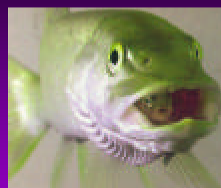
4 Questions

(On Platers' Minds)



By: Frank Altmayer, CEF, President,
Scientific Control Labs, Inc.
Technical Director, AESF

Questions:

1. What is the current status of zinc alloys as cadmium replacements?
2. What is the status of hexavalent chromium replacements?
3. Is nickel plating in trouble?
4. What role is nanotechnology playing in electroplating?

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Galvanic Series (V)

E^0 ($SO_4^=$)			Galvanic Series, E (Cl^-)				
Mg	-2.37		Mg	-2.37		Mg	-2.37	
Al	-1.66		Al	-1.66		Al	-1.66	
Zn	-0.76 } 0.32		Zn	-0.76		Zn	-0.76	
Fe	-0.44 }		Cd	-0.54 } 0.10		Cd	-0.54	
Cd	-0.40		Fe	-0.44 }		ZnNi	-0.50 } 0.06	
Co	-0.29		Co	-0.29		Fe	-0.44 }	
Ni	-0.25		Ni	-0.25		Co	-0.29	
Sn	-0.14		Sn	-0.14		Ni	-0.25	
H	0.00		H	0.00		Sn	-0.14	
Cu	+0.34		Cu	+0.34		H	0.00	
Au	+1.68		Au	+1.68		Cu	+0.34	
						Au	+1.68	

Zinc-Nickel

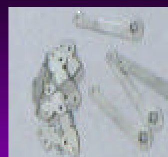
- 5-15% Ni
- Excellent salt spray performance
- Alkaline or acidic solutions
- Good Kesternich performance
  - Zinc-cobalt is better
- Chromate performance enhanced by heating
- Favorable galvanic couple with aluminum
- Good formability & weldability

Zinc-Cobalt Processes

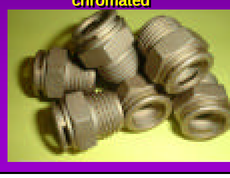
- Alloy = 0.2-0.6% cobalt.
- Deposit is bright/level Chromating solutions will require modification
- Rack or barrel plated
- Lower cost
- Co is not regulated (yet)
- No high-temperature-resistant chromates

Tin-Zinc Alloy Plating

- Alloy is 25-30% Zinc
- Cyanide or Acidic Solutions Available
- High Corrosion resistance (especially in sulfur atmosphere)
- Excellent solderability
- Good frictional properties
- Excellent ductility
- Soft (subject to damage)
- Dull, matte finish
- Excellent couple with Al



Tin-zinc, as Plated and chromated



Salt Spray Comparison, John Stropke, Battelle Institute and Glen H. Graham, CEF, Tinker AFB (Proceedings of 31st Aerospace/Airline Plating & Metal Finishing Forum, April 25, 1995)

Coating	Panel	Hrs To WR	Hrs To RR
Cadmium[1]	Scribed	504	>1000
Cadmium[1]	Not Scribed	672	>1000
Cadmium[2]	Scribed	168	>1000
Cadmium[2]	Not Scribed	672	>1000
Zinc-Nickel[3]	Scribed	168	336
Zinc-Nickel[3]	Not Scribed	168	336
Zinc-Nickel[4]	Scribed	>1000	>1000
Zinc-Nickel[4]	Not Scribed	>1000	>1000
Zinc-Tin[4]	Scribed	168	>1000
Zinc-Tin[4]	Not Scribed	672	>1000
Zinc-Cobalt[3]	Scribed	168	504
Zinc-Cobalt[3]	Not Scribed	168	336
Zinc-Cobalt[4]	Scribed	168	504
Zinc-Cobalt[4]	Not Scribed	336	672

1=chromated, 2=not chromated 3=acid solution 4=alkaline solution

Fatigue Resistance Comparison

Coating	Avg. FLC* (0.1 s r**)	Avg. FLC* (0.43 s r)
Unplated	242,456	----
Cadmium[1]	760.038	40,452
Cadmium[2]	730,733	run-out
Zinc-Nickel[3]	15,262	5,438
Zinc-Nickel[3]	39,819	39,819
Zinc-Nickel[4]	9,941	11,911
Zinc-Nickel[4]	run-out	42,311
Zinc-Tin[4]	7,620	no data
Zinc-Cobalt[3]	7,459	no data
Zinc-Cobalt[4]	22,521	no data

*Fatigue Life Cycle
**stress ratio
1=chromated, 2=not chromated 3=acid solution 4=alkaline solution

