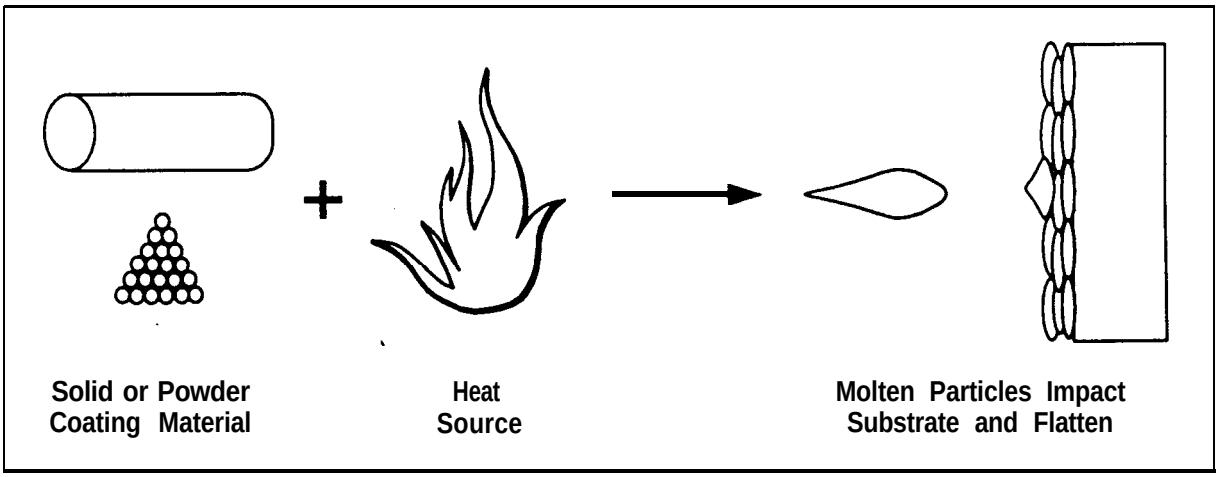

Figure IV-7: Thermal Spraying

8.1.1 Atmospheric Thermal Spraying (Flame Spraying)

Atmospheric thermal spraying, also known as flame spraying, is a technique performed under ambient temperature and atmospheric pressure. Oxygen and fuel gas is combusted to create a flame that is used to melt the coating materials, which may be in rod, wire, or powder form. This technique offers high deposition rates, efficient use of materials, ease of operation, low maintenance, and low operating costs.

8.1.2 Electric (Wire) Arc Spraying

Electric arc spraying is different from other thermal spraying methods because no external heat source is utilized. An arc between wire electrodes comprised of the coating material melts and evaporates the wires. A stream of gas strips the molten metal from the wires and carries the droplets to the substrate. Electric arc spraying offers high transfer efficiency due to the extreme heat generated by the arc. Since a relatively small amount of heat is imparted to the substrate, this method can be used to apply coatings to heat-sensitive materials.

8.1.3 Plasma Arc Spraying

Plasma arc spraying utilizes a high intensity arc as the heat source. Argon or nitrogen gas passes through the arc, ionizes, and forms plasma. The plasma then heats a powder of coating material to its plastic state. Plasma arc spraying is often used for depositing materials with high melting points since very high temperatures are obtainable with this method.

8.1.4 Detonation Gun (D-gun) Spraying

Detonation gun spraying is a combustion flame spraying process. A mixture of oxygen and acetylene is fed into a combustion chamber of long-barreled gun. Powdered coating material is then added and suspended in the gas. The gaseous mixture is ignited by a spark plug and the powder is transformed to a plastic state. Particles from the D-gun are accelerated by a high-velocity shock front produced by detonation of the mixture. Kinetic energy of the particles is converted to heat as particles strike the substrate, bonding the material to the surface. Due to the high velocity impact, D-gun spraying is typically only used to coat metal substrates.

8.1.5 High Velocity Oxygen-Fuel (HVOF) Spraying

High velocity oxygen fuel spraying is a flame spraying process similar to D-gun spraying. However, in this method, the oxygen and acetylene gases are not mixed with the powdered coating material. Instead, the mixed gases are combusted around the powdered material, causing it to melt. The molten particles impact the substrate at very high velocities. HVOF is a low-cost technique that offers high deposition rates.

