Pb, Cd, Cr\textsuperscript{+6} and Ni
Alternatives
for Surface Finishing

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My Journey to Toxics Use Reduction

• 1980s...Process Optimization, Waste Minimization, Pollution Prevention (P2) or Toxic Waste Reduction (TWR)

• 1990s...Focus shifts to TUR
  – TUR isn’t synonymous with TWR
  – TUR can increase hazardous waste generation
  – TUR can be a distraction from working the low hanging fruit of TWR
  – TUR gets all the money
  – TUR can be a distraction from effective hazard management

• Present...TUR, Hazard Management (HM) and TWR
  ...Lean and Six Sigma
Hazard Management...the Other Side of Green

Purely Green Chemistries/Processes are Currently Not Viable for Most Surface Finishing Requirements so we Must Devote as much Effort to Effectively Manage Hazards as we do to Seek New Alternatives!
1. Second and Third Generation Processes may be Temporary.
2. Will we run out of metals? Even greener processes need improved management!
3. Improved Properties Critical for Successful Implementation
4. Easier to implement change on new designs than on legacy products
5. Some New Materials do not require Coatings…CRES, Ti, Composites
787 Composites Use
Boeing Technology

Primary Structure Weight
by Material

- Carbon laminate: 50%
- Carbon sandwich: 10%
- Fiberglass: 20%
- Aluminum: 10%
- Titanium: 10%
- Other: 5%
- Aluminum/steel/titanium pylons: 5%

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### Cadmium Plating Alternatives - JSF

**Table 7. Summary of recommendations by rough order of usefulness for the JSF.**

<table>
<thead>
<tr>
<th>Components</th>
<th>Critical issues for application</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD N (patent)</td>
<td>Needs alternative to chromate conversion</td>
<td>Full production process, available in deposits - ID coating method not available</td>
</tr>
<tr>
<td>Sn-Zn</td>
<td>Hydrogen embrittlement, chemical instability</td>
<td>Concern over whether growth and phase changes</td>
</tr>
<tr>
<td>Zn-Ni</td>
<td>Hydrogen embrittlement, chemical instability</td>
<td>More subject to failure than Sn-Zin</td>
</tr>
<tr>
<td>USM</td>
<td>Property and performance database</td>
<td>Under development at NAWC; may be used in future if performance is good and cost comparable to deposits.</td>
</tr>
<tr>
<td>High strength steels</td>
<td>Property and performance database</td>
<td>Qualification necessary for landing; can be qualified in time. QM development possibility. Anxiety over corrosion resistance failures.</td>
</tr>
<tr>
<td>Aluminum-oxide (DuraTab)</td>
<td>High curing temperature, embrittlement issues seen in some cases</td>
<td>Production use on landing gear, hinges</td>
</tr>
<tr>
<td>Thermal spray Al</td>
<td>Roughness, line-cut</td>
<td>Limited production use on landing gear</td>
</tr>
<tr>
<td>Fasteners</td>
<td>Hydrogen embrittlement</td>
<td>Under evaluation by Boeing</td>
</tr>
<tr>
<td>Sn-Mn</td>
<td>Hydrogen embrittlement</td>
<td>Not for high strength alloys</td>
</tr>
<tr>
<td>Electropolished Al</td>
<td>Availability</td>
<td>Sole source, proprietary coating</td>
</tr>
<tr>
<td>AHN</td>
<td>Property and performance database</td>
<td>Under development at NAWC; may be best option if performance is good.</td>
</tr>
<tr>
<td>Metal-polymer</td>
<td>Stress-life performance, damage to lightning strike?</td>
<td>Taps well for tank vehicles</td>
</tr>
<tr>
<td>MOCVD N</td>
<td>Deposition temperature</td>
<td>Sole source, proprietary coating</td>
</tr>
<tr>
<td>Electrical connectors</td>
<td>Sn-Zn</td>
<td>Under evaluation by Boeing</td>
</tr>
<tr>
<td>Electropolished Al</td>
<td>Availability</td>
<td>Sole source, proprietary coating</td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>Hydrogen embrittlement, soliciting</td>
<td>Especially for Al</td>
</tr>
<tr>
<td>AlN</td>
<td>Property and performance database</td>
<td>Under development at NAWC; for high-temperature resistance for Al alloys</td>
</tr>
<tr>
<td>MOCVD N</td>
<td>Deposition temperature</td>
<td>Sole source, proprietary coating. For high deposition temperature for most Al alloys</td>
</tr>
</tbody>
</table>

