RDT&E Progress and Plans for Hexavalent Chromium (Cr\textsuperscript{6+})

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Environmental Technology Development Process

**SERDP**
- Service Requirements
  - Basic/Applied Research
  - Advanced Development
- Demonstration/Validation

**ESTCP**
- Implementation

**DUSD(I&E)**
**DDR&E**
Total four-year investment = ~ $30.2 million
Recent SERDP Cr\textsuperscript{6+}-Related Projects

FY2008

- Scientific Understanding of Non-Chromated Corrosion Inhibitors Function
  - WP-1618: *Corrosion Protection Mechanisms of Rare-Earth Compounds Based on Cerium and Praseodymium* (Missouri University of Science and Technology)
  - WP-1619: *Morphology and Mechanism of Benign Inhibitors* (University of Cincinnati)
  - WP-1620: *Scientific Understanding of Non-Chromated Corrosion Inhibitors Function* (Ohio State University)
  - WP-1621: *Scientific Understanding of the Mechanisms of Non-Chromate Corrosion Inhibitors* (Southwest Research Institute)
Recent SERDP Cr\(^{6+}\)-Related Projects

**FY2009**

- Dynamic Accelerated Corrosion Test Protocol
  - WP-1673: *Accelerated Dynamic Corrosion Test Method Development* (Southwest Research Institute)

- Environmentally Acceptable, Direct-To-Substrate Pretreatments for Multi-Material Systems
  - WP-1675: *Wash Primer Replacement Based on the Superprimer Technology* (University of Cincinnati)
  - WP-1676: *Environmentally Friendly Zirconium Oxide Pretreatment* (PPG Industries Inc.)
Recent SERDP Cr$^{6+}$-Related Projects

**FY2011**

- Understanding Corrosion Protection Requirements for Adhesive Bond Primers
  - WP-2144: *Understanding Corrosion Protection Requirements for Adhesive Bond Primers* (NAVAIR Pax River)
Scientific Understanding of Non-Chromated Corrosion Inhibitors Function (Project WP-1620)

Project Team – Main Performers

- Dr. Gerald S. Frankel and Dr. Rudolph G. Buchheit
  Fontana Corrosion Center, The Ohio State University
  Specialists in corrosion

- Dr. Greg Swain
  Dept of Chemistry, Michigan State University
  Specialist in electrochemistry/surface analysis

- Dr. Mark Jaworowski
  United Technologies Research Center
  Specialist in surface treatments
Project Team – Advisory Group

- Mr. Bill Nickerson, Naval Air Systems Command, Patuxent River, MD
- Mr. Brian Placzankis, Army Research Labs, Aberdeen Proving Ground, MD
- Dr. Joel Johnson, Air Force Research Labs, WPAFB
- Dr. Bill Fristad, Henkel Corp., Madison Heights, MI
- Dr. Joe Osborne, Boeing Phantom Works, Seattle, WA

These team members are deeply involved in the development and application of chromate-free coating systems for military applications.
The primary objective of this work is to develop fundamental understanding of the existing chromate-free inhibitors and inhibitory coating systems with the ultimate goals of:

• Providing scientists and engineers developing such coatings with information that will help them improve their products.

• Providing engineers designing structures with information that will help them utilize non-chromate coating systems more effectively.
Technical Approach

Tasks/Projects

Surface treatments and soluble inhibitors:
1. Fundamental studies of the Trivalent Chrome Process (TCP)
2. Mechanisms of selected inhibitors

Paint/pigment properties:
3. Active inhibition, barrier properties and adhesion
4. Paint adhesion strength and mechanism
5. Inhibitor activation and transport in the primer layer

System level:
6. Interactions between polymer matrix, pigment, surface treatment, and alloy
7. Characterization of local environments in coating systems

The tasks will be performed in parallel by various team members.
Interactions between polymer matrix, pigment, surface treatment, and alloy

Background

• In chromated coating systems, chromate released from SrCrO₄ pigment dissolution in a primer layer, stabilized the artificial passivity of an underlying chromate conversion coating.

• Such a cooperative may not exist in arbitrary combinations of non-chromate passivation treatments and non-chromate primers or paints.

Questions:

• How well is the artificial passivity conferred by TCP, NCP and REM coatings reinforced by inhibitors leached from chromate-free pigments in overlying organic coatings?

