Replacement of Hexavalent Chromium on DOD Weapons Systems

Bruce Sartwell
Weapons Systems and Platforms Program Manager
SERDP/ESTCP

MERIT Quarterly Meeting
13 January 2009

Acknowledgements

Keith Legg
Rowan Technology Group

Bill Nickerson
Craig Matzdorf
NAVAIR Patuxent River

Christian Richter
The Policy Group

Charla Wise
Tony Phillips
Lockheed-Martin

Jack Benfer
NAVAIR Jacksonville

Matt O'Keefe
Missouri University of Science and Technology

Weapons Systems and Platforms

- **Manufacturing and Maintenance**
  - Green materials and processes (principally related to surface engineering technologies)
  - Control and monitoring
    - Depots, Field, Shipyards & OEM
- **Green Energetics**
  - New Materials
  - Alternative Manufacturing
- **Air and Noise Emissions**
  - Diesels and Gas Turbines
  - Weapons and Munitions
  - Ship and Industrial

Partner with Acquisition and Maintenance Community

Hexavalent Chromium in Metal Finishing

- Cr^{6+} is ubiquitous in its use for corrosion protection
  - Metal finishing pre-treatments
  - Primers and Paints
  - Sealants

- Standard for best corrosion-resistant products
  - Very mature, used for more than 50 years
  - Very robust, inexpensive, and easy to use
  - Inhibits corrosion on multiple materials: Al, Fe, Mg, Zn, Cd, etc.
  - Comfort level of users is "high"

- Known carcinogen
  - Regulatory burden of use is increasing

Key Regulatory Drivers

- **Globalization of Regulation – European Union environmental requirements affecting market access (ELV, WEEE, RoHS, REACH)**
- **Policy evolution in U.S. – Questions about adequacy of existing regulatory framework**
- **Greening of the supply chain – Sustainability has evolved from the margin to the mainstream as a competitive advantage on the commercial front (shift in corporate procurement policies)**

NEXT ON THE HORIZON

- **Litigation related to 2006 OSHA hex-chrome Permissible Exposure Limit (PEL)**
- **NIOSH hex-chrome recommendation**
- **EPA Residual Risk Requirements related to air emissions**

Occupational Exposure Limits for Chromium: Comparison of Selected Countries

Country	Occupational Exposure Limit
United States	
◆ *New OSHA Cr(VI) PEL (2006)*	*5 ug/m³*
◆ *Previous OSHA Cr(VI) PEL*	*52 ug/m³*
Japan	50 ug/m³
European Union	50 ug/m³
France, Germany, UK, Finland	50 ug/m³
China	50 ug/m³
India	50 ug/m³
Sweden	*20 ug/m³*
Denmark	*5 ug/m³*

OSHA's Approach in Doubt?

Factors OSHA Must Consider	*OSHA's Conclusion in Setting Final PEL*
Health Risk	**Still "significant risk" at PEL of 5 µg/m^3**
Technical Feasibility	***Aerospace Painting*** **– PEL of 5 µg/m^3 not technologically feasible***
Economic Feasibility	***Electroplating*** **– PEL of 5 ug/m^3 is economically feasible, but NOT 1 µg/m^3**

"Significant Risk" in Final Standard: Cr^{6+} vs. Other OSHA Risk Estimates

Standard	Cancer Risk (per 1000)	Final Rulemaking Date
Asbestos	6.7	June 1986
Benzene	*10*	*September 1987*
Formaldehyde	.0056 – 2.64	December 1987
Cadmium	*3 – 15*	*September 1992*
1,3-Butadiene	1.3 – 8.1	November 1996
Methylene Chloride	3.6	January 1997
Chromium VI	*10 – 45*	*February 2006*

Cr^{6+} OSHA Litigation

- **Legal challenge – 3rd Circuit Court of Appeals**
- **Oral Arguments heard on November 21, 2008**
  - ***Public Citizen* – recommends that PEL be lowered to 0.25 µg/m^3 (states that "OSHA's own analysis shows standard of 1.0 µg/m^3 is feasible")**
  - ***Industry* – OSHA should set variable standards**
    - ***Nuclear power industry***
    - ***Welding operations***

- **Potential outcome of litigation**
  - **Court may remand rule back to OSHA**
  - **OSHA could consider other PEL levels**
  - **Key issues associated with "reasonableness" and "feasibility" – affects various industries differently**

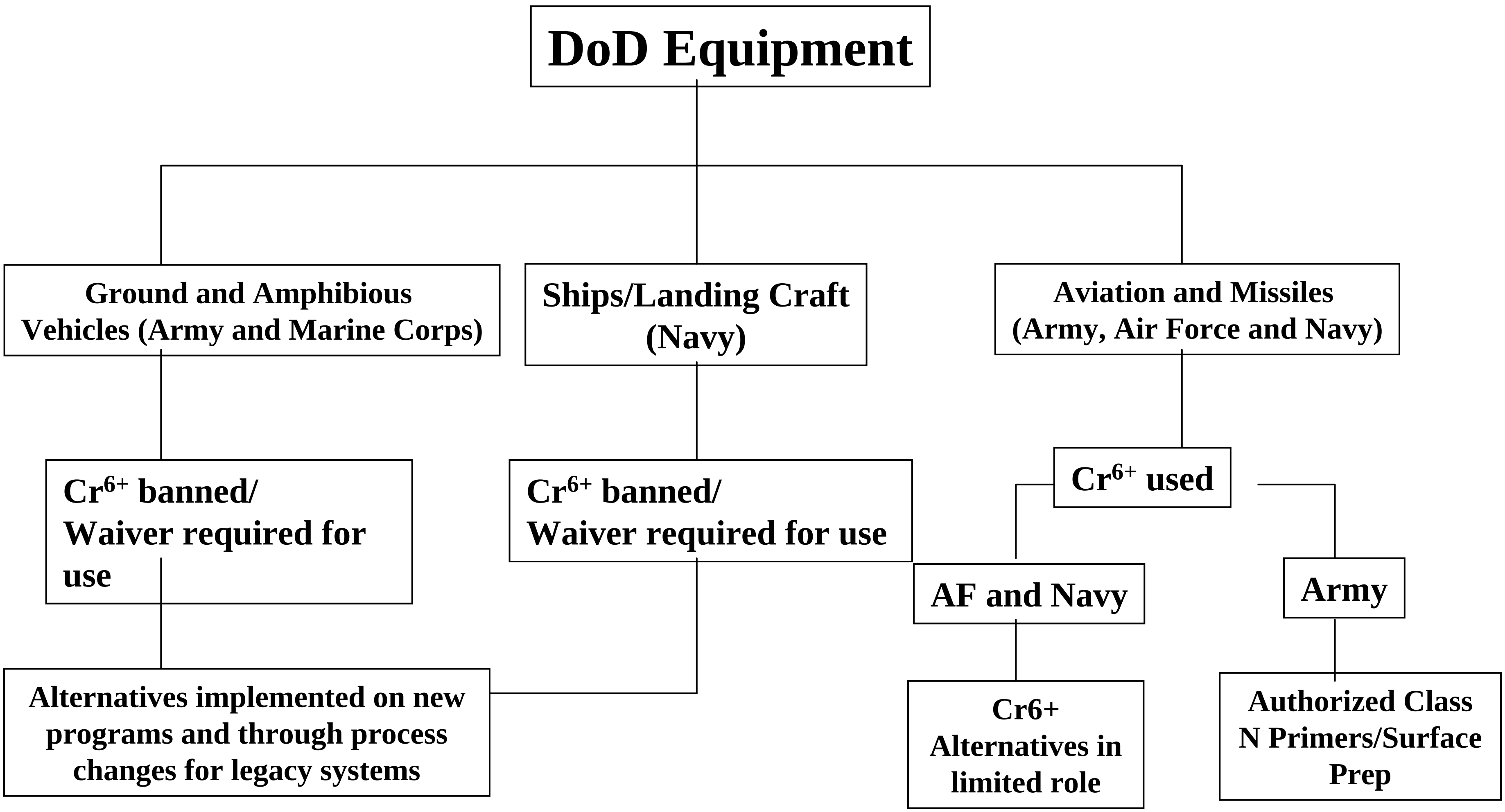
NIOSH Draft Hex-Chrome Criteria Document