**Color code:**
- Best options: Innovative technologies
Alumiplate

• Very Good Coating
• Limited Availability (one supplier)
• Expensive
• Hazardous
  – Toluene Based
  – Pyrophoric
IVD Al and Sputtering

- Corrosion Resistance not equal to Alumiplate
  - Cleaners & Deicing Fluids
- Solderability
- Cost
- Line-of-Sight (limited ID plating with sputtering)
New Metal Alloys

FERRIUM® S53
Corrosion Resistant Ultra-High-Strength Steel for Aerospace Structural Applications

Ferrum® S53 Mechanical Properties (typical)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>YS (ksi)</td>
<td>225</td>
</tr>
<tr>
<td>UTS (ksi)</td>
<td>285</td>
</tr>
<tr>
<td>B (%)</td>
<td>15-18</td>
</tr>
<tr>
<td>Rm (ksi)</td>
<td>60-70</td>
</tr>
<tr>
<td>Hardness (HRC)</td>
<td>54</td>
</tr>
<tr>
<td>CVN (ft-lb)</td>
<td>29</td>
</tr>
<tr>
<td>Kc (ksi-in)</td>
<td>70</td>
</tr>
<tr>
<td>Kic (ksi-in)</td>
<td>44</td>
</tr>
</tbody>
</table>

Other Key Properties
- Corrosion resistance has been measured in accelerated sea water tests and is less than 0.4 mils per year, comparable to 15-5PH.
- Limited fatigue testing at a number of R-values and stress levels has shown equivalent performance to typical 300M-values.
- S53 yields a Class A Weld. Welding studies have shown minimal impact on mechanical properties.

Materials by Design® Objective
Steels currently used in numerous aerospace applications, specifically landing gear, are not corrosion resistant and therefore require a protective cyanide-based cadmium plating process. Cadmium, a known carcinogen, represents significant environmental risks in both primary aerospace manufacturing and at overhaul and repair facilities. The design objective of Ferrium® S53 was to create an ultrahigh-strength stainless steel that would eliminate the need for basic metal plating.

Description
Ferrium S53 is a corrosion resistant ultra-high-strength steel for structural aerospace applications. Ferrium S53 was designed to provide mechanical properties equal to, or better than, conventional ultra-high-strength steels such as 300M and SAE 4340 with the added benefit of general corrosion resistance similar to 15-5 PH. This eliminates the need for cadmium coating processes, which are environmentally unfriendly and require substantial hydrogen bake-out operations in order to avoid hydrogen embrittlement. Ferrium S53 has a greatly improved resistance to stress-corrosion cracking (SCC) over 300M and SAE 4340.

Ferrium S53 utilizes an efficient M/C strengthening dispersion precipitated through tempering while avoiding other carbides. This maximizes strength, wear resistance, and toughness, resulting in a unique combination of mechanical properties for a stainless steel.

Ferrium S53 uses a stable passive oxide film for optimum corrosion resistance. It also has high hardenability, permitting less severe quench conditions for a given section size and resulting in less distortion during heat treatment.

Processing
Processing of Ferrium S53 is similar to other quench and tempered martensitic secondary-hardening steels. Vacuum heat treatment and vacuum tempering is recommended to avoid surface decarburization. After quenching to room temperature Ferrium S53 is subjected to cryogenic treatment to assure a complete martensitic transformation. Ferrium S53 is typically double-step tempered around 900°F (482°C) and has excellent thermal resistance approaching this temperature. This allows for higher grinding speeds without risk for grinding burns and more reliability in service.

