**Electrochemical Technologies for Replacement of Hexavalent Chromium and Cadmium**

**Functional Cr Plating from a Trivalent Chemistry**

NEED: Develop an environmentally benign coating for functional military and commercial applications with ≥ or equivalent properties

THREE APPROACHES:
- Change the process (plating) to eliminate hexavalent (Cr+6)
  - Such as Ni or Co plating
- Change the plated coating to eliminate hexavalent (Cr+6)
  - Such as HVOF WC-Co-Cr or DLC
- Change the plating bath from hexavalent (Cr+6) to trivalent (Cr+3)
  - Cr+3 used for decorative chrome coatings/not restricted
  - Maintain same chrome documentation

“Conventional Wisdom”: Thick functional chromium coatings cannot be plated from Cr+3 due to hydroxide formation at the cathode (alkaline interface)

**Optimization Testing**

- Thickness (AMS 2460, 3.4.1)
  - Microhardness via cross-section
  - As-plated and post 375°F (190°C)
- Current Efficiency
- Microhardness via cross-section
- Corrosion Resistance (ASTM B117)
- Roughness
- Plating Performance:
  - Current Density, Current Efficiency
  - Microhardness via cross-section
  - Hardness
  - Thickness (AMS 2460, 3.4.1)

- As-plated and post 375°F (190°C)

**Trivalent Chromium: Grinding Adhesion**

**Trivalent Chromium: Baking Effect on Microstructure/Hardness (AMS 2460, 3.4.3)**

**Cracks with Cr Thickness**

Application to Tri-Chrome Cracking

- Apply 1st plating condition to generate sufficient tensile stress to exceed yield stress in situ during plating
  - Cause crack formation in first layer
- Apply 2nd plating condition to cover cracks in first layer and generate sufficient tensile stress to exceed yield stress in situ during plating
  - Cause crack formation in second layer
- Loop or sequence between 1st and 2nd plating conditions
  - Generate coating with discontinuous micro-cracks

**Boric-Acid Free Looping Study [As Plated]**

Through cracks not minimized with thicker layers using initial protocols

WF1: 24 mins, 5.5 µm; WF2: 13 mins, 4.5 µm; Loop 5 times


**Evidence of Discontinuous Cracking [As Plated]**

**in Boric-Acid Free Chemistry**

Looping studies showing some discontinuous micro-cracks, in addition to through cracks

**REACH Compliant Chemistry Preliminary Coatings Overview Property Comparison**

**Acknowledgements**

- DOD Funding, Contract No. W911NF-11-2-0014
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**Coventya**
Electrochemical Technologies for Replacement of Hexavalent Chromium and Cadmium

**Application of Pulse/Pulse Reverse Electrochemistry to Stripping and Coating Processes**

- **Electrochemical Machining, Polishing, Stripping, Through-Mask Etching**
- **Electrodeposition/Plating**

**Electrolyte Screening Summary**

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Electric Field Conditions</th>
<th>Cu²⁺ Formation</th>
<th>Cr³⁺ Formation</th>
<th>Steel Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mil-spec solutions</td>
<td></td>
<td>DC</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Mineral acid solutions</td>
<td></td>
<td>DC</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Low concentrations</td>
<td></td>
<td>DC</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
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<tr>
<td>Organic Acid solutions</td>
<td></td>
<td>DC</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Organic acid solutions</td>
<td></td>
<td>PRC</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
</tbody>
</table>

**Cathodic Pulse Tuned to:**
- **Control current distribution**
- **Enhance mass transfer**
- **Remove reaction products**

**Anodic Pulse Tuned to:**
- **Remover H⁺**
- **Acidify interface**
- **Transition Planning:**
  - Characterization Tests:
    - Composition and thickness with XRF (ASTM B568/AMS 2460)
    - Adhesion by Bend to Break (ASTM B571)
    - Visual examination (AMS 2460)
    - Hydrogen Embrittlement (ASTM F519)
    - Corrosion resistance (ASTM B117)
  - Transition Planning:
    - Economic analysis that compares FARADAYIC® Electrodeposition with conventional plating
    - Preliminary transition plan to outline implementation of this process at ALCAs, depots, and partners

**Environmental Friendly Chrome Stripping Process**

- **DC stripping (MIL-STD-871) of Cr plate:**
  - NaOH (68-82 g/L) or NaOH (45-60 g/L) + Na₂CO₃ (60-75 g/L)
  - Requires conversion of Cr⁶⁺ to Cr³⁺
  - Low Hydrogen Embrittlement
  - Fatigue resistance
  - Economically viable compared to the conventional process
  - Enables immobilization or recovery/recycle of the chrome

**FARADAYIC® Stripping**

- Inverse Chrome Plated Part in FARADAYIC® Stripping Electrolyte
- Apply FARADAYIC® Stripping Waveform to remove chrome
- Recycled Stripping Electrolyte
- YES: N (Cr⁶⁺) high enough for FARADAYIC® Electroplating?
- NO: Adjust FARADAYIC® Stripping parameters to favor Cr³⁺
- YES: N (Cr⁶⁺) < OSHA PEL?
- NO: Continue FARADAYIC® Stripping
- Chromite Recovery / Recyclce

**FARADAYIC® Stripping of Cr Coated Panels**

- Flat cell for initial testing of Cr stripping in small electrolyte volumes
- Larger cell for testing of masked panels with Cr and bare steel exposed

**Stripping in Mil-Spec Solution – DC vs. PC/PRC**

- DC Stripping: Run time = 180 minutes
  - Hatch test kit: 2600 ppm Cr⁴⁺
- PC/PRC Stripping: Run time = 840 minutes
  - Hatch test kit: 100 ppm Cr⁴⁺
  - 95% less Cr⁴⁺ compared with DC

**Economic Impact**

- Many DoD systems require Cadmium (Cd) plating for:
  - Corrosion Resistance, conductivity, EMI Shielding/electrical bonding (2.5 mtd)
  - Thermal, mechanical, or electrical shock resistance, etc.
- However, Cd plating processes are known carcinogens for plating personnel and are highly regulated
- Alkaline Zn-Ni plating is an environmental benign process for Cd replacement
  - Low Hydrogen Embrittlement
  - Excellent throwing power and adhesion
  - Economically preferred considering the less cost for the waste treatment and worker safety
  - Zinc-Nickel connector finish is electrically conductive

**Objective**

- Develop a LHE alkaline zinc nickel plating line for steel and aluminum electrical connectors, back-shells, and components on aircraft/propeller systems

**Plating of Zn-Ni on Aluminum and Steel**

- Kaufman solution
- Typically requires hydrogen scrubbing
- Typically requires chelating agents

**Experimental Setup**

- Aluminum and steel samples:
  - 1" x 4" Flats
  - 1a or 2a Hydrogen Embrittlement Bars
- Retrofitted plating line for Dipol 12-C17+ Alkaline ZnNi

**Next Steps**

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**Acknowledgements**

- Program partners
  - The Boeing Company
  - Corrdesa
  - Dr. Bruce Popov

**2008 Blum Award for Pulse Reverse Finishing**

**2016 R&D 100 Finalist for Nb Electroplating**

**Electrochemical Machining, Polishing, Stripping, Through-Mask Etching**

**Pulse Electrodeposition/Plating**

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