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Non-Chromate Alternatives

Bill C Nickerson
Materials Engineering Division
NAVAIR 4.3.4

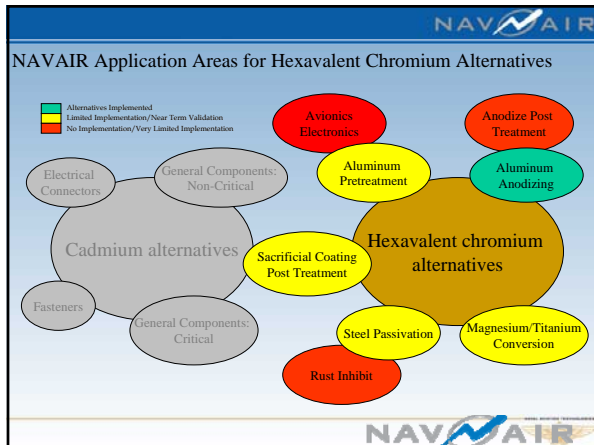
NACE Corrosion 2007

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Technical Challenges Facing Department of Defense

- Reducing the amount of money spent on corrosion prevention and control
 - DOD currently spends 10-20 billion dollars per annum*
- Eliminating hexavalent chromium from the life cycle of the coating system
- Increasing performance of coatings providing materials protection against corrosion

*Corrosion Prevention and Control Planning Guidebook, Spiral Number 2- July 2004, Issued by PDUSD (AT&L)



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Metals Finishing

- Hex Cr in Finishing - Cr⁶⁺ is ubiquitous in its use for corrosion protection
 - Basis of best corrosion resistant products. Very mature: used for 50 plus years, Very robust, inexpensive (to purchase), and easy to use, Inhibits corrosion on multiple materials: Al, Fe, Mg, Zn, Cd, Comfort level of users is “high”
 - EO 13148 stipulates a 50% reduction in use of priority chemicals by EY06
 - European Union Directive 2000/53/EC “End of Life Vehicle Directive” – Article 4, Section 2 (a): bans Cr⁶⁺ after July 1, 2003 – except for 2 gm/vehicle
 - OSHA – Current PEL: 100 ug/m³ Chromic Acid/52 ug/m³ Cr⁶⁺ (ceiling concentration) – New PEL expected CY06

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Metals Finishing Applications

Technology –

- Conversion Coatings – Aluminum, Magnesium, Titanium, Zinc
- Anodizing Sealing – Aluminum Anodizing Sealing
- Sacrificial Coatings – Cd, Zn/Zn Alloys, IVD-Al/Aluminum Plate
- Phosphate Rinsing – Zn/Mn/Fe Phosphate
- Rust Inhibiting Coatings – Fe & Steel Alloys

Technology Drivers –

- Major Issue – Hexavalent Chromium Reduction/Replacement
- Safety & Health, Environmental

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Objectives

- Optimization of compositions and processes
 - Follow-on evaluations from current implementations
 - Evaluate products/processes through lab and field testing
 - Transition technology improvements for improved DoD & Industrial capability
- Higher performance “green” coatings for corrosion control
 - Cr^{VI} is toxic – Listed as known carcinogen by IARC, basis for all of the high-performance coatings for military/industry standard
 - Focus on ESOH has led to the implementation of coatings/processes that offer **greatly reduced corrosion protection**

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Objectives

- Demonstrate and validate the in-service performance of non-chromate treatments on DoD aircraft and ground vehicle assets
- Aircraft – Rotary and Fixed-wing platforms for US Naval Aviation, US Army Aviation, US Air Force
- Vehicles – US Army Ground Combat Systems, US Naval Sea Systems, US Marine Corps Amphibious

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NAVAIR Application Areas for Hexavalent Chromium Alternatives

- Alternatives **MUST** be compatible with secondary finishing technologies
 - Organic Primers/Paints, Baked Resin Coatings, Adhesives, Sealants

<p>CURRENT NAVY AUTHORIZATION: NON-Chromated Conversion Coating (TCP) + Chromated Primers</p>	<p>Non-chromated Conversion Coating</p> <p>Non-chromated Primer</p>
<p>Chromated Conversion Coatings</p> <p>Chromated Primers (BASELINE)</p>	<p>Chromated Conversion Coating</p> <p>NON-Chromated Primer</p>