8.1.6 Vacuum/Plasma Arc Spraying

Vacuum/plasma arc spraying is considered the most-technologically advanced, and often the most expensive, thermal spraying process. Vacuum/plasma arc spraying is similar to plasma arc spraying, except the spray gun and substrate are within an evacuated chamber. Lower operating pressures allow higher molten particle velocities. This method is usually employed for coatings of **critical** nature in which maximum bond strengths and densities are essential.

8.2 Advantages/Disadvantages

This technique offers corrosion, oxidation, and abrasion resistance; electromagnetic, electrostatic, radio frequency, and cathodic protection; and thermal and electrical properties. Since this is a line-of-sight method, limitations exist such as the inability to effectively coat complex substrates.

8.3 Health and Safety

Thermal spraying generates dust, fumes, overspray, noise, and ultraviolet (UV) radiation. Spraying should be done in well-ventilated areas and high voltage sources must be isolated. Worker protection for ears, eyes, and skin is required.

8.4 Environmental

Treatment or recycling of dust, fumes, overspray, and exhaust gases is required.

8.5 Relevant Abstracts

Air Force Cuts Electroplating Wastes.
Ted Olsen
Defense Cleanup July 19, 1991 Vol. 2 No. 14
Pasha Publications, Inc.

FulI Text: The Air Force is spending nearly $5 million to cut down on toxic metal wastes produced by electroplating.

Researchers at Tyndall Air Force Base's Engineering and Services Center in Florida say three "cleaner" technologies -- one of which has been around since the 1960s -- could reduce or **even** eliminate the 675,000 metric tons of hazardous chromium, cadmium and cyanide DOD gets rid of each year.

Some 70 metric tons of cadmium are released to the atmosphere each year from these processes, which are used to protect aircraft parts from corrosion and wear. Air Force officials estimate the savings in the Air Logistics Command could be in the millions of dollars each year.

Progress on at least two of the replacements is still in the testing stage, but the center is demonstrating a full-scale unit and training personnel at Robins Air Force Base in Georgia, in a process that would replace cadmium electroplating with aluminum.

The center's Lt. Phil Brown says the objective is to totally replace cadmium electroplating with ion vapor deposition (IVD) aluminum at Warner Robins Air Logistics Center this year.

"IVD is not a new technology, but one that hasn't been utilized much since it was developed in the 1960s" Brown said. The process consists of backfilling a vacuum chamber with argon gas and ionizing it to force the aluminum to be deposited on the part.

IVD aluminum has outperformed cadmium in acid corrosion and actual service tests. These coatings withstand higher temperatures and can be used with high-strength steel and titanium and in fuel areas.

Brown also says laserjet enhanced electroplating has been shown to plate 50 times faster than conventional processes. Researchers don't know exactly how it works, but the laser is used to illuminate the spot being electroplated and allow the coating to be applied quicker.

That means the same results can be achieved with less metal, Brown reports. Figures indicate that lasejet could save the logistics command $450,000 a year and provide "lifetime" aircraft coatings that would cut down on costly maintenance.

A third process, Brown said, is replacing chromium electroplating with spray-casting, which involves introducing alloys into a hot gas flow passing through a venturi nozzle.

A pilot-scale process is being developed to test spray-coating which, said Brown, produces no hazardous waste and could save the command nearly $500,000 per year over electroplating.

Ceramic Coats Resist Diesel Wear at Cummins and Caterpillar.
Advanced Coatings & Surface Technology February, 1992 Vol. 5 No. 2
Technical Insights, Inc.

Full Text: Cummins Engine spent three years evaluating wear-resistant ceramic coatings thermally sprayed onto diesel engine piston rings. Its three top candidates are: (1) high-velocity oxygen fuel (HVOF) Cr_3C_2-20%NiCr/WC-12%Co cermets; (2) cathodic arc physical vapor deposited (CAPVD) CrN; and (3) plasma-sprayed Cr_2C_3. All three were tested against pearlitic grey cast iron liner on a high-temperature reciprocating wear rig that simulates a heavy-duty diesel engine. All three wore better than the commercial standard, electroplated chromium (EP Cr).

Why replace EP Cr, which lasts about 500,000 miles when applied as a 150 microns to 250 microns piston ring coating? Oak Ridge National Lab, which funded the project (DOE/ORNL Sub-86X-SA581C) believes ceramics can make more durable components that require less maintenance. Ceramics better withstand the higher engine temperatures needed to improve fuel economy and reduce emissions. They also retain their dimensional stability better and prevent oil from leaking into the combustion chamber.

