Emerging Safer Alternatives for Chromate Conversion Coatings and Primers

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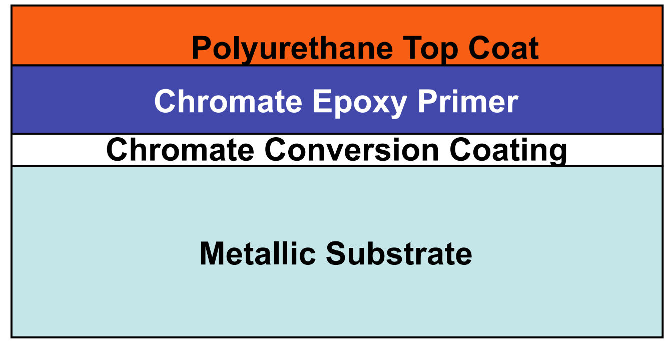
Research goal: Reduce technical risk of implementing chromate alternatives on military aircraft by investigating corrosion protection mechanisms

Problem

- **Corrosion and oxidation cost the U.S. DOD ~$20B annually**
  - **Maintenance cost is about $100,000 per aircraft per year**
  - **Protective coatings based on chromates**

Background

- **Chromates are effective corrosion inhibitors**
  - **Low cost, highly protective**
  - **Can overcome processing issues**
  - **Robust protection mechanism**
- **Many different potential replacements**
  - **More than 90% by weight of chromate is in the primer**
  - **Conversion coatings provide corrosion protection and adhesion**
  - **Primers provide long-term corrosion protection**



Deft non-chromate primer on an Apache helicopter fuselage

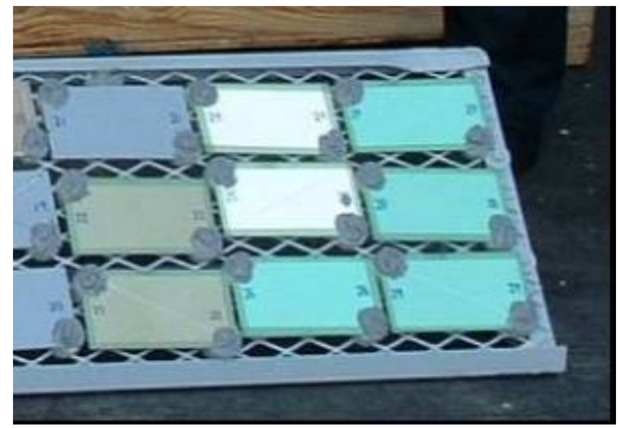
Rare-Earth Corrosion Inhibitors

- **RE compounds are potential replacements for chromates**
  - **Environmentally friendly corrosion inhibitors**
- **RE phases are NOT inherently protective**
  - **Protection depends on phase of RE compound, type of coating, and pH of the environment**
  - **Both Ce/Pr and mixed oxidation state (i.e. $Ce^{3+/4+}$ $Pr^{3+/4+}$) compounds are of interest**

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Outline

- Conversion coatings
  - Promising alternatives
  - Cerium-based conversion coatings
    - Deposition methods
    - Characterization and testing
    - Corrosion protection mechanisms
- Primers
  - Promising alternatives
  - Pr-based inhibitor package
    - Phase stability
    - Formulation and evaluation of model primers
    - Proposed corrosion protection mechanism



Primers with rare earth inhibitors during a six month field evaluation on the John C. Stennis

