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CLEAN METAL FINISHING ALTERNATIVES

SERDP/ESTCP Metal Finishing Workshop
May 22, 23, 2006

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **MAY 2006**	2. REPORT TYPE	3. DATES COVERED **00-00-2006 to 00-00-2006**

4. TITLE AND SUBTITLE **Clean Metal Finishing Alternatives**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Rowan Technology Group,1590 S. Milwaukee Ave., Suite 205,Libertyville,IL,60048**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**34**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

SUMMARY

Summary of chrome replacement alternatives.

Technology	Principle	Capabilities/Notes	TRL OD	TRL ID
Wet plating				
Electroless Ni and Ni composites	Electroless Ni-P/B (+ SiC, Teflon, diamond, etc), Amplate	Ni-P, Ni-B, and particle-filled alloys. Ni-B contains some Pb or Tl. Good ID alternative. Must heat treat for hardness	9	9
Electroplated Ni and composites	Electroplating, some with hard particles	Not as hard as chrome. Particles can pose production issues	4	4
Nanophase Co-P	Pulse plating	Softer than Cr, must heat treat for hardness	4	4
Trivalent chrome	Trivalent plating chemistry	Varying success, some must be brush plate	3	3
Alloy plating	Electroplating of simple alloys	Ni-W-B, Co-W. Little used	4	4
Co-composites, Tribomet®	Co electroplate + Cr_3C_2 particles	Co alloy, proprietary. Only used for GTEs	9	N/A
Thermal spray				
HVOF	Powder + high temperature flame	Primary OD alternative. WC-Co(Cr), alloys	9	>11” ID
Plasma spray	Powder + plasma	1.5” ID, WC-Co, alloys, metals	4	>1.5” ID
Cold spray, supersonic spray	Powder in high velocity gas stream	Dense coatings, mostly soft metals. Hard coating deposition unproven.	3	N/A
Weld coating				
Electrospark Deposition/ Alloying (ESD/ ESA)	Microarc welding	Localized repair of non-fatigue-critical components. Low deposition rate, portable. Not a coating replacement	5	4 (>1/2”)
Explosive cladding	Explosive bonding	Metals, Ta being evaluated for gun barrels	N/A	3
PVD/CVD				
Post-magnetron sputtering	Sputtering from high current rod or flat target	Metals, alloys, nitrides; Ta (Army). Scaled for large gun barrels. 0.008” thick		Development/ large dia
Flat target sputtering	Sputtering from target	Primarily nitrides, carbides	3	N/A
Ion Beam Assisted Dep	PVD with ion beam	Metals, nitrides. Low build	3	N/A
Hollow cathode evaporation	Small internal hollow cathode	Diamond-like carbon. Low build	N/A	3
CVD, MOCVD, plasma CVD	Deposition from gas	Very small, long holes. High temperature/dangerous precursors	2	2
Combustion CVD	Precursors combined in flame	Compounds (oxides, etc). VOC solvents used	3	N/A
Other methods				
Plasma, gas nitride	Nitriding at about 500C	Surface treatment (no build-up, high temperature)	9	N/A
Laser deposition	Laser evaporation, alloying, and CVD	Diamond. No build-up	3	N/A
Laser Induced Surf. Improvement (LISI)	Laser alloying	Alloys with surface material (not coating). No build-up	3	N/A
In production	Advanced development	Development	R&D	

Summary of Cd replacement and other corrosion resistant alternatives.

Technology	Principle	Capabilities/Notes	TRL OD	TRL ID
CRES Alloys				
Titanium alloys	Ti alloys, commonly Ti-6Al-4V	Lower weight, cost and volume penalty	9	9
15-5PH, 13-8Mo, etc	Precipitation-hardened steels	Lower strength than 4340, 300M	9	9
Stainless steels	A286, 400 series, etc.	Fasteners	9	N/A
S53 ultrahigh strength CRES	Computationally designed CRES	Mechanically same as 300M, somewhat less corrosion resistant than 15-5PH	4	N/A
Vacuum Al				
IVD Al	Al evaporation with weak plasma	Widely used for aircraft components	9	N/A
Sputtered Al	Sputtering with intense plasma	Commercial equipment available	N/A	5
CVE Al	Chemical vapor deposition	Relatively high deposition temperatures	3	3
Spray Al				
Wire arc spray and flame spray Al, AlZn	Thermal spray	Excellent for large structures, vehicles, ground support equipment. Some aircraft usage	9	N/A
Cold spray	Al powder + high velocity gas	Under evaluation for Mg, steels	3	N/A
Electroplates				
Zn-Ni	Acid and alkaline aqueous	Aircraft, vehicles	9	9
Sn-Zn	Brush or tank	Not as good as Zn-Ni, good for brush plate repair	5	5
Al (AlumiPlate)	Non-aqueous, toluene bath	Excellent performance, cost and ESOH issues	6	5
Electroplasma Zn-Al	High voltage aqueous plating	Zn-Al alloys, not pure Al	2	2
Al-Mn	Molten salt bath	Good performance but problems - abandoned	4	N/A
Other methods				
Al and Zn filled polymers	Spray and dip-spin	Standard for automotive fasteners	9	9
Metallic-ceramic coatings	Spray or paint Al particles in ceramic matrix	SermeTels and equivalents	9	9
In production	Advanced development	Development	R&D	

Commercial non-chromate alternatives for bulk Al and Al coatings.

Substrate	Process	Chemistry	Comments
Alternatives to chromate conversion coatings			
Al	TriChrome Pretreatment (TCP)[*] – AnoChem TCP, Aluminescent, TCP-HF	Trivalent Cr^{3+} conversion with Zr inhibitor	Developed by NAVAIR Light blue iridescent color
Al	Other Cr^{3+} treatments	"	"
Al		"	"
Al		"	"
Al	Alodine 5200/5700[*]	Non-chrome, Zr conversion	Alodine 5200 for nonferrous alloys, 5700 specifically for Al Light tan iridescent color
Al	Safegard CC-3400	Non-chrome, permanganate conversion	For Al, Mg, Zn
Al	Oxsilan AL-0500	Non-chrome, silane conversion	For Al, Mg, galvanized steel
Al	Dorado Kote #7	Non-chrome conversion	Gold-to-purple iridescent
Al	EMC	Silicate	Electrolytic
Al	AC-130, AC-131[*]	Sol-gel coatings, organo-siloxanes and zirconates	Developed by Boeing Clear and colorless
Al	PreKote[*]	Organic adhesion promoter (not a conversion coating)	Poor bare corrosion resistance Minimal color change
Steel, Zn	Various	Phosphate (without usual chromate sealer)	Not as corrosion resistant as chromate
Anodizing alternatives for Al and Mg alloys			
Al, Ti (in development)	Keronite (for Al alloys)	Plasma electrolytic oxidation (high-voltage anodizing)	Corrosion and wear resistance - fused alumina layer
Mg	Tagnite	Plasma electrolytic oxidation (high-voltage anodizing)	Corrosion and wear resistance - fused oxide layer
Mg	Anomag	Low ac voltage anodization	Corrosion and wear resistance
Al	Thin film sulfuric anodize	Sulfuric acid	Qualified for most NAVAIR applications
Al	Boric-sulfuric anodize	Sulfuric + boric acid	

[*] Ranked best in NAVAIR testing

Note: The Technology Readiness Levels (TRLs) in the above tables are for guidance only as applied to DoD components. The TRL for the same process will be different for different applications.

Further information:

ESTCP: http://ESTCP.org

SERDP: http://SERDP.org

Web portal for alternatives to hazardous materials and processes:

http://www.hazmat-alternatives.com

HCAT web site for detailed data:

http://www.materialoptions.com

DoD corrosion information:

http://www.dodcorrosionexchange.org

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1. Introduction

Cr^{6+} is a known carcinogen and Cd is a known heavy metal poison. Both of these materials are heavily used in DoD maintenance operations and pose a risk to maintainers in the field, especially during corrosion control and paint touch-up operations. Personnel exposure is regulated by OSHA under the Cd and Cr^{6+} PELs. Usage and disposal on products is regulated in Europe.

1.1. Impact of European and other overseas legislation

Three major European Union environmental rules on materials have a significant effect on metal finishing[1]:

- ❑ ELV (end-of-life vehicles) – The first of the three major EU environmental directives, effective since 1993, the ELV rule restricts the use of lead, mercury, cadmium and Cr6+ on new vehicles.
- ❑ WEEE (waste electrical and electronic equipment) – WEEE applies to new electrical and electronic equipment. The WEEE directive is a broad set of regulations that, like the ELV mandate, is designed to keep toxic pollutants out of the waste stream.
- ❑ RoHS (restriction of hazardous substances) – The far-reaching RoHS rule places strict limits on the use of lead, mercury, cadmium, Cr6+ and two brominated fire retardants in a wide range of electrical and electronic products.

