Technical Alternatives to Nickel, Chromium, Cobalt and Cadmium

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Summary

- Environmental regulations
  - US/Canadian regs – effects on manufacturing, MRO
  - REACH and other overseas regs – indirect effects on defense manufacturing, sustainment; direct effects on deployed assets

- Effects on current materials and processes, and on alternatives
  - Loss of alternatives
  - Development of better alternatives

- Way forward
  - Better science understanding
  - Better data
  - Faster, more rational development, testing, design, qualification
  - International collaboration
  - Alternatives that work better than originals
Why do aerospace and defense worry so much about corrosion?
To fight corrosion you need the right weapons.
Regulations affecting chromates – US

Defense regs
- OSD–ATL Memo, Apr 8, 2009, Minimizing the Use of Hexavalent Chromium
- DFARS, FR 75, 25569, May 5, 2011, Minimizing the Use of Materials Containing Hexavalent Chromium

DFARS affects OEM coatings >0.1%Cr6+
- Primers, SermeTels, sealants
- Conversion coatings exempt
Memo affects all uses of Cr6+ in all DoD depots, operations

OSHA – Feb 28, 2006, Occupational Exposure to Hexavalent Chromium
- 8 hr TWA Cr6+ reduced from 52 to 5µg/m³
- Requires careful control, housekeeping, showers, etc

Harder to meet standard – engineering controls
Reconfiguration of plating, anodizing, sanding, painting operations – high capital cost, lower efficiency
- Same with Cd

EPA 2012 – Stack emissions halved to 6–15 µg/dcs

Better engineering controls needed
More citations, fines
No more PFOS fume suppressant
Regulations affecting chromates – Europe

**RoHS**
- $\text{Cr}^{6+} < 0.1 \text{wt\%} \text{ in any coating}$
- Aerospace, defense exempt

**REACH**
- Registration – cannot use if not registered for that use
- Authorization – cannot use unless authorized for that use; limited duration
- Restriction – certain uses not permitted
- NO AERO/DEFENSE EXEMPTION
  - Can exist, but limited and not all countries

- Affects electronics
- Little other aero/defense impact
- Recast has not changed this

- Affects everything
- Loss of chemicals from market
- More difficult sustainment in EU
- Constant change, hard to predict

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Applications (MacDermid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium trioxide, Acids generated from chromium trioxide</td>
<td>Hard chrome plating, chromate conversion (Al, Zn, Cd, etc), chromic acid anodizing – High priority</td>
</tr>
<tr>
<td>Sodium dichromate</td>
<td>Chromate conversion (Al, Zn, Cd, etc) – High priority</td>
</tr>
<tr>
<td>Sodium chromate</td>
<td>Extensively used in chromates and trivalent chrome passivates – High priority</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>Used in Al chromates, limited use in other chromates, impacts chromate conversion – Medium priority</td>
</tr>
<tr>
<td>Ammonium dichromate</td>
<td>Not commonly used – Low priority</td>
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<tr>
<td>Potassium dichromate</td>
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<tr>
<td>Cobalt(II) sulphate</td>
<td>Trivalent passivates for Zn alloys, Co plating – medium priority</td>
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<tr>
<td>Cobalt dichloride</td>
<td>Trivalent passivates for Zn alloys – medium priority</td>
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<tr>
<td>Cobalt(II) dinitrate</td>
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</tr>
<tr>
<td>Cobalt(II) carbonate</td>
<td>Co plating – medium priority</td>
</tr>
<tr>
<td>Cobalt(II) diacetate</td>
<td>Not commonly used – low priority</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>Vapor degreasing, now seldom used – Low priority</td>
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</tbody>
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Note: Co salt rules will prevent use of nCo-P chrome plate alternative, and Cr3+ passivates for Zn, and ZnNi (i.e. Cd alternatives)
If your processes are not in the list of Authorized uses by the Application dates you can no longer do them or have them done in the EU after the sunset dates, except on-base with US citizens.
Chromates

- Chromic acid (e.g. Alodine 1200) and Na dichromate (e.g. Alodine 1600) are primary conversion coatings for aircraft skins, Al components
  - Corrosion control, repaint, touch-up

- Chromic acid used for
  - Hard chrome plating – rebuild, wear resistance
  - Chromic acid anodizing – corrosion resistance and paint adhesion on Al

- Primary aircraft sustainment chemicals
So what happens if Na$_2$Cr$_2$O$_7$, CrO$_3$ etc. go into Annex XIV?