- Issued on 14 November 2008
- Lowers recommended exposure limit (REL) for hex-chrome from 1 $\mu g/m^3$ to 0.20 $\mu g/m^3$, a level that NIOSH claims carries a 1:1000 risk of cancer death to workers
- NIOSH cites two studies of chromate chemical production workers that demonstrate a "significant risk of lung cancer mortality to workers exposed to hex-chrome at the previous REL"
- Document includes:
  - Animal, human, and in vitro studies
  - Relevant quantitative risk assessments
  - Methods for workplace sampling
  - Basis for revised REL
  - Recommendations for protecting workers from exposure
- Document available at www.cdc.gov/niosh/topics/hexchrom/
- Comments due from public by 31 January 2009

EPA "Residual Risk" Standards Limiting Cr^{6+} Air Emissions

- Industry MACT Standards under review for Cr^{6+}
  - Aerospace manufacturing and rework facilities – chromium and other hazardous air pollutants (HAPs)
  - Electroplating/anodizing operations
- Regulatory Approach
  - Review of existing technology-based standards
  - Evaluate "residual risk" or risk remaining after achieving MACT
  - Limit cancer risks to no higher than 100-in-1 million
  - Revised MACT standards as necessary
- Timeframe for EPA Action
  - Aerospace – Spring 2009 proposed rule
  - Electroplating/anodizing – Fall 2009 proposed rule
- Considerations
  - EPA has authority to be flexible
  - Priorities and focus of new Administration

Chromate Applications



Lockheed-Martin Cr^{+6} Policy Memorandum Issued on December 20, 2007

– *Continue and expand the use of non-hexavalent chromium products with the goal of reducing / eliminating hexavalent chromium from LM products, processes and supply chain,*
– *Continue and expand research to identify additional acceptable alternatives to hexavalent chromium as a priority,*
– *Prioritize and apply resources to resolve corrosion issues while reducing / eliminating the use of known hazardous materials,*
– *Ensure that adequate qualification is completed prior to release of material change to products and processes.*

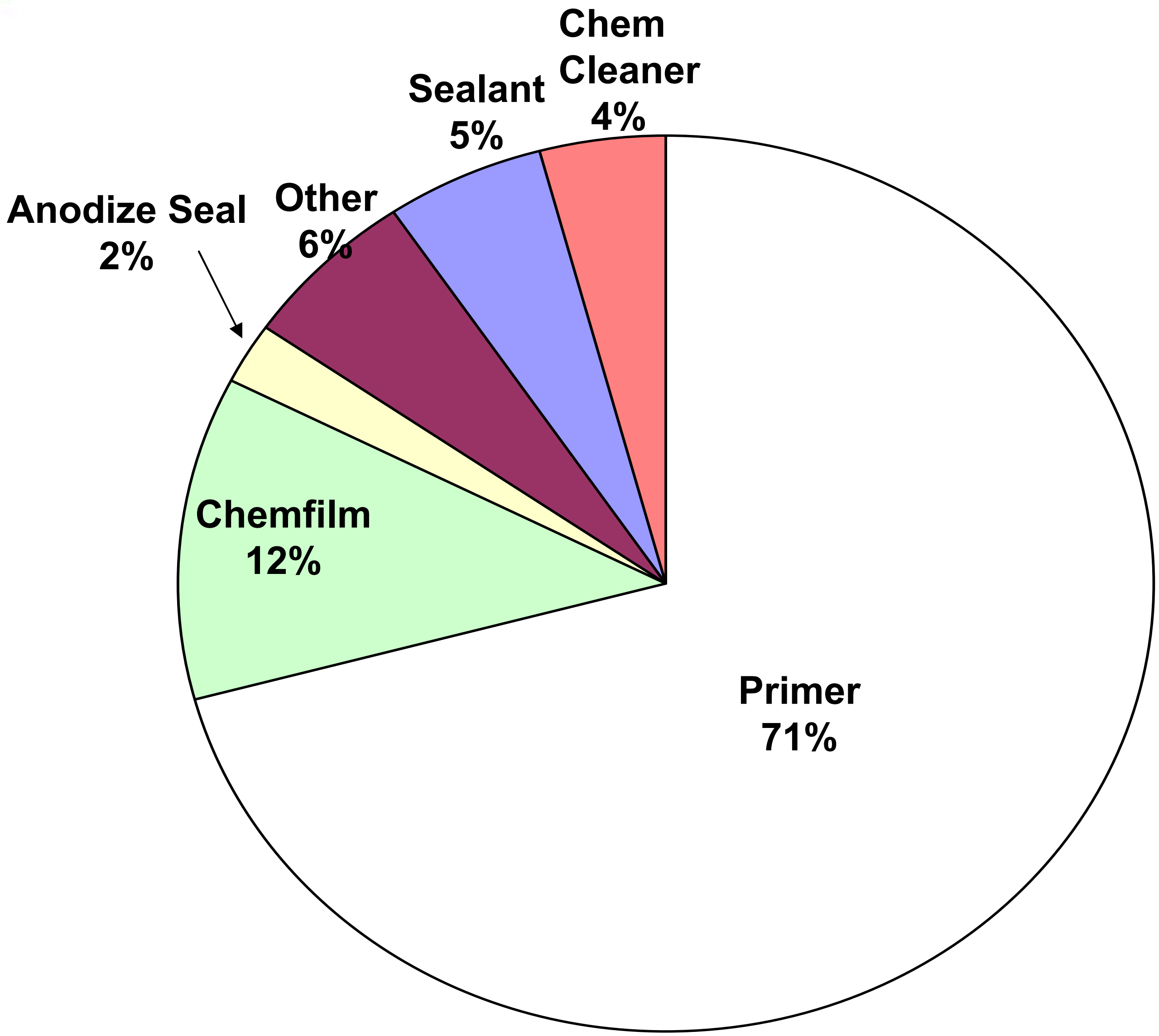
As an interim step, reversion to hexavalent chromium products and introducing new applications of hexavalent chromium products, are undesirable and will require written concurrence of the Vice President of Engineering at the affected Business Unit and approval of the Senior Vice President and Chief Technology Officer at the Corporate level. Appropriate Materials and Processes handbooks and guidelines should be updated accordingly

Impact of LM Policy Letter

"Policy Showed Customers That LM Had Top Level Management Direction To Reduce Cr^{+6}."

