Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative

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**Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative**

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<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>unclassified</td>
<td>unclassified</td>
<td>unclassified</td>
</tr>
</tbody>
</table>

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Same as Report (SAR)

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41

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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
Why Chrome plating?

Engineering hard chrome (EHC) coatings are used extensively in both industry and military applications due to their excellent performance characteristics.

- Wear
- Corrosion Resistance
- Dimensional Restoration

Where is Chrome Plating Used?

- Manufacturing and repair
- Dynamic components
- Hydraulic actuators
- Propeller hubs
- Engines
- Landing Gear
Hard Chrome Plating Environmental & Health Hazards

- Hard chrome plating utilizes chromium in the hexavalent state (Cr$^{6+}$)
- Cr$^{6+}$ is a known carcinogen and poses a health risk to operators
- OSHA lowered the Cr$^{6+}$ PEL from 52 µg/m$^3$ to 5 µg/m$^3$

8 Apr 09, Memorandum, DoD Directive

- Hexavalent Chromium Management Policy
- NAVAIR Cr$^{6+}$ Authorization Process

![Diagram showing the process of hard chrome plating with Cr$^{6+}$ contamination and management steps.](image)
Coating applied by electrodeposition
- Pulsed Current Waveform Engineering
  - Frequency (Hz) = $1/(t_{on}+t_{off})$
  - Duty Cycle (%) = $t_{on}/(t_{on}+t_{off}) \times 100$

Electrodeposited nanocrystalline materials
- Favors nucleation of new grains over growth
- Results in an ultra-fine grain structure
- Uniform throughout thickness

Leads to unique properties
- ↑ Yield Strength, wear, ultimate tensile strength
- ↑ Density
- ↓ Coefficient of friction

(Smaller grain size impedes dislocation movement and increases yield strength)
## Hard Chrome Alternative

### Nanovate™ CR

#### Process Comparison

<table>
<thead>
<tr>
<th></th>
<th>Nanovate™ CR</th>
<th>EHC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition Method</strong></td>
<td>Electrodeposition (Pulse)</td>
<td>Electrodeposition (DC)</td>
</tr>
<tr>
<td><strong>Part Geometries</strong></td>
<td>LOS and NLOS</td>
<td>LOS and NLOS</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>85-95%</td>
<td>15-35%</td>
</tr>
<tr>
<td><strong>Deposition Rate</strong></td>
<td>0.002”-0.008” /hr</td>
<td>0.0005”-0.001” /hr</td>
</tr>
<tr>
<td><strong>Emission Analysis</strong></td>
<td>*Below OSHA limits</td>
<td>Cr+6</td>
</tr>
</tbody>
</table>

#### Cathode Efficiency

Approaches 100% Efficiency

- Up to 8X faster than Chrome plating
- Increased throughput
- One Nanovate CR tank can replace several EHC tanks
- More efficient (~ 90% Reduced power consumption)
- Bath is Stable

*Co PEL is 20 µg/m3
- Developed and demonstrated at the lab scale
- Scaled up to industrial production & moved to DoD depot
- US Patents 5,433,797, 5,352,266, 7,320,832, 7,553,553
**Technology Dem/Val Site**

*(Full Operating Capability)*

CIP # 0466

**NAVAIR Fleet Readiness Center Jacksonville**

- Dem/Val line in operation since 2006
- 250 gallon Plating Tank
- Pulse Power supply (1500A Peak Current)
- Activation tank used for most all alloys

![Dem/Val Plating Tank](image)

![Power Supply](image)

![Remote Controller](image)

![Acid/Fluoride Activation tank](image)
Corrosion Properties

**Nanovate™ CR**

**ASTM B537 Ranking following ASTM B117 Salt Spray**

- **Hard Chrome (0.004”)**
- **Nanovate CR (0.002”)**

*Photos shown following 165 hrs*

**Nanovate™ CR**

**μ-EDXRF Spectra**

- **Coating Oxidation**
- **Substrate Corrosion**
Fatigue Properties

Rotating Beam Fatigue
4340 substrate (UTS: 260-280 ksi)
Significant credit vs. EHC
Comparable to bare

Axial Fatigue (R=-1)
4340 substrate (UTS: 180-200 ksi)
Significant credit vs. EHC
Credit vs bare
Nanovate CR hardness comparable to EHC after annealing at standard conditions for hydrogen embrittlement bakeout (375°F)

Max Hardness (750 VHN) achieved at 550°F w/ 5hr
Technical Progress
(Masking Evaluation)

- Maskants evaluated and downselected
  - Enthone: Enplate Stop Off No. 1
  - Tolber: Microshield
- No adverse effects on bath or deposit quality
- Demonstrated on T45 pivot component

T-45 pivot shown with Enthone Maskant
Strippants evaluated and downselected
- (3) nitro-organic oxidizers with amino compounds
- 0.001”-0.004”/hr removal rates
- MacDermid METEX SCB Electroless Nickel Stripper was tested at JAX successfully.

