Cadmium replacement options

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Definition

- Cd used on almost all exposed steel, usually chromated, primed, painted

Specs

- QQ-P-416
  - Class 1 0.0005”; Type I as-deposited
  - Class 2 0.0003”; Type II chromated
  - Class 3 0.0002”; Type III phosphated
- BAC 5701
- AMS 2400
Usage

**Steel Components**
- The “cure-all” corrosion coating
- Good salt spray and scribed corrosion protection
- No hydrogen embrittlement or stress corrosion cracking
- ODs and IDs
- Plate steel to protect Al

**Fasteners**
- Correct lubricity (avoid changes to torque-tension specs)
- No hydrogen embrittlement
- Retain thread profile

**Connectors**
- For electrical equipment
- Low contact resistance
- Non-insulating corrosion products
- Solderable a plus
Cd – a life-cycle issue

- Deposition – Cd and CN solution
- Scuff-sanding for repaint
  - Personnel exposure
- Wash-down of engines
  - Environmental contamination
- Strict new European Cd rules
  - End-of-life vehicles
Requirements

- Cd is a sacrificial material
  - Meets B117 and SO$_2$ salt fog tests
  - If scratched it still protects
  - Compatible with Al so a Cd-plated bolt or rivet does not corrode an Al aircraft skin
  - Ni and other barrier coatings are not replacements

- For threaded fasteners need right lubricity
  - Consistent break-away torque and torque-tension
    - Otherwise have to redo all the manuals

- Need to be able to repair during manufacture
- Need to be able to prime and paint
Galvanic series

- Al and Al alloys
- Zn-Ni
- Al-Mn
- Zn
- Be!!

Mother Nature left us short on options!
Summary of Cd alternative options

Cd alternatives

Vacuum Al alternatives
- IVD aluminum (Ivadizing)
- ID sputtered Al for IDs

Aqueous electroplated alloys
- Zn-Ni
- Sn-Zn

Non-aqueous electroplates
- Electroplated Al (Alumiplate)
- Molten salt bath Al-Mn

Niche alternatives
- SermeTel ceramic coatings

Alternative base alloys
- New high strength stainless
- Metal-filled polymers
- CVD Al (small IDs)

AI is the only “global” replacement
Almost everything needs chromate conversion

In use  In test  In development
JSF Cd Alternatives Report

- Requirements
- Alternatives
  - Zn-Ni, Sn-Zn electroplates
  - Alumiplate
  - Al-Mn molten salt bath
  - IVD and CVD Al
  - Sputtered Al
  - Thermal spray
  - SermeTels
  - Filled polymers
  - High strength stainless steel
Joint Test Report

- Cd alternatives report for low strength steels (<220 ksi)
  - Boeing, JGPP
  - Sn-Zn
  - Acid Zn-Ni (Boeing)
  - Alkaline Zn-Ni
  - IVD Al

http://www.materialoptions.com/w2g/cgi/kmcgi.exe?O=DI R0000000l6D&V=0

Engineering and Technical Services for Joint Group on Pollution Prevention (JG-PP) Projects

Joint Test Report
BD-R-1-1

for Validation of Alternatives to Electrodeposited Cadmium for Corrosion Protection and Threaded Part Lubricity Applications

October 1, 2002

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Submitted by:
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IVD Al

Vacuum PVD process
Fully qualified and quite widely used by OEMs and depots
Spec MIL-C-83488 for Al coating does not define deposition method
IVD Aluminum (Ivadizing)

**Pros:**
- Long history of successful use
- Clean process (except chromating)
- High volume chamber (up to 5’x1.5’x15’ load)

**Cons:**
- Vacuum process - expensive
- Requires shot blasting and chromate conversion
- Poor throwing power (especially in holes)
- Solid lubricant for torque-tension
- Limited data on fasteners, electrical connectors

**Stage of development:**
- Commercial
- Available at many depots

Vacuum evaporation of Al
Bead blasting to densify
Chromate conversion

Abar Ipsen Depots
Description

- **Deposition**
  - Al evaporated from bottom of chamber
  - Substrates hang on frame, biased for weak plasma
  - Gives coating poorly adhered and porous

- **Consolidation**
  - Glass bead peen

- **Convert**
  - Chromate convert
    - Iridite 14-2

- **Dry lube (threads)**
  - MoS$_2$ in resin binder
Applications

- **Military**
  - F-4
  - F-14
  - F-15
  - F-16
  - F-18
  - AV-8B
  - A-12
  - V-22
  - Apache

- **Commercial**
  - Boeing 737, 747, 757, 767
  - McDonnell-Douglas DC9, 10, MD-80, 90, 11
  - Bombardier Dash 7, 8
  - Airbus A300, A310
## Specification – MIL C-83488

