Report: 2nd ASETSDefense Workshop
Sustainable Surface Engineering for Aerospace and Defense

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EXECUTIVE SUMMARY

This summary is intended only to pick up and highlight the major trends and recent developments discussed in the workshop. All the briefings are available on the ASETSDefense website at

http://www.asetsdefense.org/PastWorkshops.aspx

The workshop was focused principally on Cr^{6+} reduction and elimination, but also covered Cd, topcoats, accelerated testing and stripping.

Side meetings were held on

1. Beryllium regulations and alternatives
2. DoD training in new processes
3. Cr^{6+} authorization and adoption in DoD
4. Pure Al as a Cd alternative for fasteners and electrical connectors
5. Potential international programs – primarily ionic plating.

Significant progress is being made, with increasing implementation of Cr^{6+} alternatives in paint systems and hard chrome plating replacement by DoD organizations. On the commercial side, Boeing has just shipped its first Boeing 777 with a chromium-free finish (AC-131 pretreat with chromium-free primer). Nevertheless much remains to be done in both the commercial and defense worlds to develop and implement effective alternatives at a reasonable speed, but without risk of failures or increased life cycle costs due to corrosion. To advance this effort various test methods are being developed to accelerate testing while minimizing risk.

Table of Contents

List of Tables

List of Figures

1. Agenda

Side meeting - Beryllium: ESOH Issues and Alternatives	
Introduction	Jean Hawkins JSF ESOH Team Lead
Beryllium: Occupational Health Issues	John Bishop Navy/Marine Public Health Center
Beryllium Issues from a Mfg/OEM Perspective	Scott Fetter Lockheed Martin
Depot Usage & Manufacture of CuBe Bushings	Stacey Luker FRC-E
Replacement for CuBe Bushings	Scott Fetter Lockheed Martin
Lightweight Composites for Replacement of AlBe	Dean Baker Advanced Powder Solutions

Meeting the Chromate Challenge - Control and Replacement	
Overview of OSD-ATL Cr^{6+} Memo and OSHA Cr^{6+} PEL	Bruce Sartwell, SERDP/ESTCP Keith Legg, ASETSDefense
Corrosion Control Requirements for DoD	Dan Dunmire OSD
Lockheed Martin's Progress in Hexavalent Chromium Reduction	Tony Phillips Lockheed Martin
User Perspective on New Technology Adoption	Wayne Patterson OO-ALC
RDT&E and ASETSDefense	Bruce Sartwell SERDP/ESTCP
Overview of DoD Chromate Usage and Database	Keith Legg ASETSDefense
Implementation of Chromate Free Finishes at NAVAIR	Craig Matzdorf NAVAIR

Coating Systems	
Scientific Understanding of Non-Chromate Inhibitors	Rudy Buchheit Ohio State University
Coating Systems for Vehicles	John Escarsega ARL/WMRD
Coatings for Ships	Farrel Martin Naval Research Laboratory
Chromium-Free Exterior Painting for Commercial Aircraft	Joe Osborne Boeing
Aerospace Non Chrome Corrosion Inhibiting Primer Systems	Roger Brown AkzoNobel
UV Cure Powdercoat	Corey Bliss AF CTIO
UV Cure Paint	Randy Straw WPAFB
Electrocoat Primers for the Aerospace Industry	Mike Pawlik

	PPG
Multifunctional UV Cure Coatings	Matt O'Keefe Missouri S&T
Non-Chromate Surface Treatments	
Evaluation and Demonstration of Non-Hexavalent Chromium & Sealers for Steel Substrates	Jack Kelley ARL
Keronite Treatment for Light Metals	Stephen Hutchins Keronite
Magnesium-Rich Primers	Kevin Kovaleski NAVAIR
Chromate-Free Inhibitors and Non-Chromate Fuel Tank Coatings	Jeannine Elliott TDA Research
Low VOC Materials	John LaScala ARL
Supersonic Particle Deposition for Repair and Corrosion Protection of Mg Gearboxes	Brian Gabriel ARL