- **Motivated LM Programs To Accelerate Testing / Implementation Of Nonchromated Primer**
- **LM Sites Leveraged The Policy Letter Into Starting Several Chrome Replacement Efforts**
  - **Aided In Approving Replacement Efforts**
  - **Customer Program Offices Were Receptive**
  - **Aided LM In Discussing Cr^{+6} Reduction Efforts With DoD, Program Offices**
- **Prioritized Testing, Increased Awareness, Empowered Change**
- **LM Corporate is funding chrome reduction projects**

Annual Lockheed Martin Usage of Cr^{6+} Compounds



Category	% Cr^{+6} Compound
Anodize Seal	2%
Chem Cleaner	4%
Chemfilm	12%
Primer	71%
Sealant	5%
Other	6%
TOTAL	100%

Represents 2007 Usage Including Some '06 data

LM Use of Nonchromated Primers

<u>Exterior Surface Uses</u>:

- **U-2 Authorized To Apply NCP In June 1996**
- **F-117 Began Using NCP Between Coatings In Feb '99**
  - **Approved NCP (10PW22) For All Exterior Layers In Aug '03**
- **F-22 NCP Implementation Started in Late 2002 (Exterior Only)**

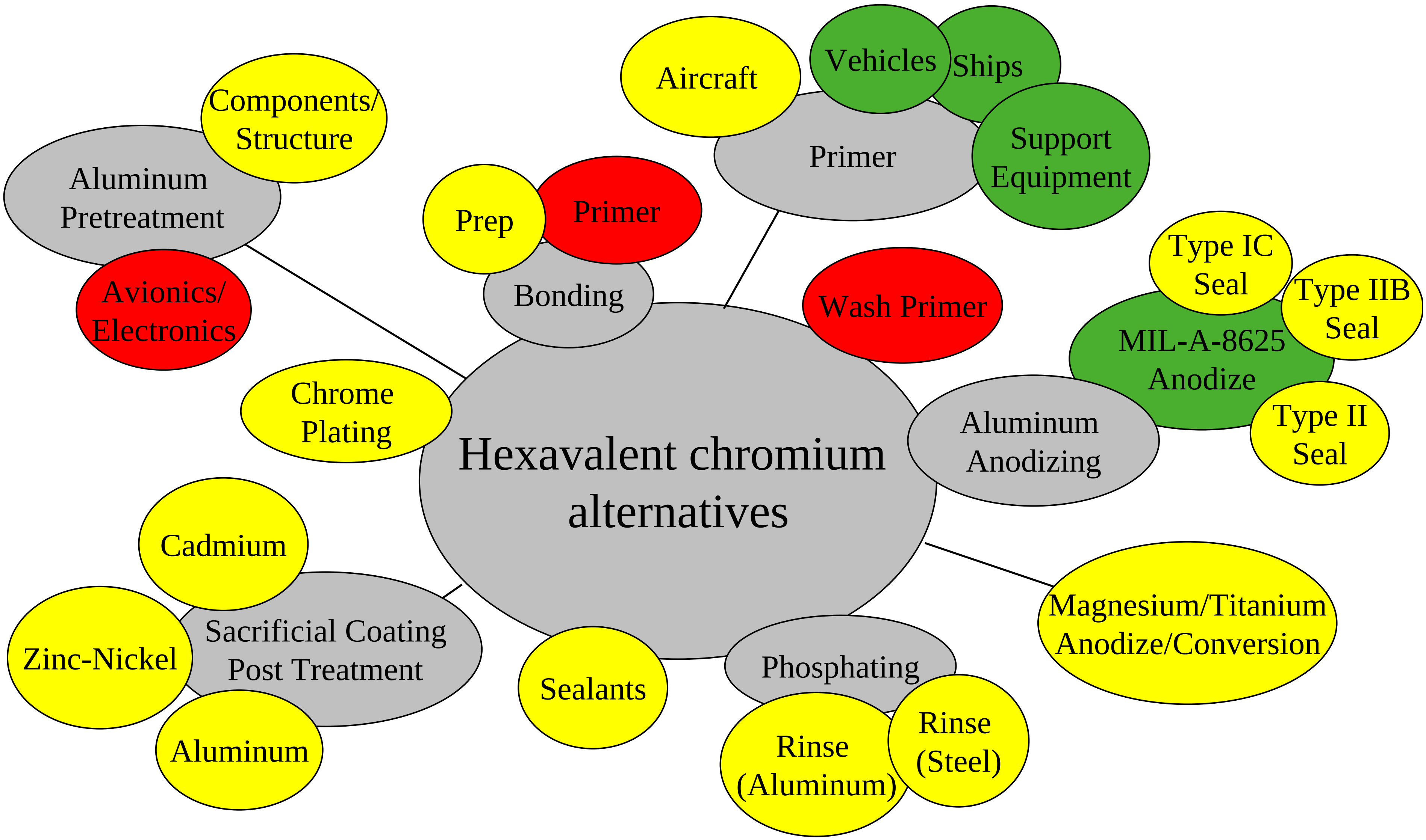
F-35 Implement NCP (44GN098) in Late 2005

– ***First Aircraft To Use On Internal Structure***

NCP: Nonchromated Primer

Application Areas for Chromate Alternatives

Green: Alternatives implemented; niche chromate use remains
Yellow: Limited implementation; near-term validation
Red: No or very limited implementation



