

BACKGROUND PAPER ON AEROSPACE & MISSILE NEEDS

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1.0 INTRODUCTION

This brief background paper or overview focuses on the major known and anticipated needs for environmentally acceptable materials and processes used in the original manufacture (OEM), and subsequent maintenance, repair and overhaul (MRO) of aerospace weapon systems, including missiles, and support equipment necessary for sustainability and mission readiness. The term “environmentally acceptable” is used here in a broad sense, and includes worker occupational safety and health issues, productivity, and compliance issues, as well as cost effectiveness. The latter is important, as will be shown later, because most changes are not driven by environmental issues alone. In addition, “aerospace weapon systems” in this context refer to rotary and fixed wing aircraft, for offensive, defensive, support, and training missions, and the ground support equipment needed to keep these assets available, ready and operational in a wide range of environments. These environments include cold weather, tropical, desert, and marine locations around the world, and the performance requirements associated with existing metal surface treatments cannot be compromised in the search for non-hazardous and non-polluting alternatives. As a corollary, for any given application (weapon system, surface treatment requiring an alternative, and operating environment) a satisfactory solution may not be appropriate for a different application. As a result, there may be a need for several alternatives for a coating replacement depending on the end use.

The surface finishing of metallic materials is a broad topic. There are many pretreatments, coatings or surface modifications, and post-treatments that may be employed in defense MRO operations. In Figure 1 an attempt has been made to classify these different processes and summarize the main compliance and/or occupational safety and health associated with each¹. While not necessarily a complete representation of all DoD metal surface requirements, it does provide an useful starting point and frame of reference for the following discussions. Typical substrate materials used in defense applications are aluminum alloys; steels; high-strength steels and alloys; titanium alloys, and magnesium alloys.

This background paper focuses on coatings and, in particular, on replacing electroplated cadmium and chromium coatings because these metals are heavily regulated. While currently nickel is not as heavily regulated, many of the near-term chromium coating alternatives are nickel-based alloy or composite coatings. At some time in the future it may be necessary to find substitutes for such alternatives!

Figure 1 is useful in showing that a systems approach must be used in finding acceptable alternative processes. In practice, finished components that are treated in a MRO facility are often stripped, cleaned, activated, coated, and many times post-treated with a chemical (chromate-containing) conversion coating. If a coating is replaced, then it must be compatible with the pretreatment(s) used, and the coating itself must be compatible any post-treatment used, which should be chromium-free. Consequently, some of the discussions during the Break Out Sessions at this workshop will focus on non-chromated conversion coatings for protecting metallic surfaces from corrosion, or providing a base to improve the adhesion of a primer if the component is to be painted.

¹ Taken from the USAF Air Force Research Laboratory “Inorganic Coatings Pollution Prevention Technology Roadmap”, (2003).
RDT&E Needs for the Metal Surface Finishing for Defense Applications Workshop
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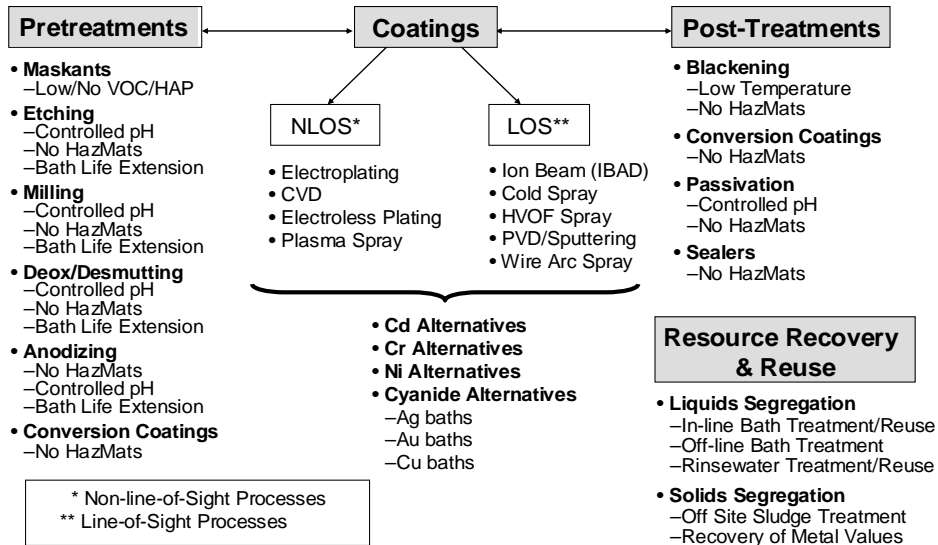


Figure 1. Metal Finishing Processes and Compliance Issues for Each Primary Activity Area

Finally, the objective of this background paper is to stimulate discussion in the Break Out Sessions in order to identify technology gaps. This overview has been written to complement the briefing that will be given at the Workshop, and covers the following topics to provide a background to what is needed, what has been accomplished so far, what technologies may have promise in the future:

- Environmental Drivers
- Technical (Performance) Requirements
- Approaches Taken and Alternatives in Use
- Promising New Technologies
- Barriers to Technology Insertion
- Lessons Learned.

The technology discussed relates primarily to aerospace requirements, but where it makes sense U.S. Navy and U.S. Army needs have been incorporated. U.S. Marine and U.S. Coast Guard requirements - in large part - will be similar, and amenable to the solutions identified for the Tri-Services. In addition, the OEMs that manufacture military aircraft usually consider leveraging solutions successfully applied on commercial aircraft, and *vice versa*. Many of the alternatives discussed may be good candidates for other than aerospace applications. Consequently, good communication and cooperative efforts are necessary to facilitate and expedite change, in a cost effective manner, without duplication of effort.

2.0 ENVIRONMENTAL DRIVERS

A wide variety of chemicals are used in inorganic finishing operations and waste streams are generated. Some of these have to be controlled as "listed" or "characteristic" wastes according to Environmental Protection Agency (EPA) regulations. Others are hazardous to health or toxic, and can be found on various EPA lists, including the EPA National Waste Minimization Partnership Program list of 30 chemicals. Many have to be below concentration levels in the environment promulgated by the Occupational Safety and Health Administration (OSHA).

The primary hazardous chemicals of concern include cadmium, chromium, and nickel. However, there are other chemicals and materials used for inorganic operations that are considered to be toxic and/or hazardous, or reactive (e.g., cyanides), corrosive (e.g., various acids such as hydrochloric, sulfuric, nitric; and various alkalis such as sodium hydroxide). In related operations, such as cleaning and applying and removing maskants, solvents are used that can lead to emissions of volatile organic compounds, and/or produce hazardous air pollutants.

2.1 Federal, State and Local Regulations

Table 1 highlights legislation and regulations relating to chemicals that impact, or are expected to affect inorganic finishing operations conducted at DoD facilities. It should be noted that these regulations and mandates also may impact some of the alternative technologies being considered for implementation.

Table 1: Summary of Important Environmental Legislation and Regulations

Regulation/Legislation	Focus/Content
Clean Air Act Amendments (1990)	<p>Amendments include more than 20 separate air quality standards and lists 189 chemicals that are regulated as toxic air pollutants by the EPA. Also listed are the requirements for permitting metal finishing and other facilities.</p> <p>Chromium plating and chromic acid anodizing facilities are targeted for implementing Maximum Achievable Control Technology (MACT) to meet the National Emissions Standards for Hazardous Pollutants (NESHAPs). The Aerospace NESHAP Rule (1995), Section A: Pretreatment/ Cleaning rules apply to all cleaning operations and housekeeping measures.</p>
Clean Water Act Amendments (1991)	<p>The CWA as amended lists standards for discharges from electroplating and metal finishing operations. Within the CWA text, there are exact limit levels set for specific chemicals.</p> <p>The proposed Metal Products and Machinery (MP&M) legislation was expected to greatly reduce allowable metal-laden water discharges from metal finishing operations; however, the EPA stated in 2003 that “no further regulation is necessary for job shop and captive metal finishing operations”. As a result, such facilities will continue to be regulated by the existing discharge limits for wastewater under 40 CFR 413 and 40 CFR 433.</p>
Resource Conservation and Recovery Act	<p>The storage, transportation, treatment, and disposal of hazardous wastes generated from inorganic finishing operations is governed by RCRA. It applies to solid, liquid, and gaseous wastes even if the chemicals are to be used, recycled, reclaimed, stored, or accumulated. Wastes are classified as being “characteristic” (i.e., corrosive, ignitable, reactive or toxic) or “listed” (e.g., F006 wastewater treatment (plating) sludge). Chemicals used in a plating shop may exhibit more than one characteristic; e.g., cyanide compounds are reactive and toxic.</p>
Comprehensive Environmental Response, Compensation, and Liability Act	<p>CERCLA (also known as “Superfund” Act) is a combination of the Superfund Amendments and Reauthorization Act (SARA) and the Emergency Planning and Community Right to Know Act (EPCRA). This legislation should be taken into consideration every time an alternative technology is transitioned to a DoD facility. Emergency Plans may have to be modified.</p>

Table 1: Summary of Important Environmental Legislation and Regulations (cont'd.)