There is a general perception that DoD does not have to be concerned about European WEEE, RoHS and other legislation since it exempts military hardware and aircraft. This does not mean, however, that this legislation does not and will not impact DoD operations and equipment. The most immediate effect is that standard materials and processes that use targeted materials (Pb, Hg, Cd, Cr^{6+}) are becoming unavailable. The military market is too small in general to command special production facilities and methods. A military exemption is of no value if the exempt item is unobtainable. This is already happening with lead-free solder. Military and aircraft electronics are exempt, but leaded solder is becoming difficult to obtain and most COTS items are lead-free. The exemption actually makes it more difficult to maintain leaded systems since non-lead electrical components become mixed in with the leaded components, making it difficult to ensure reliable processing.

Where exemptions currently exist they are not expected to remain indefinitely. The legislation provides a strong competitive incentive for companies with clean alternatives to seek removal of exemptions in order to place their products as sole source alternatives. This is already beginning to happen in some areas.

We expect that the EU legislation will ultimately make commercial Cd plate, chromate conversion coatings and chromated primers unavailable. Although it is driven by performance rather than legislation, aircraft landing gear and ultimately hydraulic actuators are likely also eventually to be manufactured with HVOF as the standard coating and chrome plate as a higher-cost special option.

2. DoD Usage of Metal Finishing Processes

DoD is a heavy user of metal finishing, primarily in depot overhaul.

2.1. Hard chrome plating

Hard chrome plating is the most common method for rebuilding worn or corroded components and restoring dimensional tolerances. It can be built to a thickness of 0.015", although some users permit thicker layers. Hard chrome is deposited in several different forms for OEM use and rebuild (Table 2-1). The major usage in DoD is rebuild hard chrome, which is often deposited on top of a thicker sulfamate nickel coating when a thicker layer is needed. Because it is used for rebuild hard chrome is often plated onto components that were never originally plated by the OEM.

Table 2-1. Common types of hard chrome plating.

Type	Thickness	Comments
OEM hard chrome	0.003"	Wear resistance on new items
Rebuild hard chrome – D-level	0.003-0.015"	Dimensional restoration after wear or corrosion
Thin dense chrome (TDC) - OEM	0.0002-0.0006"	OEM coating to provide wear, corrosion, lower friction. Nodular. Often used for IDs
Flash chrome – OEM and D-level	0.0002-0.0006"	Often used instead of TDC – not nodular
Brush chrome – D- and O-level	0.003-0.015"	Hand deposited by brush plating (aka selective or stylus plating)

Hard chrome specification: MIL-STD-1501C; QQ-C-320B

TDC specifications: TDC – AMS 2438; BAC 5709

Typical applications for hard chrome plating are:

- ❑ Hydraulic actuator rods and rams – aircraft, trucks and vehicles, ships. Almost every commercial and military actuator rod is chrome plated.
- ❑ Aircraft landing gear inner cylinders and journals
- ❑ Shaft journals for bearings on many engine shafts in turbines and other machinery.

2.2. Cadmium plating

Cd plating is used almost anywhere that sacrificial corrosion resistance is needed. Applications fall into three main categories:

1. **Components**

   These include almost any exposed item that must be protected from corrosion, including steel landing gear components, hydraulics, drive-screws, etc. Corrosion resistance and paint adhesion are critical to these applications.

2. **Fasteners**

   These are primarily rivets, washers, bolts, and screws, especially in exposed locations. Most threaded fasteners are made of high strength steels and are easily embrittled. Well-defined lubricity and torque-tension characteristics are critical for threaded fasteners. In turbine engines, most Cd-plated fasteners can be replaced by high strength stainless steel fasteners,[2] but stainless steel fasteners cause severe galvanic corrosion in contact with aluminum on airframes.

3. **Electrical connectors**

   These are primarily connector bodies, or shells, that surround multi-pin connectors, or plugs, used to interconnect electronic equipment. Long-term low electrical resistance and avoidance of insulating corrosion products are essential for this application.

The following specifications are commonly used:

- QQ-P-416 - Federal Specification for Cadmium Plating on Low and High Strength Steel up to 200,000 psi.
- BAC 5701 - Boeing specification for Cadmium Plating on Low Strength Steel.
- DPS 9.74 - Douglas Process Specification for Cadmium Plating.
- AMS 2400 - Aerospace Material Specification for Cadmium Plating.

The Federal specification for cadmium, QQ-P-416, defines classes and types of cadmium as in Table 2-2.

Table 2-2. QQ-P-416 Classes and Types of electroplated Cd.

Class	Thickness	Type	Finish
1	0.0005”	I	As deposited
2	0.0003”	II	Chromated
3	0.0002”	III	Phosphated

Cadmium provides the following properties to plated surfaces:

1. **Corrosion resistance**
   a. Cd is anodic relative to steel and protects the steel sacrificially
   b. Continues to provide protection even when scratched
   c. Small volume of corrosion products – good for fasteners.
2. **Mechanical properties**
   a. Lubricity – low torque for fasteners
   b. Ductility – coated parts can be formed
   c. Soft – poor wear resistance.
3. **Electrical conductivity**
   a. Good electrical conductivity
   b. Low contact resistance
   c. Solderable.

2.3. Chromate processes

Chromates are used whenever self-healing corrosion protection is needed – i.e. corrosion protection that reseals over damaged areas. While various compounds can do this, the traditional materials are chromates such as zinc and strontium chromates. However these materials do more than provide extra corrosion resistance: they also improve the bonding of paint or other organic finishes (including powder coatings) to metals. Epoxy primer, for example, which does not adhere well to bare aluminum, has very good adhesion when applied over a chromate conversion coating. The better bonding on a chromated surface helps to enhance corrosion protection even more by ensuring the integrity of the paint system. In addition, chromate coatings impart a characteristic color to the surface that is a reliable indicator of the film thickness, and hence the degree of corrosion protection.

Chromating processes are used to treat bulk metal alloys such as steel, aluminum, zinc and magnesium, as well as other corrosion-resistant coatings such as galvanizing on steel and anodized layers on aluminum. When used to supplement the corrosion resistance of a sacrificial coating such as cadmium or zinc, the chromate treatment is often referred to as a sealant. As well as their use in conversion coatings, chromates are often incorporated in paint primers for increased defense against corrosion.

The major applications of chromates are summarized in Table 2-3.

Table 2-3. Major applications of chromate coatings.

Application	Substrate	Purpose
Steel sheet	Electrogalvanized, hot-dipped Zn or ZnAl	Mill passivation, paint base (coil stock)
Fasteners, household hardware (screws, hinges etc.)	Galvanized steel	Corrosion protection, color
Paint primers	Bulk or plated metal (usually steel, Al)	Extra corrosion resistance, paint adhesion
Electrical connectors	Cu, brass, steel	Corrosion protection
Electrical chassis, cabinets	Galvanized steel, Al	Corrosion protection, soldering
Aircraft skins, components	Al	Base for chromated primers, polyurethane topcoats
Aircraft landing gear	Cd-plated steel	Corrosion resistance
Diecastings	Al, Mg, Zn	Corrosion protection
Extrusions	Al	Decorative paint base
Marine environments	Al	Resistance to chloride attack

In common with Cd, chromates are an ESOH problem, not just because of exposure during the initial coating process, but also because of continued uncontrolled exposures of maintainers throughout the life of a weapons system, especially during corrosion control and paint touch-up operations.

3. Alternatives to hard chrome plating

A great many coatings have been claimed to be “hard chrome alternatives” but there are not many that meet all the criteria for more than a niche product. Simply being hard and wear resistant does not make a coating a hard chrome alternative. For general use as a hard chrome replacement it must meet the criteria of Table 3-1. For more restricted or niche use, it need only meet the requirements for that application.

3.1. Hard chrome replacement criteria

Table 3-1. Hard chrome replacement criteria.