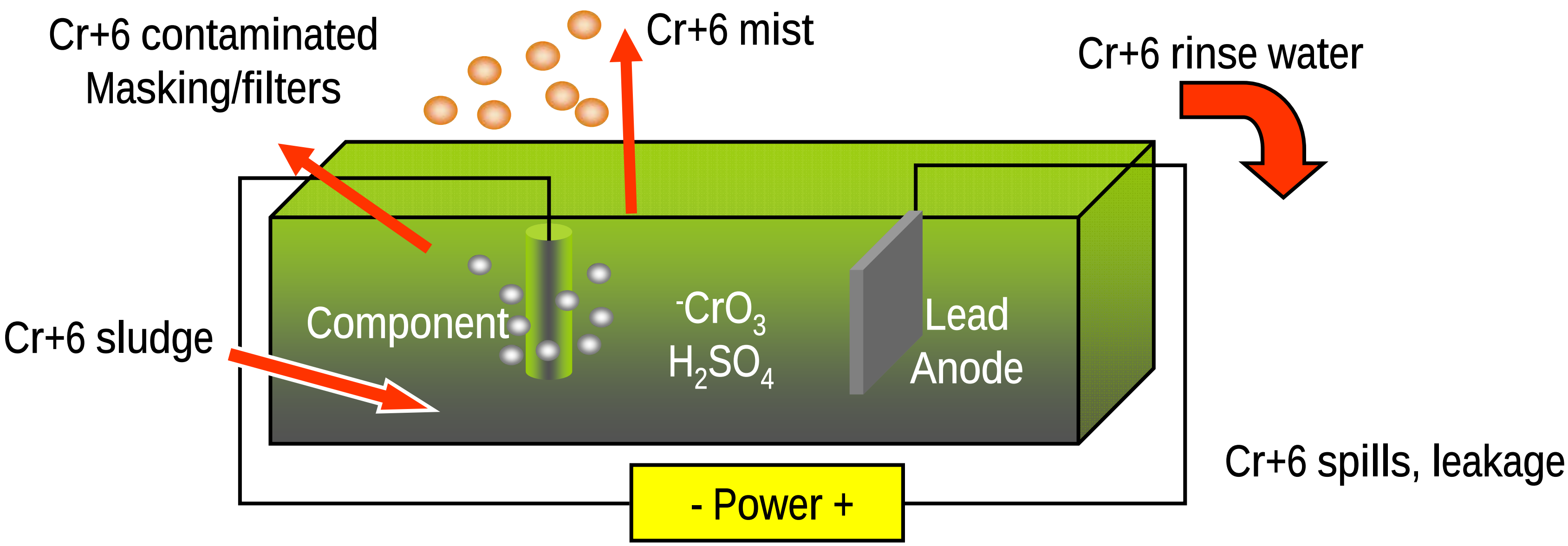
The Real World of Aircraft Processing

Fleet Readiness Center Southeast - Jacksonville

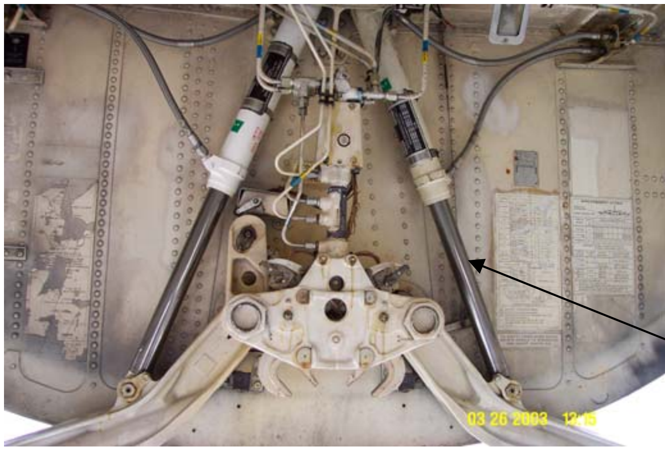
Click on Screen to Watch Video

Chrome Electroplating

- **Electrolytic hard chrome (EHC) plating uses chromic acid solutions**
- **Coatings applied to thicknesses ranging from 0.001” to 0.015” to impart wear resistance or for dimensional restoration to worn or corroded components**



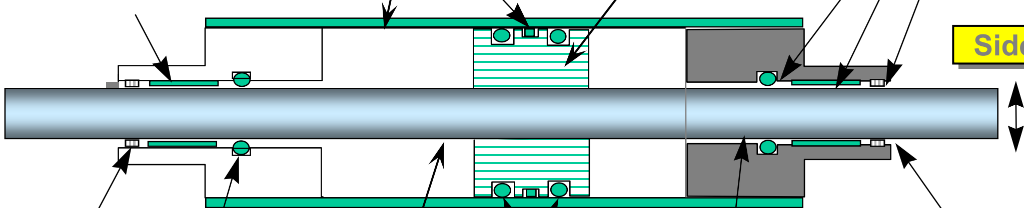
Examples of Usage of EHC on Aircraft Components



Chromed utility actuator rod

Corrosion

Pin



Chromed rod

Impact

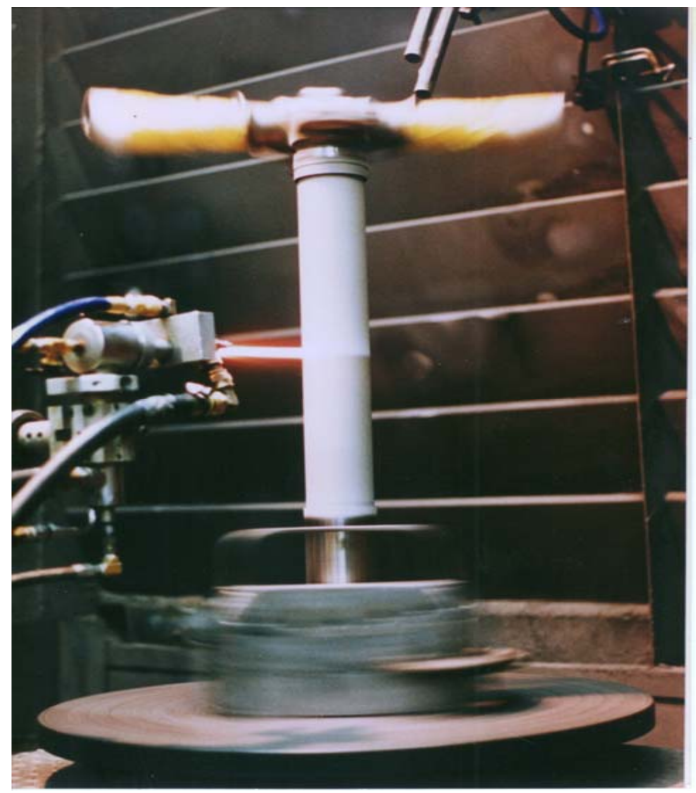
Chromed axle

Scoring

Qualification of HVOF Coatings on Different Types of Aircraft Components

- **Separate ESTCP projects were executed for EHC replacement related to:**
  - **Landing Gear**
  - **Propeller Hub Components**
  - **Hydraulic Actuators**
  - **Gas Turbine Engine Components**
  - **Helicopter Dynamic Components (rotor heads, transmissions, gearboxes, etc.)**
- **Projects ran from 1996-2006**

HVOF Thermal Spraying of WC/17Co onto nose landing gear cylinder




VAQ-138 EA-6B A/C 502
First carrier landing with HVOF coated
MLG Strut Assy installed at NADEP JAX
USS Carl Vinson 9-14-04

HVOF Implementation - Military aircraft

- Joint Strike Fighter (F-35) landing gear – all variants
- Boeing X-45C UCAV has some HVOF WC-CoCr coated landing gear components
- F-18 steering covers and shock absorber piston heads with Tribaloy 400
- CH-53 blade damper internal-surface coatings of Tribaloy 400 have been approved
- Canadian F-18 main landing gear axle hexagon repairs with WC-CoCr have been successfully tested and are awaiting approval
- C-17 nose landing gear post: HVOF WC-Co has replaced hard chrome to prevent heat-burning
- F-22 convergent nozzle actuators: shafts coated with WC-Co, internal surfaces coated with Tribaloy 400 alloy.