Hard Chrome Plating Alternatives	
HVOF Hard Chrome Alternatives - Developments, Approvals, Implementations, Performance	Ben Evans Goodrich
HVOF on Hydraulic Actuators for Off-Road Vehicles	Brad Beardsley Caterpillar
Progress in USAF HVOF Implementation at Ogden	Brad Martin Hill AFB
EA-6B HVOF-Coated Landing Gear: Post-Deployment Inspection Results	Tai Ngin FRC-SE
Design of HVOF Coatings and Seals for Hydraulic Actuators	Steve Okladek Greene, Tweed
Development of HVOF Superfinishing Spec. Development of Grinding Spec. for High Strength Steel & Cr Plate	Jon Devereaux NASA
USAF Hydraulic Actuator Chrome Replacement	Bill Southwell ARINC
ID Coating with Nano HVOF	Alan Burgess Northwest Mettech
nCo-P for ODs and IDs	Diana Facchini Integran
Microcomposite Coatings for Chrome Replacement	John Kleek, AFRL Greg Engleman, MesoCoat

International Programs	
IONMET - Ionic Liquid Technology	Pascal Negre, Khalid Shukri IONMET
Slurry and MOCVD Al Coatings for Cd Replacement	Alina Aguero INTA, Spain
Aerospace ESOH Coatings Tech Map	Farzan Jamarani Industry Canada

Cadmium Alternatives	
1) Progress on LHE Zinc-Nickel and Other Cadmium Alternatives 2) Cadmium Plating Replacement Zn-Ni Plating Technology for Boeing Commercial Airplane	Steve Gaydos, Louie Tran Boeing
1) Cadmium Coating Alternatives for High-Strength Steel JTP – Phase II 2) Implement Replacement Coating for Cadmium Brush Plating on Department of Defense Weapon System	Elizabeth Berman AFRL
Cd Alternatives for Vehicle Fasteners - Test Results and Path to Implementation	Carl Handsy TARDEC
Fastener Coating	Matt Scott PPG
Amphenol Cd-Free & CrVI-Free Connector Finishes	Edmond Fey, Mark Barnes Amphenol Aerospace
Nanostructured Zn-Based Alloys as an Alternative to Cd Plating on High Strength Steel Fasteners	Jon McCrea Integran
Computational Evaluation of ZiNi Electroplating	Alan Rose Elsyca
Shockwave Induced Spraying: A New Cost-Effective Solid-State Spraying Process	Julio Villafuerte Centerline

Test and Inspection Methods	
Rapid Testing Method for Corrosion Coatings	Craig Matzdorf NAVAIR
Accelerated Corrosion Test Method	Jim Dante SWRI
Embrittlement Test Development	Steve Gaydos Boeing
Acceptance Criterion for Hydrogen Embrittlement Testing of Coated Fasteners	Lou Raymond LRA/FDI/RSL
IR Inspection of Coatings	Jack Benfer FRC-SE
Microwave Inspection of Coatings	Gary Schmidt SMRC

Stripping and Welding	
Laser Stripping	Randy Straw WPAFB
Color Selective, Zero-Damage, Laser Decoating Process	Robert Cargill General Lasertronics
Pulse Water Jet Stripping	Jay Randolph ES3
Welding Emissions in Shipbuilding and Repair	Kathleen Paulson NAVFAC, Port Hueneme

2. General information

Because OSD had issued a policy memorandum on "Minimizing the Use of Hexavalent Chromium" the Workshop's main focus was on Cr^{6+}, with sessions on other issues such as Cd. There were several side meetings, on

1. Beryllium
2. Training needs
3. Authorization and implementation of Cr^{6+} alternatives
4. Cd replacement on fasteners, connectors
5. Potential international programs.

The briefings from the workshop are available from the ASETSDefense website at

http://www.asetsdefense.org/PastWorkshops.aspx.