Issue	Criteria	Notes
OD and ID coating requirements		
Coating thickness	OEM: 0.003” – 0.015”	
Smoothness	16μ” Ra typical, some replacements may need to be 4μ” Ra	Highly useful to be able to be able to deposit thin coatings to replace thin dense Cr, without need for grinding. (As-deposited Ra<8 μ”.)
Deposition temperature	High strength steels: <375°F (190C) Aluminum alloys: <300°F (150C)	Critical issue is time-at-temperature. Critical issue is fatigue reduction due to changed surface microstructure.
Dimensions	Aircraft: ½” to 15” OD, ½”-7” ID, 2”-60” long Ships: up to 36” OD, 15 feet long	Ability to coat outside and inside diameters important
Hole geometry	Open, blind, some internal grooves	
Technical issues		
Wear resistance and hardness	Match performance of chrome on actual components	Critical issue is wear life (wear rate x thickness) in service, and avoidance of seal wear in hydraulics
Corrosion resistance	Must match chrome - primarily B117 salt fog, Naval requirement FG85 SO_2 salt fog	Microcracks make chrome a poor corrosion inhibitor - may require sealer or Ni underlay.
Hydrogen embrittlement	None	This is a critical safety issue with high strength steels
Fatigue	Fatigue debit must not exceed chrome	Some debit usually allowed for
Producibility		
Reproducibility	Process must be stable	Both OEM and O&R environments
Cost	Life-cycle cost < chrome Reasonable capital cost	Production cost includes cleaning, masking, finishing, heat treating, waste disposal, etc.
OEM and O&R fit		
Stripping	Must be able to be stripped - safe chemicals, water jet, etc	Strippability is crucial to O&R.
Field and O&R chemical stability	Must withstand O&R cleaning, chemicals, hydraulic fluid, etc.	Must not deteriorate when put through O&R process
Environment/safety	Must be environmentally benign and safe for workers	Note that O&R operations are more diverse and less easily controlled
Acceptance issues		
Specifications	AMS and/or aircraft company specifications needed	Cannot be specified and put on drawings without specs.
Proprietary technology	Cannot be proprietary to one company	If possible, should be able to be done at general O&R site to avoid sending out

3.2. Summary of hard chrome alternatives

Table 3-2 shows the most commonly used chrome alternatives.

Table 3-2. Summary of chrome replacement alternatives.

Technology	Principle	Capabilities/Notes	TRL OD	TRL ID
Wet plating				
Electroless Ni and Ni composites	Electroless Ni-P/B (+ SiC, Teflon, diamond, etc), Amplate	Ni-P, Ni-B, and particle-filled alloys. Ni-B contains some Pb or Tl. Good ID alternative. Must heat treat for hardness	9	9
Electroplated Ni and composites	Electroplating, some with hard particles	Not as hard as chrome. Particles can pose production issues	4	4
Nanophase Co-P	Pulse plating	Softer than Cr, must heat treat for hardness	4	4
Trivalent chrome	Trivalent plating chemistry	Varying success, some must be brush plate	3	3
Alloy plating	Electroplating of simple alloys	Ni-W-B, Co-W. Little used	4	4
Co-composites, Tribomet®	Co electroplate + Cr_3C_2 particles	Co alloy, proprietary. Only used for GTEs	9	N/A
Thermal spray				
HVOF	Powder + high temperature flame	Primary OD alternative. WC-Co(Cr), alloys	9	>11” ID
Plasma spray	Powder + plasma	1.5” ID, WC-Co, alloys, metals	4	>1.5” ID
Cold spray, supersonic spray	Powder in high velocity gas stream	Dense coatings, mostly soft metals. Hard coating deposition unproven.	3	N/A
Weld coating				
Electrospark Deposition/ Alloying (ESD/ ESA)	Microarc welding	Localized repair of non-fatigue-critical components. Low deposition rate, portable. Not a coating replacement	5	4 (>1/2”)
Explosive cladding	Explosive bonding	Metals, Ta being evaluated for gun barrels	N/A	3
PVD/CVD				
Post-magnetron sputtering	Sputtering from high current rod or flat target	Metals, alloys, nitrides; Ta (Army). Scaled for large gun barrels. 0.008” thick		Development/ large dia
Flat target sputtering	Sputtering from target	Primarily nitrides, carbides	3	N/A
Ion Beam Assisted Dep	PVD with ion beam	Metals, nitrides. Low build	3	N/A
Hollow cathode evaporation	Small internal hollow cathode	Diamond-like carbon. Low build	N/A	3
CVD, MOCVD, plasma CVD	Deposition from gas	Very small, long holes. High temperature/dangerous precursors	2	2
Combustion CVD	Precursors combined in flame	Compounds (oxides, etc). VOC solvents used	3	N/A
Other methods				
Plasma, gas nitride	Nitriding at about 500C	Surface treatment (no build-up, high temperature)	9	N/A
Laser deposition	Laser evaporation, alloying, and CVD	Diamond. No build-up	3	N/A
Laser Induced Surf. Improvement (LISI)	Laser alloying	Alloys with surface material (not coating). No build-up	3	N/A
In production	Advanced development	Development	R&D	

3.3. Alternative electro- and electroless plates

Alternative electroplates and electroless plates are obviously the closest to drop-in alternatives since they use the same basic technology and can therefore in general be done on the same components.

Electroless Ni is often cited as a good chrome plating alternative because its hardness is in the same range (900-1,100 VHN, or up to 1,200 VHN for Ni-B). Unfortunately these hardness values are only achieved by heat treating at 400°C, well in excess of the 375°F allowed for structural high strength steels, and too high a temperature for many other structural alloys. As-deposited, the hardness is typically 500-750°C, and the abrasion resistance is significantly less that that of hard chrome.

For internal diameters and other low-stress areas, however, the highest hardness is not usually needed, and electroless or electroplated Ni is often used for IDs of aircraft landing gear outer cylinders and other hydraulics. Maintenance of electroless plating bath chemistry is much more critical with than for hard chrome baths, since electroless baths must maintain a delicate balance of keeping the metal salts in solution, yet autocatalytically depositing on substrates placed in the bath.

A variety of electroless Ni composites are available commercially. Some contain hard particles such as diamond or SiC for wear and/or PTFE for lubricity. For example, NiPlate 700, which AFRL has identified as the best ID chrome alternative, contains SiC particles. Process control and uniformity are always more difficult when using particle-filled plates. In the past electroless Ni was self-limiting to a thickness of about 0.001", but this is no longer the case with most modern formulations.

There are several commercial and near-commercial electro- and electroless plates:

- ☐ Alloy electroplates such as Ni-W-B, W-Co and Ni-W-SiC (the Takada process). Some of these are being evaluated as chrome alternatives. Boeing evaluated the Takada process extensively but ultimately rejected it because it was too hard to obtain uniform SiC content and the SiC particles caused rapid erosion in the air handling system.
- ☐ Co-Cr_3C_2 composite (Tribomet) is used almost exclusively on turbine engine components, and is available only from Praxair's UK plant..
- ☐ AFRL has been evaluating various Ni composite and alloy plating technologies for IDs. Some of these, such as the primary candidate, NiPlate 700, are composites and some are alloys or nanophase materials.
- ☐ Nanophase Co-P is a coating developed by Integran Technologies under a SERDP program[3], that is being validated in an ESTCP program[4] at NADEP JAX as a chrome alternatives for IDs. This is a pulse plating technology that relies for its hardness on the creation of a nanophase grain structure.

There is debate on the acceptability of Ni plating since some localities (notably CA) regulate Ni salts and emissions, and Ni is regarded as being more problematic in Europe. The same will doubtless become true of Co, W and other chemistries as they begin to move into the mainstream of plating technology.

3.3.1. Trivalent chrome plating

Trivalent chrome chemistry is widely used for decorative chrome plating, but it is not capable of producing thick, hard coatings. A great deal of R&D worldwide has gone into developing a trivalent chrome chemistry that could replace today's hexavalent chrome. The results have been mixed and no clear drop-in alternative has emerged:

- ☐ A worldwide Ecochrom team led by the French Bureau des Mines has been developing and evaluating various trivalent approaches. While one or two approaches appear promising, none was a clear drop-in alternative. Some required heat treating to achieve high hardness.
- ☐ A pulse tank plating technology has been developed by Faraday Technology, while a brush plating technology has been developed by LDC.

There is also debate on whether trivalent chrome alternatives are acceptable. The EPA and OSHA regulations are clearly concerned only with Cr^{6+} air emissions, but both Cr^{6+} and Cr^{3+} wastes must be disposed of as hazardous wastes. Consequently, while some users would consider trivalent plating ideal others do not distinguish between trivalent and hexavalent technologies and regard all chrome plating as unacceptable.

3.4. Thermal sprays

Thermal spray is a coating method in which a coating material, usually in the form of a powder or wire, is heated in a flame or plasma and fired onto the surface entrained in a high-velocity gas stream. Of the thermal spray processes, High Velocity Oxy-Fuel (HVOF) coatings have the highest quality and best performance.