HSC Comparison

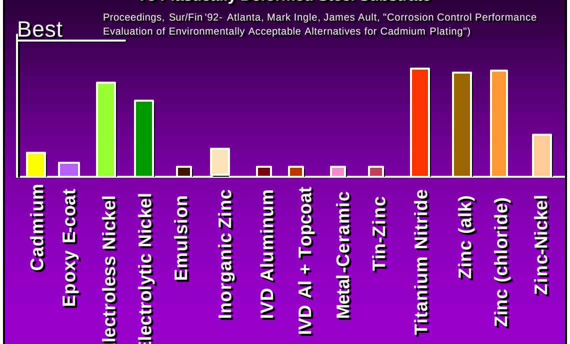
Coating	#-Tests	Time (Hrs.) To Failure/Pass
None	2	(2) >200, (2-Pass)
Cadmium[1]	6	(1) 183 (Fail), (5) >200, (5-Pass)
Cadmium[2]	3	(3) 213, 213, 213 (3-Pass)
Zinc-Nickel[3]	3	(3) 0.5, 0.4, 0.5 (3-Fail)
Zinc-Nickel[3]*	3	(3) 240, 240, 240 (3-Pass)
Zinc-Nickel[4]	6	(1) 141 (Fail), (5) >200 (5-Pass)
Zinc-Tin[4]	3	(3) 0, 0, 0.2 (3-Fail)
Zinc-Cobalt[3]	3	(3) 0.8, 5.7, 4.4 (3-Fail)
Zinc-Cobalt[4]	3	(3) 4.5, 4.5, 8.3 (3-Fail)

* Alternate Solution Supplier
1=chromated, 2=not chromated 3=acid solution 4=alkaline solution

Adhesion of Cadmium Substitutes

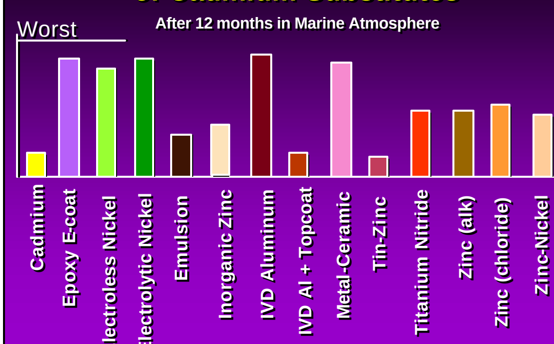
To Plastically Deformed Steel Substrate

Proceedings, Sur/Fin '92- Atlanta, Mark Ingle, James Ault, "Corrosion Control Performance Evaluation of Environmentally Acceptable Alternatives for Cadmium Plating")



Breaking Torque of Cadmium Substitutes

After 12 months in Marine Atmosphere



Questions:

1. What is the current status of zinc alloys as cadmium replacements?

2. What is the current status of hexavalent chromate replacements?

3. Is nickel plating in trouble?
4. What role is nanotechnology playing in electroplating?

Background History & Issue

- The European Parliament & the Council of European Union signed the End-of-Life vehicle (ELV) directive on 9/18/00
- Directive 2000/53/EC, Annex II, limits Hexavalent Chromium to 2.0 grams per vehicle for corrosion protection purpose only; 00.0 gram for any other application in a motor vehicle
- Implementation (Cr^{+6}) - January 2003, now delayed to July, 2007
- The Directive covers 4 heavy metals- Hexavalent Chromium, Lead, Mercury, and Cadmium

Details of ELV Directive 2000/53/EC (from European Union)

- Objective is the prevention of waste from vehicles and also the reuse, recycle, & recovery of end-of life vehicles & components
- Vintage & historic vehicles are exempted
- Components, materials, as well as spare & replacement parts are also covered
- Automotive component manufacturers to provide appropriate information to treatment facilities, concerning dismantling, & reuse

End-of-Life vehicle (ELV) Directive - 2000/53/EC

- Re-use & recovery @ 85% minimum by 1/1/2006 for all ELVs (presently 70%)
- Re-use & recovery increased to 95% by 1/1/2015
- The OEMs must publish information to prospective buyers & in their literature
- Member States already have all laws, regulations & administrative provisions to comply with the Directive

Why is this so important?

- OEMs may not accept any components with Cr^{+6} after 07/2007 (for 2003MY)
- Currently an average vehicle = 4 to 8 grams of Cr^{+6} *(some > 10g)*
- NOT an Option; MUST comply to meet customer's requirements & stay in business

Cost Factor

- Estimated cost increase in NA 10%-30%?
- Several Reasons –
  - Raw material cost ~ 10% to 30% higher
  - Concentration of Cr^{+3} @ 10-12% Vs 2-4%
  - Heated bath Vs ambient, Shorter bath life
- Initial study indicating cost factor @ 1.0-1.7
- Volume, selection of coating, as well as supplier's capability could be some of the major determining factors for higher cost

Technical Issues

- Chromium exists in four valence states:
  - Cr^{o}
  - Cr^{+3}
  - Cr^{+2}
  - Cr^{+6}
- Trivalent and Hexavalent Chromium:
  - corrosion protection coatings and application
  - process intermediates
  - sometimes changes states (Cr^{+3} to Cr^{+6}) during the application process
  - Hexavalent is self healing trivalent is not
- Neither Cr^{0} nor Cr^{3} are legislated in the European Union Directive at present

Where Is It?