Regulation/Legislation	Focus/Content
Comprehensive Environmental Response, Compensation, and Liability Act (continued)	As part of the SARA rule, the Toxic Release Inventory (TRI) is established and maintained. This is a public document that provides numbers that characterize the magnitude of a particular listed substance released into the air. However, it does not contain information on human exposure, level of toxicity, or health risks posed by the levels released.
Department of Transportation/Research and Special Programs Administration	DOT requires generators and shippers of hazardous wastes to comply with several requirements, including proper packaging and labeling. The Hazardous Materials Table (49 CFR 172.101) is useful when determining what materials are classified as being hazardous. Similar to the SARA TRI regulation, the DOT sets acceptable limits and any chemical that exceeds its specific limit must be reported. Recently, in response to the terrorist attacks of 11 September, 2001, the DOT Research and Special Programs Administration (RSPA) issued (effective 25 March, 2003) new security requirements for the transportation of hazardous materials. These are referred to as the Hazardous Material Regulations (HMR) and require security plans and training for "suppliers and transporters of hazardous materials.
Occupational Health and Safety Administration	OSHA rules cover worker safety, hazard communication, personal protective equipment, and chemical specific standards. The latter includes cadmium and chromium. OSHA has indicated that it will revisit previously established air contamination permissible exposure levels (PEL) because they were first published 25 years ago. As an example, the PEL for chromium has been reduced to 5 mg/m ³ from the previous 100 mg/m ³ level. Additional chemicals expected for reduction include cadmium (new limit = 0.2 mg/m ³), nickel (new limit = 1 mg/m ³), and cobalt (new limit = 0.1 mg/m ³).
National Waste Minimization Program	The EPA on September, 2002 introduced its National Waste Minimization Program (NWMP) that challenged everyone to find "creative approaches for helping Americans recycle, recover energy, minimize waste and revitalize the landscape". Of the two stated goals, one is to reduce by 50% the use/generation of 30 listed chemicals . This list consists of 27 organic chemicals and three metals, and replaces the "waste minimization persistent, bioaccumulative, and toxic (PBT) chemicals list drafted in 1998 for the RCRA. While the NWMP is not directly applicable to government facilities, the three metals listed - cadmium, lead, and mercury - include two found in inorganic finishing operations performed at DoD facilities.

2.2 DoD Directives and Environmental Drivers

Two DoD Directives of interest are listed below.

- **DoD 5002-R**, Section 4.3.7 "Environmental Safety and Health Considerations". This Directive stipulates a total system approach to acquisition programs, including equipment, personnel, system operations in intended environments (as well as non-intended environments), compatibility and interoperability with other systems, operational and support infrastructure, and *potential environmental impact and environmental compliance*.

- **DoD 4210.15** on hazardous materials and pollution prevention. This directive is used to implement Section 1003(b) of the RCRA. It states that DoD policy places the highest priority on reduction of volume and toxicity of wastes generated through *pollution prevention*, rather than waste treatment. If a less hazardous material can be used to accomplish an activity, it must be used.

Other pressures for hazardous material elimination include:

- DoD and company hazardous material elimination plans, directives, and/or instructions for OEM and MRO operations
- Acquisition documents that call out materials substitutions; e.g., **MIL-STD 1388** referred to conducting a comprehensive “logistics support analysis” for the life cycle of systems and equipment, but it was cancelled in 1997. **MIL-STD 882** states that “Within mission requirements, the DoD will also ensure that the *quality of the environment is protected* to the maximum extent practical. The DoD has implemented environmental, safety, and health efforts to meet these objectives. Integral to these efforts is the use of a system safety approach to manage the risk of mishaps associated with DoD operations. “This standard practice addresses an approach ... useful in the management of environmental, safety, and health mishap risks encountered in the development, test, production, use, and disposal of DoD systems, subsystems, equipment, and facilities.

Finally, there is the **Programmatic Environmental Safety and Health Evaluation (PESHE)** as part of systems engineering. The Program Manager (PM) “*shall prevent environment, safety, and occupational health (ESOH) risks*, where possible, and shall manage ESOH risks where they cannot be avoided. The process for integrating ESOH into systems engineering is to manage ESOH risks as part of the program's overall risk management system. The PM should use the principles and practices described in the government-industry standard for system safety, MIL-STD-882D”. In compliance with DoD 5000.2, E7.7, the PESHE will include, as a minimum, the following:

- Strategy for integrating ESOH considerations into the systems engineering process
- Identification of ESOH responsibilities
- Approach to identify ESOH risks, to prevent the risks, and to implement controls for managing those ESOH risks where they cannot be avoided
- Identification and status of ESOH risks including approval authority for residual ESOH risks (based on MIL-STD-882D, the approval authorities are the Component Acquisition Executive [CAE] for high risks, the Program Executive Office [PEO]-level for serious risks, and the PM for medium and low risks)
- Method for tracking progress in the management and mitigation of ESOH risks and for measuring the effectiveness of ESOH risk controls
- Schedule for completing NEPA/Executive Order 12114 documentation including the approval authority of the documents (the CAE or designee [for joint programs, the CAE of the Lead Executive Component] is the approval authority)
- Identification of hazardous materials used in the system and the plan for their disposal or demilitarization, as well as the remainder of the system.

The PESHE is not intended to supersede/replace other ESOH plans, analyses, and reports (e.g., System Safety Management Plans/Assessments, HAZMAT Management Plans, NEPA/E.O. 12114 documents, Health Hazard Assessments, etc.) but should incorporate these documents by reference. However, environmental management programs should minimize duplication of effort and documentation and give preference to recording ESOH information in the PESHE, as opposed to maintaining a series of overlapping, redundant documents.

2.3 Executive Orders

- **EO 13101** “*Greening the Government through Waste Prevention*” (1998), which revoked EO 12873, is a directive to all federal agencies to procure products and/or services that are environmentally acceptable, i.e., manufactured with recycled materials. Core groups within federal agencies were established to monitor and ensure that federal entities were working to meet the environmental objectives outlined in the EO.
- **EO 13123** - “*Greening the Government through Efficient Energy Management*” (1999) revoked EOs, 12759, 12845, and 12902. While not a pollution prevention or compliance mandate, it dictates that any alternative technology implemented should try to conserve resources, including water and energy.
- **EO 13148** entitled “*Greening the Government through Leadership in Environmental Management*” (2000) replaced EOs 12843, 12856, 12969, and Sections 1 through 4 of EO 12088. Its objective is to ensure environmental accountability in the use of toxic chemicals, including cadmium, chromium, and nickel. This EO calls for a 50% reduction of toxic chemicals by December 31, 2006. It proposes that effective, long-term planning, environmental management decision-making, and the integration of pollution prevention programs should be established to meet environmental goals.

EOs 13101 and 13148 are complementary. The 13101 order explains how environmental goals are to be achieved and monitored, while the 13148 order calls for the quantitative reduction or elimination of listed chemicals.

2.4 Foreign Country Regulations

Some MRO activities are performed at foreign bases or facilities. The Air Force, for example, has stated that it will conform to local environmental regulations, which can be different, and sometimes more stringent than those that apply to the contiguous United States. Consequently, meeting local requirements is an issue that has to be addressed, or all MRO operations must be performed at facilities governed by United States regulations.

Many bases and facilities are located in Europe; as a consequence, the European Union (EU) regulations may apply. The Council of the European Communities has issued two directives that apply to hazardous wastes. These are **Council Directives 91/689/EEC** and **75/442/EEC** that describe types of hazardous waste, and how hazardous waste must be collected, identified, stored, labeled, transported and recorded, as well as directives for waste reduction, recycling, re-use disposal and the development of clean technologies. **Commission Decision 2000/532/EC** lists the wastes covered in the above directives by the type of activity that generates it (e.g., category 06 - “Wastes from Inorganic Chemical Processes”).

In addition, **Council Directive 96/62/EC** on “Ambient Air Quality Assessment and Management” defines the principles for establishing quality objectives for ambient air, including the regulation of benzene and carbon monoxide, but “daughter legislation” must be enacted to set the air quality limit values and alert thresholds.

Wastewater discharges are covered by **Council Directive 2000/60/EC**, which sets out an integrated approach to reducing discharges of cadmium, nickel, and other chemicals to ground waters (i.e., the ecological environment). Cadmium and nickel are listed as “Priority Pollutants”, and Article 16 classifies cadmium as a “priority hazardous substance”.

Finally, on 1 July, 2006 the **Council Directive 2002/95/EC** on “Restriction of Use of Certain Hazardous Substances in Electrical and Electronic Equipment” (RoHS) comes into effect. This places limits on the use of certain inorganic and organic chemicals, such as cadmium, chromium (VI), lead, and mercury.

2.5 Guidance for Selecting Alternative Technologies

The Pollution Prevention Act passed in 1990 establishes the general hierarchy or priorities for managing pollution, which should be used for guiding the identification and evaluation of environmentally acceptable alternative materials and processes. This hierarchy is logical, and briefly stated, is as follows:

- Prevent or reduce pollution at the source
- If prevention is not possible, reduce or recycle in an acceptable manner
- If reduction or recycling is not possible, then treat the pollutant
- If treatment is not possible, then dispose or release in an environmentally safe way.

Guidance in selecting the highest priority compliance issues also may be obtained by conducting a pollution prevention opportunity assessment, in which the following actions occur:

- Identify the material or process to be evaluated
- Establish the objective and baseline or benchmark
- Examine the process to identify/asses hazardous materials usage and waste streams
- Identify opportunities/technologies to eliminate/reduce hazardous material use and waste
- Rank the opportunities using a decision matrix with appropriate evaluation criteria
- Select and evaluate the chosen alternative material and/or process.