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<th>Class</th>
<th>Thickness (min)</th>
<th>Type I</th>
<th>Type II</th>
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<td>504</td>
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<tr>
<td>3</td>
<td>0.0003”</td>
<td>168</td>
<td>336</td>
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</tbody>
</table>

Type I – Deposit + glass bead peened  
Type II – Deposit + peen + chromate convert
Advantages and limitations

Advantages
- Qualified commercial process
  - Commercial coating shops
  - IVD-coated fasteners available commercially
- Clean and safe
- Good performance
- No H embrittlement

Limitations
- Vacuum process
  - Expensive
  - Awkward
- Poor quality coating as-deposited
  - Peen and chromate
- Poor throwing power
- Soft and easily damaged
  - Cannot easily be repaired
- Dissolves in alkaline cleaners
  - MRO users may have to change cleaning process
Data available
Boeing/JGPP low strength steel report

- Boeing/JGPP report on Cd alternatives for low strength steels
  - Also on HCAT site for convenience
  - Covers 4 alternatives:
    - Sn-Zn
    - Neutral Zn-Ni (Boeing process)
    - Alkaline Zn-Ni
    - IVD Al

- IVD and neutral Zn-Ni best
  - Scribed B117 inconsistent
  - Lubricity on fasteners acceptable with
Corrosion

- Data from B117 testing at 3 locations
  - Unscribed excellent
  - Scribed – variable corrosion from scribe
Fluid compatibility

- Weight loss after immersion, scrubbing
- In most cases IVD gains weight
  - Ascribed to adherent oxide
  - Could be absorption in porosity
Fatigue

- No difference between uncoated and soft Cd alternatives
- Fatigue debit with harder alkaline Zn-Ni
Breakaway torque and torque-tension

- MoS$_2$ lubricated IVD passes testing
PVD Al for IDs – sputtered Al

- Marshall Labs Plug and Coat
  - Works inside IVD chamber
- Makes it possible to coat OD and ID simultaneously Plug & Coat
  - Add-on to existing IVD chamber
- Status
  - Being installed at Hill AFB
  - Commercially available
  - Meets MIL Spec.
- Note: All Al coatings require use of proper aqueous cleaners (avoid alkaline cleaners)
ID sputtering data

- Report # BOEING-STL-01P0041
  - Meets MIL-83488
  - Better coating quality than IVD
  - Higher plasma density
  - Lower porosity
    - no need for glass bead peening
    - may be able to get away without chromating
  - Only uncertainty is environmental embrittlement
    - testing issues
    - not part of MIL spec
    - Avoid alkaline cleaners
Developments needed

- Some additional environmental embrittlement data needed
- Plug and Coat miniaturization needed for smaller IDs
  - Under way at Marshall Labs
- Porosity and need for peening always an issue
  - Various approaches for better coating quality
    - Higher plasma density
    - Sputtering instead of IVD
    - Pulse biasing
Electroplated Al (Alumiplate™)

Alumiplate, Minneapolis
Deposited from organic solution
Alumiplate

Pros:
- Excellent corrosion resistance
- No H embrittlement
- Looks good for components, fasteners, connectors

Cons:
- Potentially hazardous bath - toluene-based
- Requires enclosed tank
- Sole production source, but willing to license

Stage of development:
- Under extensive DoD evaluation
- No aerospace qualification yet
- Probable part numbers shortly for Alumiplated composite connectors
- Being evaluated for landing gear

Electroplating using organic Al salt in a toluene bath

Alumiplate, Inc
Minneapolis

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Alumiplate description

- **Organic electroplate**
  - Requires enclosed tank and plating line in inert environment
    - Similar to vacuum processing but less
  - Al salts in toluene solution
  - Reasonable throwing power
    - Needs conformal or secondary electrodes for complex shapes, IDs
  - Frequently uses Ni strike for adhesion
  - Recent development uses grit blasting and activation with no Ni strike
    - Equivalent adhesion
  - Metallic strike needed for insulators such as composites
  - Coating thickness 0.0001 – 0.001"
    - Usually 0.0003 – 0.0005"
  - Conversion coat (traditionally chromate) for best corrosion performance (as with all other Cd alternative)
Applications and specifications

- **Applications**
  - Hydraulic hose fittings
  - Various others in production
  - No current aerospace
    - Has successfully passed all testing for electrical connectors
    - Alumiplated connectors from Amphenol will probably be assigned part numbers shortly
    - Under testing for landing gear (Goodrich)

- **Specifications**
  - Meets MIL-C-83488
  - No AMS or other specs at this point
Advantages and limitations

Advantages
- “Drop-in” replacement
- Able to coat complex shapes
- Higher quality coating than as-deposited IVD AL
- Suitable for components, connectors, fasteners (with dry lube)
- Directly compatible with Al skins
- Can be anodized for better wear and abrasion