Corrosion Resistance
The general corrosion resistance of Ferrium S53 is similar to typical precipitation-hardened stainless steels such as 17-4 PH and 15-5 PH. Linear polarization testing of Ferrium S53 measured an average corrosion rate of 0.40 mils per year versus a saturated Ag/AgCl reference electrode in 3.5% sodium chloride (NaCl) solution at ambient temperature. Ferrium S53 is rust resistant in 3.5% NaCl solution.

Density
The density of Ferrium S53 is 7.88 g/cc.

Product Forms
Ferrium S53 may be manufactured in typical ingot, bar, and billet forms. Sheet and plate also available upon request.

Other
Patent pending.

For additional information regarding Questex’s Ferrium S53 contact Charles E. Birtleman by email or call 947, 623, 6222.
# Alkaline Zinc Nickel

## Zinc-Nickel vs. Cadmium Score Sheet

<table>
<thead>
<tr>
<th>Properties</th>
<th>LHE Cadmium</th>
<th>IZ-C17 LHE Zinc-Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion - Salt Spray</td>
<td>1000 hours</td>
<td>+ 1000 hours</td>
</tr>
<tr>
<td>Hydrogen Embrittlement (1a.1)</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Hydrogen Re-Embrittlement - Water</td>
<td>Marginal</td>
<td>Pass</td>
</tr>
<tr>
<td>Hydrogen Re-Embrittlement - Salt Water</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>Throwing Power</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Fatigue</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Lubricity</td>
<td>Good</td>
<td>Needs Lubricant</td>
</tr>
<tr>
<td>Electrical Properties</td>
<td>Good</td>
<td>TBD</td>
</tr>
<tr>
<td>Fluid Immersion</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Strippability</td>
<td>Good</td>
<td>Good*</td>
</tr>
</tbody>
</table>

* Dilute HCl Solution - Strips Zn-Ni in 10 seconds and is Non-Embrittling
Chromate Conversion Coatings

- Trivalent “Passivates” or “Chromites” are available for zinc plating and cadmium plating alternatives
  - Results vary for clear, yellow and black processes and top coats may be required to duplicate corrosion resistance and torque values with fasteners
  - No self healing with some exceptions
- Trivalent Processes based on the Navy TCP processes are effective on aluminum
  - 2024 alloy has been a greater challenge
  - Chromate/Primer Synergy...you can eliminate the chromate in the primer or the “chromate” but not both
    - Chromate primers are 25% by weight strontium chromate and relatively thick...chromates are thin films
# Chromate Alternatives

## Options – Chromate conversion of coatings and Al alloys

<table>
<thead>
<tr>
<th>Current tech Options</th>
<th>Commercial Status</th>
<th>DoD Status</th>
<th>Best DoD options</th>
<th>Gaps</th>
<th>Implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Cr conversion</td>
<td>NASA, TACOM, JSMC: Alodine 5200, 5700</td>
<td>Boeing production</td>
<td>USAF flight testing: Prekote</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paint adhesion promoters (sol-gels, Prekote)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>Production (steel sheet)</td>
<td>Army vehicles</td>
<td></td>
<td>Wash primers</td>
<td></td>
</tr>
<tr>
<td>Polymer coatings</td>
<td>Production (steel sheet, Kobe Steel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Tri-Chrome Treatments (ESTCP)

Description – Tri-chrome treatments

- Developed by NAVAIR and tested under ESTCP WP-0025
- Drop-in replacement for Cr\textsuperscript{6+} conversion coatings/sealers
- Cr\textsuperscript{3+} with Zr inhibitor
- Licensed and sold as
  - B-K Aklimate
  - Lusteron Aluminescent
  - Iridite TCP
  - Metlast TCP HF
  - Surtec ChromitAl TCP
- Other Cr\textsuperscript{3+}, such as Alodine 5900
- Commercial systems now often contain Co inhibitors and SiO\textsubscript{2} nanoparticles