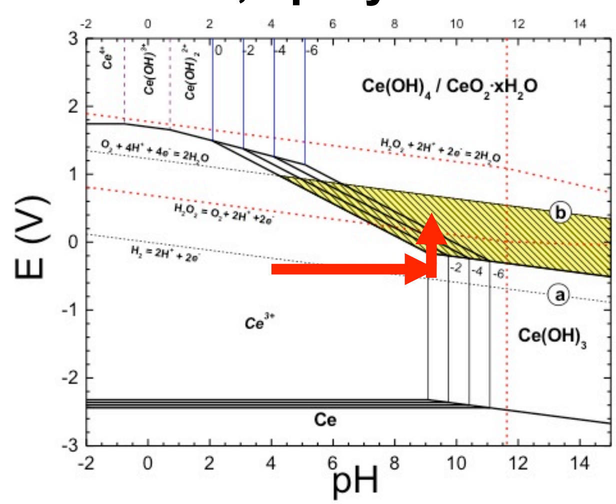
Chromate Alternatives

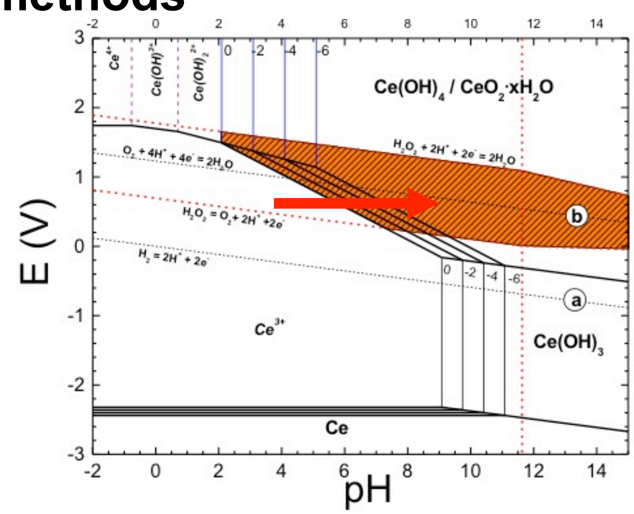
- **Trivalent chromium passivation (TCP)**
  - **Developed and patented by U.S. Navy (NAVAIR)**
  - **U.S. Patents 6,375,726; 6,511,532; 6,521,029; 6,527,841; 6,663,700; 6,669,764**
  - **Commercial product (e.g., METALAST TCP-HF, Alodine T-5900)**
- **Fluorozirconate coatings**
  - **Replacement for phosphating processes**
  - **Commercial product (e.g., PPG Zircobond)**
- **Oxy-anion analogues to chromates**
  - **Molybdates and vanadates**
- **Sol-gel coatings, anodizing, and others**

None is a drop-in replacement for CrCCs on all alloys

Ce-Based Conversion Coatings

- **Originally investigated by Hinton**
  - **1000 ppm $CeCl_3$ in water, deposition time 100's of hours**
  - **Coating deposited selectively on intermetallics, cathodic inhibitor**
- **Subsequent research by many groups including Missouri S&T**
  - **Oxidizing additive reduces deposition time to minutes**
  - **Immersion, spray and electrolytic methods**





B.R.W. Hinton, D.R. Arnott, and N.E. Ryan, Materials Forum, 9(3) 162-173 (1986).

P. Yu, S.A. Hayes, T.J. O'Keefe, M.J. O'Keefe, J.O. Stoffer, J. Electrochem. Soc., 153(1) C74-C79 (2006).

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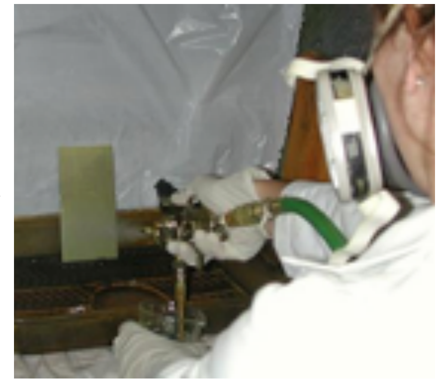
Coating Deposition

