Chromate and Cadmium: Use and Alternatives

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Cadmium

- Primary uses of cadmium at Tyco
  - Colorants in plastics (eliminated Feb, 2003)
  - Contact buttons in relays
  - Plating for corrosion protection
  - Low temperature solders (tin/lead/cadmium)

Cadmium - alternatives

- Cadmium plating restricted to MIL-Aero applications and electronics per 2002/95/EC (Cd restricted in most other applications)
- Note: Cadmium is susceptible to sublimation at certain high vapor pressures and low temperatures. Thus Cd is prohibited for space based electronic applications. (6)
- Cadmium solder
  - Looking at low temp replacements, like Sn-Bi
    - Can be brittle – looking for close temperature match
    - Very limited use
- Cadmium in relays
  - Contact buttons
  - Silver-cadmium-oxide
  - Silver-tin-oxide is targeted replacement
    - Not a drop-in replacement
    - Not as readily available/ Reduced cycle life
  - Many RoHS compliant versions in use

Hexavalent Chromium

- ❑ Primary use of Cr^{+6} is in conversion coatings used for enhanced corrosion protection, also for appearance & as adhesion film for organic coatings
- ❑ Coatings can be applied to:
  - Zn Coated Steel
  - Zinc Plate & Castings
  - Zn Coated Cu & Brass Substrates
  - Directly to Aluminum
  - Silver (electroplate for connectors)
  - Magnesium
  - Cadmium

- ❑ Tyco Products Affected:
  - Die cast products (e.g., Rf)
  - Shells (e.g., D-Sub connectors)
  - Fasteners
  - Electrical Chassis/ Cabinets

Hexavalent Chromium

- Coatings are very thin
  - Thickness generally expressed as grams/ m^2 (1)

    (IBM: specification # M-H 6-4109-000)
  - 0.4 grams/ m^2 – clear chromate
  - 1.0 grams/ m^2 – yellow chromate

Film Comparison (2)

Type	**Film Thickness/ nm**	**Cr+6/mg m^2**	**Tot Cr/mg m^2**
Clear (Cr^{+3})	25 – 80	<0.1	30 – 40
Iridescent (Cr^{+3})	250 – 500	<0.1	100 – 180
Iridescent (Cr^{+6})	250 – 500	80 – 220	200 – 460
Green (Cr^{+6})	250 – 1000	80 – 400	1000 – 1800
Black (Cr^{+6})	250 – 1000	80 – 400	1000 – 1800

Hexavalent Chromium - Alternatives

- No universal replacement for Cr^{+6}
- Trivalent chromium is most common replacement offered
  - Automotive industry has approved use of Cr^{+3} for many applications
  - Corrosion resistance can be slightly inferior to Cr^{+6}
  - Corrosion can be improved through use of an organic top-coat
- Tyco is evaluating alternatives
  - Initial results look favorable for Cr^{+3}
  - Testing clear resin coating on steel stock prior to stamp & form
  - Testing permanganates as a chromate free coating

Hexavalent Chromium - Testing

- Prolonging the onset of corrosion is the biggest issue
- Generally accepted testing conditions use salt spray
  - ASTM B-117-03
    - Salt Spray/ Fog
    - 96Hours Minimum time to white rust (zinc base) red rust (steel base)
  - MIL-C-5541E
    - Salt Spray
    - 336 Hours minimum (1000 hours max)
- Electrical resistance testing
  - ASTM D-257
  - MIL-C-81706

Cr^{+6} Attributes

- Prevents oxide formation of barrier plate/ inhibits corrosion through formation of passive surface boundary layer
- Conductive: Predictable surface resistance/ continuity characteristics
- Satisfactory substrate for paint applications (e.g. Mil-Aero)
- Predictable “Run-In” and “Break Away” torque values (Threaded hardware – automotive applications)
- Sacrificial relative to Zn & Cd substrates. Re-passivates exposed base metal, becomes soluble in presence of moisture
- Can be modified: Olive drab or black color options
- Process drying temperatures should not exceed 140 deg. F as thermal decomposition is likely above this point due to dehydration and microcracking, thus self regeneration will not occur. [2]
- Cr^{+3} offers improved resistance to heat (300 deg.F/ 150 deg C 1hr. dwell without adverse affects) [2]