Information on alternatives to chromate processes and other processes and materials with ESOH concerns can be found at

http://www.asetsdefense.org

Information on alternatives to the following is either available or in process of being added:

- Cadmium plating
- Chromate conversion
- Chromate metallic-ceramics
- Chromate primers
- Chromate sealants
- Chromic acid anodize
- Hard chromium plating
- High VOC materials

A document database is being assembled that contains engineering information such as reports and data on performance of alternatives, as well as authorization and implementation of alternatives in DoD and the commercial sector. This database can be reached from the ASETSDefense website, and is available directly at

http://db.asetsdefense.org/

These public websites do not require a login. A few of the database documents have restricted distribution statements that make them available only to DoD or contractors. They can only be downloaded with a username and password, which is available by contacting

asetsdefense@rowantechnology.com.

3. Overviews of DoD and commercial Cr^{6+} replacement

Dan Dunmire, Director, DOD Corrosion Policy and Oversight has set up a Cr^{6+} elimination task force team to identify alternatives and develop mitigation strategies. His office is funding various projects to develop and validate alternatives to Cr^{6+} and Cd. Alternatives must be substantially benign and **must meet or exceed all of the current corrosion protection performance specifications**. For more information see

http://www.corrdefense.org/default.aspx

Bruce Sartwell, Weapons Systems and Platforms Program Manager, provided an overview of

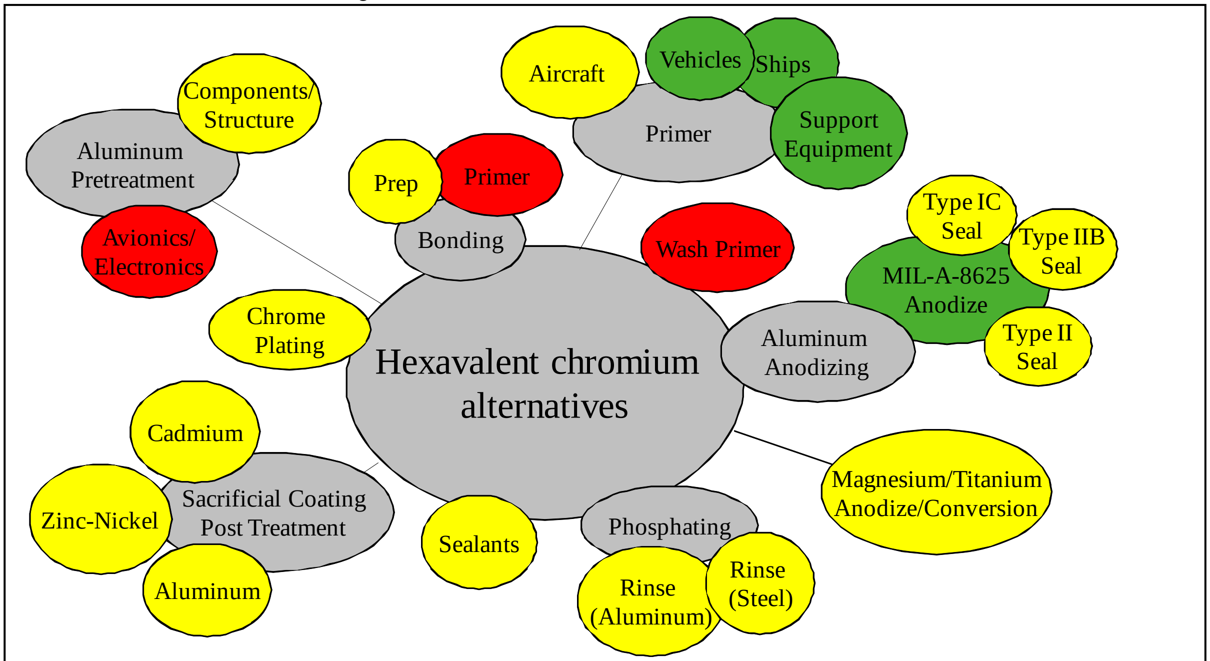

Figure 1. Progress in developing Cr^{6+} alternatives. Green, alternatives implemented; yellow, near validation, limited implementation; red, little or no implementation (courtesy NAVAIR).