USAF HVOF Implementation
Ogden ALC

- Approximately 40 components converted at this time
  - Approximately 300 components flying with HVOF coating
- Several hundred to be added in next 3 years
- Aircraft currently flying with HVOF components
  - A-10
  - B-1
  - B-52
  - C-5
  - C-130
  - F-15 C/D
  - F-16 HW
  - F-16 LW
  - KC-135
  - T-38
- Examples
  - A-10 MLG Piston
  - A-10 NLG Piston
  - B-1 MLG Axle
  - C-130 MLG Piston
  - C-141 MLG Bogie Beam
  - C-141 Outer Cylinder
  - C-5 MLG Roll Pin
  - C-5 MLG Ball Screw
  - C-5 MLG Outer Pitch
  - F-15 Drive Keys
  - KC-135 MLG Axles

HVOF Implementation – Commercial Aircraft

- All new Canadian landing gear designs specified with HVOF WC-CoCr
  - 4 HVOF shops set up to meet demand
- In commercial use for
  - Boeing 767-400
  - Boeing 787
  - Airbus A380
- Maintenance, Repair and Overhaul
  - Boeing has approved for thickness < 0.015”
  - Delta now using for maintenance
  - HVOF now used for repair of flap tracks

Nanocrystalline Co-P Alloy Plating

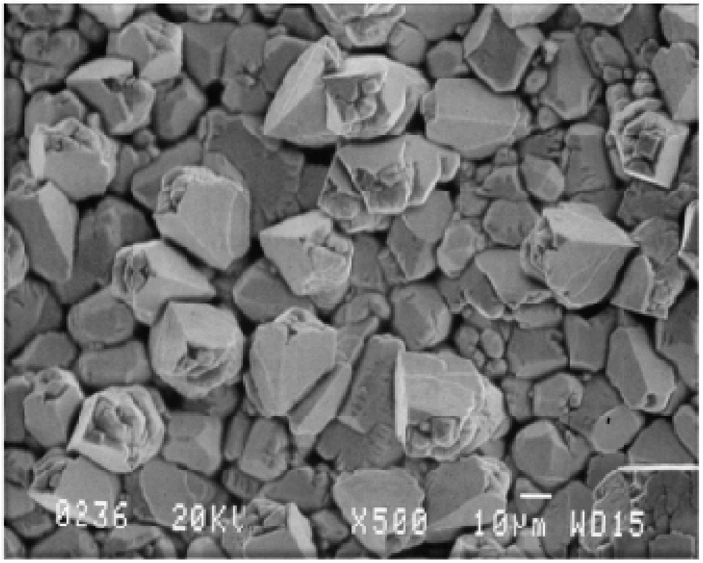
- Technology developed by Integran Technologies Inc.
- Potential replacement for EHC plating
- SERDP Project PP-1152
- ESTCP Project WP-0411
  - Industrial scale-up at Integran
  - Process Line NAVAIR JAX
    - Dem/Val system installed
    - Initial component plating trials
    - IH assessment on Co emissions
  - Performance Testing
    - Fluid immersion testing
    - Hydrogen embrittlement testing
    - Fatigue testing
    - Wear testing
    - Corrosion samples prepared
  - Apply coatings to demonstration components

Chrome Plating Tank at FRC-SE

nCoP tank at FRC-SE

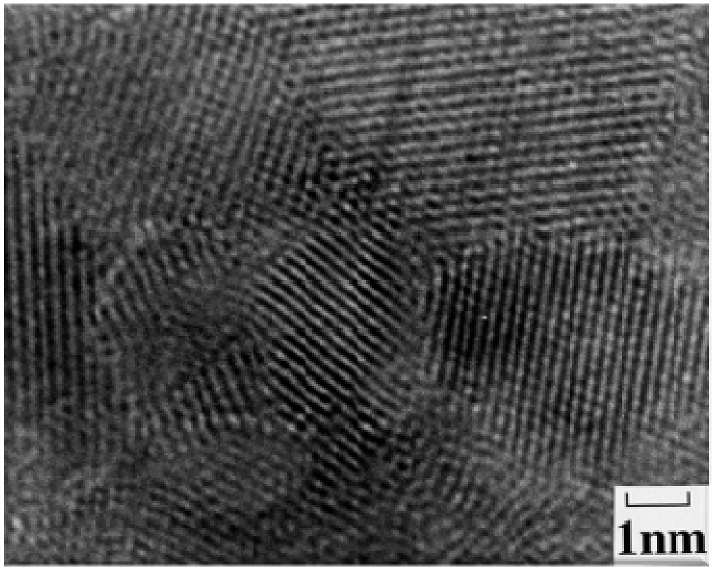
Technology Description

Typical Structure



Typical electrodeposits have crystalline structures with average grain sizes of 10 – 100 µm.