Limitations
- Size limited
  - Landing gear about 3’ long
  - Limited by current bath size
  - Appears scalable
- Requires dry lube for threads to prevent galling
- Sole source is Alumiplate, Minneapolis
  - Willing to license, but no current licensees
  - Not yet available in Europe
- High capital cost
- Toluene bath not suitable for DoD depot use
- Cannot brush plate Al repair
  - Can brush plate Sn-Zn to repair Al
Data available

A great deal of data becoming available as a result of ongoing JSF and Army testing. Rowan is currently putting together a report on the technology – available by year’s end.
General corrosion data

- With chromate conversion passes 5,000 hr B117 salt fog and >336 hr SO$_2$ salt fog
- 0.0007” Al lasts for 1,000hr to red rust with no Ni strike or chromate conversion
  - Ni strike helps a bit
  - Chromate conversion is major contributor (as with most Cd and alternative coatings)
- Tests on connector shells show excellent corrosion resistance with Ni strike and chromate conversion
  - Better than Cd
Hydrogen embrittlement

- Does not appear to cause hydrogen embrittlement
  - Passed F-519 and RSL tests conducted by NAVAIR
  - Embrittlement seen in CTC tests, but tests not reliable
    - specimens stripped and replated several times
    - standard plating process not used

- Note: Cd causes major embrittlement
  - Hence need for LE Cd
Fatigue

Small fatigue debit with and without Ni strike
Electrical connectors

- Meets all tests for qualification on connector shells (MIL-DTL-38999K testing)
  - Al and C-fiber/PEEK composite
  - Corrosion, conductivity stability in salt fog
  - Mate/unmate testing (wear, torque, conductivity)
  - No insulating corrosion products

- Amphenol expected shortly to offer process with part numbers

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Threads and lubricity

- Requires thread lubricant (as with IVD)
- MoS\(_2\) in thin polymer binder looks good
  - Acceptable torque-tension and breakaway torque
  - Long term stability looks good (many cycles)
  - No change during salt fog testing
- Passes tests for connectors
- Will probably work for threaded fasteners
Other issues

- **Repairability**
  - Al can be repaired by brush plating Sn-Zn after suitable activation (Boeing)
  - Can also be repaired with brush-on SermaTel

- **Anodizing**
  - Can be anodized, leaving Al layer beneath anodize layer
  - Will improve wear and abrasion, but hard coating on soft underlay not a good high load wear surface

- **Any form of Al avoids Cd embrittlement**
  - Very bad form of embrittlement
  - Can occur when aborted takeoff heats brake discs and nearby landing gear components
Developments needed

- Non-toluene solution needed for depot use
  - Present chemistry cannot be used in depots
- Additional sources for plating service
- Additional embrittlement testing
- Well-defined brush plate or other repair
  - Both for OEM and MRO use
Other ways to deposit Al

- **Arc or flame spray**
  - Used on some Bombardier aircraft
  - Thick coating (0.001 – 0.003”)
  - Rough
  - Al-Zn arc spray used on support equipment, radar towers, bombs

- **CVD**
  - Generally high temperature
  - Used for cooling passages in hot section blades

- **Slurry Al – developed by Liburdi Engineering**
  - High temperature heat treat
  - For hot section turbine blades (oxidation resistance)
SermeTel®

Metal-filled ceramics from SermaTech
SermeTel

- Al flakes in ceramic matrix
- Brush or spray on
- Older formulations contain Cr\(^{6+}\)
- Heat treat 375-700°F
  - Hard, glassy coating
- Grit blast to uncover Al

Figure 17. SermeTel aluminum-ceramic coating cross sections 500x. Left chromate-containing coating; right chromium-free coating.
Applications

- Used in turbine engines
  - Cases and discs
- Landing gear in some older aircraft (commercial)
- F-22
  - Extensive use of SermeTel coatings on landing gear and other systems
  - See Baltimore meeting on Materials Substitution for P2 in Advanced Aircraft (2002)
Specifications

- Specs from SermaTech
Advantages and limitations

Advantages

- Simple spray or paint
  - Can be used for repair
- Hard coating
  - Abrasion resistant

Limitations

- Sole source
  - Licensing to major users only (e.g. Goodrich)
  - Others (inc. depots) must send to SermaTech
  - Very high cost
- Requires heat treat
  - Can be low enough T for HSS
- Embrittlement from acids in formulation
  - When using 984/985 HE on A100 for F-22
  - New formulation, not yet tested or approved
- Contains chromates
  - New non-chromate formulations now available

Note: There are now some other similar coatings on the market
Data available

Little publicly available data
Data

- Little publicly available data
  - Boeing test data showed poor B117 performance
  - Successful performance in commercial aircraft
Zn-Ni electroplate
Zn-Ni

