Overview of Plating and Inorganic Coatings – Available Alternatives and Future Developments

Results of SERDP-ESTCP Metal Finishing Workshops

Keith Legg, Rowan Technology Group
CSIMP Workshop, Monterey, CA
February 21, 2007
DoD’s most widely used metal finishes

Chrome plate
- Ni – strike, sulfamate
- Alloy
  - Hydraulics, landing gear
  - Topcoat
  - Chromated primer
  - Chromate conversion
  - Al alloy
  - Aircraft skins, electronic cabinets

Topcoat
- Chromated primer
- Chromate conversion
- Cd plate
- Steel
  - Vehicles, hydraulics, fasteners

If it wears, chrome plate it. If it corrodes, chromate it.
Regulatory trends worldwide

Growing concerns

- Nanotechnology
- Cobalt
- Zinc
- Other Metals

Already heavily regulated

- Nickel
- Hex Chromium
- Cadmium
- Lead

Next against the wall

- Notice: Current regulations hit our current finishes
Future regulations will hit our best alternatives

From: SERDP/ESTCP Metal Finishing Workshop, May 06. Christian Richter

klegg@rowantechology.com
Regulations – US

- **OSHA Cr\(^{6+}\) limit (Feb 2006)**
  - PEL 5µg m\(^{-3}\) (tenfold reduction)
  - Lawsuits still ongoing and limit could be lowered again
  - Primary impact for DoD and aerospace is uncontrolled emissions from painting, sanding, corrosion control

- **California RoHS**
  - Likely to say that anything restricted in Europe is equally restricted in CA
    - Hg, Pb, Cd, Cr\(^{6+}\), brominated fire retardants
Regulations - Europe

- EU Precautionary Principle
  - If we don’t know assume it’s bad
  - Screaming trumps science
- WEEE (Waste Electrical and Electronic Equipment)
  - RoHS (Reduction of Hazardous Substances)
  - China RoHS, California RoHS
  - Big issue coming up is how to measure Cr⁶⁺
- ELV (End of Life Vehicles)
- REACH (Registration, Evaluation and Authorization of Chemicals)
- Lesser known regs
  - Stockholm Convention on Persistent Organic Pollutants (POPS), Convention on Long Range Transboundary Air Pollution (LRTAP) and Heavy Metals protocols

From: SERDP/ESTCP Metal Finishing Workshop, May 06.
Christian Richter
Impact of regulations on DoD

- DoD and aerospace exempt from regulations
- But we are not immune to their effects
  - Weapons system reliability
  - Fewer suppliers of chemicals and processes, higher prices
  - Already seeing these effects in Pb-free solder
- Forcing adoption of modern, more effective technologies that improve performance and workforce health and safety
  - HVOF, Al coatings, CRES alloys, composites
- But, we still have only one periodic table
  - “Green” alternatives are already becoming brown - Zn, Ni, Co, Cr³⁺
  - Need to assure rational approaches that enhance, not impair, our capabilities

F-35 Lightning 2 CTOL first flight Dec 15, 2006

Totally green F-36 Lightning 3 CV carrier landing (circa 2050)
Pb, Cd, Cr⁶⁺, Ni, Zn, Co, EHC - free
Getting superior alternatives into depots and contractors

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klegg@rowantechnology.com
SERDP/ESTCP sponsored workshops on metal finishing

- Metal Finishing Workshop, Washington DC, May 22, 23, 2006
  - What is the state of the art and what remains to be done

- Metal Finishing Session and Side Meeting, Partners in Environmental Technology Symposium, Washington DC, November 2006
  - Session summarized workshop for broader DoD community
  - Side meeting to start DoD/industry collaboration

- Chromates Workshop, to be held in Ogden, UT (near Hill AFB), May 16, 17, 2007
  - DoD/finishing industry collaboration to identify viable alternatives and engineering data
Metal Finishing Workshop, Washington DC
May 22, 23, 2006

Objective: “Strategically guide future environmental research development testing and evaluation (RDT&E) investments and to support the transition of demonstrated technologies in the area of metal plating and finishing.”