Nanocrystalline Structure

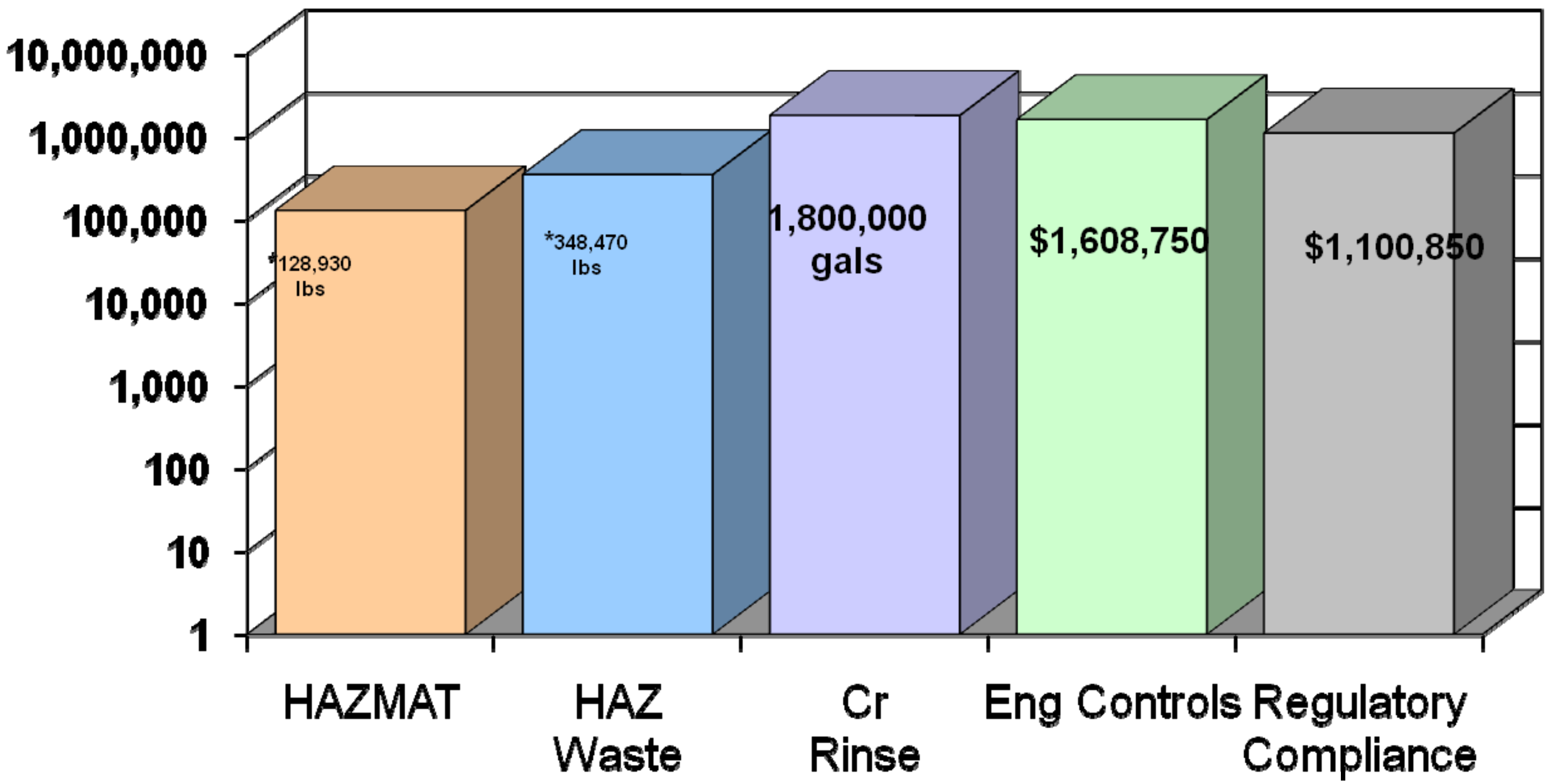


nCoP process creates electrodeposits with grains of 20 nm or less (1000 times smaller).

Cost/Benefit of Technology

(Hexavalent Chromium Plating at Navy FRCs)

- **Estimated NAVAIR P2 Savings over 10 Yrs**

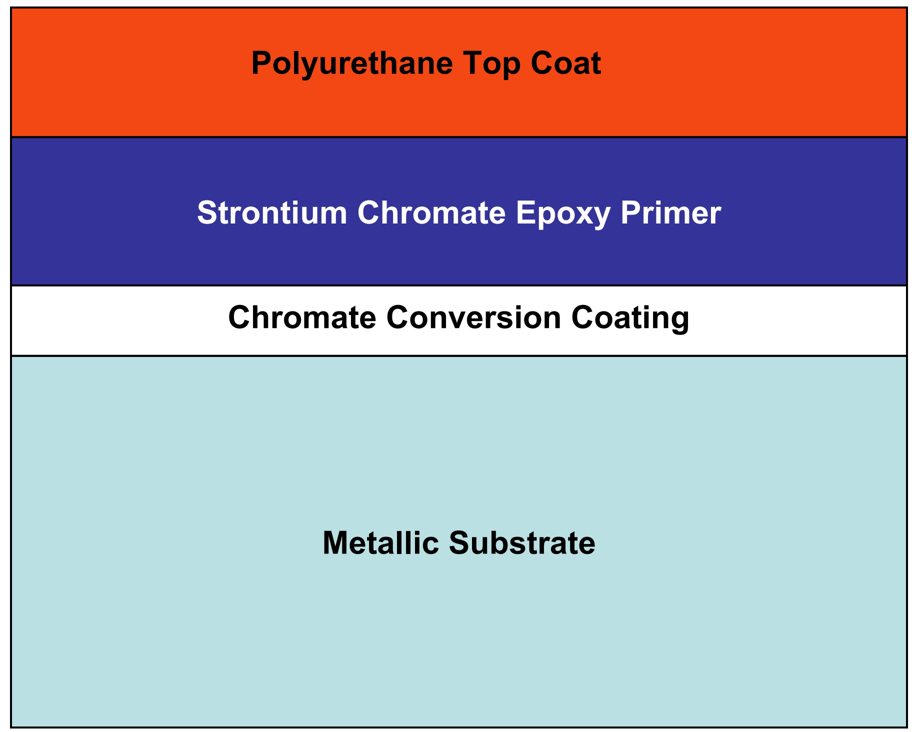


Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs

** Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period*

“Conventional” Coating Stack-Up

- Coating stack-up very common on aircraft, especially for protection of aluminum alloys
- Chromate conversion coating thickness usually only about 0.0001” (2.5 µm)
  - Used to impart corrosion resistance and to improve adhesion of primer
- Primer thickness ranges from about 0.002”- 0.004” (50 – 100 µm)



SERDP Projects to Address Cr^{+6}

Understanding Mechanisms

- **WP-1119:** Critical Factors for the Transition from Chromate to Chromate-Free Corrosion Protection **(Ohio State Univ.)**
- **WP-1618:** Corrosion Protection Mechanisms of Rare Earth Compounds Based on Cerium and Praseodymium **(Missouri University of Science & Technology (MUST))**
- **WP-1620:** Scientific Understanding of Non-Chromated Corrosion Inhibitors Function **(Ohio State Univ.)**
- **WP-1621:** Scientific Understanding of the Mechanisms of Non-Chromate Corrosion Inhibitors **(Southwest Research Institute)**

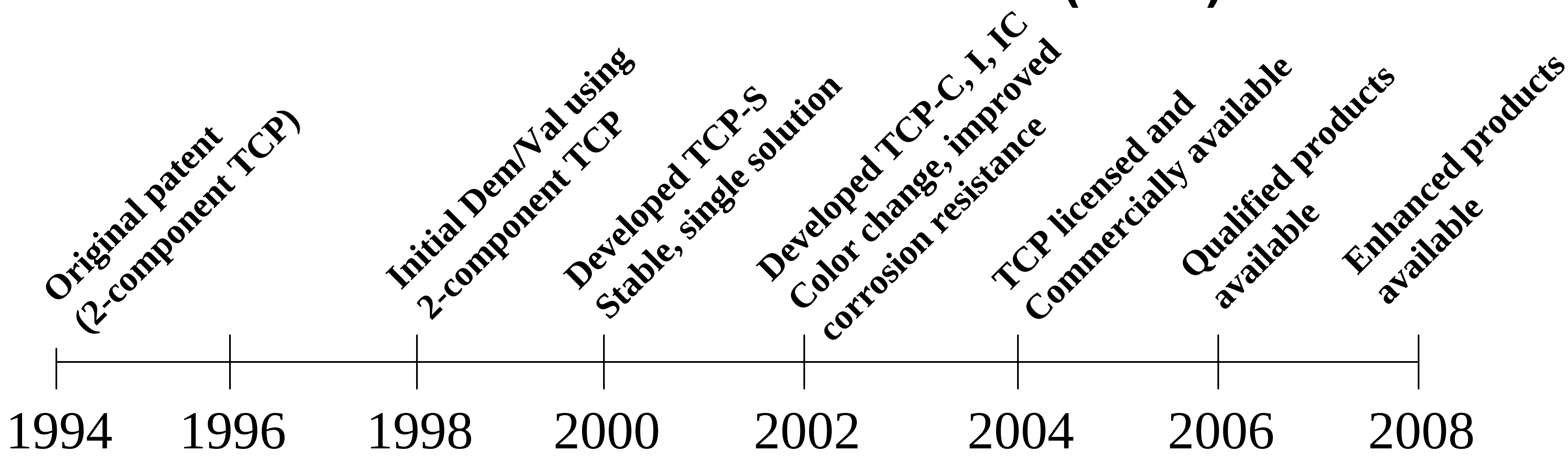
Developing Alternatives

- **WP-1341:** Chromium-Free Coating System for DoD Applications **(Univ. of Cincinnati)**
- **WP-1342:** Zeolite Coating System for Corrosion Control to Eliminate Hexavalent Chromium from DoD Applications **(Univ. CA Riverside)**
- **WP-1519:** Corrosion Finishing - Coating Systems for DoD Metallic Substrates Based on Non-Chromate Inhibitors and Ultraviolet-Curable, Zero-VOC Materials **(MUST)**
- **WP-1520:** Ultraviolet-Curable Non-Chrome Primer and Advanced Topcoat System **(Foster Miller)**
- **WP-1521:** Non-Chromate/No-VOC Coating System for DoD Applications **(Army Research Lab)**