- **Consortium set up** to pursue Authorization for CrO$_3$
  - >$2$ million and no certainty
  - >$50,000$ to get authorization if not from vendor

- Will they be authorized?
  - Probably, as essential for EU aero industry (Al and Mg conversion, chrome plating, probably CAA, sealing and passivation)
  - But Authorization is time–limited (X yrs)
  - Any user must derive authorization from vendor or other authorization holder, or have own

- Same for each of the other substances

Will there be Authorization Consortia for the other chromates? Have not seen any, and if not they are gone

X<3–5yrs?
What about other materials?

Cd

- Cd also covered under RoHS (<0.01wt%)
- Cd salts also SVHCs under REACH
  - Will be authorizable/restricted sooner or later
- Cd already restricted for most EU vehicles
- OSHA enforcing similar housekeeping issues for Cd as for Cr⁶+
- Navy requires Cd–free connectors for new replacement submarines
  - First time DoD has banned Cd
  - Covered at ASETSDefense 2012
Cd alternatives

- LHE Zn14wt%Ni without brighteners
  - Available from Dipsol, Atotech, Coventya
  - This chemistry is single-phase material
- Qualified by USAF Hill AFB for landing gear
  - Being implemented component by component
- Close to qual by Boeing for components and fasteners
  - Seattle and St Louis not yet decided whether to spec by chemistry supplier or performance
  - Discussion of this at ASETSDefense 2012
Dingwerth, SUR/FIN 2012

**Zinc-nickel alloy coatings**

Corrosion protection and alloy composition / NO post-treatment

**Zn/Ni in ISO 9227 NSS / time until red corrosion alloy**

- Zn(H)Ni (14 % Ni)
- Zn(L)Ni (6.5 % Ni)
- Zn

- 0.01 µm/h
- 0.03 µm/h
- 0.05 µm/h

**Ni$_2$Zn$_{11}$ γ-phase conc. vs Ni fraction in**

**Best cathodic corrosion protection with γ-zinc-nickel alloy!**

“Stray but a little and it will fail”
Computational fixture design for uniform thickness, chemistry

Plating with ZnNi is more complex than Cd because we must keep the correct Zn/Ni ratio to get single phase coating.

Hill AFB uses Elsyca computational software to design plating fixtures.

C-5 MLG Rotation Collar

Website: www.rowantechnology.com  Email: klegg@rowantechnology.com
Is ZnNi the drop-in replacement?

- Not really. Works well for structural components, but not for electrical connectors (see ASETSDefense 2012 Connector side meeting)

- Connectors far more complicated
  - Electroless Ni–PTFE being adopted by most connector companies
    - Good electrical performance
    - But galvanic corrosion of shell when coating breached
  - ZnNi usually fails conductivity testing
  - Electroplated Al works well, but high capital cost
What about Co?

- Electroless Ni used as hard Cr alternative
- HVOF WC–Co, WC–CoCr and pulse plated nCo–P developed as non–Ni alternatives to hard chrome (also Co–P+SiC, Ni–W)
  - Co salts now priority chemicals under REACH
  - WC–Co “hard metal disease” rising concern
- ZnNi developed as alternative to Cd
  - Uses Ni
  - Needs Co–based passivate
Ni alternatives

- Ni coatings are alternatives to hard Cr
- ZnNi is alternative to Cd
- Ni is essential for aircraft MRO
- Ni salts added to CLP list as SVHCs
  - Will be Restricted or Authorizable at some point
- Thus far Ni Institute in Brussels has kept them off the Priority List
  - Hope is to keep them off until the EU realizes that they are losing all their manufacturing
“We are the Knights who say Ni!”
Nickel: the versatile metal

A perfect communication tool with the French Authorities!

France Capon, ASETSDefense 2012

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All these are transition elements, so have some chemical similarities that allow some substitutions among them. Is there an escape from this circle?
Yes, we can escape, and there are some good options. For corrosion the most common options are stainless, Ti, composite. There are now some organic corrosion inhibitors.

But every alternative has limitations and costs (usually higher costs, sometimes far higher).

Legg’s Law: “Any material active enough for corrosion control will be a health and environmental hazard”
What else is on the REACH hit list?