**Technical Progress**
*(Coating Removal Evaluation)*

**Mass removal over time**
(slope of linear fit used as performance metric of stripping rate)

- Pre-plate coupon
- Plated coupon
- Stripped coupon
24 Core Tests Defined in JTP

- Coating Quality
  - Appearance, Thickness, Porosity, Hardness, Grain size
- Ductility
- Stress (internal)
- Fatigue (Axial)
- Corrosion (B117, SO₂, Beach, OCP)
- Adhesion
- HE, HRE
- Fluid Compatibility
- Wear
  - (Taber, PoD, Rig, Falex, Gravelometry, SATEC)
Fatigue/Wear Testing

**Axial Fatigue Test**
- 4340 steel (260-280 ksi)
- Shot peened
- R ratio: R = -1

**SATEC Oscillating Load Test**
- Boeing Specific Test
- Pin/Bushing Oscillating Wear Test
- Constant/ Sinusoidal load-motion profile
Wear Testing

**FALEX Block on Ring**
- Test per ASTM G77
- Determines the resistance of materials to sliding wear
- Different Alloy/Coatings against Ring

**Gravelometry**
- Test per ASTM D3170
- Specimens mounted perpendicular to projected path
- Pea size gravel; air pressure 70 psi
- Assess wear performance vs. chrome as an ID actuator
- Test developed by Messier-Dowty
  - 20,000 Cycles
  - Observe the effect of surface finish, seal types, and hardening condition

### Endurance Rig Testing

**Test Matrix***

<table>
<thead>
<tr>
<th>Coating</th>
<th>Surface Finish (Microinches)</th>
<th>Piston Seal</th>
<th>Rod Seal</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHC</td>
<td>12-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EHC</td>
<td>4-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCoP</td>
<td>12-16</td>
<td>Buna-NTee Seal Nitrile Butadiene Rubber</td>
<td>Buna-NTee Seal Nitrile Butadiene Rubber</td>
</tr>
<tr>
<td>nCoP</td>
<td>4-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCoP HE Bake</td>
<td>12-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCoP HE Bake</td>
<td>4-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCoP Hardenin g Heat Treat</td>
<td>12-16</td>
<td>Buna-NTee Seal Nitrile Butadiene Rubber</td>
<td>Buna-NTee Seal Nitrile Butadiene Rubber</td>
</tr>
<tr>
<td>nCoP Hardenin g Heat Treat</td>
<td>4-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EHC</td>
<td>12-16</td>
<td>Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer</td>
<td>Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer</td>
</tr>
<tr>
<td>nCoP</td>
<td>12-16</td>
<td>PTFE Cap</td>
<td>Spring Energized PTFE</td>
</tr>
<tr>
<td>EHC</td>
<td>12-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCoP</td>
<td>12-16</td>
<td>Buna-NO- Ring/Back-up - Nitrile Butadiene RubberO-Ring</td>
<td>Buna-NO- Ring/Back-up - Nitrile Butadiene RubberO-Ring</td>
</tr>
</tbody>
</table>

*In kind funding (Messier-Dowty)
Dem/Val Components
T-45 Pivot Assembly

- T-45 Arresting Hook Pivot Assembly

NAVAIR JAX Dem/Val for Air Vehicle Components

Plated Area

Pivot Assembly

T-45 Goshawk Trainer Aircraft
Dem/Val Components
T-45 Pivot Assembly
Electrochemical Modeling

- Conducted chemical characterization for model input
- Optimize current density distribution
- Control composition of electroplate
- Optimize coating properties
- Applied simulation to a complex geometry – T45 Pivot Assembly
Potential Dem/Val Component
Lifting Arm Pin

- Spotting Dolly - Lifting Arm Axel Pin
- EHC vs. Nanovate Cr vs. E-Ni

Various Lifting Pin Systems

Spotting Dolly Lifting Arm
NAVSEA Leveraged Effort
LVS Hydraulic Cylinder

NAVSEA (NESDI & OSD Leveraged Effort)

- Marine Corps MK48
  LVS (Logistic Vehicle System) Hydraulic Cylinders

  1. Evaluate coatings on steel and carburized steel laboratory panels
  2. Evaluate optimum coatings with accelerated corrosion testing (GM9540P)
  3. Field test on MK48 vehicles

Goals:
- Develop selection criteria for implementation into system repair / rebuild and spare parts sourcing
- Reduce corrosion maintenance requirements and repair costs of vehicles
Phase I: (*Carburized 1018 Steel Coupons)  
- Unofficial test results
  - ASTM B117 (passed)
  - ASTM F1978 Taber Abrasion (passed)
  - ASTM B571 Impact, Chisel/Knife, Peel (passed)
Component Producibility
NAVSEA Refueling Parts