Al 2024-T3 panel
Alcohol wipe

Alkaline Degreasing
5 min at 55ºC

Acid Activation
1 wt% H_2SO_4
5 min at 50°C



5 Sprays with
35 sec delay

Post-Treatment
5 min at 85°C
phosphate sol'n

As-deposited

Sealed

Coated Panels

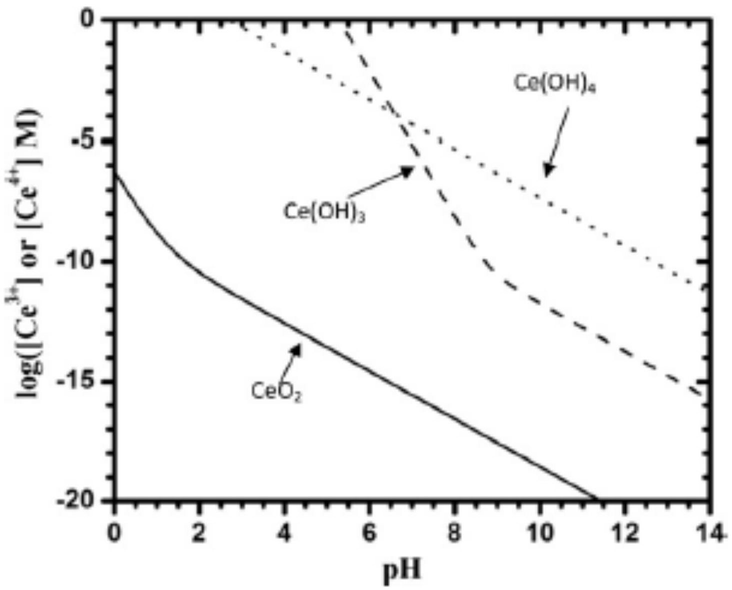
Water Rinsing
after each step

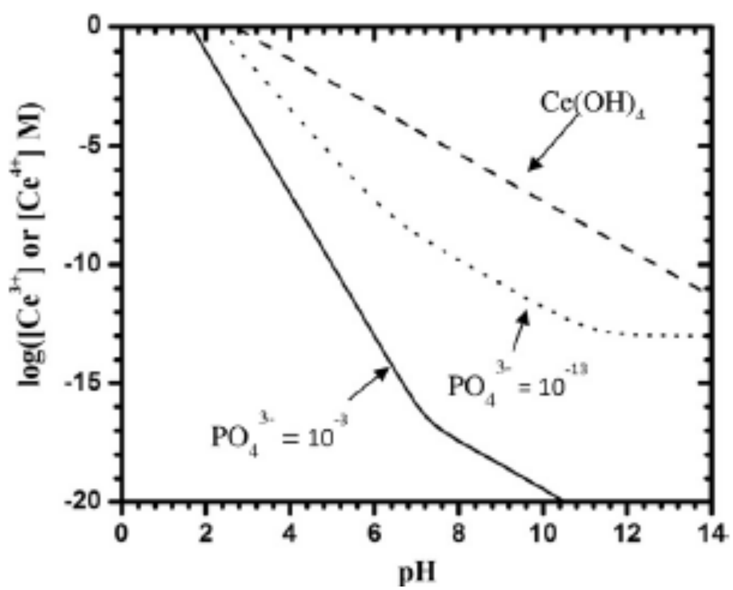
- Coating solution: 0.11 M $CeCl_3 \cdot H_2O$, 1 M H_2O_2, 2.4 g/L gelatin, pH to 2.3 w/ HCl
- Post-treatment (sealing) solution: 2.5 wt% NaH_2PO_4

Best coatings ~400 nm thick, 336 hours protection is ASTM B117 salt spray

Cerium Solubility

- **As-deposited CeCCs consist of hydrated cerium oxide species**
- **Ce oxides are more soluble at low pH**
  - **$Ce(OH)_4$ is the most soluble**
  - **CeO_2 is the least soluble**
- **Post-treated CeCCs contain hydrated cerium phosphate species**
  - **Ce phosphates less soluble than oxides**
  - **Increasing phosphate concentration decreases Ce solubility**
- **Dissolution of Ce species during corrosion seems unlikely**