SERDP-ESTCP programs, which have totaled more than $70 million over the past decade. Figure 1 shows the many uses of Cr^{6+} in DoD and the extent to which alternatives are being implemented. An important current focus is development of better accelerated corrosion tests, since we cannot afford the poor prediction accuracy and enormous delays inherent in extensive laboratory and beach exposure testing if we are to implement successful alternatives in a reasonable time. For more information see

http://www.estcp.org/, http://www.serdp.org/

In 2007 Lockheed-Martin issued a memo severely restricting the use of Cr^{6+} on their weapons systems, requiring concurrence from the VP level for its use on new systems or to revert to it on legacy systems (Tony Phillips). The OSD memo of April 2009 used a similar approach. Cr^{6+} is now being removed from existing Lockheed products under a series of projects.

NAVAIR has continued to work on improving Cr^{6+}-free processes and materials and implement them in the fleet. The status of NAVAIR implementation efforts is summarized in Table 1 (Craig Matzdorf).

NAVAIR is developing an implementation approach for non-Cr primers based on risk, which depends on the platform and the application. Non-critical applications and training aircraft have the lowest

Alternative Implemenation Status

M&P Area	Sub Area	Location	Process Status	wt vol% of Cr6+ in NAE	%of Cr6+ eliminated
Painting	Support Equipment	Depot and Field	Non-chromate primer in use (MIL-C-53022) for all applications	0	100
	Aircraft and Components	Depot and Field	Non-chromate primer authorized scuff sand and overcoat	TBD	TBD
Bonding		Depot and Field	Alternative not authorized	TBD	0
Sealing		Depot and Field	Chromated and non-chromated sealants in use	TBD	TBD
Aluminum Pretreatment	Avionics/Electrical	Depot and Field	Alternative not authorized	TBD	TBD
	Components/Structure	Cherry Point-Aircraft re-paint (spray)	Authorized for use under chromated primer (TCP). Demontration and validation underway assessing TCP with leading NC primer on aircraft	TBD	100
		North Island- Aircraft re-paint (spray)		TBD	0
		Jacksonville- Aircraft re-paint (spray)		TBD	0
		Cherry Point- Component Immersion tanks		TBD	0
		North Island- Component Immersion tanks		TBD	0
		Jacksonville- Component Immersion tanks		TBD	0
		Field		TBD	0
Aluminum Anodizing	Sealing Type II & III	Cherry Point	Authorization of alternative (TCP) pending authorization letter. Jacksonville planning to implement TCP as soon as authorization is completed.	TBD	0
		North Island		TBD	0
		Jacksonville		TBD	0
	Sealing Type IC	Cherry Point	Authorization of alternative (TCP) pending results of fatigue testing.	TBD	0
		North Island		TBD	0
		Jacksonville		TBD	0
	Sealing Type IIB	Cherry Point	Type IIB not authorized currently. Dem/val underway to produce data for potential authorization as Type IC alternate. Being considered by Jacksonville as part of single tank Type II, IIB and III anodize system. Authorization of alternative (TCP) pending results of fatugue testing.	TBD	0
		North Island		TBD	0
		Jacksonville		TBD	0
Sacrificial Coatings	Cadmium Post Treatment	Cherry Point	Authorization of alternatives pending review of available data	TBD	0
		North Island		TBD	0
		Jacksonville		TBD	0
	IVD Aluminum Conversion	Cherry Point	Authorization of alternative (TCP) pending resutls of field testing.	TBD	0
		North Island		TBD	0
		Jacksonville		TBD	0
	Zn-Ni Post Treatment	Cherry Point	Authorization of alternatives pending review of available data	TBD	0
		Jacksonville		TBD	0
Magnesium Conversion Coating		Cherry Point	Authorization pending for alternative use in component recoating and touch up (Alodine 5700 and TCP)	TBD	TBD
		Jacksonville	Authorization pending for alternative use in component recoating and touch up (Alodine 5700 and TCP)	TBD	0
		Field	Authorization pending for alternative use in component coating touch up (Alodine 5700 and TCP)	TBD	TBD
Hard Chrome Plating		Cherry Point	HVOF coatings authorized; limited to low stress/spalling risk applications	TBD	TBD
		North Island		TBD	TBD
		Jacksonville		TBD	TBD
Titanium Conversion Coating		Depot and Field	Authorization of alternatives pending review of available data	TBD	TBD
Phosphating	Steel, "rinse"	North Island	Mn-phosphate process with chromate rinse. New alternative being assessed (ChromiPhos).	TBD	0
		Cherry Point	Zn-phospahate process with chromate rinse. New alternaitve being assessed (ChromiPhos).	TBD	0