HVOF composite coatings (usually WC-17Co or WC-10Co4Cr) are generally regarded as the method of choice for replacing hard chrome on ODs of aircraft components such as landing gear inner cylinders and hydraulic actuator rods. All new commercial and military landing gear programs now specify HVOF instead of hard chrome on most wear areas (the inner cylinder OD, bearing journals, and associated actuator rods). Commercially, large hydraulic actuator rods are now being made by Caterpillar with an HVOF Cr_3C_2 composite coating, and this same material is increasingly being offered as a rebuild coating for actuators on off-road and mining equipment.

HVOF technology has been validated and qualified by the Hard Chrome Alternatives Team (HCAT) under a series of ESTCP-funded projects.[5,6,7,8] The final reports and many other reports and briefings can be found on the Hazardous Material Alternatives portal at www.hazmat-alternatives.com under DoD Programs/DoD Reports/Chrome Alternatives. The extensive materials test data on ongoing projects can be obtained at the HCAT Teaming Website at www.materialoptions.com.

HVOF wear performance is significantly better than hard chrome and the corrosion performance in service is also better (although B117 test performance is usually worse). The only respect in which HVOF coatings are known to be inferior to hard chrome is in their performance under high strain. HVOF carbide coatings are more brittle than hard chrome and have a strain-to-failure of about 0.7%. When cycled at strains approaching the yield point of high strength steel, the coating will crack or spall. When cycled in-service at far lower strain for times approaching fatigue run-out (typically 10^6 cycles), HVOF coatings often develop circumferential cracks at the highest tensile strain points of landing gear cylinders or journals. This has not been found to cause either substrate fatigue or corrosion, but would be grounds for stripping and recoating.

HVOF can be used for IDs where the ID can be reached from outside at an angle of no more than 60° off-normal. It cannot be used for deeper IDs. Plasma spray coating with the same materials can be used for IDs>1.5”, although the coating performance is not as good as HVOF, and is typically similar to that of hard chrome.

Thermal sprays can be used for small components such as snubber rods, as well as for very large components such as hydraulic rams for ships. For most components turnaround times are significantly shorter than for hard chrome because the process itself is fast (typically 30 min spray time for a landing gear inner cylinder) and there is no need for a hydrogen bake. However, unlike chrome plating, the larger the component the longer the process time. Because the coating technology and materials are both very different from hard chrome HVOF coatings require different processes or conditions for masking, grinding, finishing and quality control.

Ogden ALC is currently in the process of replacing chrome plating with HVOF WC-Co throughout the depot. HVOF is also used in a more limited way at NADEPs Jacksonville and Cherry Point.

3.5. Vacuum coatings

Various very hard PVD and CVD coatings have been put forward as general-use chrome alternatives, including TiN, diamondlike carbon and WC (Hardide). While these types of coatings are widely used commercially (TiN for dies, molds and drills, diamondlike and WC-C carbon for diesel fuel injector rods, PVD ZrN for “lifetime coatings” on faucets and door hardware for example) most of them are suitable only for niche products. In general CVD coatings require too high a temperature for use on structural alloys and all of these types of coatings are limited by the size of the chamber and the cost of the process. Most present DoD applications of these types of coatings are as thermal barriers on turbine blades, which are not recoated in depots. There is a current SERDP project on CVD Ta for gun barrels[9].

Wear resistant PVD and CVD coatings are generally very thin (a few microns) and are very expensive to deposit to high thickness. Some of the hard PVD nitride and carbide coatings have highly compressive residual stress and will spall if made more than a few microns thick, so that they cannot be used for rebuild. Vacuum deposition equipment used for hard coating (which is much more complex than IVD Al equipment) is not in general suitable for factory or depot use, and must be run by specialist companies.

There is some usage of coatings such as TiN on aircraft components such as engine bearing races and APU components. Potentially they may be cost-effective for small components that wear and are remove and replace items rather than repair components, such as small hydraulic rods, hydraulic spool valves and pumps.

Ion beam assisted deposition (IBAD) is frequently put forward as a chrome replacement. In terms of performance it can be better than standard plasma PVD. However, it combines the complexities both of PVD deposition and of ion beams, and cannot be used for rebuild, making it unsuitable for most depot use. It is being used in production to deposit hard, multi-layer erosion-resistant coatings on turbine blades for helicopter engines (a Russian process carried out commercially for GEAE).

The only DoD uses of vacuum coatings as a chrome alternative that we are aware of are:

- ☐ B-2 bomb bay door manual lockout – DLC used for hardness and lubricity.
- ☐ PVD Ta on the ID of gun tubes for tanks and large guns, developed by Benet Labs[10]. This is at the full-scale demonstration stage, but is not yet in production. This is obviously an important application for DoD, but it is not a general ID chrome replacement, although it may be a viable approach for thick ID coatings, primarily for certain OEM applications.

3.6. Laser processes

As the power, stability and simplicity of lasers have improved in recent years, they have begun to be used for materials processing. Laser cladding is the general name for a method of coating in which coating material is brought to the surface (usually in powder or wire form) and melted (or welded) onto the substrate using a high power laser such as a Nd-YAG or CO_2.

Laser cladding requires sufficient surface heating to weld the materials together, which means that the surface heat treat is modified by the process, leaving a heat-affected zone beneath the coating. The coating tends to be very rough, with a “ploughed field” effect of raised strips of weld material.

Because of the surface temperature, laser cladding tends to be used for high temperature materials such as turbine blade alloys. For example, the method is used for rebuilding the tips of some hot section turbine blades. It is not easy to set up the correct processing parameters, but once they are determined the method can be very reliable.

Although it has been put forward as a chrome replacement, its processing temperature at the surface makes it unsuitable for most structural applications in which hard chrome is used.

3.7. Weld coatings

Weld coatings are used quite widely in agricultural and industrial equipment for wear control. However, they are not generally suitable for replacing hard chrome because they are rather crude, thick and require high temperature.

Recently a microwelding process, electrospark deposition, ESD (or electrospark alloying, ESA), has been validated as a localized repair technology[11]. It is used by Rolls Royce Aircraft Engines for in-factory repair of non-fatigue-critical components, and repair methods using it have been developed by Anniston Army Depot for corroded Abrams gun cradles and a gear shaft.

Because of its very low deposition rate (mg per minute), it cannot be used, as hard chrome is) for large area coating, but it is a simple method for repairing localized damage in components and coatings resulting from corrosion, scratching and impact.

Explosive welding or bonding is a method for joining dissimilar metals. It is being evaluated as a potential alternative to chrome plating in the IDs of medium caliber gun barrels[12], which cannot be coated by PVD.

3.8. Heat treatments

Heat treatments such as nitriding and carburizing are widely used industrially (in fact most gears in military equipment are carburized, as they are in most commercial equipment). However, they are only suitable for OEM use as the high processing temperatures (typically 500°C or above) require a post-processing heat treat in most cases. Furthermore, they cannot be used for rebuild. Nitride treatments are used for some components, such as gun barrels.

4. Alternatives to cadmium plating

Cadmium plating is used where sacrificial corrosion protection is needed. As with hard chrome alternatives, many corrosion protection coatings are put forward as "Cad alternatives" that are not in sacrificial, but are simply barrier coatings such as Ni or ceramics.

Cadmium alternatives are currently under evaluation by the Joint Cadmium Alternatives Team (JCAT) under an ESTCP program[13].

4.1. Cadmium plate replacement criteria

There are three principal applications for Cd, each of which has different requirements:

1. **Components**

   These include almost any exposed item that must be protected from corrosion, including steel landing gear components, hydraulics, drive-screws, etc. Corrosion resistance and paint adhesion are critical to these applications.

2. **Fasteners**

   These are primarily rivets, washers, bolts, and screws, especially in exposed locations. Most threaded fasteners are made of high strength steels and are easily embrittled. Well-defined lubricity and torque-tension characteristics are critical for threaded fasteners. In turbine engines, most Cd-plated fasteners can be replaced by high strength stainless steel fasteners,[14] but stainless steel fasteners cannot be used for most airframe or other aluminum alloy structures because they severe galvanic corrosion in contact with aluminum.

3. **Electrical connectors**

   These are primarily connector bodies, or shells, that surround multi-pin connectors, or plugs, used to interconnect electronic equipment. Long-term low electrical resistance, ability to survive lightning strikes, and avoidance of insulating corrosion products are essential for this application.