Click for additional Info
Chromate/Primer Synergy

Best current options, gaps – Non-Chrome Primer

Substitution

- Depends on application
  - Chromated systems usually better than non-chromated, but non-Cr⁺ has greatly improved recently
- Chromate primer over non-chromate sealer
  - Current NAVAIR requirement
- Non-chrome primer over chromated conversion coat
  - Good intermediate step with minimal Cr⁺ and equivalent performance in many applications
  - Currently used on F-35
  - Uses minimum Cr⁺ as pretreat far thinner than primer

- Long-term: Single-component low temperature powder coat with inhibitor may provide better performance

Control

- PPE

Gaps

- Internal fuel tank coatings
- Fully chromate-free paint system with better or equal performance
  - F-35 development, testing in process
  - More difficult (longer term) on 2000 and 7000 series alloys
# Hard Chromium Plating Options

## Options - Hard chrome plating

<table>
<thead>
<tr>
<th>Current tech</th>
<th>Commercial Status</th>
<th>DoD Status</th>
<th>Best DoD options</th>
<th>Projects</th>
<th>Gaps</th>
<th>Implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HVOF</td>
<td>All OEM mill and comm landing gear systems, GTE, acts</td>
<td>Being implemented at DD ALC, Depot, some GTE usage</td>
<td>✔</td>
<td>✔</td>
<td>ESTCP HCAT HVOF: Completed</td>
<td>Spall-resistant coating for AVS/LG - new/MRO, carrier a/c/LG, hydraulics</td>
</tr>
<tr>
<td>Electroless Ni internals</td>
<td>Primary ID alt. Moderate and growing use, F-35</td>
<td>Some R&amp;D, testing</td>
<td>✔</td>
<td></td>
<td>APRL NLOS, completed, Niplate 700, Not implemented</td>
<td>No qual ID chrome alt, hydraulic IDS</td>
</tr>
<tr>
<td>Ni-based plate</td>
<td>Limited OEM use</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other electroplates</td>
<td>Limited OEM use Co-electroplates - GTE, nCo-P electroplate, dem/val, JAX</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas/ion nitride</td>
<td>Some actuator rod</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti electroplate</td>
<td>Decorative only</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta (gun barrel, large)</td>
<td>Dem/val, firing test</td>
<td>TBD</td>
<td>“Green gun barrel” Qual alt for gun barrels</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta (gun barrel, small)</td>
<td>R&amp;D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta (gun barrel, small)</td>
<td>R&amp;D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CONTROL OPTIONS**

- Segregated line: in use (FRC-SE) ✔
- Enclosed line: in planning (WR ALC) ✔
- Surfactants: in use ☑

**Implementation**

- Fit: FRC-SE
- Cost:
Hard Chromium Plating Alternatives

- HVOF (Various)
- Nanocrystalline Co/P (Integran) looks promising but it has not scaled up well

Issues
  - Cost
  - Line-of-Sight
Status – HVOF

Commercial/OEM

- Specified on all new landing gear programs
  - B787, B767-400, A380, A350
  - F-35 (all variants)
- Increasing use for hydraulics
  - Aircraft (OEM, MRO)
  - Caterpillar vehicle hydraulics (OEM, MRO)
- Specifications
  - AMS 2447, 2448, 2449
  - Boeing 5851

DoD

- Project to replace all EHC on LG at Ogden ALC
  - 38-128 qualified so far
- Advanced testing, Qualifications
  - Flight testing EA-6B (JAX), CH-53 (FRC-E)
  - C-2, P-2, P-3, C-130 propeller hubs WR-ALC, FRC-E
  - H-1 drive and rotor components, FRC-E
  - P-3 LG (FRC-SE) qual’d but not in production
  - TF33 GTE (OC-ALC)
Decorative Chromium Plating