ESTCP Projects to Address Cr^{6+}

- **WP-0025:** Non-chromate Aluminum Pre-treatments **(NAVAIR Pax River)**
- **WP-0527:** Validation of Novel Electroactive Polymers as Environmentally Compliant Coatings for Replacement of Hexavalent Chromium Pretreatments **(NAVAIR China Lake)**
- **WP-0614:** Low Temperature Powder Coatings **(Hill AFB)**
- **WP-0731:** Joint DOD Demonstration and Validation of Magnesium Rich Primer Coating Technology **(NAVAIR Pax River)**
- **WP-0801:** Ultraviolet Curable Powder Coatings **(AFRL)**
- **WP-0804:** Ultraviolet Curable Coatings for Aerospace Applications **(Hill AFB)**
- **WP-0904:** Validation/Demonstration of Anti-Corrosion Inhibitor Primer Formulations as Replacements for Hexavalent Chromium Military Primer Coatings **(NAVAIR China Lake)**
- **WP-0906:** Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles **(ARL)**

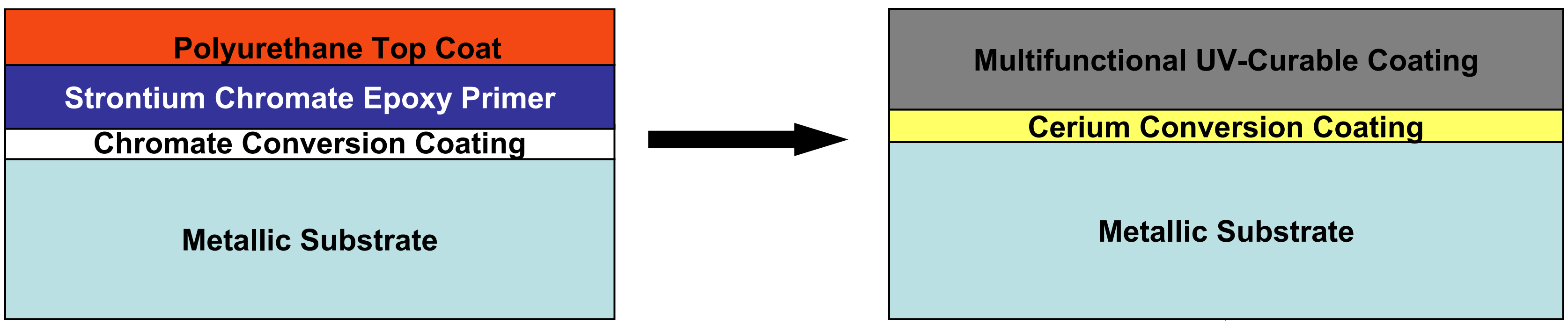
NAVAIR Development of Trivalent Chromium Pretreatment (TCP)



- **ESTCP funded effort from 2000-2007**
- **TCP initially focused on spray application at NAVAIR depots as potential option for spray-applied chromate conversion coating (1998-2000)**
- **TCP-S developed as single, stable solution**
- **Multiple versions have been developed and are being implemented**

SERDP Project
Missouri University of Science and Technology

Develop a Two Layer, Chromate-Free, Zero TRI/VOC/HAPs Corrosion Coating System for DoD Metallic Substrates



Current 3 Layer, Cr(VI) Based Coating System

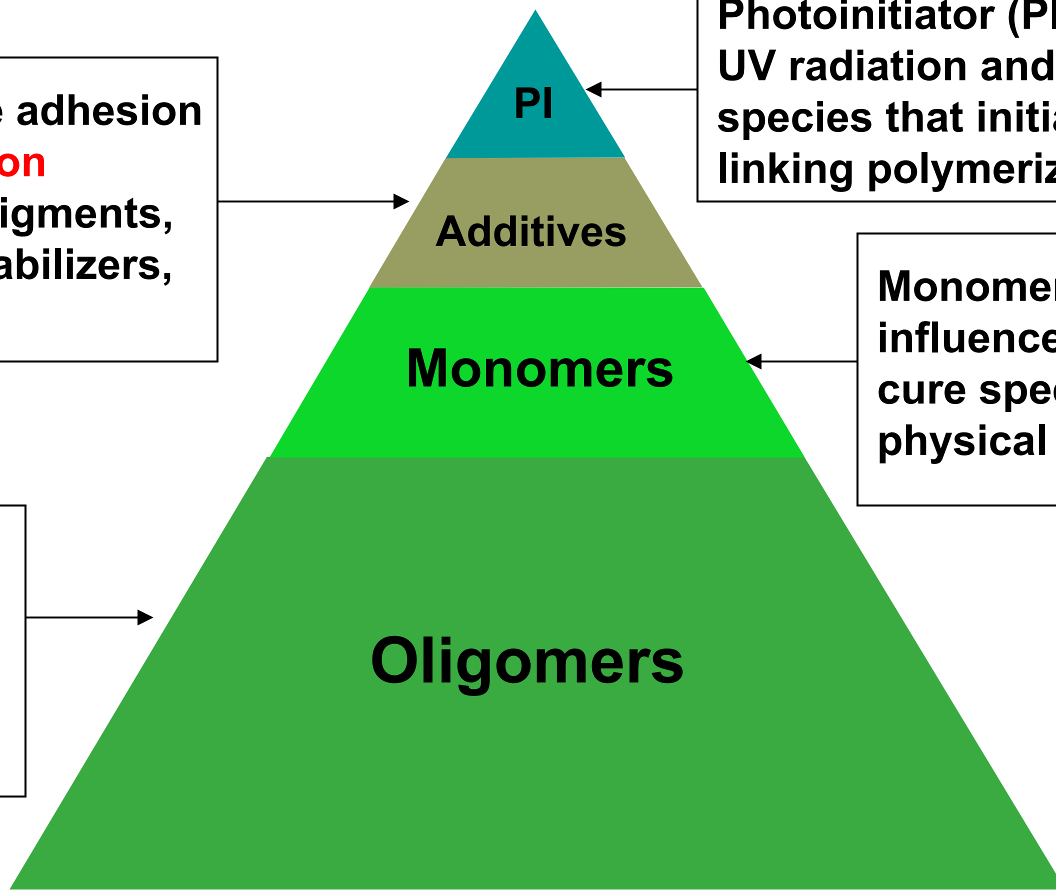
2 Layer, MUV Curable Coating System With No Cr(VI)

Note: Working with Boeing Phantom Works on project

Identify Oligomer, Monomer, Photoinitiator and Additive Chemistry of UV Curable Self-Priming Topcoat System

Additives – include adhesion promoters, corrosion inhibitors, fillers, pigments, dispersing aids, stabilizers, rheological agents