Another consideration in choosing alternative technologies is the guidance OSHA has published for minimizing worker exposure to hazardous materials. For example, the following is presented in decreasing order of preference:

- Substitute less/non hazardous material
- Isolate worker from hazardous material
- Provide ventilation – general and localized
- Use personnel protective equipment (PPE).

OSHA states that engineering and work practices must be applied before using PPE to meet Permissible Exposure Limits.

3.0 TECHNICAL/PERFORMANCE REQUIREMENTS

The trend continues to converting military specifications to industrial specifications, and to use performance specifications rather than material specifications, which provide a greater degree of flexibility in identifying, evaluating, and qualifying alternatives. However, when defining performance requirements to be met, the baseline originally often was set rather arbitrarily. For example, electroplated chromium coatings were available and fulfilled the requirements for a wear and corrosion resistant coating when needed many decades ago. Subsequent specifications, engineering drawings, and technical/work orders then called out these EHC coatings with perhaps not much thought being given to why EHC was originally chosen and what was needed for the changing requirements, more advanced designs, and new substrate materials. As a consequence, much effort is spent nowadays in trying to define realistic baseline data and performance requirements, then getting concurrence and acceptance among

the user community. An accepted approach for achieving consensus in the defense aerospace industry is the use of Joint Test Protocols, which have been written by all the stakeholders that eventually will have to sign off when the technology is transitioned into the OEM and MRO facilities. These protocols incorporate all the tests (and criteria for passing) that an alternative must pass for a wide range of end use applications. However, in practice, some alternatives may not meet all the performance requirements but may meet those for a specific application, and be an acceptable alternative for it.

4.0 ALTERNATIVES IN USE OR BEING EVALUATED

Two approaches to improving performance and eliminating the need for coatings are design changes and material changes. For example, cadmium coatings to prevent corrosion could be eliminated by substituting a more corrosion resistant substrate material, such as a corrosion resistant steel (CRES) or a titanium alloy, depending on the end use application. However, for the purposes of this workshop the focus is on surface finishing. There are a variety of inorganic coating processes in use at DoD facilities and supplier facilities. Some require the use of liquid processing chemicals (i.e., “wet” processes such as plating, electroless plating) while others are performed in a vacuum chamber (i.e., “dry” processes such as physical vapor deposition).

One of the most common types of inorganic finishing process is electroplating, often referred to as just plating. During plating, the part to be coated (cathode) is immersed in a tank containing a suitable counter electrode (anode), and a direct or pulsed current is passed through the electrolyte solution (plating bath) that contains the metal(s) to be deposited as a coating. A variety of additives in the bath help to facilitate and control the plating process. Electroplating, as well as other forms of inorganic coating processes, commonly involve toxic metals, such as cadmium, chromium, and nickel. In addition, most baths contain concentrated alkaline or acidic solutions, while some plating baths contain cyanide solutions, which are reactive, and when in contact with acids produce a toxic gas. For this reason, cyanide waste streams must be separated from other inorganic waste streams.

Alternative technologies may be sorted into the following categories for convenience: “long-term”, “mid-term”, and “short-term”. Descriptions of these categories are provided below.

- **Short-term Alternatives**

Short-term technologies are alternatives that are either commercially available or soon to be available commercially (less than three years). Each alternative process may require additional military or aerospace-specific testing to verify its ability to be transitioned to a specific depot or weapon system application. Evaluation of technologies falling under this classification could be funded by the ESTCP.

- **Mid-term Alternatives**

Mid-term technologies are those may not be commercially available for three to five years due to technical or economic issues. Investigation of technologies falling under this classification could be funded by the SERDP, or by the ESTCP, depending on process maturity.

- **Long-term Alternatives**

Technologies classified as long-term are those that require research and development work (five to ten years time frame) and optimization, and have a higher risk associated with eventual implementation. Emerging technologies falling under this classification could be explored under the SERDP.

4.1 Cd Alternatives: Wet and Dry Deposition Technologies

Cadmium coatings are used on a wide range of components and parts, such as those in landing gear, hydraulics, gear boxes, engines, fasteners, other small parts, on aircraft and missile surfaces, as well as on ground transportation equipment and in structures. These coatings are used because of their desirable properties, such as good coverage and adhesion, corrosion protection; lubricity; low electrical contact resistance for bonding surfaces; and providing a surface suitable for subsequent painting (see SAE-AMS-QQ-P-416, MIL-STD-870, SAE-AMS-C-81362,-8837). Cadmium electroplating baths are established, relatively inexpensive to operate and maintain, and the process is applicable to components of all dimensions from landing gear to fasteners (non-line-of-sight applications). There is a possible problem with hydrogen embrittlement with cadmium plating because hydrogen may be generated during processing. Also, due to the environmental and health issues associated with cadmium, there is a need to investigate alternative coatings. Some of the alternatives investigated are briefly discussed below, and a summary (Table 1) is provided at the end of this section. Further information may be found in the published literature.^{2,3}

4.1.1 Implemented Technologies

Ion Vapor Deposited Aluminum: In the mid 1980s, the Air Force and Navy investigated ion vapor deposited (IVD) aluminum as a cadmium alternative for the outside diameter surfaces of low strength steel parts. IVD is a type of physical vapor deposition process developed by the McDonnell Aircraft Corporation and relies on the evaporation of atoms of aluminum from a target to coat the surface of a part. Aluminum was considered to supply similar sacrificial corrosion properties, and when lubricated it could be used for applications where torque/tension properties might be an issue (e.g., threaded fasteners). IVD aluminum is now allowed as an alternative to cadmium by MIL-DTL-83488 for thin aluminum coatings, and is used at DoD and at some OEM facilities. Surface post-treatments, such as glass bead peening and applying sealers, may be necessary to improve corrosion resistance for some applications. However, these additional steps make this alternative process more labor intensive.

Sputtered Aluminum: The Air Force worked with Boeing and Marshall Laboratories on an IVD alternative that would allow internal diameter parts to be coated with sputtered aluminum. In 2001 a demonstration of the “Plug-N-Coat” proprietary process showed that this sputtering (PVD) technology had potential. The following year this process was performed in a production environment at OO-ALC, and the demonstration on landing gear parts was successful. The process is now undergoing production trials on B-2 and C-17 landing gear components.

One issue to be resolved with sputtered aluminum coatings is that they cannot be “spot” repaired if damaged in service. However, for internal diameters on some parts, this may not be a severe problem and cadmium brush plating can be used as an interim measure.

Alkaline Zinc-Nickel Alloy Plating: By the middle 1990s, OO-ALC converted many of their heat sensitive and torque critical cadmium workloads over to Zn-Ni alloy coatings deposited from alkaline plating baths. This type of coating generally has corrosion (sacrificial) properties similar to cadmium, as well as some desirable lubricity (torque/tension) characteristics. In general, this alloy coating exhibits good adhesion, thickness build, and has better hydrogen

² E. W. Brooman, “Corrosion Behavior of Environmentally Acceptable Alternatives to Cadmium and Chromium Coatings: Cadmium, Part I”, *Metal Finishing*, **98**, No. 4 (2000) 42.

³ E. W. Brooman, “Corrosion Behavior of Environmentally Acceptable Alternatives to Cadmium and Chromium Coatings: Cadmium, Part II”, *Metal Finishing*, **98**, No. 6, (2000) 106.

embrittlement (HE) properties than deposits from acidic baths. Development work with different alloy compositions may eliminate the HE issue. The corrosion resistance of alloys containing 12-15% Ni was found to be “average”. There are several vendors of the chemicals required to operate this alloy deposition process.

Nickel-Phosphorus Electroless Plating: OC-ALC uses this process as a barrier coating for applications where the part has no torque requirements and it has internal diameters needing protection. This process does not require an applied electric current and is not line-of-sight limited, but the thickness of the deposit is self-limiting. The amount of phosphorus incorporated into the deposit (as a result of the reducing agent used) and the subsequent low temperature, precipitation hardening heat treatment, determine the hardness of the deposit and its corrosion resistance. A borohydride compound is sometimes used as a reducing agent, which produces Ni-B coatings. The properties of these coatings differ from the Ni-P coatings, but they are rarely used in engineering applications because of the much higher cost.

There are numerous vendors of electroless nickel processes. Electroless Ni-P has been changed out as a cadmium alternative for a few parts at OC-ALC.

Cermet Coatings: SermaTech Power Solutions (STPS), a division of SermaTech International, Inc. (STII) is the manufacturer of a proprietary aluminum-ceramic coating known as SermeTel[®] 984/985. This coating is applied as a slurry then fired to fuse the constituents together to form an integral coating. It is marketed as a potential replacement for cadmium electroplating on high strength steel hardware and was investigated by the Air Force in the early 1990s. At that time it did not pass the hydrogen embrittlement test and did not exhibit the required adhesion, so was not considered suitable for high strength steels. However, it was found to be acceptable for some low strength steel applications.

More recently STII has modified the process, such that the coatings now pass the hydrogen embrittlement test. It is being used now on the F-117 and F-22 aircraft as a cadmium alternative for landing gear components. In addition, SermeTel 984/985 is being considered as a “primary” coating for the Joint Strike Fighter (JSF).