Desirable Characteristics for Alternatives to Cr^{+6}

- Should be easily applied using existing metal finishing equipment and have low capital installation costs
- Abrasion resistant
- Should exhibit predictable torque characteristics
- Suitable base for organics/ paints
- Conductive
- Exhibit suitable film stability over time
- Cost effective

Alternative coatings to Cr^{+6}

- Organic Polymer Films
  - Polyacrylate
  - Polyethylene Waxes
  - Solubalized Oils (used to modify torque characteristics)

    (Generally used in conjunction with organic topcoats and waxes)
  - Insulators: Poor choice where continuity to ground is needed
- Cr^{+3} – Trivalent blue:
  - Cr^{+3} with and without clear top seal coatings
  - Note: Trivalent deposits can contain trace amounts of Cr^{+6} in the film [2] *(Generally at or below the detection limits of measurement equipment)*
- Permanganates:
  - Permanganates
  - Permanganates plus clear top seal coat

Toxicity Cr^{+6} vs. Cr^{+3}

- Cr^{+6}: Group A human carcinogen [3]
  - Known to cause nasal ulcerations
  - Negative reactions with reproductive and gastrointestinal tract
  - Negative dermal affects

- Cr^{+3}: Group D carcinogen, not classifiable as to carcinogenicity in humans
  - Non oxidizer

Chemical Processing

- Hexavalent chromate protection can be enhanced with additions of Silicates (As clear top coats) or leaching with carbonate or caustic based solutions, forming an insoluble silicate barrier.

  (Note this is of limited use due to solubility of silicates in aqueous solutions) (4)

  To get around this, industry repackaged silicate in a solution/ gel formula. Drawback: Poor stability (Gel sets to quickly!)

Chemical Processing- General Chromating of Zinc

- Reaction involves metal surface, aqueous solution containing chromates & select activator ions.
- Activator types: Acidic sulfates, chlorides, fluorides, phosphates & complex cyanides.
- Generally chemistry is tailored to work with a specific base metal, i.e., Aluminum or Zinc, Zn Alloys or Cadmium.
- Processing sequence:
  1. Metal ions on part surface are dissolved by acid medium & enter solution as ions.
  2. Localized rise in pH in immediate vicinity of metal / solution interface.
  3. Metal ions combine with chromate ions to form insoluble compound at localized high pH zone which precipitate on the metal part surface as an adherent coating.

Chemical Processing- General Chromating of Zinc continued:

4. Reaction by-products enter solution
5. Thickness builds from the base metal outward – process is self limiting as metal exposure is reduced due to increase in chromate coverage. (Chemistry must diffuse through active layer to react with Zn base)

- ***Typical Process Cycle:***
  - Zn Electroplate
  - Rinse
  - Dip 0.25% - 0.5% Nitric Acid
  - Dip in chromic acid
  - Cold water rinse
  - Leach using a dilute alkali bath
  - Cold water rinse
  - Dry
  - Seal/ Top Coat?

Ongoing Industry R&D Efforts:

(Alternatives to Cr^{+6})

- ❑ Newer formulations use Zirconium, non- chrome metal oxide
- ❑ Silicate derived from Silane (Costly)
- ❑ Organometallics: Silane based chemistry, (Improved color over chromates) Limited options due to instability in water & non conductive – good base for paints [4]
- ❑ Titanates
- ❑ Partially Solubalized Silanes
- ❑ Organo-zirconates (Excellent as paint primer)
- ❑ Permanganates
- ❑ Replacement coating should be Chromium and/ or Nickel free

Color Comparisons:

- Cr^{+6}
  - Clear
  - Iridescent yellow/ bronze
  - Olive Drab
  - Black

- Cr^{+3}
  - Clear
  - Iridescent light blue
  - Dark blue (Certain suppliers)
  - N/A
  - Black – *(possible but not commercially available)* (4)

Colors Continued:

- Clear: Typical solution -Chromates **(Cr^{+6}),** sulfates & buffers. [5]
  - Deposits a yellow to gold iridescent film; subsequently leached in dilute alkali to obtain clear results [4] – leaves residual Cr^{+6} ions.
  - Used over Zinc plate
  - Is a single step process (Plate and dip)
  - Is double dip process for Cadmium
- Blue Bright: Cr^{+3}
  - Single dip process consisting of Chromates, Fluorides & Nitric Acid
  - Designed for use over Zinc Plate
  - Typical applications include fasteners, stampings & wire
  - Working chemistry </= $1.10/ L
  - Can be dyed using organics
  - Optimal thickness = 250-500 nm [2]
  - Color may shift if processing over Zn alloys

Colors Continued:

- Gold Films
  - Processed from chromic acid based solutions, with sulfate or chloride activators
  - Contains large amounts of Cr^{+6} ions, resulting in improved corrosion resistance
  - Used on:
    - Zinc Electroplate & Zinc die castings
    - Cadmium plate, Aluminum base & Silver contact finishes
- Olive Drab
  - Color derived from inclusion of organic acid modifiers
  - Improved corrosion resistance over Gold coatings
  - Functional applications for Automotive components & Mil-Aero

Colors Continued:

- **Black**: Processed from Gold chromic acid (Cr^{+6}) solution with inclusion of soluble silver salts.
  - Offers excellent corrosion resistance
  - Matte black in appearance
  - Applications include Solar collectors and Mil-Aero

- **Disclaimer**: Above mentioned colors derived from Cr^{+6} chemistry; therefore banned per 2002/95/EC RoHS *(Except Cr^{+3} Blue)*

- **Tri Chrome** - colors may vary from those described if Zn alloy plate is used, (ZnFe, ZnCo or ZnNi) and may require use of select dyes and/or passivation systems to achieve desired results.

Corrosion Testing:

- ASTM- B117: 5% Salt Fog
  - Satisfactory for comparison performance between coating types - may not be suitable to quantify specific coating performance characteristics
- CASS: Copper Assisted Salt Spray / ASTM B368 (Automotive)
- Ford World Wide Fastener Finish Spec. WX-100
  - S-437- 8.0 um min. Electro Zn,
  - Leached sealant containing integral torque control lubricant
  - Spec. # WSS-M21P17-B3
  - Corrosion protection: 96 hrs. to white rust, 384 hrs. to red rust
  - Service temp. 120 deg C, Non conductive coating
  - Not recommended for use where severe abrasion conditions occur.
- GM World Wide Fastener Spec: GMW3044- Zn plating for fasteners and non fasteners.
- Consensus specifications:
  - SAE: Society for Automotive Engineers / ASTM: Society for Testing Materials / United States Council for Automotive Research / AIFG (Automotive Industry Fastener Group)
- ASTM B202:

Industry Trends:

- Tri Chrome/ Zinc Nickel Alloys
  - ZnNi plated alloys becoming prominent
  - Favored options (via literature) is Cr^{+3} over ZnNi

    (11-15% Co-deposited Ni may offer the best alternative protection in combination with Cr^{+3} when compared to Hex Cr over Zn [(4)]
  - Cr^{+3} Not self healing (No Cr^{+6} soluble compounds in the olation polymer)
  - Cr^{+3} May require processing at elevated temperatures depending on supplier formulation
  - Cr^{+3} exhibits significantly improved heat resistance compared to Cr^{+6} (possible technical advantage)
- Increased use of Permanganates as an alternative to Cr^{+6}:
- Use of chrome free alternative coatings require multi-step systems to achieve similar results to Cr^{+6} or Cr^{+3}; applied costs are higher than Cr^{+3}

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