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Status

- NAVAIR –
 - Authorization Letter issued for TCP
 - NADEP Cherry Point Implemented Alodine T5900 Jan. 2006
 - 20 A/C delivered to fleet
 - NAS Kingsville – T-45 demo planned FY07
- AMCOM –
 - AMRDEC Materials authorized TCP for implementation
 - CH-47 FY06 Demo (1109th AVCRAD) – In service for 12+ months
 - FY07 CCAD Transition Planned
- USAF –
 - TO 1-1-8 authorizes PreKote
 - Ongoing dem/val – AC130
 - SAE Committee Specification for organic surface finishes

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Status

- TACOM –
 - Authorization Letter issued for Alodine 5700
 - 5000/6000 Series – Red River Army Depot
 - PM Combat Systems EMT TCP demo
 - 3 M2A3 Bradley's – 3+ yrs
- USMC –
 - DRPM AAA authorized Alodine T5900
 - Alodine 5700 Wipes – implemented 2005
 - AVTB, Camp Pendleton
- NAVSEA –
 - Technical warrant holder decision on implementation
 - New platforms (LCS, Swift, etc) using more "aerospace" materials

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Status

- General Dynamics –
 - Revised Finish Spec – EFV
 - Alodine T5900
- BAE Ground Systems –
 - FY06/07 demonstrating Metalast TCP-HF
 - Working with commercial finishing shops
 - Evaluating Nalco TechBond
- Boeing St. Louis –
 - Alodine 5700 Wipes for touch-up
 - Evaluating TCP products for immersion line
 - Working w/ UMR for Ce-based conversion processes
- United Technologies
 - Evaluating TCP products for Sikorsky, HS, Pratt & Whitney

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TECHNOLOGY TRANSFER

- MIL-DTL-81706 Revision B – Oct 2005
 - Updating manuals and supply system
- MIL-C-5541 Revision F – Jun 2006
 - Updating manuals and supply system
- SAE Committee B participation
- ASTM Committee F40 –
 - WEEE, RoSH Impacts
- OEM & Industrial Partnerships
 - Specs & Stds
 - Commercial Finishing Vendors

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Implementation

- NAVAIR Class N Authorization
 - Ser AIR 4.9.7/7.4801 March 1, 2005
 - 23377/85582 QPL Class N – Scuff-sand & Overcoat
 - FRC NI Component Paint Shop
 - MIL-PRF-85582 Type II, Class N – PPG EWAE118A
 - No authorization for Class N with MIL-DTL-81706 TyII
 - Pursuing Class C1 primers
 - MIL-PRF-85582 – 2nd Source
 - MIL-PRF-23377 – In progress
 - MIL-PRF-85582 Class N – PPG
 - Poor field testing results, adhesion and corrosion issues
 - TT-P-2756
 - Implemented for S-3, E-2, H-53

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Implementation

- USAF Class N Authorization
 - F-15 Program Approval – Deft 02GN084
 - Only being used at Sioux City, IA due to induction time issues
 - Pursuing coating SYSTEM specification
 - Cleaner/Surface Treatment/Primer/Topcoat/Stripper
 - Qual as total system
 - Sico epoxy Class N – Failed initial MIL-PRF-23377 QPL Test
 - Also pursuing SAE NC pretreatment specification
 - Have baselined “ELT/APC” topcoats – Deft/ANAC
 - Known detriment to overall system corrosion performance
 - MIL-PRF-85582 Class N – PPG
 - Field testing late 90’s – Poor results, extra corrosion reported

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Implementation

- AMCOM Class N Authorization
 - AMSRD-AMR-AE-U Memo TN12144 12 February 2005
 - 23377 Class N recommended over 85582 Class N
 - Approves use of MIL-DTL-81706 Type II w/ Class N primers
 - Specifies 85582 Class N for wet-install – non-aqueous reduction
 - 1109th AVCRAD – Oct. 2005
 - Began field testing of Class N system – TCP/Hentzen 23377 N
 - Currently in process of implementation for H-47, H-60, H-58
 - Corpus Christi Army Depot
 - Currently implemented Hentzen 23377 N
 - Evaluating Deft 23377 N and 85582 N for implementation
- USMC Class N Authorization
 - EFV Implementation – MIL-PRF-23377J TyI, Class N
 - All surfaces, including interior and wet install applications