Table 1. Status of Cr^{6+} replacement at NAVAIR (Matzdorf).

risk, while uninspectable areas on high-performance ship-based aircraft have the highest risk:

Application risk:

1(L) – Composite/Fiberglass Surfaces

2(L) – Non-critical Metallic Surfaces – External Fuel Tanks, etc.

3(M) – Airframe Tie-Coat Applications

3A – OML

3B – IML – Topcoat or inspectable areas

4(M-H) – Airframe Direct-to-Metal Applications

4A – OML

4B – IML

5(H) Interior/Faying Surface/HS Components

Platform risk:

1(L) – Trainer Aircraft – T-45, T-34, etc.

2(M) – Land based Aircraft – KC-135, C-40, etc.

3(M-H) – Special Land – P-8, H-53, etc.

4(H) – Ship-based Aircraft – E-2, H-60, etc.

5(H) – Ship-based Aircraft and Specialty Coatings

F/A-18, EA-18G, F-35, etc.

4. Coating systems and surface treatments

The use of chromates varies markedly between vehicles, vessels and aircraft.

- Ships (Farrel Martin)): There is very little use of Cr^{6+} for shipboard coatings. No chromate is used in structural coating Primary ESOH issues with ships are anti-fouling coatings.
- Ground Vehicles (John Escarsega): The only major Cr^{6+} usage is in wash primers. Major issues are in topcoats (camouflage and CARC, Chemical Agent Resistant Coatings).
- Air vehicles (Joe Osborne): Aircraft remain the primary users of chromated systems, including chromate conversion of Al airframes and skins, chromated primers and chromate treatments of Mg alloy gearboxes.

All systems use Cr^{6+} (usually as a conversion coating on Cd) for fasteners and electrical connector shells.

There is as yet no military use of Cr^{6+}-free finishes for aircraft. However, Boeing has now replaced chromate conversion with AC-131 (Boegel) for all commercial aircraft (Joe Osborne). In August 2009 Boeing shipped the world's first commercial aircraft with a chromium-free finish, a B777-300ER to KLM (Figure 2).

A major development over the past few years is in the area of UV curable coatings (Corey Bliss, Randy Straw). These are powdercoats or liquid paints that cure in a few minutes under a UV light, eliminating the hours to days involved in curing standard coating systems. This approach promises to remove a major logjam in recoat operations. Primers are eliminated all together in UV cured powdercoat systems

NAVAIR continues to work with Akzo Nobel on the development and evaluation of Mg-rich primers (Kevin Kovaleski). The early generations of these materials showed severe pitting through the primer itself in corrosion tests. This is a different failure mechanism from that typically seen in paint systems, where corrosion occurs only in and around the scribe. The third generation of this material has promise, but it is not yet comparable either with chromated primer or with the best available chromium-free primers. Testing of a fourth generation product is under way. It must exceed the performance of the current chromium-free products to make it worthwhile for NAVAIR to continue testing.

Coatings for internals of fuel tanks have been a significant challenge for some time. Because of their location and criticality they are a high-risk area. TDA, in partnership with Akzo Nobel, has developed a fuel tank coating that appears to have promising corrosion performance (Jeannine Elliott).