Approaches:

• Interrupted exposure testing, in situ EIS and destructive forensic characterization at local defects.
Accelerated Dynamic Corrosion Test Method Development (SERDP Project WP-1673, SwRI)

- **Objective**
  - Develop an improved test method to assess corrosion of new systems
    - Excite appropriate failure modes
    - Integrate representative sample designs into accelerated corrosion testing
    - Integrate mechanical loading into accelerated corrosion testing

- **Approach**
  - Characterize and compare the development of corrosive electrolytes for “real world” and current accelerated corrosion tests
  - Determine the effect of critical environmental and mechanical parameters on degradation modes of system components
  - Develop a framework to tailor the accelerated corrosion test to real world failure modes
Project Team

- **James Dante, Southwest Research Institute**
  - PI, electrochemistry, atmospheric corrosion, corrosion test method development
- **Craig Matzdorf, NAVAIR Pax River**
  - Co-PI, atmospheric testing, accelerated corrosion testing, qualification
- **Dr. Joseph Osborne, The Boeing Company**
  - Co-PI, coating system integration, coating and surface prep development, Cr and Cd replacement
- **Drs. Robert Kelly and Bill Keene, University of Virginia**
  - Measurement of thin film and localized electrolytes, electrochemistry, corrosion mechanisms
  - Atmospheric chemistry
- **Brian Placzankis, Army Research Lab**
  - Accelerated corrosion testing, materials qualification
- **Steve Carr, Army Aviation and Missile Command**
  - Accelerated corrosion testing, materials qualification
- **Francine Bovard, Alcoa Corporation**
  - Corrosion test method development, SAE Task Leader for accelerated aluminum corrosion test
- **Fritz Friedersdorf, Luna Innovations Inc.**
  - SCC sensors and coating properties
Sample Design

- **Sample design needs to simulate:**
  - Geometry with exposed and occluded areas
  - Galvanic couples between substrates and fasteners
  - Coating across discontinuities
  - Coating defects

- **Sample design needs to allow for:**
  - Selection of paint, fastener materials, and substrate alloys
  - External mechanical loading

- **Initial design based from NAVAIR sample geometry**

- **Working to develop guidelines and definitions for selection and characterization of exposed panels**
Effect of Environment on Cracking

- RH and NaCl effect SCC behavior
- SCC sensor being modified for measuring SCC in outdoor or laboratory environments

![Graph showing da/dN vs. Relative Humidity (%RH)]

- RH only
- RH + NaCl

DRH

![Image of modified SCC sensor]

![Image of V-Notched Aluminum Fracture Sample]
Selected ESTCP Projects Related to Cr$_{6}^{+}$

- **FY2000:** Non-chromate Aluminum Pre-treatments (NAVAIR Pax River)
- **FY2003:** Development of Ferrium S53 High-Strength, Corrosion-Resistant Steel, (Hill AFB)
- **FY2005:** Validation of Novel Electroactive Polymers as Environmentally Compliant Coatings for Replacement of Hexavalent Chromium Pretreatments (NAVAIR China Lake)
- **FY2006:** Supersonic Particle Deposition for Repair of Magnesium Components (Army Research Lab)
- **FY2006:** Low Temperature Powder Coatings (Hill AFB)
- **FY2008:** Ultraviolet Curable Powder Coatings (AFRL)
- **FY2008:** Ultraviolet Curable Coatings for Aerospace Applications (Hill AFB)
- **FY2009:** Validation/Demonstration of Anti-Corrosion Inhibitor Primer Formulations as Replacements for Hexavalent Chromium Military Primer Coatings (NAVAIR China Lake)
Selected ESTCP Projects Related to Cr\textsuperscript{6+}

- **FY2009**: *Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles* (ARL)
- **FY2009**: *Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Plating Alternative* (NAVAIR Jacksonville)
- **FY2010**: *Electrocoat Process for Non-Chromate Primers in DoD Manufacturing* (NAVAIR Pax River)
- **FY2011**: *Chromium Elimination and Cannon Life Extension* (Benet Weapons Lab)
- **FY2011**: *Comprehensive Evaluation and Transition of Non-Chromated Paint Primers* (NAVAIR Pax River)
Development of S53 Ultra-High-Strength (UHS) Corrosion-Resistant Stainless Steel

- Ultimate objective was to develop UHS stainless steel to replace UHS low-alloy steels such as 4340 that require cadmium plating and Cr⁶⁺ post treatment for corrosion protection
- Started as SERDP Exploratory Development (SEED) project in December 1999; SERDP full project started in June 2001
- Transitioned to ESTCP project in March 2003
- Developed under Accelerated Insertion of Materials (AIM) program
- First military component (A10 drag brace) fabricated in December 2005
Demonstration Tests at Hill AFB

A-10 Main Landing Gear Piston
- Performed landing gear strut testing of S53 Main Landing Gear Piston to qualification standards per Mil-A-8866 - Successfully Completed 4 Lifetime Test
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - Awaiting Approval