- SERDP and ESTCP have spent a lot on money on metal finishing
- Where are we now? What remains to be done?
- Current state of the art in the Defense sector – OEM and MRO
- Emerging regulatory trends – US and overseas
- Currently used non-hazardous materials and processes
- Barriers to adoption of clean alternatives
  - Performance shortcomings,
  - Cost and other non-technical barriers

Read-ahead papers and briefings
- Breakouts by application and technology

Materials:
- Hard chrome
- Cd
- Chromates: Conversion coats, pretreats, sealers, anodizing – Not primers
Agenda

1. Bridging the Valley of Death, Carol Handwerker, Purdue
2. Environmental Issues and Corrosion, Lew Sloter, OSD
4. Clean Alternatives, Keith Legg, Rowan Technology Group

DoD Operations and Sustainment
1. Tactical Vehicles, John Beatty, ARL, Tom Sachar Picatinny
2. Aerospace and Missiles, Eric Brooman, AFRL, Sheldon Toepke
3. Gun Barrels, Mike Audino, Benet Labs

New Platforms
1. Joint Strike Fighter, Scott Fetter, Lockheed
2. UAVs and UCAVs, Steve Gaydos and Joe Osborne, Boeing
3. Future Combat System and Stryker, John Beatty, Geoff Hoerauf, FCS
Agenda - breakouts

Applications
1. Hydraulic and pneumatic actuators
2. Turbine engines for vehicles, ships and aircraft
3. Structural (load-bearing) components
4. Gun barrels and small components (fasteners, pins, etc)

Technology
5. Chrome plating (line-of-sight and non line-of-sight)
6. Cd plating (line-of-sight and non line-of-sight)
7. Cr$^{6+}$ pre- and post-treatments
Final Report

- Worked out well, with a lot of detailed information and good discussions
- Final Report
  - Authors: Keith Legg and Christian Richter
  - Available on web
    - Cleared for distribution
    - Link from www.materialoptions.com
Alternatives
Hard chrome alternatives

Thermal spray
- HVOF carbides
- Plasma spray
- Cold spray

Aqueous electroless, electroplates
- Electro -, Electroless Ni
- nCo-P electroplate
- Other alloys, composites

Vacuum coatings
- Post magnetron sputtering
- Other sputter, arc coatings
- Hollow cathode

Weld coatings
- Electrospark deposition
- Explosive cladding
- Laser cladding

Heat treatments
- Plasma and gas nitriding
Hard chrome alternatives

Alternatives adopted
- HVOF WC-CoCr now specified for all new Landing Gear programs, many aircraft hydraulics
- HVOF baselined for JSF (all)
  - nCo-P promising for IDs and TDC alternative
- OO-ALC major project to replace EHC with HVOF across depot
- NADEPs JAX and CP use HVOF for engine parts
- WR-ALC, OC-ALC beginning to adopt
- New Army vehicles using electroless Ni, Ni-W-B and Ni-W-SiC electroplate
- HVOF Cr$_3$C$_2$-NiCr beginning to be used for commercial hydraulics
- Gun barrels – sputtered Ta nearing production for large caliber

Remaining needs
- Alternatives mostly identified but adoption rate still low
- HVOF spalling still an issue
  - So far looking good for typical 0.003” thick OEM use
- IDs still uncertain
- Gun barrels still under development
- Ni likely next against the wall, so Ni alternatives are interim solution
Cd alternatives

Vacuum and spray Al
- IVD Al (vacuum)
  - Sputtered Al
  - Arc and flame spray Al, Al-Zn
  - Cold spray Al and alloys

Aqueous electroplates
- Acid and alkaline Zn-Ni
- Sn-Zn
- Electroplasma Zn-Al

Non-aqueous electroplates
- Electroplated Al (AlumiPlate)

Alternative alloys
- Titanium alloys
- High strength stainless steels
- Ultra-high strength CRES
- CVD Al coatings

Niche products
- Metallic-ceramic coatings
- Al- and Zn-filled polymers
**Cd alternatives**

### Alternatives adopted

- Stryker has no Cd plated hardware or fasteners
- F35 uses CRES fasteners, AlumiPlated steel or composite elec. Connectors
- IVD-Al used at OO-ALC, CCAD, NADEPs JAX, NI, CP
- F-35 likely to replace LG Cd with AlumiPlate
- Metallic-ceramic (SermeTels) esp. on F-22 LG etc
- Carmakers use Zn-Ni and similar alloys