Cadmium plating is governed by the following specifications:

- ☐ QQ-P-416 - Federal Specification for Cadmium Plating on Low and High Strength Steel up to 200,000 psi.
- ☐ BAC 5701 - Boeing specification for Cadmium Plating on Low Strength Steel.
- ☐ DPS 9.74 - Douglas Process Specification for Cadmium Plating.
- ☐ AMS 2400 - Aerospace Material Specification for Cadmium Plating.

The Federal specification for cadmium, QQ-P-416, defines classes and types of cadmium as in Table 4-1.

Table 4-1. QQ-P-416 Classes and Types of electroplated Cd.

Class	Thickness	Type	Finish
1	0.0005”	I	As deposited
2	0.0003”	II	Chromated
3	0.0002”	III	Phosphated

Cadmium provides the following properties to plated surfaces:

- **Corrosion resistance**
    - Cd is more electronegative than steel, which it protects sacrificially
    - Continues to provide protection even when scratched
    - Small volume of corrosion products – good for fasteners.
- **Mechanical properties**
    - Lubricity – consistent, low torque for fasteners
    - Ductility – coated parts can be formed
    - Soft – poor wear resistance.
- **Electrical conductivity**
    - Good electrical conductivity
    - Low contact resistance
    - Solderable.

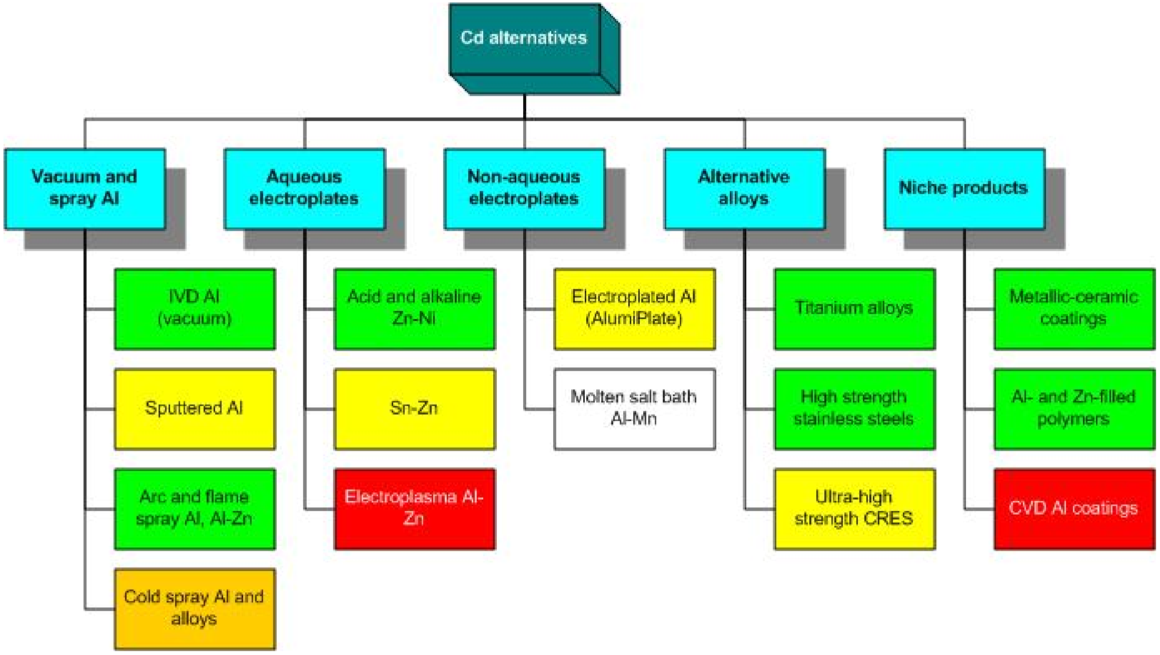

Figure 4-1. Families of Cd plating alternatives.

4.2. Summary of Cadmium alternatives

It is clear from the galvanic series of Figure 4-2 that there are very few materials that can provide galvanic protection similar to that of Cd, the most common being Al, especially for high strength steels, and Zn for low strength alloys.

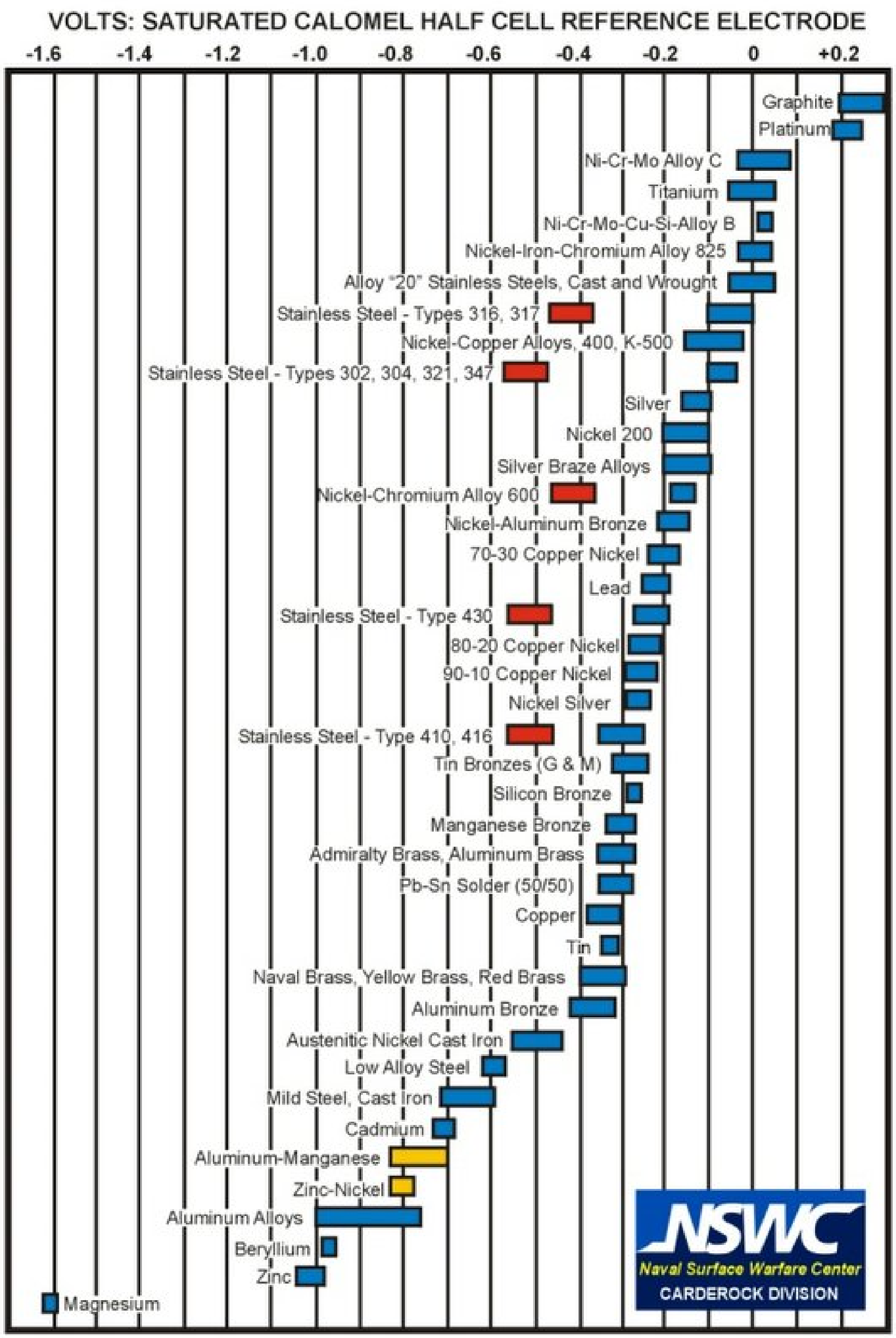

Figure 4-2. Galvanic series in seawater (NAWC-CD).

Table 4-2. Summary of Cd replacement and other corrosion resistant alternatives.