- Aqueous electroplate
- Acid zinc-nickel developed and used
  - Boeing patented process
  - BAC 5637 Class 2 Type II (SAE AMS2417E)
  - E-Chrome 864 chromate conversion coating
- Alkaline zinc-nickel under development
  - AMS 2417 – Dipsol Gumm Ventures DGV Zinic IZ-260
  - DGV Zinic IZ-268S chromate conversion coating
Description

- Alloy electroplate
  - 5-15% Ni
  - Aqueous solution – mixture of chlorides
  - No CN
  - Coating chemistry depends on bath chemistry, current density, process parameters

- Can also be brush plated for repair
Applications

- Boeing uses acid Zn-Ni
  - Restricted to UTS<220 ksi because of embrittlement issues

- Oklahoma City ALC
  - Replaced Cd and TiCd with brush Cd, Zn-Ni and IVD in 1991
Specifications

- Acid Zn-Ni
  - BAC 5637
- Alkaline zinc-nickel
  - AMS 2417
Advantages and limitations

Advantages
- Aqueous electroplate
  - Easier application in open tanks
- Qualified process
- Tank and brush plate

Limitations
- Alloy chemistry
  - Difficult to ensure reproducibility and uniformity, especially on complex shapes
- Embrittlement
Data available

Data available from Boeing, JGPP report
http://www.materialoptions.com/w2g/cgi/km cgi.exe?O=DIR000000016D&V=0
Corrosion

- Alkaline Zn-Ni best alternative in scribed tests
Galvanic corrosion

- Generally acceptable against common materials
Torque-tension

- Alkaline Zn-Ni quite different from Cd
  - Difficult to run onto bolts
  - Note, however, test done with no lubricant, so may be fine with dry lube
Embrittlement

- Zn-Ni embrittles on deposition
  - Zn-Ni (acid and alkaline) can be H baked with the normal 375°F for 23 hour bake
Fatigue

- Alkaline Zn-Ni has significant debit
  - Endurance limit - 11%
  - Some substrate issues
  - Retesting recommended
Developments needed

- Extension to high strength steels
  - New JTP for HSS under way – Boeing, JGPP
- Brush plating
  - Is Zn-Ni a good repair for IVD or electroplated Al?
High strength stainless steel

S-53 – new steel developed by QuesTek Innovations LLC
High strength stainless steel

- Developed using Materials by Design
  - Design using a variety of models and databases

- Normal development time for a steel
  - 10 years and hundreds of heats

- S-53 developed in half a dozen heats
  - Aim – meet the mechanical specs of 300M, but with the corrosion resistance of 15-5PH stainless
  - Developed under SERDP funding
  - Now in ESTCP program to validate at Ogden
Advantages and limitations

**Advantages**

- No coating to come off
- Eliminates corrosion
  - Primary cause of landing gear overhaul and parts condemnation
- Avoids SCC
  - Primary mechanism for major landing gear failure

**Limitations**

- Cannot be used uncoated against Al
Developments needed

- Full validation of properties and performance
- Development of materials database
- Licensing to steel producers so commercially available
  - QuesTek’s intent is licensing to several steel companies
    (QuesTek is a steel developer, not a producer)
Data available

Extensive data will become available over next 2 years from ESTCP program
Summary of S-53 heats

- Note: Edisonian method takes several hundred heats!
- Meets 300M properties
  - Corrosion resistance = 15-5 PH stainless
  - Much better $K_{IC}$ (88 $\sqrt{\text{in}}$)
  - $K_{ISCC}$ (50-60 $\sqrt{\text{in}}$)

HSSS properties

UTS

Fty

Yield Strength and Ultimate Tensile Strength [ksi]

SHT-OQ-3 hrs LN z=8 hrs 422°C-LN z=8 hrs 482°C
SHT-OQ-1 hr LN z=8 hrs 482°C-LN z=8 hrs 482°C
SHT-OQ-3 hrs LN z=8 hrs 482°C-LN z=8 hrs 482°C
SHT-OQ-3 hrs LN z=8 hrs 482°C-LN z=8 hrs 482°C and methanol+8 hrs 482°C-dry ice and methanol
Current status

- Appears to be mechanically equivalent to 300M but much better fracture strength and SCC
- Being tested and validated at Hill AFB
- Work to be complete in 3005
- Will obtain data needed for qualification
  - Not MIL Handbook 5 (requires 10 heats at $300,000/heat)
  - Will do three heats to 20,000 lb
    - Then use AIM method (Accelerated Insertion of Materials) to interpolate between and extend lab data using modeling data
Conclusion

- Al is the best overall option, but deposition methods are not straight “drop-in”
- High strength stainless exciting new development
  - Will be 2 or 3 years before it is fully qualified at Ogden
  - Even then, no MIL Handbook 5 numbers
  - Modeling will tell us more about this steel than we know about most others
- There are niche products for other Cd alternative applications