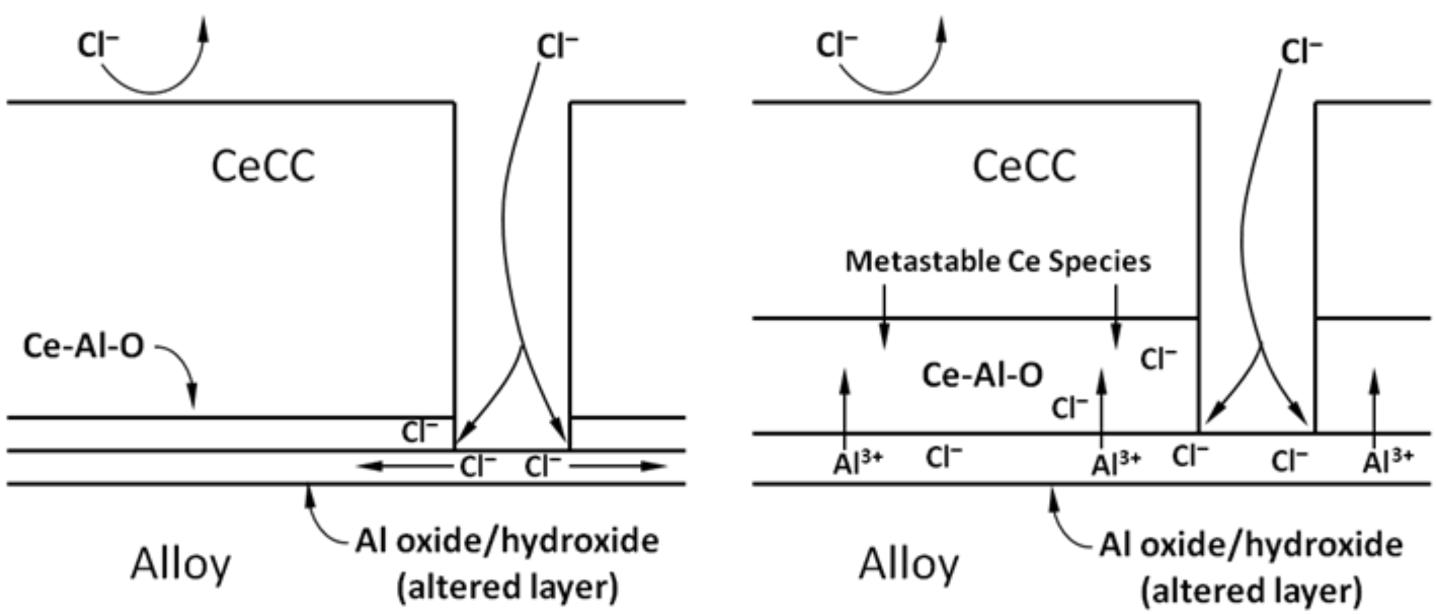




S. Joshi, E.A. Kulp, W.G. Fahrenholtz, and M.J. O'Keefe
Corrosion Science **60** 290-295 (2012)

Formation of Altered Layer

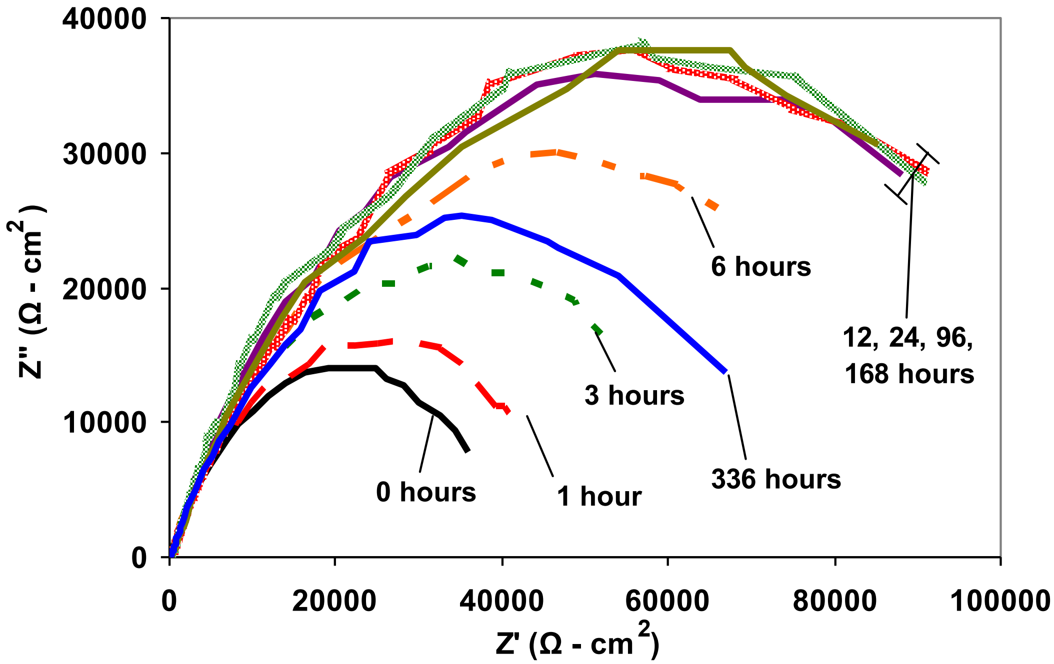
- **Interfacial layer formation and structural changes demonstrate CeCCs are not static barriers, but actively inhibit corrosion**
- **Chloride ions attacked at crack/substrate interfaces**
  - **Al^{3+} ions released from altered layer may react with metastable Ce species**
  - **Transition of cerium hydrogen phosphate species to $CePO_4 \cdot H_2O$ may affect pH**
  - **Facilitate formation of more stable phase(s)**