- Boric acid
- Almost all Ni salts
- Pb salts
- Cd and Cd salts
- Co salts
- Phthalates (plastics)
- Flame retardants
- Large numbers of organics
- Arsenic salts
- Refractory fibers
- Nanomaterials in future?
The story so far

- All our primary coatings and treatments are becoming harder to do
- Risk of regulation, deselection by customers
- Loss of chemicals from the market
- Alternatives are in the same boat
  - As soon as we qualify an alternative it is likely to be next against the wall, as already found
  - Especially since most inhibitors must be chemically active by definition
What can we do about it?

- Be aware what is in your products
- Be aware of chemicals used to make them
- Keep on top of technology/material developments
- Anticipate from lists, databases, suppliers
- Plan on how/when to change
- Use databases to identify alternatives
- Minimize risk, cost by better test and design methods
- Be aware what is in your products
Anticipating change

- Lists
  - 67/548/EEC, List of Lists, SIN
  - REACH Annex XIV Candidates
  - Suppliers

- Similarity to existing SVHCs

- Database
  - Shows current restrictions
  - Potential for future restrictions

- Some changes unanticipated
  - Especially as register smaller quantities (so far only 1,000 tonne)

I’ve got them on the list, They’d none of them be missed
Often the problems will not be the major constituents, but the essential minor or even trace chemicals.
Keeping up with technology

- NASF (National Assoc for Surface Finishing)
  - Coating technologies
  - Environmental regulations US, EU
- Trade magazines
- ASETSDefense covers alternatives to Cd, Cr\(^{6+}\), VOCs for military and aerospace
  - Not very useful for most commercial automotive
- Coatings database for comparisons
- We are considering whether there is enough of a market to provide service for keeping up with regulations and materials alternatives
Both Granta and ASETSDefense Coatings Databases provide performance and usage data. Coatings never as well-defined as bulk materials and alloys.
Planning

- Most alternatives are more expensive, often not as effective (at least not at first), process often requires more care, better QC
- E.g. Zn sealers: $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+} \rightarrow \text{non-Cr} \rightarrow \text{organic}$
  - How long will each option last in EU then US?
  - How broad a supply base?
  - Should you migrate to the next closest option for better availability, lower cost and technical risk?
  - Hold out for better performance, lower cost?
  - Wait and see what everyone else does?
  - Or make a big jump in hope it will last longer in the market and maybe give you “green” kudos?
More efficient testing

- Testing and redesigning are expensive
- How do you know a new material will work?
- Wear and corrosion tests very poor indicators of service performance
  - Even worse when alternatives work differently so mechanisms are not the same
    - Cr$^{6+}$ vs Cr$^{3+}$ vs Ce as corrosion inhibitors
    - Hard Cr vs E–Ni composite vs thermal spray for wear
- People are trying to develop better tests (esp corrosion), but will be 5+ years
  - Really hard to do a 2–yr service test in a month
Predictive design

- We have data and models to predict stress, thermal properties
- But all we have for corrosion are rules of thumb for corrosion
- One of the biggest problems is galvanic corrosion between dissimilar materials
  - Rules of thumb not much use as change coatings and their surface treatments
    - On galvanic chart where is Zn vs Zn8Ni vs Zn15Ni vs Al vs Zn/Al–filled polymer vs Mg rich primer?
      - With Cr$^{3+}$ vs Mn vs Zr vs Mo inhibitor?
Currently we rely on half-century old galvanic data for our coatings. New coatings and treatments require better data to use them successfully.
Prediction of Wing/lug galvanic corrosion

Cd-plated CuBe bushing in anodized Al lug

Since anodized Al layer is porous and more cathodic causes galvanically dissolves Cd plating from bushing.

Once CuBe is exposed it galvanically attacks Al through porosity or damage in anodize.
Integrating performance data, corrosion prediction, design

Corrosion Rate
Corrosion Potential

Stainless Steels
Zn, Zn-Ni
Steel
Cadmium

BOEING

CORROSION RESISTANT DESIGN

Website: www.rowantechnology.com Email: klegg@rowantechnology.com
Environmental regulations will make coatings and corrosion control increasingly difficult, but there are ways to meet the challenge.
Toward a brave new world – free of Cr, Cd, Ni, Co, Zn, and all nasties

- Without Zn steel is useless
- Without Ni, Co we can have no stainless steel
- Without steel we can have no industrial society
- But we can all become great artists again!

The problem is that REACH is based on the Precautionary Principle = HAZARD
US Regulation is supposed to be based on RISK
THERE IS A BIG DIFFERENCE BETWEEN HAZARD