In practice, OO-ALC has indicated that they have no interest in SermeTel coatings for small parts, hydraulics, and landing gear components because of difficulties experienced in their application and the variable results in service. OO-ALC personnel prefer to use sputtered aluminum as a cadmium alternative.

4.1.2 Short-term Candidates

Aluminum Plating: AlumiPlate[®] is a process patented by AlumiPlate, Inc. for electroplating high purity aluminum. It is marketed as a potential cadmium replacement. An organic solvent, primarily toluene, is used in the commercially available AlumiPlate plating bath to electrodeposit a very dense aluminum coating on small parts in a batch process. The process has been evaluated for adhesion, quality, thickness, corrosion resistance (scribed and unscribed in salt fog and sulfur dioxide conditions), and HE with good results.

While not viable as an alternative for many cadmium coating applications, Lockheed-Martin is investigating it for certain F-22 and F-35 aircraft applications. The Defense Logistics Agency is interested in using the process for purchased threaded components as their traditional cadmium plating sources decrease in number. Barriers to implementation are scale-up, equipment complexity, worker safety, cost, and licensing issues.

Aluminum-Manganese Alloy Plating: Under an ESTCP Project (PP-9903), the Naval Air Command has been investigating the potential for using Al-Mn alloy coatings deposited from a molten salt (non-aqueous) bath. However, because the molten salt bath must be operated at elevated temperature, and is sensitive to moisture, there still are significant environmental, health, and safety concerns. NAVAIR (Patuxent River, MD) is the only known developer of this patented Al-Mn electroplating process. The process is operated in accordance with QQ-P-416, Federal Specification for Electroplated Cadmium, because it was developed as a potential replacement for cadmium electroplating. While the performance of the aluminum alloy coating met expectations, production trials with a scaled-up version of this process conducted recently at the North Island Depot revealed some difficulties with operating this molten salt technology. Consequently, further development work has been halted.

Zinc-Nickel Alloy Brush Plating: Commercial Zn-Ni alloy coatings using conventional alkaline plating bath chemistries have shown promise as an alternative to brush cadmium plating for providing protection and lubricity on low strength steel applications. In a study conducted by Boeing for the C-17 program Office⁴,

Acid Zinc-Nickel Alloy Plating: An “acid” Zn-Ni alloy plating bath was developed by Boeing (Phantom Works). While the coatings containing 7-12% nickel exhibited good adhesion and corrosion resistance (salt fog exposure) properties, the process had poorer throwing power than the alkaline Zn-Ni plating bath, so did not provide as uniform a coating over complex shaped parts. In addition, the resistance to HE was not as good as that provided by coatings deposited from an alkaline plating bath

Tin-Zinc Alloy Plating: This electroplated coating composition is a commercially available alternative to cadmium on threaded fasteners. For DoD weapon system applications, the biggest problem remains matching the torque values to those of cadmium. Commercial, electroplated Sn-Zn processes have been evaluated under numerous projects funded by the ESTCP, SERDP, and government agencies. An example of one of these projects was the JG-PP effort entitled “*Alternatives to Electrodeposited Cadmium*”. Sn-Zn brush plating might be a candidate for cadmium alternative coating repair and touch up.

Metal-filled Inorganic Coatings: These are water-based coatings that consist of a binder and metal flakes or particles that impart sacrificial corrosion protection to ferrous substrates. The metal fillers typically are either zinc or aluminum, but sometimes may be a combination of these. Some of these coatings contain hexavalent chromium compounds that provide a binding action with a corrosion inhibition function. These types of coating are considered to be “self-healing”. Other formulations may incorporate chromium-free corrosion inhibitors. GEOMET[®] and DACROMET[®] coatings manufactured by Metal Coatings International, Inc. (MCII) are examples of this type of coating, and are used on threaded fasteners in the automobile industry. These coating processes were evaluated by the Air Force and were found to be unsatisfactory as a cadmium alternative for ALC use.

4.1.3 Mid- and Long-term Candidates

Magnetron Sputtered Aluminum: Inverted cylindrical magnetron sputtering of aluminum would extend the “Plug-N-Coat” sputtering technology discussed earlier for internal diameters of landing gears to be suitable also for external diameters, and other components requiring an alternative to a cadmium coating. This PVD process uses proprietary technology to control the magnetron to yield very uniform target utilization, which increases process efficiency. The part

⁴ M. A. Gilman, C-17 PTP 113F Report “Qualification/Demonstration of Cadmium Plating Alternatives”, (November, 2005).

to be coated is placed in the center of the vacuum chamber and the aluminum target is placed inside the circumference. A bias voltage between the target and the part ensures a flux of coating material is efficiently directed to the surfaces to be coated. The resulting coatings are denser than IVD coatings and do not require a post-treatment. The Air Force currently is evaluating this technology in conjunction with several vendors.

Laser Assisted Surface Improvements: Several techniques have been developed that use laser beams directed at the surface of a part to modify the surface or produce a coating. Some examples of interest are described briefly below. Because of the heat input, these processes may be suitable only for low strength steel substrates.

1. *Laser Glazing or Shock Peening*: There are some current initiatives to investigate laser-based technologies to improve surface properties for a wide range of applications. These are commercially available processes in which a focused laser beam modifies a deposited coating to enhance its performance. In laser glazing the surface layers are melted and fused, porosity is reduced, and density is increased. In laser shock peening (LSP) the mechanical properties are modified to improve fatigue properties. Some of the other alternative technologies being considered as providing alternatives to cadmium might benefit from this treatment if some of the coating properties do not meet performance specifications.
2. *Laser-induced Surface Improvement (LISISM)*: This process was invented by scientists at the University of Tennessee Space Institute and it is licensed to Surface Treatment Technologies, Inc. (ST²). Thus far, the later has evaluated modifications to several substrates, including 1010 and 4340 steels, as well as 6061 and 7075 aluminum alloys. ST² also has evaluated several precursors for surface alloying; examples being Ni/Cr/TiC and WC. The LISISM process is achieved by using a 3 kW, YAG laser with a fiber optic focusing device to perform surface modifications. The resulting coatings are alloys that can be engineered to have the required properties. The process at this time, however, is slow and very noisy. It is not suitable for large areas and cannot be used on heat sensitive substrate materials. Currently the process is not mass production ready.

Zinc-Nickel-Phosphorus Alloy Plating: The Zn-Ni-P alloy coating is obtained from an electroless plating process developed at the University of South Carolina (USC). This coating provides sacrificial protection to ferrous substrate materials. The pretreatment/cleaning of the steel substrate is a single step, one-minute immersion process utilizing a solution developed by USC. The typical post-treatment for this process is a silicon dioxide coating, which is a patented, single step process, also developed by USC in collaboration with Elisha Technologies. This process was evaluated by the Air Force under a GSA Task entitled "*Testing of Cadmium Alternatives*". Test results revealed that further development work is needed before it can be considered for DoD applications. Although the salt fog corrosion resistance was acceptable, the coatings failed the adhesion and hydrogen embrittlement tests.

Zinc-Nickel+Silicon Dioxide Plating: The Zn-Ni+SiO₂ coating is a composite composed of an electrodeposited Zn-Ni alloy with occluded SiO₂ particles. It is a sacrificial coating for ferrous substrates. This plating process was developed by USC for the Office of Naval Research. The coating can be deposited using constant voltage or constant current power supply settings. The pretreatment/cleaning of the steel substrate is a single step, one-minute immersion process utilizing a pretreatment solution developed by USC. Similarly to the Zn-Ni-P alloy coating, test results showed that USC needs to conduct further R&D on the process. The salt fog corrosion resistance was acceptable, but the coatings failed adhesion and hydrogen embrittlement tests.

Multi-layer Coatings: Northrop-Grumman's Quality Services Laboratory has developed a proprietary coating system - known as TigerPlate[®] - that was marketed as a possible cadmium replacement. This coating combines a number of commercially available processes in a patented, unique fashion, as follows: nickel strike + IVD Aluminum + conversion coating + heat treatment. The conversion coating can be a conventional (chromated) product or a proprietary, patented, chromium-free formulation developed by Northrop-Grumman.

Test results confirmed the developer's contention that further development work is needed before this coating can be considered a serious candidate to replace cadmium. With an appropriate pretreatment (coupling agent) adequate adhesion may be obtained, but thickness control needs to be improved (for replacing cadmium, thinner coatings are required). In addition, the post-treatment (heat treatment) temperature has to be reduced if heat sensitive substrates are to be coated. The coating, however, passed the hydrogen embrittlement test. An additional issue is that there is currently no single source to apply all the processing steps at one facility. The individual processing steps are outsourced by NG, which introduces the potential for lowering quality control.

Ion Beam Assisted Deposition: Ion beam assisted deposition (IBAD) is a vacuum deposition process that combines PVD and ion-beam bombardment. An electron-beam evaporator is used to generate a vapor of coating atoms, which are deposited on a substrate. At the same time, ions are extracted from a plasma and accelerated into the PVD film at high energy levels (hundreds to several thousand electron volts). IBAD coatings such as nitrides have been investigated as replacements for cadmium through a variety of projects, but because it is a batch process, requires high vacuum equipment, and deposits only thin films, other less expensive, more conventional approaches have been favored.

