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Indium Alloy as Cadmium Brush Plating Replacement



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Report Documentation Page

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Project Details



- **Second Year of Effort**
- **Numerous Agencies / Companies Involved (partial list)**
 - Air Force Research Laboratory (AFRL)
 - Air Force Depots
 - NAVSEA (Naval Avionics Support Equipment Appraisal)
 - Concurrent Technologies Corporation (CTC)
 - Boeing
 - Matco Associates
 - Harris Consulting



Problem Statement



- Cadmium (Cd) plating is used on steel mating surfaces on a Department of Defense (DoD) Weapon System
 - Federal regulations of Cd have increased to protect human health and the environment
 - Rate of phase-out and cost have also increased
- Maintenance, repair, and overhaul operations of a component of the same weapon system have recently been transitioned to a different DoD facility
 - New DoD facility had previously eliminated Cd plating
 - DoD facility requested the United States Air Force (USAF) for replacement coating in the weapon's component



Conduct Electricity During Service



Mating Surfaces Must Remain Conductive



- ❖ Mating surfaces have dimensional tolerances
- ❖ Iron oxide is insulating and expands part volume
- ❖ Cd oxide is semi-conductive and non-voluminous



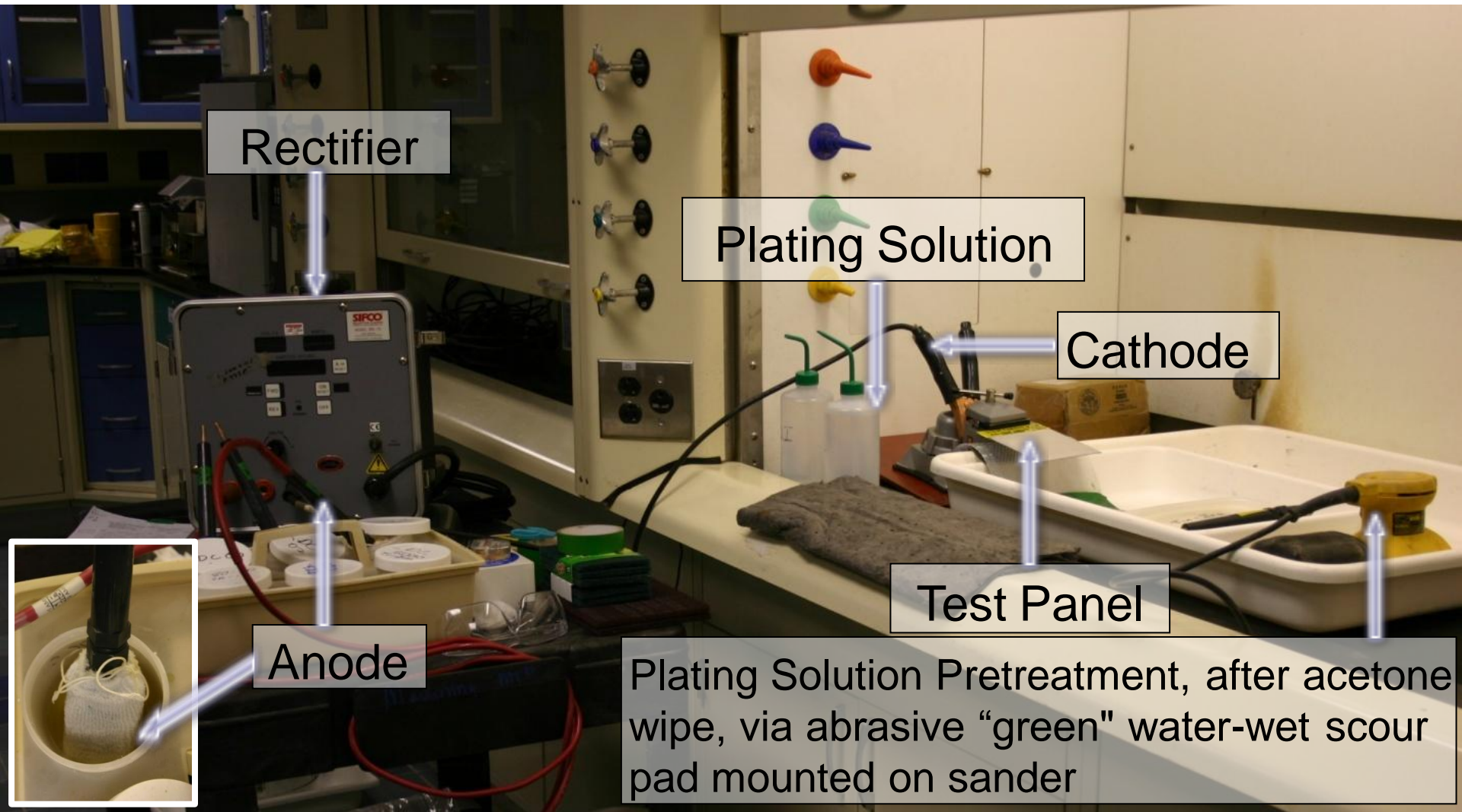
Objectives



- Identify replacement chemicals and required equipment for processing at DoD facility
- Investigate replacement repair plating process
- Define the process and testing criteria for alternatives
- Perform optimization testing on candidate coatings
- Recommend the process to be implemented after passing the demonstration / validation testing



Example Brush Plating Set-up