Figure 2. World's first commercial aircraft with a chromium-free finish (Boeing 777-300ER).

This coating uses nanoparticles to carry the inhibitors, which are released on demand when the coating is damaged.

Magnesium alloy gearboxes have always presented a severe corrosion challenge since Mg is very susceptible to corrosion and the only corrosion treatments have traditionally been Dow 17 and HAE, both of which are chromated. Keronite, a plasma electrolytic oxidation (PEO) process, is now available in the US for use on Al, Mg and Ti (Stephen Hutchins). Tagnite is another PEO process that is widely used for Mg alloys such as gearboxes. Both of these processes use benign solutions and create a surface that is much more resistant to corrosion and damage. Supersonic particle deposition (cold spray) of Al is being developed and tested by ARL, DSTO (Australia) and Sikorsky to repair damaged Mg gearboxes and improve their corrosion resistance (Brian Gabriel). This approach is showing promise for both corrosion and fatigue.

5. Hard chrome plating

HVOF WC-CoCr is now being used commercially for almost all new design landing gear. Ogden ALC (Brad Martin) is implementing HVOF WC-Co throughout their landing gear overhaul shops, except on items that are not suitable for HVOF (e.g. thin wall, high stress, where spallation is a concern). A stress analysis is carried out on all items, and the conversion to HVOF includes all ancillary processes such as masking and grinding.

A landing gear inner cylinder from an EA-6B that was coated with HVOF WC-Co and put into flight test in 2004 had recently been returned to FRC-SE because of a major seal failure (Tai Ngin). The aircraft had had only about a year at sea, with 153 carrier takeoffs and landings. There was no flaking or loss of coating from the HVOF surface. The surface finish, which had originally been a 4μ" Ra superfinish, had roughened to 8-18μ" Ra in the center and lower areas of the piston, and re-superfinishing revealed corrosion pits with rust spots over much of the surface. Discussion concluded that this was a more rapid failure than would have been expected for hard chrome, and that WC-Co was not the best material for a highly corrosive shipboard environment – WC-CoCr would have been a better choice. It was not clear whether or not the HVOF coating was the cause of the seal failure, and a analysis was being conducted by Trelleborg.

***Note**: The Trelleborg report was received shortly after the workshop. Unfortunately it was unable to throw much light on the reason for the failure. The seals did show presence of particles (although apparently not an uncommon quantity), but there was no indication of their chemistry and hence their source. Seal distortion and extrusion were seen, as well as evidence of excessive heating. However, none of the damage could be linked to any clear cause. Further analysis is expected to be completed in a few weeks.*

Steve Okladek of Greene, Tweed and Jon Devereaux of NASA discussed the details of surface finishing of HVOF coatings. This information is critical to reliable long term seal performance.

Beginning in 2000 Tinker AFB began delta qualification testing of HVOF on a variety of actuators, including rig and service tests. Some tests are still incomplete and some components have become lost from the system; but all those components whose tests are complete have passed. Jennifer Ewy at Tinker is now in charge of this testing.

6. Cadmium plating

Two primary Cd alternatives have emerged

1. Electroplated Al (AlumiPlate), which is in low volume production for several aircraft
2. LHE ZnNi, which is being validated at Hill AFB

Both of these materials were tested under the JCAT program (Elizabeth Berman) and neither was perfect.

TARDEC has proposed an OSD policy that would largely replace Cd plating on fasteners and electrical connectors with pure Al with a chromate-free finish, but would allow alternatives where needed (Carl Handsy). This was discussed at more depth in a side meeting.

Amphenol has been moving toward adopting ZnNi and electroless Ni-PTFE for 38999 connectors (Edmond Fey).

Computational methods are now being applied to alloy electroplating (Alan Rose) and show that the chemistry of ZnNi electroplate varies with current density and fluid flow rate in the bath. This shows that care must be taken when electroplating alloys such as ZnNi to ensure that its chemistry does not stray outside spec on any area of a complex component.