4.1.4 Summary of Candidate Status

Table 1 provides a brief summary of the principal candidates to replace cadmium discussed in this section. Additional information may be found in the published literature.⁵

4.2 Cr Alternatives – Metal Coatings: Wet and Dry Technologies

Chromium coatings meeting AMS QQ-C-320B are used on a wide range of components and parts, such as those in landing gear, flap tracks on aircraft wings, hydraulics, gear races, engines, and propellers hubs. They are used because of their desirable properties, such as good coverage and adhesion, hardness; wear resistance; barrier corrosion protection; and lubricity (by retaining oil in microcracks). Hard chromium electroplating baths are established, relatively inexpensive to operate and maintain, and the process is suitable for components of all dimensions from large landing gear to small flanges (line-of-sight and non-line-of-sight applications). Because EHC is a strong, wear resistant coating, it is suitable for building up worn or damaged areas for repair operations. For some parts such as bearings, "thin dense" or "nodular" chromium is sometimes called out where a thin, protective coating (sometimes referred to as a "flash" layer) is required. There is a possible problem with hydrogen embrittlement with chromium plating because hydrogen may be generated during processing. Also, hexavalent chromium is a known carcinogen and is considered to be environmentally detrimental. Therefore, there is a need to replace chromium plating with a more worker and environmentally acceptable process.

⁵ G. C. Wright, et al., "Evaluation of Alloy Coatings Being Developed as Alternatives to Cadmium Coatings", Proc. SUR/FIN '03, Session P, The AESF Society, Milwaukee, WI (2003).

Table 1. Summary of Candidate Cadmium Alternative Coatings

Alternative Coating	Comments	DoD Status
IVD Al	Proprietary PVD LOS* coating process; requires vacuum chamber; qualified alternative but because of porosity requires post-treatments to match Cd properties	In use on landing gear and many small steel parts
Sputtered Al	Proprietary (“plug and coat”) magnetron sputtering PVD process; requires vacuum chamber; dense coatings, but may require post-treatment	In limited use on inside diameter surfaces of landing gear components
Cermets (Al based)	Proprietary spray and fuse process; substrate material must not be heat sensitive; might be suitable for touch up and repair	Commercial sole source; being evaluated for use on aircraft
Electroless Ni-P	Proprietary NLOS** coating process	Commercial; limited use as a barrier coating
Electroplated Al	Proprietary AlumiPlate® NLOS coating deposited from an organic plating bath; results from performance testing good except for lubricity ; no problems with hydrogen embrittlement; some scale up and safety issues with bath chemicals	Near commercial – sole source; being evaluated for use on small parts (e.g., fasteners, electrical contacts)
Electroplated Al-Mn	Molten salt NLOS plating process developed by the Navy; full size dem/val testing revealed process was difficult to control in a production setting	Withdrawn as a candidate replacement
Electroplated Sn-Zn	Proprietary NLOS alloy coating; not as corrosion resistant as Zn-Ni alloy coatings; good candidate for touch up and repair (brush plating) of Cd and Zn-Ni coatings	Commercial; being evaluated for use on aircraft
Electroplated Zn-Ni (acid)	Proprietary NLOS alloy coating deposited from an acidic plating bath; not as good as the alkaline bath – harder to operate and more risk of hydrogen embrittlement on high-strength steels	Commercial; evaluated for use on aircraft
Electroplated Zn-Ni (alkaline)	Proprietary NLOS alloy coating deposited from an alkaline plating bath; widely used on low-strength steels;	Commercial; being evaluated for use on aircraft

* LOS = line-of-sight limited to accessible surfaces. **NLOS = can be used to coat complex shapes and inside and outside diameter surfaces.

Some of the alternatives evaluated are briefly discussed below, and a summary (Table 2) is given at the end of this section. Further information may be found in the published literature.^{6,7}

4.2.1 Implemented Technologies

High-Velocity Oxy(gen) Fuel Coatings: HVOF (thermal spray) coating facilities have been installed and used at the ALCs and depots for some time now to deposit coatings on landing gear and engine parts to replace hard chromium coatings. For example, Air Force facilities

⁶ E. W. Brooman, “Corrosion Behavior of Environmentally Acceptable Alternatives to Cadmium and Chromium Coatings: Chromium, Part I”, Metal Finishing, **98**, No. 7 (2000) 38.

⁷ E. W. Brooman, “Corrosion Behavior of Environmentally Acceptable Alternatives to Cadmium and Chromium Coatings: Chromium, Part II”, Metal Finishing, **98**, No. 8 (2000) 39.

apply tungsten carbide-cobalt (e.g., WC-17Co) coatings on outside diameter surfaces of some landing gear components. However, the U.S. Navy prefers to use WC-Co-Cr coatings because of its greater corrosion resistance. While this is not a chromium-free solution, worker exposure and emissions will be reduced compared to conventional hard chromium plating.

4.2.2 Short-term Candidates

High-Velocity Oxy(gen) Fuel Coatings: The ALCs and depots are working demonstration and validation projects to further implement this type of thermal spray process on some of their major outer surface (line-of-sight) workloads. A variety of metallic and cermet coatings can be applied, such as WC-Co and Tribaloy 800[®]. These coatings are anticipated to reduce the chromium plating workloads by 60 to 80 percent once they are fully implemented. The remaining 20 to 40 percent of *non-line-of-sight* applications will require a different alternative coating technology. HVOF coatings have been evaluated extensively under numerous projects funded by the ESTCP, SERDP, and others. Some of these projects that have, or are evaluating HVOF-applied coatings as potential chromium replacements are as follows:

- SERDP Pollution Prevention project PP-1151 – *“Clean Dry-Coating Technology for ID Chrome Replacement”*
- ESTCP Project PP-9922 – *“Replacement of Chromium Electroplating on Propeller Hubs Using HVOF Thermal Spray technology”*
- ESTCP Project PP-0023 - *“Replacement of Chromium Electroplating on Gas Turbine Engine Components Using Advanced Thermal Spray Technologies”*
- ESTCP Project PP-0038 – *“Replacement of Chromium Electroplating on Hydraulic Actuators Using HVOF Thermal Spray Technology”*
- ESTCP Project PP-0127 – *“Replacement of Chromium Electroplating on Helicopter Dynamic Components Using HVOF Thermal Spray Technology”*.

Non-Line-of-Sight Nickel Alloy Coatings: Chromium-free plating technologies are being investigated as “drop-in” substitutes for hard chromium plating. Most of the processes identified to date have been nickel-based alloys, which may only provide an interim solution if nickel becomes more heavily regulated. Under the initial phases of the NDCEE Task entitled *“Non-Line-of-Sight (NLOS) Hard Chromium Alternatives”*, six proprietary alternatives were evaluated:

- Nanoplate[®] (manufactured by Babcock & Wilcox)
- Enloy 500[®] (manufactured by Enthone-OMI, Inc.)
- Niklad 797[®] (manufactured by MacDermid, Inc.)
- Millenium KR[®] (manufactured by Sirius Technology)
- Enfinity HX[®] (manufactured by Stapleton Technologies)
- NiPlate 700[®] (manufactured by Surface Technology, Inc.).

The above listed processes were first subjected to Screening Tests that evaluated adhesion, thickness, quality, hardness, stress, composition, and surface roughness. Following these tests, Performance Tests were conducted and the results showed that NiPlate 700 coating was the best candidate overall to replace EHC and it is currently undergoing qualification testing by the U.S. Air Force. This coating is comprised of an electroless nickel matrix containing silicon carbide particles in the 200 to 2,000 nm range. Precipitation hardening provides the hardness while the SiC particles contribute to the wear resistance.

Other nickel-based alternative coatings are briefly described below.

Nickel-Cobalt Alloy Plating: Several commercially offered coatings fall under this category. Of particular interest are the two coatings offered by NANON Technologies (formerly Shining Surface Systems); namely, NANON 6[®] and NANON 8[®].

- **NANON 6:** This coating (formerly called Mettex 6) is marketed as an alternative to hard chromium plating. It is applied by an electroplating process and the coating consists of 50-70% nickel and 30-50% cobalt. The NANON 6 process produces a nano-crystalline structure that is claimed to provide three times the wear resistance of conventional hard chromium.
- **NANON 8:** This coating (formerly called Mettex 8) also is marketed as a hard chromium alternative. It has a similar composition to NANON 6 and, based on the preliminary test results reported, appears to possess similar properties.

Nickel-Boron Electroless Coating: One vendor (Universal Chemical Technologies, Inc.) offers its UltraCem[™] coating as a replacement for hard chromium or hard electroless nickel-phosphorus coatings. It is deposited by an electroless process in an alkaline bath that is claimed to produce a 95% nickel and 5% boron coating. UltraCem is used commercially in a variety of applications, which include the aerospace, armament, foundry, pulp and paper, and tool and die industries.

This process was evaluated under by the Air Force and test results indicated that this coating may be a promising hard chromium alternative for use on steel substrates. Post heat treatment (meeting the requirements of AMS QQ-C-320B) enhances the coating properties (hardness and adhesion) to acceptable levels, but the heat treatment (temperature and time) must not have a detrimental effect on heat sensitive substrates such as some aluminum alloys and high-strength steels. Other UltraCem properties, such as appearance, quality, composition, and surface roughness also were considered to be acceptable. Thickness, however, was less than required. The Taber wear resistance of the UltraCem coating has to be determined.