- Trivalent Chromium Plating and PVD are the best alternatives to Hexavalent Chromium Plating.
- PVD “top coats” provide lifetime finish over nickel plating with excellent wear/abrasion resistance...decorative hardware and plumbing.
  - Capital Costs
  - Process Flow
- Trivalent Chromium Plating provide a good alternative for automotive trim and other similar parts where corrosion resistance is primary non-decorative requirement.
  - Hexavalent Chromium Plating can be Operated in a Closed Loop
  - Color is the only issue to complete conversion.
PVD Coatings

- Decorative Thin Films Only
  - Synergistic Coating over Electroplated Nickel
Nickel vs. Cobalt

- Continued debate regarding which element is more toxic
- Many alternatives to Cadmium Plating include Nickel Alloy Coatings or Substrates
- Most alternatives to Chromium Plating include Nickel and/or Cobalt Alloy Coatings
- Many alternatives to chromates include Cobalt in addition to trivalent chromium
Hazardous Material vs. Hazardous Process Perspective

- Alumiplate...hazardous process produces nonhazardous material...pure aluminum
- Chromium Plating...hazardous process produces nonhazardous material...pure chromium
- Chromate...hazardous process produces hazardous material
- Cadmium...hazardous process produces hazardous material
Hazard Management for Wet Processes

• Minimize Operator Exposure
  – Automation and Tooling
  – Enclosures
  – Automatic Covers
  – Ventilation System Design
  – Minimize Mist with Agitation Design

• Spill Prevention & Control – Asset Management & Preventative Maintenance

• PPE
RAFB AMFF
Designing for LEED
Leadership in Energy and Environmental Design
Robins AFB Process Automation

Fully Automated Wet Process Lines Provide Better Quality, Productivity and Safety
Integrated Hazard and Energy Management

Air in Operator Setup Area is Positive Relative to Wet and Dry Process Areas

Bulkhead with Automated Doors Separates Operator Setup Area from Wet Process Area
Integrated Hazard and Energy Management

Air in Operator Setup
Area can be Cost
Effectively Comfort
Cooled due to Reduced
Ventilation Rate
Push/Pull Ventilation is Very Efficient with Improved Capture due to Front and Back Shields
Integrated Hazard and Energy Management

Obstructions of Push/Pull Ventilation System are Minimized
Integrated Hazard and Energy Management

Sliding Isolation Shields Protect Operator from Splashes and Fumes and Improve Capture Efficiency

Interior Washdown of panels and hoods is Integrated in Design with Spray Manifolds and Collection Troughs
Preventative Maintenance and Asset Management

Facility Design facilitates Frequent Washdown of Process Equipment to Control Corrosion

Robust Corrosion Resistant Materials and Coatings are Required to Minimize PM Costs and Protect Assets
Design for Maintenance

Efficient Mechanical Design and Layout Reduces Maintenance Time and Cost
Main Level Maintenance Aisles

Alternating Operator and Maintenance Aisles Facilitate Efficient Equipment Maintenance

Instrument Sensors are Located for Easy Access
Integrated Spill Prevention/Control and Corrosion Management

Floor Coating Penetrations are Above Spill Zone.

All Equipment Sits on Pads Above Spill Zone.
Integrated Spill Prevention/Control and Corrosion Management

The Basement Level Floor Slopes to Collections System of Trenches
Integrated Spill Prevention/Control and Corrosion Management

Trenches Slopes to Collections Sumps
Integrated Spill Prevention/Control and Corrosion Management
Resources

- NASF Online Data Library
  - www.nasf.org
- ASETSDefense (HCAT/JCAT)
  - www.hcat.org
  - www.materialoptions.com
  - www.asetsdefense.org
  - www.hazmat-alternatives.com