Dip anode in chemical; supplement from squirt bottle



Processing & Performance Replacement Requirements



- Meet SAE-AMS-QQ-P-416, Type I Class 2 Specification
 - No chromate conversion coating
 - 0.3 to 0.5 mils coating thickness
- Process the part coating within the repair production period
- Be compatible with DoD facility and worker capability
- Preserve the dimensional tolerance for the mating parts
- Sacrificially protect mild steel from corrosion
- Comparable or lower electrical resistivity than Cd during the service life
- Negligible change in volume between as-plated and end of service life (similar to Cd).



Eliminate Cd, Pb (and Nickel [Ni]?) Alternative (Alts)



- | | | |
|--------------------------------|----------------------------|-----|
| 1. Aluminum | 10. Tin-cadmium | |
| 2. Cadmium-titanium | 11. Tin-nickel | X? |
| 3. Zinc | 12. Tin-zinc | |
| 4. Lead | 13. Acrylic | X?* |
| 5. Zinc-cadmium | 14. Epoxy | X?* |
| 6. Nickel | 15. Fluorocarbons | X?* |
| 7. Zinc-nickel | 16. Nylon | X?* |
| 8. Nickel-cadmium | 17. Polyester | X?* |
| 9. Tin | 18. Polyurethane | X?* |

* Organic coatings are unknown to be sacrificial sufficiently, when applied at 0.5 mils or less



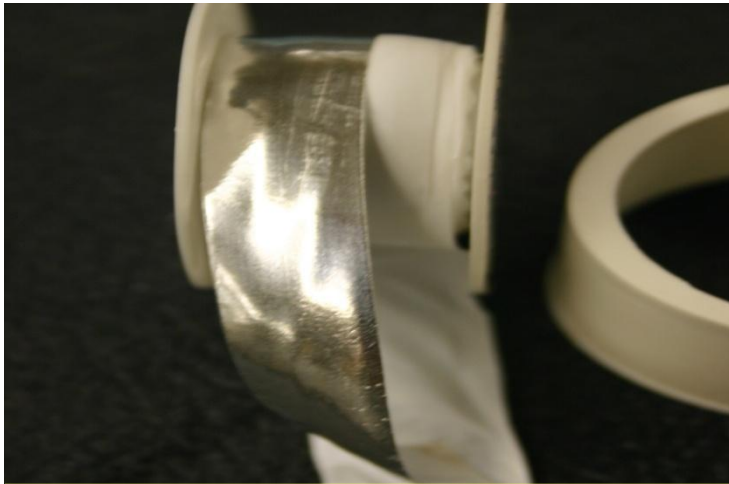
Remaining Alts. per QQ-P-416



Alternative	Notes
1. Aluminum	Sacrifices to protect steel, converting to an alumina, which is an electrical insulator
2. Zinc	Also sacrificial to protect mild steel from corrosion; zinc oxide is 10X to 100X more electrically insulating than cadmium oxide
3. Tin	Plated tin is sacrificial to protect mild steel in seawater, but tin oxide is 10X more electrically insulating than cadmium oxide
4. Tin-zinc	Known to be sacrificial to protect mild steel, but its oxides' electrical resistivity is unknown and needs to be tested



Could Indium / Indium Alloy be an Alternative?