Sputtered Chromium: Variations of this line-of-sight PVD technology could be used to apply thin dense chromium coatings to outside diameters of parts. Because it is a dry process, using solid chromium as a target material, worker exposure to hexavalent chromium is eliminated as well as any related waste treatment. However, this type of coating would not meet a chromium-free specification. At best, it might be considered an interim solution until alternatives are found, evaluated, and qualified for implementation. Cylindrical magnetron sputtering was evaluated under SERDP Pollution Prevention Project PP-1074 entitled “*Tri-Service ‘Green’ Gun Barrel*” as an alternative coating technique to hard chromium plating.

Cermet Coatings: The Air Force Propulsion Engine Working Group (PEWG) is evaluating SermeTel[®] coatings as an alternative to EHC for engine parts. SermaTech Power Solutions is continuously modifying its product line in response to customer requirements and improvements to the former SermeTel W coatings have been made.

4.2.3. Mid- and Long-term Candidates

Laser Assisted Surface Improvements: Several techniques have been developed that use laser beams directed at the surface of a part to modify the surface or produce a coating. These have been described in Section 4.1.3. The same technologies can be used to modify surfaces or apply hard, wear resistant coatings to replace EHC.

Ion Beam Assisted Deposition: Ion beam assisted deposition (IBAD) is a vacuum deposition process that combines PVD with ion-beam bombardment, as discussed earlier. IBAD coatings, such as nitrides, have been sought as replacements for chromium on a variety of projects. IBAD has been evaluated under numerous projects funded by the SERDP, U.S. Army, and others. Examples of these projects are as follows:

- SERDP Pollution Prevention project PP-632 entitled, “*PVD and Ion Beam Processes to Replace Electroplating*”
- Sustainable Green Manufacturing (SGM) (FY97-01) project R4-1 entitled “*Surface Finishing Processes*”
- SGM (FY99-00) project R4-6 entitled “*Ion Beam for Improved Corrosion Resistance*”

In summary, the results from these efforts have shown that IBAD coatings can provide very hard, wear resistant coatings for both line of sight and non-line-of-sight applications, depending on the coating being considered and the variation of IBAD that is used for deposition. For example, most hard, refractory coatings can only be deposited using line-of-sight methods; however, coatings such as diamond-like carbon (DLC) can be deposited using non-line-of-sight methods such as plasma immersion ion processing (PIIP). In all cases, however, the coatings are very thin (several to tens of micrometers thick) so they cannot be used alone to build up worn surfaces, such as those typically experienced in aerospace wear (e.g., on the order of several thousandths of an inch), nor do they provide significant corrosion protection. Therefore, these coatings can be considered as “next generation” coatings that may be used on original equipment manufactured parts that might not otherwise be coated in order to extend the initial wear life of components. If the initial wear life can be significantly extended, then the components of interest may have to be repaired fewer times during the component life cycle.

The coatings also may have the potential as a replacement for thin dense chromium in line-of-sight applications (e.g., when using ceramics) or non-line-of-sight applications (e.g., when using DLC in lower temperature applications when coating degradation is not a concern). In general, however, due to the complexity of fixturing required for line-of-sight methods and the reduction in the numbers of components that can be treated in a single cycle, this process typically is reserved for high-cost or value-added components. Other non-line-of-sight methods can be more cost effective, depending on the production requirements of the components to be treated.

Micro-welding-based Coatings: Electro-spark Deposition (ESD) also is referred to as Electro-spark Alloying (ESA). With this technique, metallic coatings are applied by a pulsed arc, micro-welding process. As a result, part dimensions are changed and there is a small heat-affected zone (as found in the LSI process) resulting from the short duration, but high current, electrical pulses. This could be a limitation for heat sensitive substrates, such as high strength steels. However, the deposited material is rapidly solidified, which results in a metallurgically bonded coating exhibiting excellent adhesion. The following projects involve ESD as a possible replacement for chromium plating:

- SERDP Pollution Prevention Project PP-1147 entitled “*Electro-Spark Deposited Coatings for Replacement of Chrome Electroplating*”
- ESTCP Project PP-0202 – “*Electrospark Deposition for Depot- and Field-Level Component Repair and Replacement of Hard Chromium Plating*”.

In addition, the Navy is working in conjunction with Advanced Surfaces and Processes, Inc. to determine the applicability of another type of ESD process.

Trivalent Chromium Plating: Trivalent chromium is considered to be much less toxic than hexavalent chromium. Consequently, trivalent chromium coatings are being considered as an

interim alternative to conventional hard chromium coatings. So far the major application has been as a decorative coating, and control of the baths is more difficult than the conventional chromic acid plating baths. However, electroplated, functional trivalent chromium coatings are being investigated under numerous projects funded by the ESTCP, SERDP, and others. Some known vendors of this plating process are Faraday Technologies, Inc. and Atotech (USA), Inc. In addition, the National Institute for Standards and Technology is developing an electroplated trivalent chromium process. Under the NDCEE Program, a joint effort with Atotech is focusing on coatings with desirable functional properties, such as improved hardness and wear resistance.

Nano-composite Plating: This is a type of electroplating process that holds some promise for replacing chromium and nickel coatings. Nano-composite coatings can be engineered to provide a wide range of desirable properties for specific applications. Either the coating matrix is nano-crystalline and incorporates particles to improve wear resistance, or the matrix is a conventionally electroplated or electroless material in which nano-sized particles are incorporated. The best coating compositions have yet to be identified, although an investigation funded through GSA as Task 242, entitled "*Nano-composite Plating as an Alternative to Chrome and Nickel Plating*", investigated a variety of nickel and cobalt containing deposits containing particles such as diamond or tungsten carbide (WC). Several of these coatings exhibited good adhesion, hardness and wear resistance.⁸ Another type of coating (nano-crystalline Co-P) was investigated under a SERDP funded project (PP-1152) entitled "*Electroformed Nano-crystalline Coatings: an Advanced Alternative to Hard Chrome Electroplating*"; further development work is being carried out with ESTCP funding.

Under the Advanced Non-Line -of Sight project funded by the Air Force, a review of the latest developments in candidate alternatives to EHC resulted in the down selection of the following coatings⁹:

- Electroplated nano-Co-P (Integran Technologies, Inc.) - benchmark
- Electroplated Co-P (Boeing - Seattle)
- Electroplated nano -Co-P+boron Carbide particles (Integran Technologies, Inc.)
- Electroless Co-[B or P]+diamond particles (Surface Technologies, Inc.)
- Electroplated Co-W alloy (Zinex Corp.)
- Electroplated Co+tungsten carbide particles (Inframmat Corp.)
- Electroplated Co+ tungsten carbide particles Whyco Technologies (USA), Inc.)
- PVD Ti or Zr nitride (Ionic Fusion Corp.)
- PVD Mo or Ta (CAP Technologies, LLC.).

Screening tests and further investigation of capabilities and process maturity has led to the following coatings being subjected to more rigorous performance testing:

- Electroplated nano-Co-P (Integran Technologies, Inc.) - benchmark
- Electroplated nano -Co-P+boron Carbide particles (Integran Technologies, Inc.)
- Electroplated Co-P+silicon carbide particles (U.S. Chrome Corp.)
- Electroless Co-B+diamond particles (Surface Technologies, Inc.)
- Electroless Co-P+diamond particles (Surface Technologies, Inc.).

⁸ M. L. Klingenberg, E. W. Brooman and T. A. Naguy, "Nano-particle Composite Plating as an Alternative to Hard Chromium Coatings", Proceedings SUR/FIN '03, AESF Society (2003).

⁹ M. J. Beebe, et al., "Identification of Alternatives and Recommendations Report", prepared by Concurrent Technologies Corp. for the Air Force Research Laboratory, Dayton, OH (October 2004).

The test results will not be available until late 2006. However, a series of recent articles^{10,11,12} provides a detailed discussion of the properties of some of these and other candidates, along with a preliminary risk assessment for ranking them.

Diffusion Coatings: Metallizing is an unique heat treatment process that can improve surface properties through diffusion to produce coatings. This process is still laboratory-based and the developer, Gannon University is looking for a partner to commercialize the technology. Materials that have been diffused into various substrates include boron, beryllium, silicon, tantalum, titanium, chromium, aluminum, zirconium, yttrium, rare earth elements, and other metals. The engineering properties of treated substrates are specific to the substrate material, the metal that is diffused into that substrate, and the alloys or compounds that are produced.

Plasma Anodized Coatings: The MicroplasmicTM process is an anodic process that uses a microarc induced plasma to produce an alumina coating on aluminum substrates. It was developed by the Microplasmic Corporation and produces a very hard, corrosion resistant coating (over 2,000 hours salt fog exposure). Similar types of coating may be obtained on magnesium and titanium substrates.¹³ A similar process is also offered by Keronite, Ltd. (UK), Magnesium Coating Corporation, and Ceramic Coating Technology, Inc. The authors are unaware of any projects being conducted to evaluate this particular hard chromium coating alternative for DoD applications.