A-10 Nose Landing Gear Drag Brace
- Perform landing gear strut testing of S53 Main Landing Gear Drag Brace Strut to qualification standards per Mil-A-8866 - Complete
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - Awaiting Potential Approval

A-10 Nose Landing Gear Axle
- Analysis and Design to Achieve Final Qualification - Complete
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - Awaiting Potential Approval

T-38 Piston
- Performed landing gear strut testing of S53 Main Landing Gear Piston to qualification standards per Mil-A-8866 - Successfully Completed 5 Lifetime Test
- Conduct a Field Service Evaluation with fully processed components on a T-38 aircraft - December 2010
A10 Demonstration Components

- **A-10 drag brace (300M - 270 ksi)**
  - Simple tension loading
  - No forging required
  - Corrosion related failures

- **A-10 main landing gear piston (4330V – 240 ksi)**
  - More complex loading
  - Forged component

- **A-10 nose landing gear axle**
Examples of *Ferrium* S53® Market Adoption

Application Examples

- Aircraft landing gear - parts in production and preparing for flight by USAF; commercial landing gear parts in detailed evaluation
- Auxiliary aircraft equipment - parts specified for use in major next-generation commercial aircraft platform aux equipment
- Motion control devices - parts specified for aerospace platforms
- Drive shafts - demonstration helicopter rotor driveshafts in progress
- Extensive market qualifications/property data resources -
  - CINDAS ASMD data base
  - MMPDS-04 CN1
  - SAE AMS 5922
- Robust supply chain -
  - 2 competing licensees:
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
HVOF Implementation - Military aircraft

- Joint Strike Fighter (F-35) landing gear – all variants
- Hill Air Force Base (Ogden Air Logistics Center) putting HVOF into production on hundreds of landing gear components on various types of aircraft; requiring vendors to provide HVOF on landing gear, not hard chrome
- 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
- 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.
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
Eliminating Chromium from Medium Caliber Gun Barrels


Results

- Process to explosively bond Tantalum-10% tungsten liners to the insides of medium caliber cannons.
  - Firing tests demonstrated that the lined tube showed superior wear resistance – lasts twice as long as chrome-plated tube.

Benefits

- Eliminates the use of hexavalent chromium in medium caliber gun barrels while providing superior performance and reduced life cycle costs.
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.
www.asetdefense.org

Menu
● Surface Engineering Database
● Clean Alternatives Information
● ASETSDefense Workshops
● DoD Policies, Government Regulations
● Team Workspaces
● Tools
● Assistance
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● Contact ASETSDefense

Submenus drop down on click

One-page technology descriptions

Welcome to the ASETSDefense website

This site is designed to provide background information and detailed technical data on alternatives to coatings and surface treatments that are environmental or health hazards, such as:

- Coatings that contain hexavalent chromium or use it in the deposition process
- Coatings that contain cadmium
- Coatings that contain volatile organic compounds (VOCs)

ASETSDefense
Advanced Surface Engineering Technologies for a Sustainable Defense - ASETSDefense - is a Department of Defense (DoD) initiative sponsored by Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP). Its objective is to facilitate the implementation of new, environmentally friendly technologies for surface engineering (coatings and surface treatments) by providing ready access to information and data from research, development, test, and evaluation efforts as well as the status of approvals and implementations. ASETSDefense provides defense organizations with information and assistance to improve weapons system performance and life-cycle cost while reducing or eliminating environmental safety and occupational health (ESOH) impacts.

Surface Engineering Database
This is a relational database designed with search capability to provide access to the available information needed to make informed decisions on the use of alternatives to materials and technologies used for surface engineering that pose environmental or health hazards. This information includes detailed engineering data, background documents, and information on processes and products that have been validated, authorized or implemented.

> more details...
ASETSDDefense Workshop

- Held 7-10 February 2011 in New Orleans, LA
- 241 attendees representing DoD labs and repair facilities, OEMs, and vendors
- Covered all ESOH coating and surface finishing issues in new and legacy aircraft, vehicles and ships
- Focus was on Cr$^{6+}$ as a result of USD (AT&L) memo
- 51 presentations covered research & development, demonstrations and implementations of alternative technologies
- Held side meeting on *Computational and Data Base Methods for Design and Prediction*
- Workshop summary plus all presentations are available on web site, [www.asetsdefense.org](http://www.asetsdefense.org)
- Next workshop planned for August 2012
Information Resource

For additional information on all SERDP and ESTCP projects, visit the new SERDP-ESTCP web site:

www.serdp-estcp.org