7. Rapid testing and stripping

Increasingly stringent ESOH regulations and requirements, often with short time scales to implementation, is driving the development of new methods of testing for corrosion (Craig Matzdorf, Jim Dante) and embrittlement (Steve Gaydos, Lou Raymond). The aim of these test methods is to speed up the adoption of clean alternatives without increasing risk or sacrificing performance. The corrosion test methods are seeking a way around the requirement for years of beach exposure and service testing for corrosion. The embrittlement testing methods are developing reliable tests that can be done in a reasonably short time on the best design of test specimen.

Several new methods have been developed for stripping coatings, including laser stripping for paints (Bob Cargill and Randy Straw) and a pulse water jet technique that can strip HVOF coatings (Jay Randolph). The advantages of these techniques are speed and avoidance of the use of toxic stripping chemicals. Laser stripping is being used in production and has been FAA-approved for commercial aircraft.

Appendix 1. Side Meeting on Beryllium

The primary purpose of this side meeting was to raise awareness of regulatory developments on Be. Be is the cause of Chronic Be Disease (CBD). There is increasing concern over particle size, not just quantity of Be in the air.

While the OSHA PEL is 2µgm^{-3}, the American Conference of Governmental Industrial Hygienists (ACGIH) has put forward a Threshold Limit Value (TLV) of 0.05µgm^{-3} inhalable. This limit is too low to be measurable with most current equipment and methods. A recent Academy of Sciences study on Be could not define a safe Occupational Exposure Limit (OEL), which can be interpreted to mean that any measurable beryllium exposure is an unacceptable risk. There is also some initial evidence that 1µm Be particles can be absorbed through the skin, leading to a potential for sensitization. There may also be a genetic pre-disposition to Be sensitization.

F-35 has replaced CuBe bushings throughout the airframe with Nitronic 60, except for bushings >2.5", which cannot be work-hardened sufficiently to achieve the correct properties. Ultimately these bushings will probably be replaced by ACUBE 100 alloy from Carpenter, which is a Co-Cr-Mo alloy currently used for prosthetic implants.

Because of its unique properties AlBe (Albemet) is a more difficult material to replace. Dean Baker, Advanced Powder Solutions has been developing a composite material based on consolidation of hollow spheres, but it is still in the R&D phase.

Appendix 2. Side Meeting on Training

Since this meeting was held on the Monday evening it was poorly attended and discussion was limited. In general the new coating materials and treatments require more care over process cleanliness and coating conditions than the older chromate processes. DoD depots clearly have major issues in worker retention and in getting artisans to implement different finishing methods. Training usually only lasts a few weeks before people revert to the old process methods.

In addition, people working in the cleaning shop and the paint shop have some of the worst jobs on base, and usually move out of those positions as soon as they can. This makes it difficult to keep high quality trained workers in those jobs, even though those are some of the most critical areas.

Bruce Sartwell asked if people would be interested in instituting better training approaches if funding could be made available. The answer seemed to be that there would be interest in developing improved training methods, but no clear consensus on what types of approaches would stand the best chance of success.

Appendix 3. Side Meeting on Adoption of Cr^{6+} Alternatives

Craig Matzdorf has been tasked with gathering DoD-wide information on authorization and implementation of Cr^{6+} alternatives. It was suggested that PESHEs (Programmatic Environmental Safety and Health Evaluations) might be a place to start.

Keith will provide any information available on commercial and defense usage that he comes up with for the ASETSDefense database.

Appendix 4. Side Meeting on Cd Replacement on Fasteners and Connectors

This side meeting was set up to discuss the implications of Cd replacement with pure Al and a chromate-free sealer on fasteners and connectors, as proposed by Carl Handsy.

There was no consensus on the best approach, with differing opinions as to relative advantages and disadvantages of Al vs ZnNi. ES3 (Hill AFB) and Amphenol were in favor of using alkaline ZnNi since they did not feel that AlumiPlate would meet their needs. Amphenol considers AlumiPlate too expensive, and reported galling issues, while Hill considers the AlumiPlate toluene bath a serious ESOH issue for the depot. On the other hand TARDEC and Lockheed were in favor of AlumiPlate, since its performance appears significantly better in their applications.