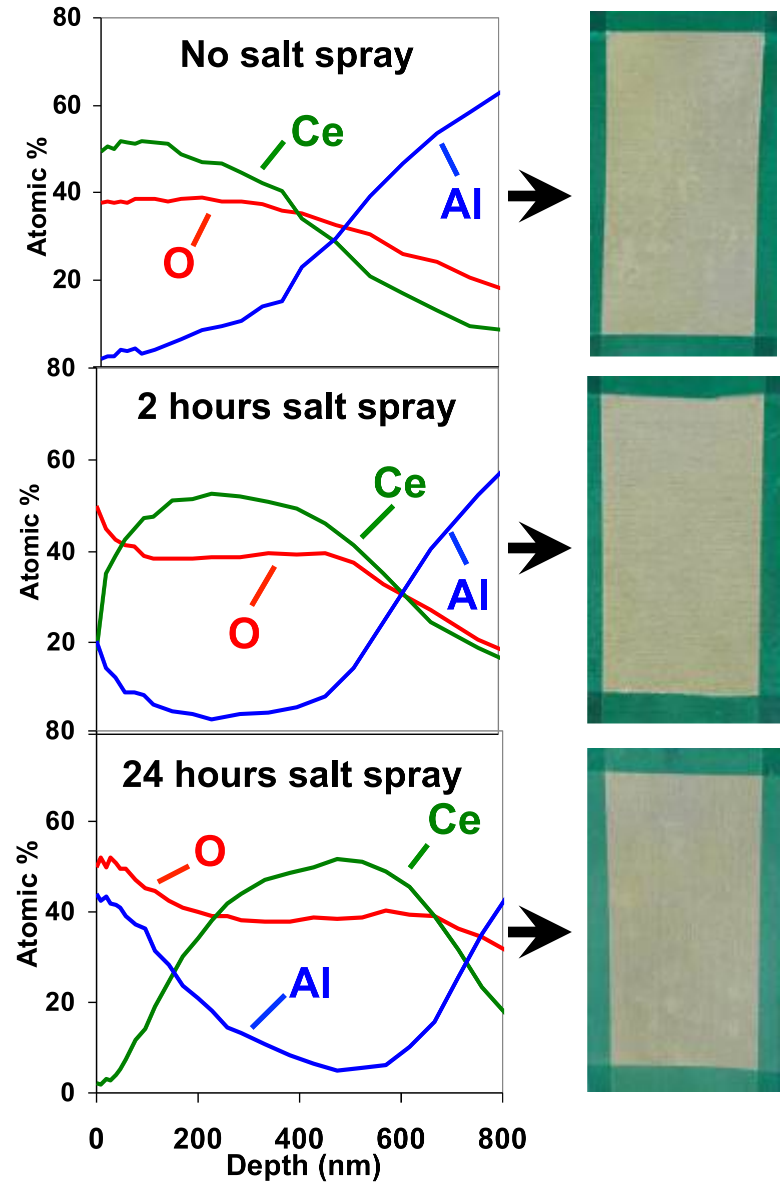


D.K. Heller, PhD Thesis, Missouri S&T, 2010

Salt Spray Changes Impedance

Changes in post-treated CeCCs during salt spray





- Impedance doubles during first 24 hrs
- Al, O rich layer develops, no visible corrosion

W. Pinc, D. Heller, W. Fahrenholtz, and M. O'Keefe, *ECS Trans*. **25** (29) 3 – 17 (2010).

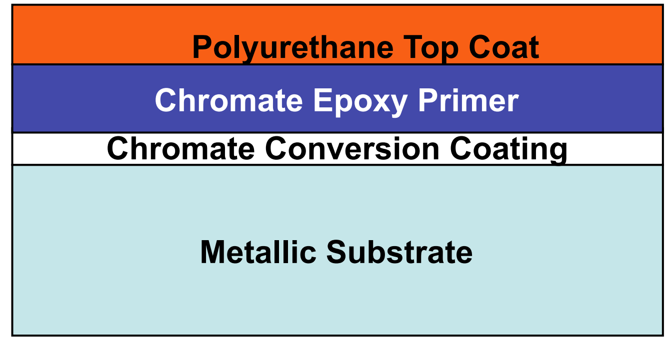
CeCC Protection Summary

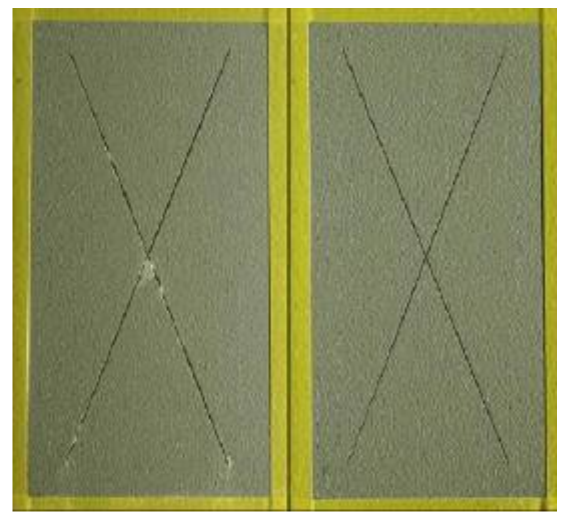
- CeCCs offer corrosion protection to high strength aluminum alloys
  - Ce species are not soluble
  - An altered layer forms between CeCCs and substrates during salt spray exposure
  - Impedance initially increases during salt spray exposure
- Overview of protection mechanisms

1. CeCCs are an insoluble barrier between the environment and the substrate
2. During corrosion, a layer containing Ce, Al, and O forms between the coating and substrate
3. Protective oxides deposit on the coating surface and in defects during salt spray exposure

Corrosion Protecting Primers

- Primers are protective coatings
  - Promotes paint adhesion
  - Provides corrosion protection
  - ~50 µm thick (2 mils)
- Chromate primers
  - Typically epoxy-polyamide based
  - Strontium chromate or similar inhibitors
  - Protects by dissolution of chromates from primer, transport to site of attack, and reaction to passivate corrosion