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Technical Status

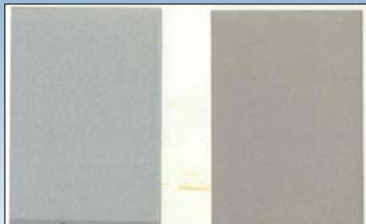
- FY04 RDT&E Efforts
 - NCP
 - NCP on anodized Al – corrosion, adhesion excellent – USAF additional testing – Navy Invention Disclosure (I.D.) filed
 - Alt. metallic corrosion inhibitors, bare corrosion/adhesion
 - NCP on Al – corrosion, adhesion, color – Navy I.D. filed
 - NCP on Sac. Coatings – corrosion, adhesion – Navy I.D. filed
 - TCP
 - TCP-C – Alt. Zn counter ions – bare corrosion, solution stability, color
 - TCP/TCP-C on Mg - bare/painted corrosion, adhesion – Navy I.D. filed
 - TCP/NCP/TCP-C on Steel - paint adhesion/corrosion, humidity testing (underway) – Navy I.D. filed
 - TCP/TCP-C applicator pens - repair applications, bare corrosion, shelf-stability and paint adhesion/corrosion (underway)

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Technical Status

- FY05 RDT&E Efforts
 - NCP
 - NCP-I Pretreatment – Bare corrosion testing (underway) – Adhesion/Painted Corrosion (Navy I.D. filed)
 - NCP-I Anodize Seal – NCP yields 1,000+hrs on Al anodize – NCP with Inhibitor sealed anodize coupons prepared (awaiting chamber space)
 - NCP w/ counter ion Additive – Bare corrosion testing completed – no improvement vs. baseline NCP
 - TCP
 - CrIII Anodize – Pushed out due to extremely high performance of TCP/NCP Sealing on SAA, TFSA, BSAA
 - FY04/5 TCP on Mg improvements to continue in FY06
 - Zn/Fe Phos Rinse – TCP as good or better than chromate in initial screening
 - TCP-I/IC for anodize sealing/sacrificial coating post-treatment (in progress)
 - TCP/NCP – Process optimized for bright Zn and ZnNi post-treatment

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TCP & TCP-C @ 336hr NSF
No Evidence of Corrosion even with TCP-C on AA2024T3

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Aluminum Anodizing

Traditional Anodizing – Corrosion Resistant Coatings

Chromic Acid Anodize (Type I) – Solution/Anodic Coating contain Hex Cr

Sulfuric Acid Anodize (Type II, IIB) – Rinse/Sealer solution contains Hex Cr, chromate film deposited on anodic coating

Hot Water Sealing greatly lowers the corrosion performance vs. chromate anodizing/rinsing

Non-Chromate Anodize Rinse –

Trivalent Chromium Process (TCP) rinsing yields consistently better corrosion performance vs. traditional chromate/chromic acid rinse (TCP more cost effective)

Non-chromium Process (NCP) rinsing performs similarly to chromates over Type II, IIB sulfuric acid anodize

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Tri-chrome seal for Thin-film SAA 2184 hrs B117

1680 hrs

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Non-chrome seal for Thin-film SAA

AA2024-T3 1008hrs B117

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Magnesium Finishing

Magnesium Alloys used for high-strength/very light-weight components

Transmission housings and gearboxes primary DoD application

Traditional Pretreatment Process (AMS-M-3171)

Contains Hex Cr, High Temp (200 F), often in conjunction with HT (180-190 F) chromic acid pickle (Dow 7)

TCP/NCP Conversion Processes yield greatly improved adhesion and corrosion performance

Touch-Up/Repair Coatings – Dow 19 – also need alternatives for in-situ repair

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Bright Zinc Post-treatment

- Activation of the panels prior to TCP treatment severely decreased the corrosion resistance
- Room temperature application of TCP outperformed commercial Cr (III)
- Optimum TCP performance was found when TCP was applied at 120 °F for a 5-10 min immersion time
- The commercial Cr(VI) performed only slightly better than 2P applied at 120° F
- The 2P applied at RT, 85° F, and 100° F outperformed the commercial Cr(III)

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Test Parameters

- Type of sacrificial coating
 - Boeing bright zinc
 - Zinc-nickel
 - IVD-aluminum
- TCP/NCP composition with and without additives
- Chromated and nonchromated primers
- Key Processes
 - Activated versus non-activated
 - Peened versus unpeened for the IVD-aluminum
 - Immersion temperature, time, and solution concentration

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26 Days Neutral Salt Fog (ASTM B117)

2P, 120 °F,
5 min

2P, 150 °F,
5 min

Commercial
Cr (III)
25 days

Commercial
Cr (VI)

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Results for IVD-Aluminum

- Activation of the panels (more apparent with the peened samples) increased corrosion protection
- At over 4000 hours, the TCP/NCP is performing as well as the chromate control
- Optimum performance for the non-Cr (VI) post-treatments was found on activated, peened samples with an immersion time of 10-15 minutes applied at room temperature
- After 6 months carrier exposure the NCP treated IVD panels look excellent