It was pointed out that there are a large number of applications where almost any Cd alternative would work, such as internal spaces on ships, where corrosion is not a serious issue and almost all connector coatings could be replaced today with little or no risk.

Both Al and ZnNi should be largely galvanically compatible with Cd, with each other, and with Al alloy and Mg alloy components. The use of either material, or both, even in mixed inventories would not appear to represent a serious issue, provided proper DFLs are used on threads to ensure correct torque-tension for fasteners and eliminate galling in connectors, which can generate metal particulates.

A more detailed report on discussion of the issues is available.

Appendix 5. Side Meeting on International Programs

The IONMET program (Pascal Negre) is an EU-funded program to develop ionic liquid electroplating technology. This technology makes it possible to electrodeposit materials that cannot be plated in aqueous baths. The method is essentially a low melting point molten salt method based on complex metalorganic salts.

Industry Canada and NRC have developed a Roadmap for Environmental Technologies for the Canadian Aerospace Industry (Farzan Jamerani).

Discussion centered on the potential for collaborative work, especially for the development of Al electroplating that might avoid the use of a toluene bath.

Appendix 6. Definitions and acronyms

Definition of chromates:

Chromates are materials that contain chromate ions CrO_4^{2-} or dichromate ions $Cr_2O_7^{2-}$, in both of which the valency of the Cr ion is 6 (hexavalent chromium or Cr^{6+}). Examples of chromates used in metal finishing:

- Chromic acid H_2CrO_4
- Chromium trioxide CrO_3
- Sodium dichromate $Na_2Cr_2O_7$
- Strontium chromate $SrCrO_4$

Most chromates are considered toxic and carcinogenic.

Trivalent chromium (Cr^{3+}) is not considered to be carcinogenic.

Chromium metal (as in hard chrome plating) is non-toxic.

Equivalent terms often used in briefings and documents:

Chromate = Hex chrome = Hexavalent chromium = Cr^{6+} = CrVI

Tri-chrome = Trivalent chromium = Cr^{3+} = CrIII

Chromate-free = Non-chromate: contains no Cr^{6+} but may contain Cr or Cr^{3+}

Chromium-free = Chrome-free = Non-chrome: does not contain chromium in any form (Cr, Cr^{3+}, Cr^{6+})

Hard Chrome Plating = Hard Chromium Plating = Engineering Hard Chrome = Electrolytic Hard Chrome = EHC (contains no Cr^{6+})

Acronyms:

Table 2. Table of acronyms.

ACGIH	American Conference of Governmental Industrial Hygienists
AFB	Air Force Base
ASETS-Defense	Advanced Surface Engineering Technologies for a Sustainable Defense
CARC	Chemical Agent Resistant Coating
DFL	Dry Film Lubricant
DoD	US Department of Defense
ESOH	Environmental Safety and Occupational Health
ESTCP	Environmental Security Technology Certification Program
EU	European Union
FAA	Federal Aviation Authority
FRC	Fleet Readiness Center
HVOF	High Velocity Oxy-Fuel thermal spray
ID	Internal Diameter
IML	Inner Mold Line (interior surface of aircraft skin)
IR	Infrared
LHE	Low Hydrogen Embrittlement
MOCVD	MetalOrganic Chemical Vapor Deposition
NAVAIR	Navy Air Systems Command
NRC	National Research Council of Canada
OD	Outside Diameter
OEM	Original Equipment Manufacturer
OML	Outer Mold Line (outside skin of an aircraft)
OSD	Office of the Secretary of Defense
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PEO	Plasma Electrolytic Oxidation
PESHE	Programmatic Environmental Safety and Health Evaluation
SERDP	Strategic Environmental Research and Development Program
TARDEC	Tank-Automotive Research, Development and Engineering Center
TLV	Threshold Limit Value
USAF	US Air Force
UV	Ultraviolet