Technology	Principle	Capabilities/Notes	TRL OD	TRL ID
CRES Alloys				
Titanium alloys	Ti alloys, commonly Ti-6Al-4V	Lower weight, cost and volume penalty	9	9
15-5PH, 13-8Mo, etc	Precipitation-hardened steels	Lower strength than 4340, 300M	9	9
Stainless steels	A286, 400 series, etc.	Fasteners	9	N/A
S53 ultrahigh strength CRES	Computationally designed CRES	Mechanically same as 300M, somewhat less corrosion resistant than 15-5PH	4	N/A
Vacuum Al				
IVD Al	Al evaporation with weak plasma	Widely used for aircraft components	9	N/A
Sputtered Al	Sputtering with intense plasma	Commercial equipment available	N/A	5
CVE Al	Chemical vapor deposition	Relatively high deposition temperatures	3	3
Spray Al				
Wire arc spray and flame spray Al, AlZn	Thermal spray	Excellent for large structures, vehicles, ground support equipment. Some aircraft usage	9	N/A
Cold spray	Al powder + high velocity gas	Under evaluation for Mg, steels	3	N/A
Electroplates				
Zn-Ni	Acid and alkaline aqueous	Aircraft, vehicles	9	9
Sn-Zn	Brush or tank	Not as good as Zn-Ni, good for brush plate repair	5	5
Al (AlumiPlate)	Non-aqueous, toluene bath	Excellent performance, cost and ESOH issues	6	5
Electroplasma Zn-Al	High voltage aqueous plating	Zn-Al alloys, not pure Al	2	2
Al-Mn	Molten salt bath	Good performance but problems - abandoned	4	N/A
Other methods				
Al and Zn filled polymers	Spray and dip-spin	Standard for automotive fasteners	9	9
Metallic-ceramic coatings	Spray or paint Al particles in ceramic matrix	SermeTels and equivalents	9	9
In production	Advanced development	Development	R&D	

4.3. Aqueous electroplates

Acid Zn-Ni was developed by Boeing[15] and has been qualified and used in aerospace for some years. Depots such as WR-ALC use Zn-Ni in place of Cd plating. Recently alkaline Zn-Ni has become the preferred chemistry and appears to cause less hydrogen embrittlement. It is under evaluation by the Joint Cd Alternatives Team (JCAT).

Sn-Zn has been put forward for some applications where better lubricity is needed. However, the deposit is not a true alloy, but can have regions of high Sn, which may pose problems of Sn whisker growth in some electronics applications.

However, Boeing has found that it is easier to brush plate using Sn-Zn than using Zn-Ni, making it easier to repair damaged Zn-Ni by using Sn-Zn.

A new process is currently under evaluation called ElectroPlasma Processing (EPP)[16]. This process is a high voltage electrochemical process similar to the Keronite process. It is possible in principle to use it to deposit alloys such as Zn-Al that cannot be deposited by standard electrochemical processing.

4.4. Non-aqueous electroplates

AlumiPlate is pure Al electroplated from an $AlCl_3$ plus toluene bath[17]. The process is aprotic (does not produce hydrogen) and is done in a completely enclosed plating line under an inert atmosphere. This eliminates oxygen, which interferes with the process, but it also prevents emission of toluene vapor.

For many applications it has proved to be the best Cd alternative:

- The quality of the coating is very high – typically better than any other electroplate.
- In corrosion testing it usually outperforms other coatings.
- Because the process is aprotic it does not cause embrittlement (in an early test that showed embrittlement the problem was found to result from stripping the coating, not from applying it).
- In the JCAT evaluations of Cd alternatives it has been the only alternative to completely avoid hydrogen embrittlement.
- It has proved to be the best alternative for steel connector shells in Lockheed testing for the F-35, and is now available on Amphenol connectors.

However, the method does have significant drawbacks for wide DoD use:

- The capital cost is high (several million dollars) because of the requirement for an enclosed plating line.
- The use of a toluene bath precludes its installation on most depots.
- The current deposition system at AlumiPlate is small (20”x23”x31”), and can just fit an F-22 landing gear inner cylinder.
- The process is sole-source from AlumiPlate Inc.

It is important to remember that any Al coating must not be treated with strong alkali cleaners or other chemical that cause Al dissolution, either in depot maintenance or in the field, since these chemicals damage the coating and can also cause embrittlement of the underlying steel.

Molten salt bath electroplating is another method for depositing metal coatings that cannot deposit from aqueous baths. An Al-Mn coating method has been developed under ESTCP funding[18], but failed to meet requirements in depot testing at NADEP-NI, and has been abandoned.

4.5. Corrosion resistant alloys

Perhaps the most widely-used alternative is the use of corrosion resistant (CRES) alloys in place of Cd plated steels:

- Titanium alloys are primarily used in aircraft because of their obvious weight advantage. Some aircraft landing gear, actuators, and components such as flap tracks are made of Ti alloys.

- Almost all new aircraft actuators are now made of 15-5PH stainless steel rather than the Cd-plated 4340 steel used in many legacy systems.
- Other precipitation hardened CRES alloys are used for structural components, including PH13-8Mo.
- Many fasteners are made of Ti alloys and stainless steels, such as A286 and 400 series stainless steels.
- A new high strength stainless steel called S53, developed under SERDP funding[19] by QuesTek Innovations, is currently being validated under ESTCP funding[20,21] at OO-ALC. This alloy has the mechanical properties of 300M (280 ksi UTS, 225 ksi yield).

4.6. Vacuum processes

The most widely used and fully qualified alternative to Cd plating is IVD Al (Ivadizing), which was developed by McDonnel Douglas Corp. IVD is quite widely used on aircraft components and fasteners, and several depots are equipped with IVD chambers. The process is done in a large vacuum chamber and involves evaporating Al in the presence of a weak plasma. After deposition the surface must be glass bead peened to densify the coating because the plasma is too weak to obtain a high-quality, low porosity structure.

IVD coatings do not have the throwing power to coat internal diameters. For this reason Marshall Labs developed the Plug and Coat system for sputtered Al. This is a sputter deposition rod that inserts into the ID of a component such as a landing gear and operates inside the IVD chamber. This approach has been validated at Hill AFB by Boeing, and Hill is the only location where it can presently be done on a commercial basis. The C-17 program is considering adopting the method for coating the IDs of C-17 landing gear at the OEM level.

The sputtered Al coatings are fully dense and do not require peening. However, this system is designed for ID sputtering, and it does not easily translate into an efficient OD coating method because of the difficulty of scaling the plasma for adequate coverage and uniformity.

Other vacuum methods include CVD Al. There is an ongoing SERDP program to develop CVD Al[22] and there is a commercial process developed by Liburdi Engineering for coating the IDs of cooling channels in turbine blades. Pure thermal CVD processes require high temperatures (typically 500°F), and depositing at lower temperature requires resorting to plasma assistance or expensive organometallic precursors.

4.7. Spray processes

Al and Al alloys can be deposited very effectively by thermal spray and cold spray methods:

- Arc spray – Spraying from an electric arc between two wires of the alloy blows molten droplets of the material at high velocity onto the substrate.
- Flame spraying – Similar to arc spraying, but using a flame and feeding the alloy in as a powder.
- Cold spray (kinetic spray, supersonic particle deposition) – The powder is fed into a high velocity cold or warm gas stream and accelerated to a velocity high enough to forge the particles into a coating on the

substrate.

Flame spray Al is used on some commercial aircraft landing gear in place of Cd. The major uses of arc spray are large structures such as bridges, communication towers, concrete piers, and vehicles such as aircraft ground support vehicles. The alloy usually used for this is 80-85%Zn/15-20% Al. For example, Patrick AFB in Florida, which is on a narrow spit of land next to the ocean, uses arc spray to protect panels on ground support vehicles. NASA has had great success with a similar approach for communication towers on islands and other high corrosion areas.

There is an ongoing ESTCP program[23] coordinated with a JSF JPO funded Australian program to dem/val cold spray for corrosion resistant coating of lugs and other high-corrosion areas of Mg gearboxes for helicopters and the F-35.

4.8. Paints and polymers

Metallic-ceramic coatings[24] are ceramic coatings incorporating Al particles. They are painted or sprayed on and then baked (375-700°F) to cure. They are usually grit blasted to reveal the Al that provides sacrificial protection, and overcoated with a sealer layer that traditionally contains chromate. These coatings used to be available only from Sermatech Inc. under the SermeTel tradename, but are now available from several companies (Alseal, Ipcote, etc). In order to eliminate the Cr^{6+} component most manufacturers have recently developed low Cr^{6+} or non Cr^{6+} formulations. Some of these perform better than others, and some may not meet the performance of chromated systems. An ongoing PEWG project is attempting to establish their relative performance[25].

The unique feature of these coatings is that they are the only coatings commonly available that combine corrosion protection with erosion and wear protection. All other sacrificial coatings (Zn, Al, Cd, etc.) are soft. Since they were originally developed for use in turbine engines they have excellent high temperature and oxidation resistant properties.