Refueling At Sea Components
(Norfolk Naval Shipyard)

4340 Steel Bearing Housings

17-4 PH Stainless Roller Shafts

Plated
Component Producibility
Boeing Aircraft Parts

Boeing Seattle – Aircraft Components

Boeing Producibility Items

737 Trunnion Pin – 4340M
787 Drive Shaft – 4340M
Messier Dowty – V-22 Components

- Messier-Dowty Producibility Items

V-22 NLG Piston

V-22 Osprey
Integran Technologies, Inc. (Toronto Canada)

- Nanovate CR prototyping line in operation since 2004
- 600 gallon Plating Tank
- In-line activation tanks
  - Mild steel, alloy steels, stainless steels, aluminum, Inconel, nickel…
- JTP sample production
- Commercial prototyping
  - Hydraulics, valves, pistons, shocks, engines, actuators, landing gear…
- OEM and R&O
Enduro Industries, Inc. (Hannibal, MO)

- Nanovate CR process line installed and in operation since 2008
- Applying Nanovate CR to mild and induction hardened steel bars for use in hydraulic actuators for fluid power
- 700 gallon Plating Tank
- Integran provides on-going support of line
- Milestone: 1,000,000 Amp-hrs of production plating
Pratt & Whitney Canada (Longueil, Canada)
- EHC replacement for R&O of engine components
- Retrofit equipment to convert to Nanovate™ CR Dem/Val Process Line
- Process line in use since Nov 2010
- 250 gallon Plating Tank

Support provided by:
Commercial Uses
P&WC

- Demonstration components plated for PT6 platform (shown after machining):
  - Prop shaft
  - Seal runner

[Images of plated components]

- Turbo Prop PT6
- Prop shaft plated at ITI (Oct 10)
- Seal runner plated at PWC (Jan 11)
- Prop shaft plated at PWC (Jan 11)
Summary

- **Nanovate CR (nCo-P):**
  - Environmentally compliant EHC alternative
  - Process compatible with existing plating infrastructure
  - Reduced energy consumption, increased throughput
  - Production process in commercial use (TRL 7)

- **Nanovate CR Material Properties**
  - Enhanced corrosion and wear
  - Non-embrittling
  - Improved fatigue performance vs. EHC

- **Future work (WP-0936)**
  - Performance testing (JTP)
  - Dem/Val at NAVAIR JAX Depot
  - OEM Producibility Components

For more information...
Questions

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**IH Assessment at NAVAIR JAX**

- NAVAIR-JAX IH assessment on Co emission on the Dem/Val tank.

<table>
<thead>
<tr>
<th>DATE</th>
<th>PERSONAL SAMPLING RESULTS (8-HR TWAS)</th>
<th>AREA SAMPLING RESULTS (8-HR TWAS)</th>
<th>VENTILATION MEASUREMENTS (TAKEN ON THE PULL SIDE)</th>
<th>DRY BULB READINGS (2)</th>
<th>RELATIVE HUMIDITY (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Aug 2007</td>
<td>Below the LOD</td>
<td>0.0023 mg/m³</td>
<td>3519 FPM</td>
<td>Initial: 79.1°F</td>
<td>Initial: 100%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final: 97.3°F</td>
<td>Final: 58%</td>
</tr>
<tr>
<td>9 Aug 2007</td>
<td>Below the LOD</td>
<td>0.0074 mg/m³</td>
<td>3545 FPM</td>
<td>Initial: 81.2°F</td>
<td>Initial: 100%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final: 97.6°F</td>
<td>Final: 58%</td>
</tr>
<tr>
<td>16 Aug 2007</td>
<td>Below the LOD</td>
<td>0.0017 mg/m³</td>
<td>4001 FPM</td>
<td>Initial: 79.0°F</td>
<td>Initial: 91%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final: 94.4°F</td>
<td>Final: 51%</td>
</tr>
<tr>
<td>22 Aug 2007</td>
<td>Below the LOD</td>
<td>Below the LOD</td>
<td>4366 FPM</td>
<td>Initial: 78.5°F</td>
<td>Initial: 94%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final: 95.0°F</td>
<td>Final: 50%</td>
</tr>
<tr>
<td>24 Aug 2007</td>
<td>Below the LOD</td>
<td>Below the LOD</td>
<td>4088 FPM</td>
<td>Initial: 77.5°F</td>
<td>Initial: 100%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final: 94.2°F</td>
<td>Final: 58%</td>
</tr>
</tbody>
</table>

**Co PEL is 20 µg/m³**
Dem/Val Component
Spread Cylinder Hydraulic Rod

- Spread Cylinder Hydraulic Rod
  (A/S32A-32 Aircraft Towing Tractor “Spotting Dolly”)
- Supply System Risk