Photoinitiator (PI) – absorbs UV radiation and generates species that initiate cross-linking polymerization



Monomers - influence viscosity, cure speed, and physical properties

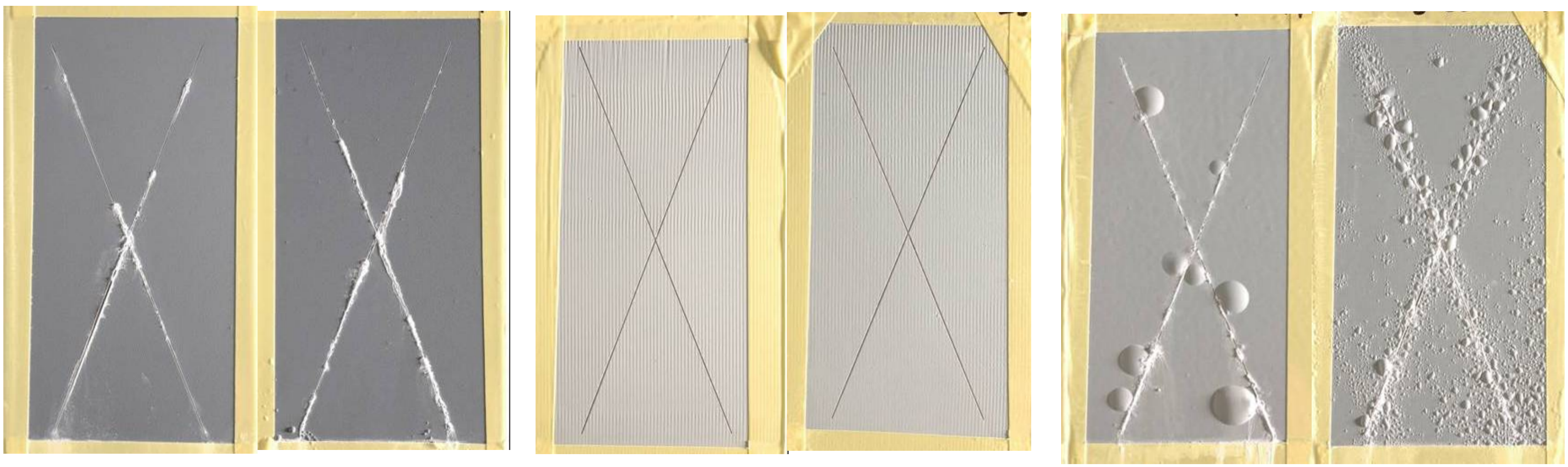
Oligomers - determine the physical properties of the coating

Integrated Coatings - 3000 Hour Salt Spray Results

Round 1, 2024-T3

Best Performance with UV Cured Inhibitor B

- Inhibitor B Performance Better Than All Others, Including Cr(VI)



Cr(VI) Control | **No Cr(VI) Control** | **Inhibitor B On CrCC** | **Inhibitor B On CeCC** | **Inhibitor A On CrCC** | **Inhibitor A On CeCC**

Non-UV (Cr(VI) Control, No Cr(VI) Control)

UV Cured (Inhibitor B On CrCC, Inhibitor B On CeCC, Inhibitor A On CrCC, Inhibitor A On CeCC)

Example of Requirements for New Coating Implementation

- Implementation Path
  - Lab validation – process and product performance
  - Field validation – process and product performance
- Implementation
  - Sign-Off
    - Engineering/Materials
    - Depot/Production
    - Program: Fleet Support Team (FST)/Class Desk/OEM
  - Revise specs (Local/MIL/AMS…)
  - Revise General Series and Equipment Manuals

Accelerated Corrosion Testing

- **Qualification of alternative corrosion-resistant coating systems requires accelerated test methods that represent real-world conditions and result in same mechanisms of corrosive attack**

Allan Grobin, IBM Corporation, member of ASTM Committee G-1 (corrosion-related), October 5, 1977: "The salt spray test while initially developed as a corrosion test was very quickly found not to be a corrosion test. Many of the metal plating specifications disqualified the salt spray test as a corrosion test. It is a comparative test for quality control and should not be used as an evaluator of corrosion resistance. It should not be used to compare the resistance of one type of plating against another."

In 2008, the salt spray test (ASTM B117) is still being specified in qualifying alternative coating systems

Technician loading test panels into salt-fog (salt spray) test cabinet (ASTM B117)

Dynamic Accelerated Corrosion Test Protocol

Because qualification of alternative coating materials and processes is critical, SERDP decided to issue Statement-of-Need for development of accelerated test methodology

Objective

- **To develop an accelerated corrosion testing protocol that more accurately reflects the operational environments of Department of Defense (DoD) end users and would be acceptable across the DoD.**

Focus

- **Stress new protective systems in an effort to understand how they perform compared to the standard systems that are currently in use.**
- **Use several material "stack-up/mock-up" geometries selected from those currently being used by the military services.**
- **Ability to adjust protocol to provide accurate predictive data for most operational environments, ranging from land-based ground vehicles to carrier-based aircraft.**

Projects Being Funded by SERDP

	WP-1673 Luna Innovations Inc. FY09 New-Start	WP-1674 Air Force CTIO FY09 New-Start
Objective	Develop a next generation accelerated corrosion test methodology.	Develop a comprehensive test protocol to accurately predict all aspects of the performance lifetime of DoD coatings.
Technology/ Approach	Measure the evolution of electrolyte composition and corrosion morphology in the lab and at outdoor sites to determine relevant solution composition as well as deficiencies in current test methods. Identify specific regimes that govern corrosion processes and different corrosion failure modes by systematically varying environmental and mechanical inputs. Integrate the data sets and calculate test chamber conditions where realistic failure modes (or combinations of failure modes) will result. Deliver a set of test coupon configurations, exposure regimes, and analysis tools to evaluate the performance of materials and structures in corrosive environments.	Investigate the corrosion products generated in various outdoor environments on a variety of substrates to accurately identify the reactive species present in each environment. Generate a simulated exposure environment that mimics the corrosion products found outdoors. Combine reactive species to duplicate synergistic effects through modification of an existing weatherometer. Kinetics of the simulated environment will be investigated to accelerate (by increasing temperature and/or concentration of reactive species) the performance evaluation.

New SERDP/ESTCP Initiative

ASETS DEFENSE

ADVANCED SURFACE ENGINEERING TECHNOLOGIES FOR A SUSTAINABLE DEFENSE

SERDP Strategic Environmental Research and Development Program

Improving Mission Readiness Through Environmental Research

ESTCP

- **Numerous surface-engineering-related projects executed by SERDP, ESTCP and other organizations to develop and evaluate new technologies that are more environmentally friendly and reduce life-cycle costs**
- **Problem is that stakeholders and weapons systems owners do not have ready access to data to determine if new technology can be implemented**
- **ASETSDefense is initiative intended to develop information data bases and organize workshops associated with technologies in the surface engineering field; web site www.asetsdefense.org is entry point to engineering data and materials selection data bases under development**

SERDP ESTCP

Conceptual Design of Main Web Page

Structure of Surface Engineering Data Base