4.2.4 Summary of Candidate Status

Table 2 provides a brief summary of the principal candidates to replace EHC discussed in this section. Further information may be found in the published literature.¹⁴

4.3 Cr Alternatives – Conversion Coatings, Adhesion Promoters

Chemical conversion coatings are applied by immersion or spraying processes to form a more protective surface thin film - usually on aluminum and magnesium alloys - and, when required, to provide a surface to which primers and topcoats can adhere more strongly. Until recently, the only products were based on a chromate or dichromate redox chemistry that provided a good bond, corrosion resistance, and a "self-healing" feature¹⁵. The latter is accomplished by the migration of soluble chromium ions to damage sites where they react with the bare substrate material to form a new, protective, thin film. More recently, some chromium-free conversion coatings have been offered that incorporate other redox couples, such as those based on cerium, cobalt, vanadium, or molybdenum chemicals. Another candidate - developed by the U.S. Navy - is based on trivalent chromium rather than hexavalent chromium, on the premise that the former is not regulated like the latter. Finally, a third approach is to provide a pretreatment that produces a thoroughly clean surface¹⁶ and deposits a thin, typically organic film (such as a sol-gel¹⁷) on the surface to promote adhesion on parts to be painted. Some of these pretreatments incorporate a non-chromium, corrosion inhibitor (or inhibitor package to take advantage of any synergy) to meet the corrosion resistance specification.

¹⁰ E. W. Brooman, "Compliant Electrodeposited and Electroless Nano-Structured and Nano-Composite Coatings to Replace Chromium Coatings – Part 1", *Galvanotechnik*, **96** (12), 2843 (2005).

¹¹ E. W. Brooman, "Compliant Electrodeposited and Electroless Nano-Structured and Nano-Composite Coatings to Replace Chromium Coatings – Part 2", *Galvanotechnik*, **97** (1), 58 (2006).

¹² E. W. Brooman, "Compliant Electrodeposited and Electroless Nano-Structured and Nano-Composite Coatings to Replace Chromium Coatings – Part 3", *Galvanotechnik*, **97** (2), 297 (2006).

¹³ A. T. Kuhn, "Plasma Anodized Aluminum – a 2000/2000 Ceramic Coating", *Metal Finishing*, Vol. 100, No. 11/12 (2002) pp.44-50.

¹⁴ E. W. Brooman, et al., "Air Force Hard Chromium Coatings Replacement Efforts", Proc. SUR/FIN '02, Session Q, The AESF Society, Orlando, FL (2002).

¹⁵ D. Baudrand, "Conversion Coatings for Aluminum and Magnesium", *Plating & Surface Finishing*, **92** (1), 30 (2005).

¹⁶ Anon., "EPA Award Recognizes Air Force Use of Non-Chromated Conversion Coatings", *Industrial Paint & Powder*, (Sept., 2004), 10.

¹⁷ M. L. Zheludkevich, et al., "Sol-Gel Coatings for Corrosion Protection of Metals", *J. Royal Society of Chemistry*, **15**, 5099 (2005).

Table 2. Summary of Candidate Chromium Alternative Coatings

Alternative Coating	Comments	DoD Status
Sputtered Cr	PVD LOS* coating process; lower ES&OH impact than EHC	Near commercial
HVOF WC-Co	Thermal spray LOS process used on landing gear, hydraulic components; thick, rough coating requiring grinding/finishing; may be an issue with Co if coatings are ground	In limited (Air Force) use
HVOF WC-Co-Cr	Thermal spray LOS process used on landing gear, hydraulic components; better corrosion resistance than WC-Co coatings; may be an issue with Co and Cr when coatings are ground	In limited use on military (Navy) and commercial vehicles
Plasma Alloys	Thermal spray NLOS process; wide range of coating materials; denser, smoother coatings than HVOF, but not as good as EHC; adhesion not as good as with HVOF; need grinding/finishing	In limited use on aircraft; commercial
Cermets	Proprietary spray and fuse process; substrate material must not be heat sensitive; might be suitable for touch up and repair	Commercial sole source; being evaluated for use on aircraft engines
Electrospark Alloys	Wide range of materials can be deposited; rough LOS coating requiring grinding/finishing; issue with heat affected zone on heat sensitive substrate materials	Commercial, sole source
Electroless Ni-B	NLOS; more difficult to control plating bath; more expensive than electroless Ni-P coatings; low impact resistance may be a problem	In limited use; commercial
Electroless Ni-P	NLOS; cannot build thick coatings; can be used as a barrier coating; properties depend on P content and post-deposition heat treatment	Commercial
Electroless Ni-P+ diamond	NLOS; difficult to keep composites suspended in bath and scale up may be difficult; tests show properties are promising	Commercial
Electroless Ni-P+ silicon carbide	NLOS; difficult to keep composites suspended in bath and scale up may be difficult; tests show properties are promising	Near commercial
Electroplated Cr ³⁺	NLOS coatings not quite as hard or wear resistant than EHC coatings; lower ES&OH impact than EHC, which uses Cr ⁶⁺ chemicals	Commercial
Electroplated Nano-Co-P	NLOS; softer than EHC, lower wear resistance; may be an issue with Co if coatings are ground	Near commercial
Electroplated Nano-Co-P+ boron carbide	NLOS; harder and more wear resistant than electro-plated nano-Co-P	Near commercial
Electroplated Nano-Ni-Co	NLOS; wear resistant but not as hard as EHC	Near commercial

* LOS = line-of-sight limited to accessible surfaces. **NLOS = can be used to coat complex shapes and inside and outside diameter surfaces.

Pretreatments are used on a wide range of small parts, fasteners, electrical components and racks, ground support equipment and structures, aircraft and missiles. A brief discussion of some of these is provided below, and a summary given in Table 3. Further information about

the wide range of candidates investigated and tested by the U.S. Air Force and the U.S. Navy may be found in their published reports.^{18,19}

4.3.1 Implemented Technologies

The U.S. Navy has developed, patented, and licensed to several commercial vendors a pretreatment - TCP - process that uses trivalent chromium compounds. While the U.S. Air Force cannot use a process based on any chromium compounds, the U.S. Navy finds this approach to be acceptable and test results comparing their chemistry to the conventional hexavalent chromium chemistry have been very positive (see Ref. 19), especially on Zn-Ni coatings used to replace cadmium coatings. However, although the performance is acceptable on pure aluminum substrates and some aluminum alloys, it does not work as well on a few other aluminum alloys. In addition, independent testing has shown that the products offered by the licensees do not all provide the same high performance. Because the chemical compositions of the commercial products are proprietary, it is not possible to determine if minor variations in the formulations has a marked effect on the corrosion protection offered by these conversion coatings.

Other companies have developed and are marketing trivalent chromium “passivation” and pretreatment processes, so the user has a choice of products. Henkel Surface Technologies has introduced their 5000 series of Alodine™ coatings (e.g., Alodine 5200 and 5700 - the latter being the premixed version) that are chromium-free and provide acceptable performance in coating systems (see Ref. 18).

Boeing developed a sol-gel pretreatment (Boegel EP-II™) that is now offered commercially by Advanced Chemistry & Technology, Inc. as AC-131. It is an adhesion promoter for Al, Ti and CRES substrates and once applied is dried in place without rinsing. It is colorless, so removing excess chemicals (“puddles”) before drying can be difficult. Another product that is a cleaner and adhesion promoter for a wide range of substrate materials is PreKote™ (formerly X-It PreKote™) sold by Pantheon Chemicals. This product has been used on F-16 aircraft with success and is being evaluated for other aircraft.²⁰

4.3.2 Short-term Candidates

The U.S. Navy also has developed a chromium-free conversion coating identified as NCP. Evaluation of this process is not as far along as that for their TCP process, but testing of both is continuing under a SERDP funded project (WP-1521) managed by the U.S. Army Research Laboratory. The University of Missouri at Rolla has been working with DoD funding to develop cerium-based pretreatments (as well as primers) to eliminate chromium in organic coatings (paint systems). These provide good adhesion but are not as effective as chromium redox chemistry in controlling corrosion when coatings are damaged. The Ohio State University has focused on hydrotalcite chemicals as replacements for chromium in conversion coatings. Neither has been commercialized, but the cerium-based processes are further along in their development and the university is working with a large commercial paint manufacturer.

4.3.3 Mid- and Long-term Candidates

Other sol-gel and silane based pretreatments have been developed in the laboratory. These also provide great adhesion, but a corrosion inhibitor has to be added to provide the required

¹⁸ C. Joseph, “Non-chromated OML Coating Systems Screening” Final Report to Air Force Research Laboratory (January, 2003).

¹⁹ C. Matzdorf, “Non-Chromate Aluminum Pretreatments”, ESTCP Phase I Report, Project PP-0025 (August, 2003).

²⁰ L. Roberts and A. Galanis, “Non-Chromated Technology Works on Aircraft”, *Plating & Surface Treatment*, **90** (10), 8 (2003).

corrosion protection. Recently, nano-particles have been added to sol-gel chemistries to impart improved properties, and this development is being funded in part by the Air Force, and under a SERDP project (PP-1341) at the University of Cincinnati. Nano-particles or encapsulated nano-particles could be used to provide a “reservoir” of corrosion inhibitor to facilitate a self-healing reaction. For example, the SNAP (self-assembled Nanophase particle) silicon sol-gel coatings contain a zirconate as inhibitor²¹. This type of coating could be formulated to be “slow release” or “release on demand”.¹⁷

4.3.4 Summary of Candidate Status

Table 3 provides a brief summary of the principal candidates to replace chromium-based chemical conversion coatings discussed in this section. Additional information may be found in the references given above and the published literature.