Spread Cylinder Rod in Assembly

Actuator Assembly
Two Different Sizes Shown
<table>
<thead>
<tr>
<th>Coating Properties</th>
<th>Nanovate CR</th>
<th>EHC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Pit, Pore, Crack -free</td>
<td>Microcracked</td>
</tr>
<tr>
<td>Ductility</td>
<td>2-7%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Hardness</td>
<td>As-Deposited 530-600 VHN</td>
<td>Min. 600 VHN</td>
</tr>
<tr>
<td></td>
<td>Heat Treated 750 VHN</td>
<td>-</td>
</tr>
<tr>
<td>Adhesive Wear</td>
<td>Wear loss 6-7 x 10^{-6} mm³/Nm</td>
<td>9-11 x 10^{-6} mm³/Nm</td>
</tr>
<tr>
<td>(Pin-on-disk)</td>
<td>Coefficient of friction 0.4-0.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Pin Wear Mild</td>
<td>Severe</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Salt Spray ASTM B117 † Protection Rating 8 (1000 h) @ 0.002”</td>
<td>† Protection Rating 2 (1000 h) @ 0.004”</td>
</tr>
<tr>
<td>Hydrogen Embrittlement</td>
<td>ASTM F519 Pass with bake</td>
<td>Pass with bake</td>
</tr>
<tr>
<td>Fatigue</td>
<td>Axial &amp; Rotating Beam Credit vs. EHC Comparable to bare</td>
<td>Significant debit vs. bare</td>
</tr>
</tbody>
</table>

† ASTM B537 Rating
- Technology transfer underway
- Integran provides on-going support for the line
- Early process monitoring demonstrates good production control
(Hexavalent Chromium Plating at Navy FRCs)

**Estimated NAVAIR P2 Savings over 10 Yrs**

- **HAZMAT** *
  - 128,930 lbs

- **HAZ Waste** *
  - 348,470 lbs

- **Cr Rinse** *
  - 1,800,000 gals

- **Eng Controls** *
  - $1,608,750

- **Regulatory Compliance** *
  - $1,100,850

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
Cobalt Air Emissions – US EPA (Environmental Protection Agency)
- Emission limit different by state
  - Typical emission limit without requiring a license is 0.1 tons per year
- EPA estimating tool employed to determine emissions
  - Variables for estimator – bath amps, bath operating hours
  - Typical results are less than 50 lbs (20kg) per year
  - Drivers size of parts being plated, number / shifts (amp hours)
- Nanovate CR emissions below limits

Aqueous System - Environmental
- Dust or fume not produced by the plating process
- Nano materials do not become airborne
  - Nano material plated directly onto the substrate material
  - No sprays to disperse nano materials in the atmosphere

Cobalt Development Institute – Additional Information

Highly Efficient Process Produces very little Cobalt emissions
Rod-Seal Wear Testing

- Four PH 13-8Mo hydraulic actuator rods
  - Plated with 0.006-0.008” Nanovate CR
  - Hydrogen baked (375°F, 23h) or heat treated (300°C, 6 h)
  - Ground to 6-9 μinch, 12-16 μinch or superfinished to Ra < 4 μinch

- Testing conducted at NAVAIR-PAX
  - similar to ID cylinder wear - wear against seals
  - Tests showed Nanovate CR comparable to EHC

Nanovate CR coated hydraulic rod

Rod-seal test apparatus
Rod- Seal Wear
(Leakage, Various O-rings)

- Black lines hard chrome from prior HCAT work
  - Different test run
  - Nanovate CR roughly comparable with hard chrome
  - Ground surfaces higher leakage

Rod/Seal Leakage
Fluorosilicone O-ring w/ PTFE Cap Vs 4 Rods

Rod/Seal Leakage
MIL-P-83461 O-ring w/ Capstrip Vs 4 Rods

Rod/Seal Leakage
Spring Energized PTFE Vs 4 Rods

Rod/Seal Leakage
MIL-P-83461 O-ring w/ 2 backup ring Vs 4 Rods
### Joint Test Protocol

<table>
<thead>
<tr>
<th>Sample Production Progress</th>
<th>Sample Completion</th>
<th>Test Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Characterization</td>
<td>Feb 2011</td>
<td>Mar 2011</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Fluid Immersion</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Corrosion</td>
<td>Feb 2011</td>
<td>Apr 2011</td>
</tr>
<tr>
<td>Adhesive Wear (PoD, BoR)</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Abrasive Wear</td>
<td>Feb 2011</td>
<td>Mar 2011</td>
</tr>
<tr>
<td>Seal Wear</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Gravelometry</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Bushing Wear</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Fatigue</td>
<td>Feb 2011</td>
<td></td>
</tr>
<tr>
<td>Embrittlement</td>
<td>Feb 2011</td>
<td></td>
</tr>
</tbody>
</table>

*With support from Messier-Dowty/Safran Group*