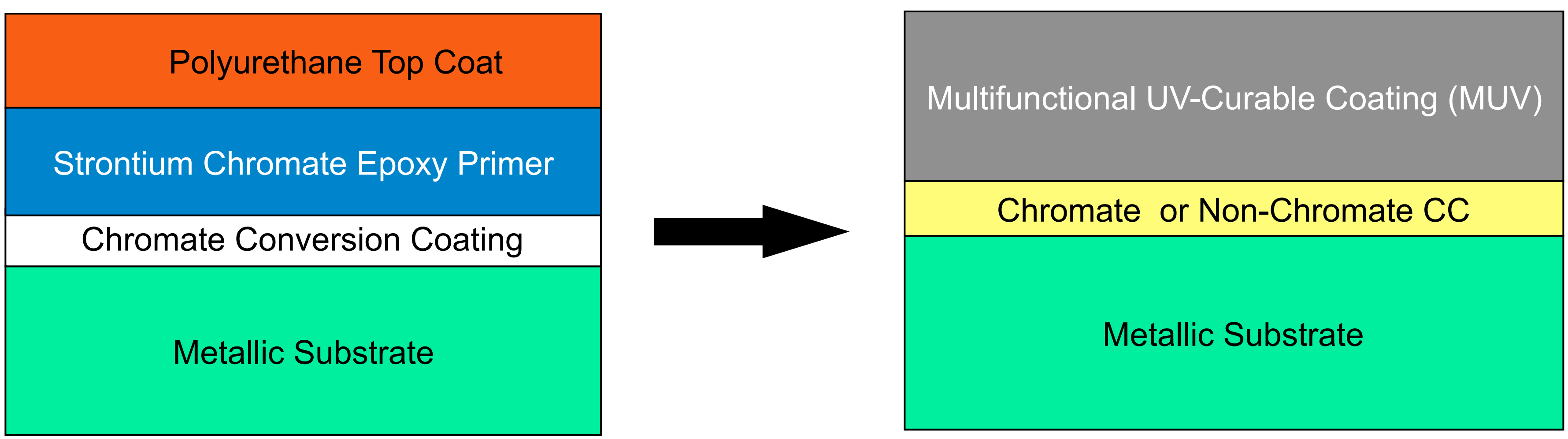




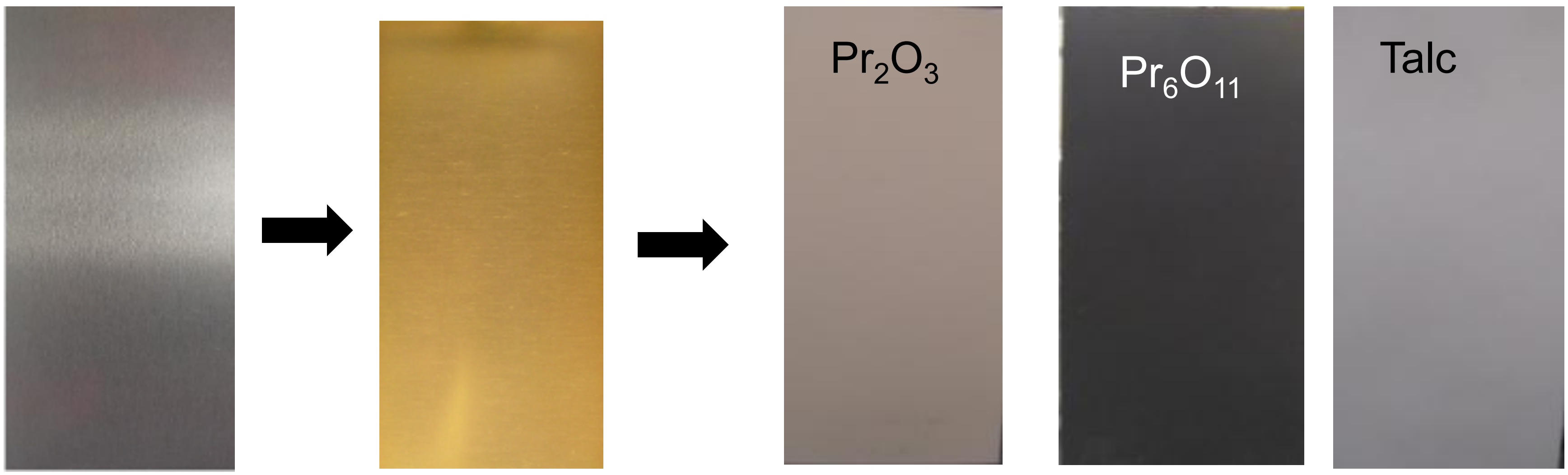
Chromate primer on CrCC after 3000 hours in ASTM B117 salt spray testing

Chromate Alternatives

- **Mg-rich primer**
  - **Licensed and marketed by Azko-Nobel (Aerodur)**
  - **Protection exceeds chromates in some tests, not sufficient in others**
- **Electrocoat primers**
  - **Widely used in automotive (e.g., body in white initiatives)**
  - **Tank based process for multiple metals**
- **Multi-functional UV-curable coating (SERDP WP-1519)**