- Hexavalent Chromium is found in the corrosion preventive and conversion coatings on numerous key steel and aluminum automotive components (usually as chromate films)
- Metal parts (such as fasteners, levers, fuel/brake lines, alloy wheels, etc.)
- Polymer pigments
- Pre-painting and anodizing sealing chromate rinse
- Phosphates (acidulated rinse)

Test Methods for Cr^{+6}

~9 test methods available, DELPHI Procedure Summary:

- 50 cm^2 minimum sample
- Chromated parts must be >24hrs. and <30 days old
- 5-7 minutes extraction in boiling water
- Remove part(s), filter water if cloudy
- Acidify with sulfuric acid
- Add diphenylcarbizide solution
- Measure color at 540nm
- Repeat extraction to confirm all Cr^{+6} removed

Choice of Alternatives

- Two Major Alternatives –

  Trivalent Chromate
  - Commercially available globally, many suppliers offer proven technology
  - Enhanced corrosion protection with a sealer or a topcoat; several color finishes
  - Black may be hard to produce

  Chrome-Free Substitutes
  - Limited universal availability
  - Application limited to spray or spin & spray in most cases (Geomet, Plus Sealers)
  - Mostly silver or gray (black finish limited)
  - Cost may be higher than Cr^{+3}

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Is Nickel Plating In Trouble?

- Sweden/Denmark Lead Ban On Nickel In Jewelry
  - <0.05% Ni in any jewelry alloy
- Denmark/Germany
  - <0.5m g/cm^2/week release to artificial perspiration
- EEC793/93 Existing Substances Regulation
  - Data Collection (completed)
  - Priority Setting (completed)
  - Risk Assessment (completed)
  - Risk Reduction (draft completed, not released)

Is Nickel Plating In Trouble?

- California, IARC & NTP have linked some nickel compounds to cancer
- TERA (Toxicology Excellence for Risk Assessment) Finds "insufficient data"

European Regulations Affected

- Directive 76/769/EEC Restrictions on marketing/use of dangerous substances
- Euro Coinage
- Consumer protection, food contact materials
- Directive 98/83/EC water quality standards
- Directive 90/385/EEC implantable medical devices
- Directive 88/378/EEC toy safety
- Directive 89/106/EEC construction products
- Directive 96/61/EC pollution prevention & control
- Directive 76/464/EEC aquatic environments
- Directive 2000/60/EC water policy
- Directive 80/68/EEC groundwater protection
- Directive 98/24/EC protection of workers
- Directive 2000/76/EC incineration of waste
- Directive 91/689/EEC No. 259/93 hazardous waste

Is Nickel Plating In Trouble?

Substitutes:

- Cu-Zn-Sn (Trade Name: Alballoy)
  - 55-60%Cu, 20-30%Sn, 10-20%Zn
  - Bright
  - Solderable
  - Hardness > nickel
  - Solution is hard to control
  - Cyanide process

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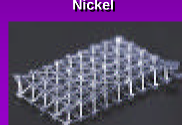
Nano-technology & Electroplating MEMS* Nickel Plating

MEM:
Nano-scale components produced by combination of lithography and electroplating

Applications:
Pressure Transducers
Medical monitors
Airbag sensors
Bio-terror sensors
Miniature power supplies
Heat exchangers
Aircraft components

Market: $5b+

Trusses, 1-100 μm MEM, Pure Nickel



*Micro-electro-mechanical systems

Micro-electrodeposition

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US Pat 6,455,233

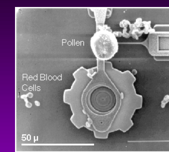
Structures of micro-miniature dimensions are formed by scanning a nearly parallel beam of high energy light ions across the surface of a resist material such as PMMA in a predetermined pattern.

The resulting chemical changes in the exposed resist material allows a chemical developer to remove the exposed material while leaving the unexposed material substantially unaffected.

By simultaneously scanning the beam and orienting the resist layer in a controlled manner, resist structures of three dimensional complexity can be micro-machined.

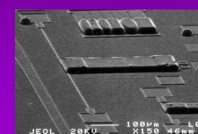
MEMS Process Details

A conductive plating base or seed layer over silicon (sputtered nickel) and a means to pattern the electro-deposit (photolithography) are needed.



Adhesion Promotion:
Application of sputtered Ti or Cr, or roughening of Si

Typically, the electrodeposit is patterned by an additive process (selective deposition) instead of a subtractive process (etching).



Solution: Nickel Sulfate, 200 g/L, Nickel Chloride 5 g/L, Boric Acid 25 g/L, Saccharin 3 g/L, pH 4, 23°C, 0.735mA/cm^2, 50% duty (pulse)

MEMS Features (According to JPL):

- 10 to 1,000 times reduction in size, weight, and power consumption over conventional technology
- Matched or better performance
- New function and capability not realizable with traditional technology
- Significant improvement in operation endurance (shock, vibration, and temperature cycling)

The End

Thank You!