Table 3. Summary of Candidate Chromium Conversion Coating Alternative Coatings

Alternative Coating	Comments	DoD Status
Alodine [®] 5200/5700	Chemical conversion coating; colored; performs well as part of a chromium-free coating system; said to provide similar features to the chromated version, 1200S; drop in replacement	Commercial sole source; being evaluated for use on military aircraft
NCP [®]	Chromium-free chemical conversion coating; undergoing laboratory testing; light colors; contains a corrosion inhibitor package	Near commercial
TCP [®]	Trivalent chromium chemical conversion coating; extensive laboratory and some field testing; light colors; contains corrosion inhibitor; used on Al alloys	Commercial, properties vary for different vendor's products
AC-131 [®]	Silane sol-gel pretreatment; multi-component system with 12-hour pot life; contains a corrosion inhibitor; colorless; dried in place; adhesion promoter	Commercial sole source
OXSILAN [®]	Silane pretreatment; multi-component system; contains fluorine compound; colorless; dried in place; adhesion promoter	Commercial sole source
PreKote [™]	Pretreatment; adhesion promoter; now contains a corrosion inhibitor package and number of processing steps has been reduced from 3 to 2	Commercial sole source; in limited (Air Force) use

5.0 BARRIERS TO IMPLEMENTATION

There are litany of reasons for not changing materials and processes that have been successfully utilized in the aerospace industry for over 50 years. Some are more real than others but most can be related to a negative desire for change. A discussion of some of these barriers, grouped into arbitrary broad categories, follows.

²¹ M Donley, “Corrosion Protection Characteristics of New Sol-Gel Based Surface Treatments for AA2024 T-3”, SERDP Partners in Environmental Technology Symposium, Session 3C (2001).

- 1. Technical/Performance:** The alternative may meet some, but not all of the defined performance requirements, or may not be optimized for a specific application. On a total system level, incompatible or non-existent pre- and post-treatments for the alternatives also may preclude their use.
- 2. Practical/Production:** The alternative material and process is found to equivalent in performance in the laboratory using test specimens, but scale up to production size parts and configurations is not feasible. Although work changes may be a high priority, some facilities have an engineering task force that is severely limited, so alternative material qualification and implementation changes are difficult. Unknown availability and costs of subcontractor/job shop supplied parts/services is another possible barrier. A facility may decide to eliminate in-house plating process by substituting an alternative material on 20-30% of high value parts and then subcontract out the remaining work. There can be a large uncertainty in costs, viability, and technical ability of subcontractor job shops. Surveys of plating shops show a mix of optimism and pessimism on continued cost effective chromium plating because of the new lower OSHA PEL. For example, facilities with modern ventilation systems are more optimistic; however, some of these now have to look at worker exposure during demasking and grinding operations. Individual weapon system “buy-in” can be a barrier for an alternative that can be used across weapon systems. In addition, Program Offices individually have to approve Environmental, Safety and Occupational Health (ES&OH) changes associated with material changes.
- 3. Financial/Funding Cycle:** Due to the magnitude of the cost making a change, funds have to be requested and budgeted for years ahead of time (e.g., OEM’s and job shops have 5-10 year capital improvement plans). Also, often there is a reluctance to project increased costs due to anticipated hazmat pressures. ES&OH life cycle costs are very difficult to project due to the ever changing regulatory pressures and wide range of potential liability costs. Each facility’s cost increase will vary due to differences in type of facilities, processes, and type of work being accomplished, as well as the local hazmat pressures. In general, weapons programs involve many different production and depot sites, and environmental costs vary widely depending on location (attainment vs. non attainment areas, toxic hot spot regions, and metropolitan vs. rural areas). Some facilities may be state of the art and others may be antiquated. Some sites may contain, or be near superfund sites, which are very sensitive to any additional emissions. Some facilities also may be required to follow OSHA expanded standards and work rules and others may not. There is a lower level of confidence in tracking overseas hazmat pressures and timing, considering how difficult it is to analyze the impact of evolving USA ES&OH costs. Due to foreign basing and subcontracting, worldwide ES&OH costs now need to be considered and analyzed. The benefits of making ES&OH material changes also vary depending on a program status. It is easier to make decisions on programs that are near phase-out or just beginning, but for programs with limited production or operational life, it is more difficult to make material change decisions.
- 4. Institutional/Specifications:** Universally used materials generally have a federal, military or industry specification, but many facilities have their own specifications with additional test requirements, or modifications to the universal specifications because of tighter process controls due to previous problems or more critical needs. This complicates alternative material qualification across multiple sites. Mistrust of data generated by “outsiders” also falls under this category. Facilities have varying levels of technical expertise and often use different test methods or equipment, for these reasons the data generated often are considered suspect by others (hence the need for joint

test protocols and cooperative and coordinated testing, as discussed earlier). The risk of creating a competitive disadvantage due to increased ES&OH costs is also a barrier, especially when DoD facilities are competing for work loads. Many ES&OH changes are believed to increase costs, although in the long term life cycle cost analyses may refute this. Downsizing in the aerospace industry puts pressure on sites to reduce costs or be eliminated. Sometimes it is economically and technically feasible to make a material change, but the cost of changing hundreds or thousands of drawings and hundreds of pages of product support manuals, technical, and work orders can block the change.

5. **Qualification/Acceptance:** Qualification test requirements are usually written for a material and often some different test and/or test methods are required for alternative materials (this is why flight tests are the best qualification tests and take a long time). Long flight time evaluations needed to gain confidence in new alternative materials, therefore, is a barrier. There is a large amount of data on the performance of cadmium and chromium plating for many different applications in a wide range of environments. It will take many years of laboratory and flight testing to gain high confidence in alternative materials and processes. There is always an inherent risk in making material changes to a proven technology, especially on flight critical hardware. Some military programs are utilizing slightly modified commercial aircraft and vehicles. Material changes in these require FAA test protocol approval and certification, which most military certified test sites are not capable of meeting. In addition, a lack of incentives or resources often means that vendors and suppliers are hesitant to qualify products themselves, especially for small markets, such as the defense industrial base.
6. **Availability/Sole Source:** Significant risks, such as limited stocks or unavailability, exist when relying on a single source vendor or process (also cost control is in jeopardy with a single source). Material changes to standard parts/commercial off the shelf (COTS) products are not governed by the OEM's or military users, which may pose a problem. In contrast, the aerospace industry utilizes many (tens of thousands) standard parts and COTS items without engineering authority or material change control.

Most of the above barriers can be overcome if customer demands the change, or if cost/risk management models support a change. Also, the timeframes for change can be significantly shortened by joint military-industry efforts.

7.0 LESSONS LEARNED

For the past 20-30 years there has been an increased awareness of ES&OH issues as a result of both regulatory pressure and scientific discovery of the detrimental effects of certain chemicals on both worker's health and the environment. A review of the material and process changes that have been made leads to several observations. Every organization that uses hazardous materials wants to protect its workers. The decisions on how to best accomplish this are made by a process that primarily uses costs to determine the type and level of protection afforded. Protection can be obtained in two ways; by substituting a less hazardous material or by limiting exposure through the use of robotics to limit worker exposure, improved ventilation, as well as PPE. Two examples of different methods of protection are; (1) elimination of asbestos in products by substitution of alternative materials and technologies, (2) when the dangers of isocyanates in paints were determined, resins were reformulated to minimize "free isocyanates" and workers were required to use air supplied respirators and protective PPE.

Compliance with environmental pressures also has followed two paths: (1) it was an easy decision to find alternative solvents for 1,1,1,TCA after the United States signed a treaty saying the production and importation of this chlorinated solvent would be stopped by a given date; and (2) the Aerospace NESHAP required a reduction in the emission of solvent (HAP'S/VOC's) in paints. Cost studies determined that it would be cheaper to reformulate paints (high solids paints) rather than to add solvent capture/recovery systems to paint booths.

After reviewing these and other observations, several lessons learned are obvious. First is that the aerospace industry has made very few material eliminations due to environmental and health pressures unless these specifically mandated a change in a material. Also, material changes have been made only when the customers mandated a change. Despite this, discussions on cadmium plating elimination have gone on for over 40 years, with only limited success, and even with increasing ES&OH pressures, there is still continuing widespread use.

Because costs drive most decisions, a second lesson learned is that often there is a lack of confidence in ES&OH cost projections. Therefore, risk based analysis is generally used to make ES&OH decisions. The aerospace industry is operating in a worldwide environment with ever changing ES&OH pressures that makes cost projections uncertain. Costs for a given material and process vary widely due to user location, facilities, current and projected workload, management practices and policies, and so on. An example of this is an European country that requires individual insurance policies for workers that must use a liquid shim containing crystalline silica. What liability costs can be projected for this? Will it be like the unbearable costs of class action suits being imposed on sites that used asbestos 40 years ago?

A third lesson learned is that if a facility is contemplating a material change, then it needs the commitment and involvement of all its customers or stakeholders early and throughout the change process. As an example, the aerospace industry has a high desire to eliminate the use of cadmium and chromium plating. This is most readily accomplished in emerging platforms and in applications where the alternative offers cost or performance improvements, or a competitive advantage. Changes will not be made to the remaining applications until a change is mandated or cost/risk models reliably predict the need for a change, or a cost effective alternative with better performance becomes available and change is hard to resist.