Primers with Pr-Based Inhibitors

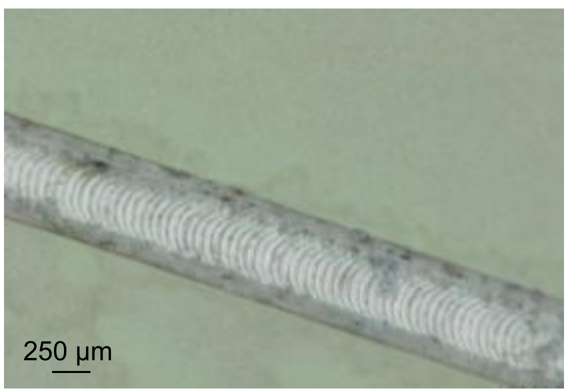


Al 2024-T3 | **Al 2024-T3 with Alodine® CrCC** | **Al 2024-T3 with a CrCC and model -primer**

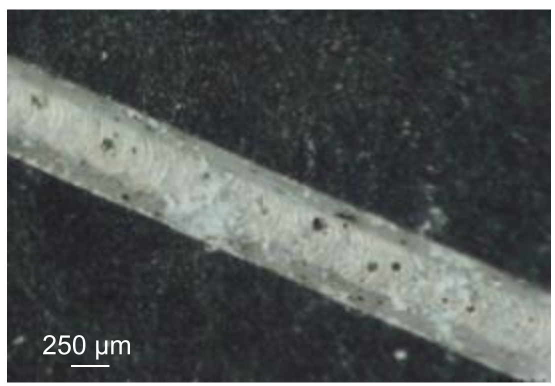
- **Pr-based inhibitors have been developed for primer coatings**
- **Panels with model primers were prepared by Deft (now PPG Aerospace)**
- **Inhibitor species were incorporated within the resin/polymer matrix**
  - **Pr_2O_3**
  - **Pr_6O_{11}**
  - **Talc as a control (should be inert)**

Salt Spray Exposure

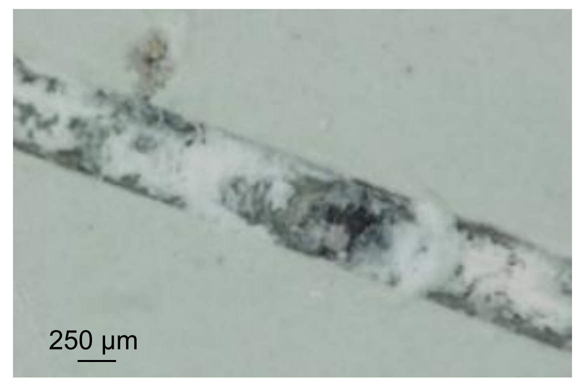
- **Scribed Al 2024-T3 panels with CrCCs and model primers were evaluated in ASTM B117 salt spray testing for up to 3000 hours**
- **Coatings were characterized before, during, and after salt spray exposure**
  - **XRD to identify crystalline phases**
  - **SEM-EDS to characterize morphology and chemical composition**
- **Goal was to identify species dissolving, transporting, and reacting**