The F-22 program adopted SermeTel 984/985[26] coatings in place of Cd on the landing gear. Hydrogen embrittlement has been reported as an apparent problem in both the F-22 and the Sikorsky Comanche helicopter, due to hydrogen embrittlement from attack by acids in the formulation. SermeTech is reported to have reformulated the product to eliminate this problem, but since these older products are now being replaced, embrittlement will have to be re-evaluated in testing the new Cr^{6+}-free formulations.

In response to the European ELV regulations, most automotive companies have now eliminated Cd and chromate conversion coatings from cars, including from all of the fasteners. Automotive fasteners are now almost universally coated with a metal-filled polymer (typically PTFE or epoxy filed with Zn or Al particles or flakes) using a simple dip-spin process. The coating may be deposited directly onto the steel, but it is often deposited onto a Zn coating. Army testing evaluated a number of these formulations and found the best at that time was Dorrltech, which is now known as Magni 555. Many other similar coatings exist such as Dacromet and Geomet.

There is a recently-completed SERDP-funded program evaluating the use of conducting polymers as a Cd replacement[27].

5. Alternatives to chromate conversion and chromic acid anodizing

In the US, exposure of personnel to chromates is covered under OSHA rules, and the permissible exposure limit (PEL) for Cr^{6+} has now been lowered an order of magnitude to $5\mu g\ m^{-3}$ 6hr TWA. Although personnel are exposed during D-level chromating and painting processes, the more serious problem is the uncontrolled exposure during O-level corrosion control and paint touch-up operations.

Chromate conversion coatings are under a great deal of pressure from the European ELV, WEEE and RoHS rules, which forbid the use of Cr^{6+} in any “homogeneous material” in a concentration in excess of 0.1 wt%. Since the definition of a homogeneous material encompasses coatings, these rules ban chromate conversion layers on vehicles and electronic equipment. Even though military equipment and aircraft are exempt from these rules most COTS items are covered by them, and it is in any case probable that the exemptions will be removed once reliable alternatives are proved to exist.

These twin drivers are leading DoD to attempt to eliminate all chromate processes used in metal finishing.

5.1. Chromate conversion processes

Chromate conversion coatings are also often termed passivation layers or sealers. They are produced by chemical or electrochemical treatment of metal surfaces with mixtures of Cr^{6+} compounds (salts containing hexavalent chrome in the chemistry Metal-CrO_3 such as strontium chromate, zinc dicrhromate, etc.) and other chemicals known as activators. As a result of the chemical attack that occurs, some of the surface metal dissolves (typically 50 microinches, or $1\mu m$), forming a protective film that consists of a complex mixture of Cr^{6+} and Cr^{3+} compounds with the base metal. Thus chromate conversion coatings are not coatings in the traditional sense, but chemical conversions of the metal surface.

Historically, chromate conversion coatings have dominated other types of conversion coating such as phosphate treatments. This is because Cr^{6+} coatings are very thin (with typical thicknesses in the microinch range), inexpensive to produce, can readily be adapted to different processes, and can be applied by immersion, spray or wipe techniques.

Chromates have the unusual property of affording corrosion protection even when scratched or damaged. They do this by going into solution in the corrosive environment, migrating to the exposed bare metal surface, and forming complexes to inhibit further corrosion. In addition, chromates often form good bonding layers, improving the bond between a paint system and a surface, which also helps to improve corrosion resistance. Consequently chromates are widely used as inhibitors and sealers wherever corrosion is a serious concern, especially where damage to the surface coating is quite likely, and they provide further corrosion resistance by improving the adhesion of paints.

Examples of the use of chromate conversion coatings include

- ☐ Aluminum and magnesium alloys are typically chromate converted to resist chloride attack in marine environments
- ☐ Sacrificial corrosion resistant coatings on steels (such as Cd, Zn, Al) are frequently chromate converted to supplement the corrosion resistance of the sacrificial coating. This type of chromate treatment is often termed a

"sealer".

- Phosphate passivation coatings on steels are typically chromate sealed
- Primers and paints
- Metal surfaces are commonly chromated prior to painting to enhance paint adhesion
- Paint primers often contain chromates so that if scratched they will continue to protect the surface.
- Metal-ceramic paint systems used on aircraft engines are usually finished with chromate-containing sealing layers for corrosion resistance.

Typical applications of chromates:

- Galvanized steel sheet
- Galvanized and Cd-plated fasteners – fasteners and other components are often color-coded for corrosion resistance (Table 5-1), since different thicknesses of chromate layer give different colors, and thicker layers provide better corrosion resistance.
- Painted steels used in corrosive service
- Aircraft skins and structural members made of aluminum alloys
- Magnesium alloy components such as gearbox housings used in aircraft
- Cadmium plated aircraft landing gear
- Electrical connectors and cabinets with predictable surface resistance and continuity characteristics and ability to be soldered
- Castings and extrusions.

The color of a chromate coating, which is due to thin-film interference, varies from clear-bright and blue-bright for the thinnest films through olive drab to matte black for thick films. Film thickness is usually expressed in mg/m^2 of total chromium: clear chromate coatings are about 400 mg/m^2 thick, yellow chromate about 1000 mg/m^2. Table 5-1 shows typical thicknesses for various colors.

Table 5-1 Chromate film comparison (MacDermid, Inc.). Yellow shaded cells are trivalent chrome.

Color	Film thickness µin (nm)	Cr^{+6} content (mg/m^2)	Total Cr (mg/m^2)
Clear (Cr^{3+})	1-3 (25-75)	<0.1	30-40
Iridescent (Cr^{3+})	10-20 (250-500)	<0.1	100-180
Iridescent (Cr^{6+})	10-20 (250-500)	80-220	200-460
Green (Cr^{6+})	10-40 (250-1000)	80-400	1000-1800
Black (Cr^{6+})	10-40 (250-1000)	80-400	1000-1800

5.2. Chromic acid anodizing and passivation

Anodizing is an electrochemical process in which a metal is immersed in an acid and made anodic (used as the positive electrode) in a low voltage DC circuit. The process grows an oxide layer that is self-limiting. This makes it possible to treat complex shapes, where holes and other difficult areas can be treated for the long periods required for full anodization without forming too thick a coating elsewhere. The oxide layer that the process forms on the surface provides better resistance to abrasion and corrosion. In addition, anodized layers can be dyed to provide color. Anodizing is most commonly used on Al, Mg and Ti.

Chromic acid passivation is used on stainless steels to create a thick oxide layer at the surface (thicker than the layer that grows naturally on these alloys), which enhances their corrosion resistance. Stainless steels are typically passivated, primed and painted.

Note that, unlike chromate conversion, chromic acid anodize and passivation layers do not contain any Cr^{6+}. Thus, while they are an OSHA concern for the workers applying them, they pose no ESOH issues for downstream users.

5.3. Summary of chromate alternatives

There are a great many chromate alternatives that are now commercially available (Table 5-2, note that this is not an exhaustive list). Some of these are not strictly drop-in alternatives that create similar surface properties, but are completely different ways of achieving improved corrosion resistance, such as anodized layers or paint adhesion promoters. Note that one of the most successful alternatives is the tri-chrome pretreatment (TCP) developed by NAVAIR and licensed to various companies.

Table 5-2. Commercial non-chromate alternatives for bulk Al and Al coatings.

Substrate	Process	Chemistry	Comments
Alternatives to chromate conversion coatings			
Al	TriChrome Pretreatment (TCP)[*] – AnoChem TCP, Aluminescent, TCP-HF	Trivalent Cr^{3+} conversion with Zr inhibitor	Developed by NAVAIR Light blue iridescent color
Al	Other Cr^{3+} treatments	"	"
Al		"	"
Al		"	"
Al	Alodine 5200/5700[*]	Non-chrome, Zr conversion	Alodine 5200 for nonferrous alloys, 5700 specifically for Al Light tan iridescent color
Al	Safegard CC-3400	Non-chrome, permanganate conversion	For Al, Mg, Zn
Al	Oxsilan AL-0500	Non-chrome, silane conversion	For Al, Mg, galvanized steel
Al	Dorado Kote #7	Non-chrome conversion	Gold-to-purple iridescent
Al	EMC	Silicate	Electrolytic
Al	AC-130, AC-131[*]	Sol-gel coatings, organo-siloxanes and zirconates	Developed by Boeing Clear and colorless
Al	PreKote[*]	Organic adhesion promoter (not a conversion coating)	Poor bare corrosion resistance Minimal color change
Steel, Zn	Various	Phosphate (without usual chromate sealer)	Not as corrosion resistant as chromate
Anodizing alternatives for Al and Mg alloys			
Al, Ti (in development)	Keronite (for Al alloys)	Plasma electrolytic oxidation (high-voltage anodizing)	Corrosion and wear resistance - fused alumina layer
Mg	Tagnite	Plasma electrolytic oxidation (high-voltage anodizing)	Corrosion and wear resistance - fused oxide layer
Mg	Anomag	Low ac voltage anodization	Corrosion and wear resistance
Al	Thin film sulfuric anodize	Sulfuric acid	Qualified for most NAVAIR applications
Al	Boric-sulfuric anodize	Sulfuric + boric acid	

[*] Ranked best in NAVAIR testing

5.3.1. Alternatives for galvanized steel

Manufacturers that use galvanized steel will not be able to meet the European RoHS rules unless they eliminate the use of chromates. As far as we know there are no US steel producers that offer chromate-free galvanized steel. Only Japanese steel companies are meeting this requirement at this time (see Table 5-3).