### Remaining needs

- HSS fasteners
  - Everyone’s problem, no-one’s responsibility
  - Carmakers use Al/Zn filled ceramic and polymer coatings
  - SERDP has issued RFP for Cd and Cr₆⁺-free fastener technologies
- LHE alkaline Zn-Ni (Boeing, Dipsol America) test/validation
- Corrosion resistant structural materials (CRES alloys, composites, etc.)
- Cd-free electrical connectors
- Corrosion-erosion resistant coatings
- Brush Cd alternatives
- More options for high density Al coatings

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Cd used for protecting steels
Military and aerospace are only remaining coating uses

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ELV, RoHS drivers

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klegg@rowantecnology.com
There are many COTS solutions widely used in industry. The question is how to qualify those that are viable and find the best solutions where COTS products cannot be used.
Chromate usage

- Chromates (strontium dichromate, zinc chromate, etc.) contain Cr$^{6+}$ and are used everywhere for corrosion protection and adhesion
  - Conversion coatings and sealers for Al, Mg alloys, Zn, Al, Cd, ZnNi and other corrosion resistant coatings
  - Anodizing, esp. where paint adhesion is essential
  - Primers and bonding primers
  - Fuel tank coatings
  - Wash primers for steels (military vehicles)
  - Metallic-ceramic paints (SermeTels)
  - Passivation of stainless steels
- EU ELV, WEEE, RoHS rules forcing elimination of chromates from galvanized sheet, fasteners, etc.
## Cr\(^{6+}\) alternatives

### Alternatives adopted
- Primary alternatives are Cr\(^{3+}\) chemistries, Zr, Mn, rare earth inhibitors; also adhesion promoters – silanes, etc.
- NAVAIR TCP (TriChrome Pretreatment) commercially available from several suppliers
  - NAVAIR approved for some Al alloys
- PreKote AF approved for F-16, T-37, T-38
- F-35 Deft non-Cr primer for internal bays
- Many commercial Cr\(^{3+}\) options
- Alodine 5200/5700 approved for USMC Expeditionary Fighting Vehicle
- Cr\(^{3+}\) on Al road wheels – Army
- NAVAIR approved boric-sulfuric anodization in place of chromic
- Phosphates on steels commercially
- Keronite (for Al) and Tagnite (for Mg) increasingly used as anodize
- Non-Cr or low-Cr metallic-ceramics approved by P&W and others in place of SermeTel W
  - SermeTel, Ceral, Ipcote, Alseal now available

### Remaining needs
- Qualify COTS alternatives
- Scientific understanding of non-Cr\(^{6+}\) inhibitors
  - New SERDP RFP
- Electrical equipment
- Anodize for use for paint adhesion
- Improve TCP for ease of use
- Chromate alternatives for Mg
- NDI of Mg through anodize layer
Needs

Particularly difficult applications

- Fasteners (esp. threaded fasteners)
  - Must have right torque-tension to avoid changing maintenance manuals
  - Must have low volume corrosion products to avoid seizing
- Al electrical boxes and electrical equipment (also coated composite electrical equipment and boxes)
  - Not primed and painted
  - Alternative must work alone and have low electrical resistance

Common needs

- Qualification of COTS products (esp. Cr⁶⁺ alternatives)
- Cost-benefit analyses people can believe
- Technical Database of Surface Finishing Technologies
  - Starting to assemble
- Better H embrittlement test – funded
- Better test and NDI methods (reduce qual cost)
- Some funding of OEM implementation
Drivers and barriers to adopting clean alternatives

- Performance is still the strongest driver
- But ESOH regulations are becoming a strong driver as well (especially in commercial products)
- Numerous DoD barriers, including
  - Technical barriers
    - Qualification cost, requirements based on existing technologies
    - Lack of data and specifications
    - Cost of implementation, paperwork and drawing changes
  - Cultural barriers
    - Inadequate depot engineering staffing, lack of management support
    - Lack of specific requirements – policies largely ignored
    - DoD contracts incentivize cost reduction, disincentivize implementing new technologies
How can we overcome the barriers to technology adoption?