Pr_2O_3 Primer



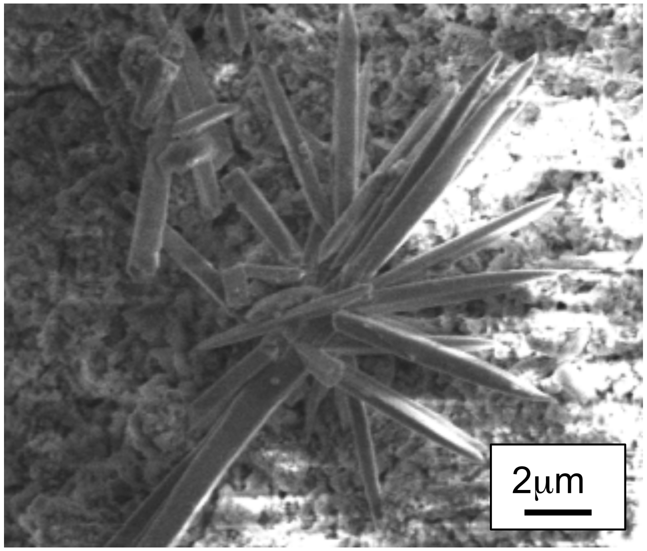
Pr_6O_{11} Primer

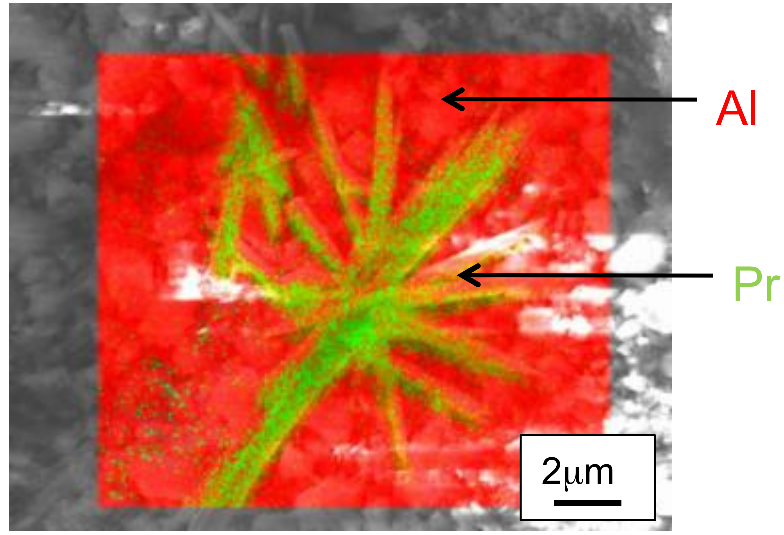


Talc Primer

Pr_2O_3 and Pr_6O_{11} primers provided corrosion protection, talc primer did not

Transport of Pr Species





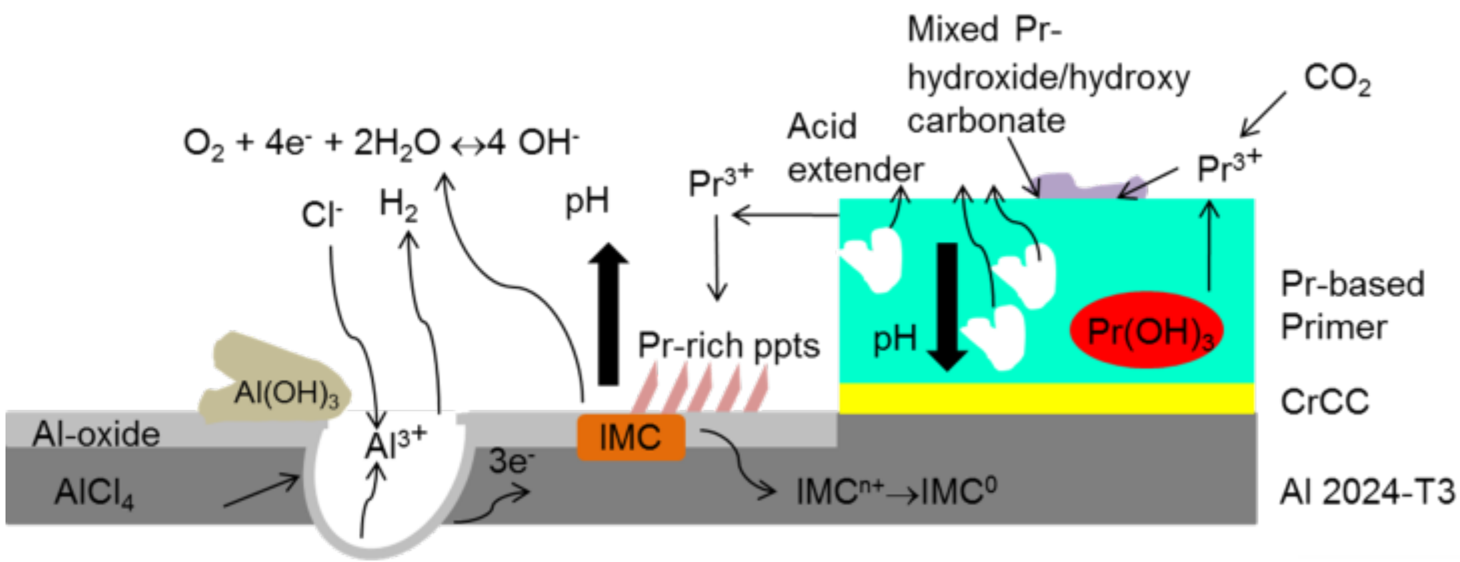
Scribe following 3000 Hours of Spray Exposure

Element	Atomic %
O	67.46
Fe	3.75
Cu	1.87
Al	15.11
Pr	11.81
Total	100

EDS identified the major elements present as O, Al, and Pr

Proposed Protection Mechanism

- **Model for primer protection has been developed**
- **Pr-rich species dissolve from primer matrix containing $Pr(OH)_3$**
- **Dissolved species precipitate as Pr-hydroxycarbonates**
  - **Coating surface and in the scribed area**



Overall Summary

- Chromate alternatives are available for aerospace applications
- Cerium-based conversion coatings
  - Deposited by immersion, spray, or electrolytic processes
  - Corrosion protection for up to 336 hours in ASTM B117 salt spray
  - Protects through barrier and interfacial reaction mechanisms
- Pr-based inhibitors for primers
  - Incorporated into current epoxy-polyamide primer bases
  - Corrosion protection up to 3000 hours in ASTM B117 salt spray
  - Protects by dissolution, transport, and reaction
- Rare-earth coatings are promising alternatives to chromates