Table 5-3. Commercial chromate-free galvanized steels.

Product	Company	Comments
Eco-Frontier Series	JFE Steel	Electrogalvanized, 6 grades available Organic composite coating with both barrier and self-healing properties
Zinkobella Greencote GX	Kobe Steel	Electrogalvanized Inorganic composite coating, probably molybdate conversion
Greencote GX-GC	"	Hot-dip galvanized Same coating as electrogalvanized
Zinkote 21	Nippon Steel	Electrogalvanized Zn-Mg phosphate coating
Moonstar Zinc	Nisshin Steel	Electrogalvanized
ALSTAR	"	Hot-dip aluminized stainless steel

For zinc coated fasteners and vehicle components there are a number of commercially available trivalent chrome alternatives. In particular, several of the same chromate alternatives used for are also sold for use on Zn.

5.4. Trivalent chrome conversion

The most obvious drop-in for hexavalent chromate is trivalent chrome. However, Cr^{3+} solutions by themselves are not good corrosion inhibitors since the inhibition process depends on the Cr^{6+} ion. Thus the most successful Cr^{3+} alternatives include other inhibitors such as molybdates or zirconates.

Of these some of the best overall performance has been measured for trivalent systems based on the TCP coating developed by NAVAIR[28]. NAVAIR has approved TCP for use on some Al alloys.

The trivalent conversion coatings are not as effective on zinc as hexavalent chrome conversion.

Note that trivalent coatings are light blue iridescent and do not have color variations that indicate the degree of corrosion protection they will provide. This can be something of a problem for users who are accustomed to specifying a particular color chromate layer.

5.5. Chrome-free conversion

There are various conversion coatings that avoid the use of chrome all together. NAVAIR is testing a non-chrome conversion coating. There are various chemistries based on permanganates, silicates, zirconates, and other inhibitors, while for primers some of the greatest success has been with rare earth additives.

Alodine 5200, which is Zr-based, has proved to be essentially similar in performance to TCP, and is approved by TACOM for vehicles.

A sol-gel organo-siloxine coating developed by Boeing (originally known as Boegel) has also proved to be an effective treatment for Al.

5.6. Paint adhesion promoters

Another approach is provided by various adhesion promoters. These coatings do not, in themselves, provide any enhanced corrosion protection, so if the paint system is scratched there is no self-healing. However, they can be very effective by greatly improving the adhesion of the protective prime and paint layers. PreKote is one such coating that has proved very effective in Air Force testing.

5.7. Alternatives to chromic acid anodizing

Approved alternatives to chromic acid anodizing are thin film sulfuric and sulfuric-boric acid anodizing. The primary situation in which chromic is still required is where paint adhesion is critical. Because the anodized layer on Al is more porous when made with chromic acid it promotes better paint adhesion, and is often still specified for this reason.

Alternative anodizing methods now available based on high voltage “plasma electrolytic oxidation” (PEO) in place of the standard low voltage method used in the traditional process. In PEO the voltage is raised to the point that a plasma forms in arc points all over the surface, forming a fused oxide layer that is thicker than traditional anodize layers. These processes use benign solutions that avoid strong acids and chromates. The most common are

- Keronite – Used primarily on Al, but also available for Mg and being developed for Ti.
- Tagnite – Used for Mg (avoiding the Dow 17 Cr^{6+} process typically used).

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[1] For more information see http://hazmat-alternatives.com/Regs-Europe.htm

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[3] SERDP Project: "Electroformed Nanocrystalline Coatings: An Advanced Alternative to Hard Chrome Electroplating" (WP1152)

[4] ESTCP Project: "Nanocrystalline Cobalt Alloy Plating for Replacement of Hard Chrome and Thin Dense Chrome (TDC) on Internal Surfaces" (WP-0411)

[5] ESTCP Project: "Replacement of Chromium Electroplating on Aircraft Landing Gear Using HVOF Thermal Spray Technology" (WP-9608)

[6] ESTCP Project: "Replacement of Chromium Electroplating on Gas Turbine Engine (GTE) Components Using Advanced Thermal Spray Technologies" (WP-0023)

[7] ESTCP Project: "Replacement of Chromium Electroplating on Hydraulic Actuators Using HVOF Thermal Spray Technology" (WP-0038)

[8] ESTCP Project: "Replacement of Chromium Electroplating on C-2, E-2, P-3 and C-130 Propeller Hub Components Using HVOF Thermal Spray Technology"

[9] SERDP Project: "Investigation of Chemically Vapor Deposited Tantalum for Medium Caliber Gun Barrel Protection" (PP1425)

[10] SERDP Project: "Tri-Service "Green" Gun Barrel" WWP 1074)

[11] ESTCP Project: "Electrospark Deposition for Depot- and Field-Level Component Repair and Replacement of Hard Chromium Plating" (WP-0202)

[12] SERDP Project: "Chromium Elimination in Medium Caliber Gun Barrels" (WP1426)

[13] ESTCP Project: "Cadmium Replacements for Department of Defense (DoD) and National Aeronautics Space Administration (NASA) Applications" (WP-0022)

[14] C. Cooper, P&W Canada, kickoff meeting, Canadian Cadmium Replacement Program, May 2000.

[15] US Patent # 4,765,871

[16] SERDP Project: "Electrolytic Plasma Processing for Sequential Cleaning and Coating Deposition for Cadmium Plating Replacement" (WP1406)

[17] US Patents # 4,145,261 and 4,759,831, AlumiPlate, Inc

[18] ESTCP Project: "Aluminum-Manganese Molten Salt Plating" (WP-9903)

[19] SERDP Project: "Corrosion Resistant Steels for Structural Applications in Aircraft" (WP1224)

[20] ESTCP Project: "Demonstration and Validation of Corrosion Resistant Steels for Structural Applications in Aircraft Using an Accelerated Insertion Methodology" (WP-0304)

[21] ESTCP Program: "Replacement of Cd Plated Steels with S-53 in Rotary Geared Actuators" (WP-0619)

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[22] SERDP Program: “Investigation of Chemically Vapor Deposited Aluminum as a Replacement Coating for Cadmium” (WP1405)

[23] ESTCP Program: “Supersonic Particle Deposition for Repair of Magnesium Components” (WP-0620)

[24] MIL-C-81751B, Coating – “Metallic-ceramic”

[25] PEWG Project: “Aternatives to Aluminu-Ceramic Coatings for Turbine Engine Components”

[26] NASA/JPL Alert QA-98-01, DOC-NO 35046 “Landing Gear, Aermet 100, Hydrogen Embrittlement, Sermetel” (1998).

[27] SERDP Program: “Electroactive Polymers as Environmentally Benign Coating Replacements for Cadmium Plating on High Strength Steels” (WP1411)

[28] ESTCP Program: “Demonstration and Validation of Non-Chromate Aluminum Pretreatments” (WP-0025)

APPENDIX – TRL LEVELS

Definition of Technology Readiness Levels.

1. **Basic scientific principles** only known and reported
2. **Technology concept/application** formulated, potential benefits identified
3. **Proof-of-concept** demonstrated in lab
4. **Primary performance parameters** – representative parts or specimens lab tested (no show stoppers)
5. **Validation** – lab specimen performance tests, relevant exposure environment tests (e.g. beach or shipboard corrosion) and producibility demonstration
6. **Rig testing** – actual or simulated components in real or closely simulated test rig
7. **Service testing** – actual components
8. **Qualification** – process/product has passed qualification tests
9. **Operational testing** – actual operating environment, operating experience gained

The Technology Readiness Level was designed by NASA to indicate the degree of development of a technology. Since the original TRL concept was developed for electronic equipment we have adapted the definitions in a manner similar to that used by Pratt & Whitney (see table above). In order to the classified at a particular level the technology must have passed the appropriate milestone. The TRL will differ for each application of a technology.