Developing a coating is no easy matter. Coaters have not found it easy to deposit thick, coherent, adherent ceramic films. Even if they can increase film thickness to 10 microns, they would still need a ceramic with a wear coefficient 15 to 25 times lower than EP Cr to achieve similar performance. Deposition must be done at temperatures low enough to prevent thermal distortion or microstructural changes in the piston rings, and reproducibly enough to do on an industrial scale. It is no easy job.

CAPVD CrN achieved the lowest lubricated wear, but researchers could not apply it thicker than 4 microns, too thin for commercial use. Plasma sprayed Cr^2O^3 and Al^2O^3-ZrO^2, wore very well at extremely high temperatures (450 ^{0}C) and when not lubricated (a situation encountered when cold starting diesels). The best ceramic films also wore better

than EP Cr ring facings when lubricated with high-soot oils (typical of diesel operation), though their sensitivity to soot varied widely.

Chromium oxide wear rose with coating porosity and intersplat cracking. HVOF cermets were sensitive to carbide dissolution in cobalt. One key finding is that cast-iron cylinder wear products can abrade ceramic-coated rings, and that liner corrosion may dominate overall cylinder-piston-ring wear. HVOF cermets had the best combination of low ring and liner wear, especially when matched with H13 hardened tool steel.

The report, Development of Wear-resistant Ceramic Coatings for Diesel Engine Components, evaluates each piston ring coating system and the process used to apply it.

Contact: Malcolm G. S. Naylor, Cummins Engine Co., Inc., 500 Jackson St., Columbus, IN 4720l-6258. Phone: 812-377-5000. Fax: 812-377-3334.

Caterpillar has undertaken a similar effort for ORNL. It has found two systems to meet its goal, 0.1 coefficient of friction, lubricated, at 350 ^{0}C with less than 25 x 10-6 mm/hr wear. The first is a plasma-sprayed high-carbon iron-molybdenum piston ring coating running against a plasma-sprayed chromia-silica cylinder liner coating. The second system also coats piston rings with high-carbon Fe-MO, and uses a low-temperature arc-vapor-deposited (LTAVD) chrome nitride to coat the cylinder liner. Under Phase II, Caterpillar will scale up both processes, boost LTAVD film thickness to 15 microns, develop inner-diameter deposition systems, and formulate cost-effective ways to grind the coatings. Contact: M. H. Haselkom, Caterpillar Inc., Mossville Plant, Mossville, IL 61552. Phone: 309-675-1000.

HVOF Materials for Internal Diameter Applications.
Dorfman, M.; Kushner, B.; DeBarro, J.; Exline, J.; Kempton, K.; Aldag, D.
Metco-Perkin Elmer
Conference: Thermal Spray Coatings: Research, Design and Applications, Anaheim, California, USA, 7- 11 June 1993
ASM International, Materials Park, Ohio 44073-0002, USA, 1993, pp. 145- 152

Abstract: Due to the emergence of HVOF technology and an increase in the number of internal diameters cylinder applications requiring buildup, materials have been developed to meet a majority of customer engineering requirements. Specific efforts are underway to develop thermal spray coatings in power cylinders as an alternative to chrome plating. Chromium plating has been applied successfully to the internal bore of power cylinders for several years; it is a way of restoring the worn surface without the expense of purchasing a new cylinder. Chromium plating also has outstanding wear resistance. The disadvantage of Cr plating is the cost of applying thicknesses > 0.020 in. (0.50 mm) and the cost of complying with environmental regulations regarding waste disposal and handling. It is for these reasons that thermal spray coatings may offer attractive alternate solutions to Cr. The paper discusses in detail the material selection process of developing HVOF materials and coatings for power cylinders. In addition, results from an actual field test site are discussed.

Descriptors: Conference Paper; Cylinders-- Coating; Gray iron-- Coating; Chromium plating; Spray coating; Flame spraying

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Locomotive diesel engine cylinder liner coatings, phase I: Evaluation of thermally sprayed coatings.
Tandon, K. N.
Transportation Development Center, Montreal (Quebec).
University of Manitoba. Dept. of Mechanical Engineering (Canada)..
National Technical Information Service, Springfield, VA, 1991 84 pp.

Abstract: Wear of the internal surfaces of a liner in a diesel locomotive engine is of concern because it eventually must be replaced using hard chrome plating, a process that uses hazardous chemicals. This project applied various coatings such as thermally sprayed metal or ceramics onto the wall surface of the liners and evaluated the adhesion, porosity and wear of these coatings. The coated liners were then tested in an experimental diesel engine to determine the performance of the new coatings and to compare them with the conventional hard chrome plating.