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ASTM B117 Results for IVD-Aluminum

5S, RT, 15 min
Activated
Peened

NCP, RT, 10 min
Activated
Peened

Commercially
Applied
5S, RT, 10 min
Peened

Commercial Cr (VI)
Peened

209 Days – Scribed IVD on 4130

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Results for IVD-Aluminum

Alumiplate™ on 4130 steel – post-treated with NCP (I) and Alodine 1200S ©
4,200 hours in ASTM B117

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NCP Conversion Coatings on 4130 Steel

Acetone wiped – 5 min. NCP

Sand-blast – 5 min. NCP

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TCP Conversion Coatings on 4130 Steel

Sand-blast – 5 min. TCP-C

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TCP/NCP Conversion Coatings on 4130 Steel

5 min. TCP – Air dried
0.9mil MIL-P-53022
168hrs B117

5 min. NCP – Air dried
0.9mil MIL-P-53022
168hrs B117

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4130 Steel Pretreatment

Control – Sand blast
0.9mil MIL-P-53022
168hrs B117

Control - Acetone
0.9mil MIL-P-53022
168hrs B117

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(numbers in parens are deox time and TCP time in minutes, respectively)

20% TCP-IC (2, 5)

20% TCP-IC (2, 10)

AA2024-T3 1008hrs B117

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Results: Pretreatment Analysis

- Chemical Analyses of Coatings** – Atomic Absorption (AA); Inductively Coupled Plasma (ICP); Energy Dispersive X-ray (EDX) Analyses.
- Oxidations States of Chromium** – Electron Paramagnetic Resonance (EPR); Ultraviolet Visible (UV-Vis.) Spectroscopy; X-ray Photoelectron Spectroscopy (XPS); Raman Spectroscopy; Fourier Transform Infrared (FTIR) Spectroscopy, Near Mid, Far; X-ray Absorption Near edge Spectroscopy (XANES); Extended X-ray Absorption Fine Structure (EXAFS); Luminescence.
- Depth and Lateral Homogeneity** – Scanning Auger Microscopy (SAM); Optical Microscopy; Raman Imaging; IR Microscopy; Atomic Force Microscopy (AFM); Scanning Electron Microscopy (SEM).
- Identification of Organic Components in Coatings** - FTIR, Raman.

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RESULTS: TCP/NCP Composition on Aluminum

FTIR

- TCP Samples – Evidence of Cr^{3+} , No Evidence of Cr^{6+}
 - Bands Near 1116 cm^{-1} Indicative of surface bound Cr_2O_3 , [i.e. Cr(III)] in TCP. (García Rodenas, Luis A. et al., Surface Complexation Description of the Dissolution of Chromium (III) Hydroxide Oxides by Oxalic Acid, *Inorganic Chemistry* (1997), 36(27), 6423-6430.)
 - Total [Cr] – from 0.024 to 0.180 ppm, via AA.
- Peaks not present in NCP
- Organic chelating compound identified in NCP-I and TCP-IC

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RESULTS: TCP/NCP Composition on Aluminum

Fig. 2 Raman spectra of powders of CrO_3 and Cr_2O_3 .

RAMAN DATA

- CrO_3 has two distinctive bands at around 1000 and 500 cm^{-1} .
- Cr_2O_3 has two distinctive bands around 600 and 300 cm^{-1} .
- $Cr(OH)_3$ has one band around 560 cm^{-1} [A]. A. J. Zhao et al., *J. Electrochem. Soc.*, 1998, 145, 2258.

- No Cr(III) in NCP
- No Cr(VI) in NCP or TCP

Raman Bands at 550 cm^{-1} in TCP

Indicative of Cr^{3+}

Wavenumber (cm^{-1}): ~3071, ~1620, ~1267, ~1234, ~1133, ~1100, ~1000, ~932, ~860, ~814, ~610

Areas of Interest

- What is the corrosion protection mechanism for TCP coatings on metal surfaces?
 - How does this mechanism change according to substrate?
 - Barrier coating, active inhibition, localized inhibition?
 - No detectable Cr^{6+} presence
- Why does the TCP outperform chromate in some applications?
- What additional chemistry modification can be made for equivalence to chromate in ALL applications?
 - Same process – Al first, then flow down to other metal finishing
- Compatibility/Synergy effects with new Non- Cr^{6+} inhibitors needs to be explored