- **Knowledge**
  - What do we really need?
  - What already exists that we can use?
    - DoD, the commercial world, other countries

- **Experience**
  - What works where?
  - What do others use successfully?
  - What performance and service information is available?
    - Just as important to know what does not work as what does

- **Data**
  - To make good, solid engineering decisions we need good, solid engineering data, and we need it readily available
Follow-on Metal Finishing Session and Side Meeting

Partners in Environmental Technology Symposium
Session 1C and Side Meeting on Metal Finishing
November 2006
Aim of meeting

- **Session 1C**
  - Make DoD attendees aware of the results of the workshop, and the options used in the commercial world.
  - 120-150 attendees

- **Side Meeting**
  - Initiate collaboration between DoD and the finishing industry on the best approaches for reducing hazardous materials in DoD weapons systems and sustainment.
  - Involved DoD engineers, commercial suppliers and users, call-in by GM, Ford
  - 60+ attendees
Session 1C on Metal Finishing - Agenda

- **Keynote: Regulatory Trends for Metal Finishing** – Christian Richter, The Policy Group
- **Surface Finishing Community Response to ESOH Regulations** – Craig Bishop, Atotech USA
- **Addressing Emerging Environmental Regulatory Requirements on DoD Tactical Ground Vehicles** – John Beatty, Army Research Lab
- **Replacing Cd and Chromates on Boeing Commercial Airplanes** – Joe Osborne, Boeing
- **Elimination of Cd and Cr platings and Cr6+ from DoD Aircraft Systems, New and Legacy** – Sheldon Toepke, Toepke Consulting
- **Fasteners for Military and Commercial Systems** – Liang Zeng, Alcoa Fastening Systems
Side meeting – next steps

- Initiated contact and collaboration between DoD and finishing industry
- Follow-on joint workshop between DoD, NASF, SFIC to discuss specific commercial solutions to DoD chromate problems
  - Will take place May 16, 17 in Ogden, UT
  - Visit to Hill AFB afternoon of May 15
- Database of engineering data
  - Engineers need ready access to engineering data on alternatives adequate for making engineering decisions
  - Under way and should take place over coming year.
- Expand and rename HCAT to encompass metal finishing in general (or materials in general)
www.hazmat-alternatives.com

Portal for information on alternatives, regulations, etc., with links to other locations. Includes databases, on-line tools
Surface Engineering Database to be added over coming year as resources available
www.hazmat-alternatives.com

- Info on regulations, including EU rules
- Publicly released reports and briefings
- **Surface Engineering Database under construction**
  - Will contain data as downloadable Excel files, reports, including rig test and service experience
  - Include sources
  - Password protected

Rowan Technology Group
Surface Engineering Database

- Hard Chrome Alternatives
- Cd Alternatives
- Chromate Conversion Alternatives
- Anodizing Alternatives (Al, Mg, Ti)
- Chromated Primer Alternatives

TEST DATA
- Test Protocols
- Technical Reports
- Briefings
- Specifications
- Approvals
- Manufacturing Guidelines
- Other Documents

Item
- Corrosion
- Embrittlement
- Fatigue
- Wear/Friction
- Impact
- Adhesion
- Integrity
- Rig Tests
- Flight Tests

- SERDP and ESTCP-generated data
- All other releasable DoD data we can get our hands on
- All commercial data companies are willing to give us
- Links to data held by others, e.g. NASF, NMFRC, etc.

klegg@rowantechonlogy.com
Improved Database

- Data will be rearranged for easy search and download
- Excel files can be downloaded for use in engineering analysis
- All reports and briefings containing data from rig and service testing will be downloadable
- Additional technologies, materials and coatings to be added as data become available
  - Including data on commercial coatings and treatments
- Push the production of proper engineering data suitable for decision-making
  - Minimize the amount of testing needed for validation and qualification
  - Make it possible to use COTS products more readily
Long term vision

Integrated system to identify and prioritize DoD ESOH needs and gaps, linked to Surface Engineering Database.

Most components already exist in JSF program.

Can be applied to almost any ESOH technology area.
Workshop – Chromate Alternatives for Metal Treatment and Sealing, May 16, 17, 2007

- Follow-on joint meeting between DoD, NASF, SFIC engineers
- Aim: Bring together DoD and finishing industry engineers to identify specific COTS alternatives for DoD metal finishing
  - Conversion coats and sealers, anodize, chromate wash
  - Not primers and paints – later workshop possible for that
  - To start working out how to fill gaps
- Date: May 16, 17, Layton, UT
  - Visit to Hill AFB afternoon of May 15 for commercial suppliers to see how DoD uses chromates