Descriptors: Coatings, Diesel motors, Foreign technology, Locomotives, Diesel engines, Engine cylinders.

Plasma-Sprayed Coatings: An Alternative To Hard Chromium?
Longo, Frank N.
METCO Inc. Westbury, NY, USA
Plating and Surface Finishing Vol. 72 No. 7 Jul 1985 pp 28-32

Abstract: Plasma-sprayed wear-resistant coatings constitute an economical alternative to chromium plating. The plasma method requires a substantially lower capital investment for facilities and equipment, and effluent treatment is all but eliminated. These coatings are being used as a substitute for hard chromium plate in certain applications where thicknesses of 0.008 in. or greater are required. Plasma spraying also has the advantage of flexibility. A hard chromium operation is largely a dedicated one - a total commitment to one coating type - whereas plasma spray automatically provides the capability to apply many different finishes for a multitude of functions.

Descriptors: Protective Coatings-- Plasma Spraying

Spray Casting.
Principal Investigator: Glovan, R. J.
MSE, Inc. Butte MT 59701
Project Monitor: Staats, G. E.
Sponsor: USDOE Environmental Restoration and Waste Management

Abstract: The spray casting technology is being jointly developed by the Department of Energy (DOE) Office of Technology Development (OTD) and the U.S. Air Force

(USAF). The process uses a controlled aspiration process (CAP) to spray liquid metal on a substrate as a coating or onto a mold for near net shape forming applications. The USAF effort is directed at replacement of chromium electroplating as a repair/refurbishment technique on aviation parts. Chromium plating will be replaced by a thermally sprayed coating of equal or superior mechanical and physical properties. The coating portion of this project will be demonstrated at Kelly Air Force Base in San Antonio, Texas. The USAF Engineering and Services Laboratory at Tyndall Air Force Base is the USAF sponsor of the project.

Descriptors: Aluminum-- Coating; Chromium steels-- Coating; Electroplating; Flame spraying; Plasma spraying; Powder spraying; Physical vapor deposition; Environment; Chemical vapor deposition

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Super D-Gun and D-Gun Coatings as Alternatives to Electroplated Chromium.
Antony, M. M.; Tucker Jr, R. C.
Union Carbide Coatings Service
Conference: Environment in the 1990s--a Global Concern, San Diego, California, USA, 21-23 May 1991
Society for the Advancement of Material and Process Engineering, P.O. Box 2459, Covina, California 91722, USA, 1991, pp 239-247

Abstract: There is a growing requirement to find alternatives to electroplated Cr for environmental and other reasons. Thermal spray coatings may satisfy this requirement, particularly in those applications where Cr is used primarily for wear resistance. Of the thermal spray coatings, detonation gun (D-Gun) coatings have been the standard of the industry for > 30 years because of their excellent wear resistance, bond strength, corrosion resistance, and mechanical properties. Recently, a new generation of coatings, Super D-Gun coatings, has been developed with properties superior even to D-Gun coatings. These processes and the resultant microstructures of selected tungsten carbide--cobalt, tungsten carbide cobalt--chromium, and chromium carbide coatings are described. Mechanical and wear properties, including bond strength, adhesion, and abrasion properties, are also described. Where possible, direct comparisons between Super D-Gun, D-Gun, and electroplated Cr coatings are made. Substrates considered in the discussion include 4340 steel.

Descriptors: Conference Paper; Nickel chromium molybdenum steels-- Coating; Tungsten carbide-- Coatings; Chromium carbide-- Coatings; Cemented carbides-- Coatings; Detonation; Flame spraying; Ceramic coatings-- Mechanical properties; Bonding strength; Adhesion; Adhesive wear; Wear rate; S N diagrams; Abrasion resistance

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thousand hours. The wear of coats did not exceed 20 mn. Engine having conventionally applied galvanic chromium coats is operable for only 8 thousand hours. Suggested coats result in significant economic efficiency and provide higher ecological cleanliness due to the replacement of galvanic process by gas thermal one.

Descriptors: Ceramic coatings; Tribology; High temperature properties; Wear of materials; Friction; Plasma spraying; Protective coatings; Diesel engines

Identifiers: Boron coatings; Oxide coatings

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'These references were used to compile general process descriptions.