Indium Foil



**Indalloy #1 Wire
50% indium, 50% tin**

- ✓ Not considered hazardous
- ✓ Commercial brush plating products can plate indium within thickness tolerances
- ✓ Sacrificial to mild steel (in sea water) and its couple to mild steel produces a potential <math><0.15</math> volts
- ✓ Electrically conductive, similar to Cd
- Metal “cold welds” to itself / Alloy
Avoids “cold weld” issue
- Metal subject to halide attack / Alloy unknown to halide attack



Indium in a Galvanic Series



Lower Number is More Anodic

Active (Anodic)

1. Magnesium
2. Manganese
3. Zinc (plated)
4. Aluminum
5. Cadmium (plated)
6. Indium
7. Tin (plated)
8. Steel 1010
9. Iron (cast)

10. Copper (plated)
 11. Nickel (plated)
 12. Cobalt
 13. Bismuth
 14. Tungsten
 15. Titanium
 16. Silver
 17. Gold
 18. Graphite
- Noble (Less Anodic)**

MIL-STD-889; Series for Seawater



Replacements Down-selection



Key Requirements	Candidate Cd Plating Replacement							
Processing	Al	Zn	Ni	Sn	Zn-Ni	Sn-Ni	Sn-Zn	Sn-In
Meet Environmental Health and Safety (EHS) Standards	P	P	?/F	P	?/F	?/F	P	P
Fits within Overhaul Schedule	?	P	P	P	P	P	P	P
Fits with Worker Capability	?	P	P	P	P	P	P	P
Performance								
Coating Thickness	P	P	P	P	P	P	P	P
Adhesion to substrate	P	P	P	P	P	P	P	P
Contact Impedance	F	F	F	F	?	?	?	?
Expansion of Corrosion Products	F	F	F	P	?	?	P	?
Sacrificial Corrosion Protection	P	P	F	P	?	?	P	P
Whisker Growth (FOR INFO)	?	F	P	F	P	P	?	?

Al = Aluminum;
“P” = Pass;

In = Indium;
“F” = Fail;

Ni = Nickel;
“?” = Unknown;

Sn = Tin;
“?/F” = Questionable Future.

Zn = Zinc.



Select Commercial Chemistries



Alternatives	Notes
1. Tin-zinc	Known to be sacrificial to protect mild steel, (but its oxides' electrical resistivity is unknown and needs to be tested). Prior work encountered processing inconsistency for target metal alloy composition.
2. Tin-indium	Sacrificial to mild steel (in seawater) and electrically conductive, similar to Cd; avoids "cold weld" issue. Possibility of halide attack is unknown. Processing inconsistency similar to tin-zinc is a concern.
Contingency	Notes
3. Zinc-nickel	Known to be sacrificial to protect mild steel when its nickel content is <25-30% by weight; its oxides' electrical resistivity is a concern and needs to be tested. Possible worker health and safety concern.



Alts. Chosen for Testing



Coating Round 1	Composition (nominal)	Coating Round 2	Composition (nominal)
Cd	100% Cd		100% Cd
Sn-Zn @ 7 volts(1)	90% Sn, 10% Zn		
Sn-Zn @ 12 volts (2)	70% Sn, 30% Zn	Sn-Zn @ 12 volts (2)	70% Sn, 30% Zn
Sn-In (1)	80% Sn, 20% In		
Sn-In (2)	90% Sn, 10% In		
In-Sn (3)	65% In, 35% Sn	In-Sn	70% In, 30% Sn
Zn-Ni (dip plated)	82% Zn, 18% Ni	Zn-Ni (brush plated)	85% Zn, 15% Ni



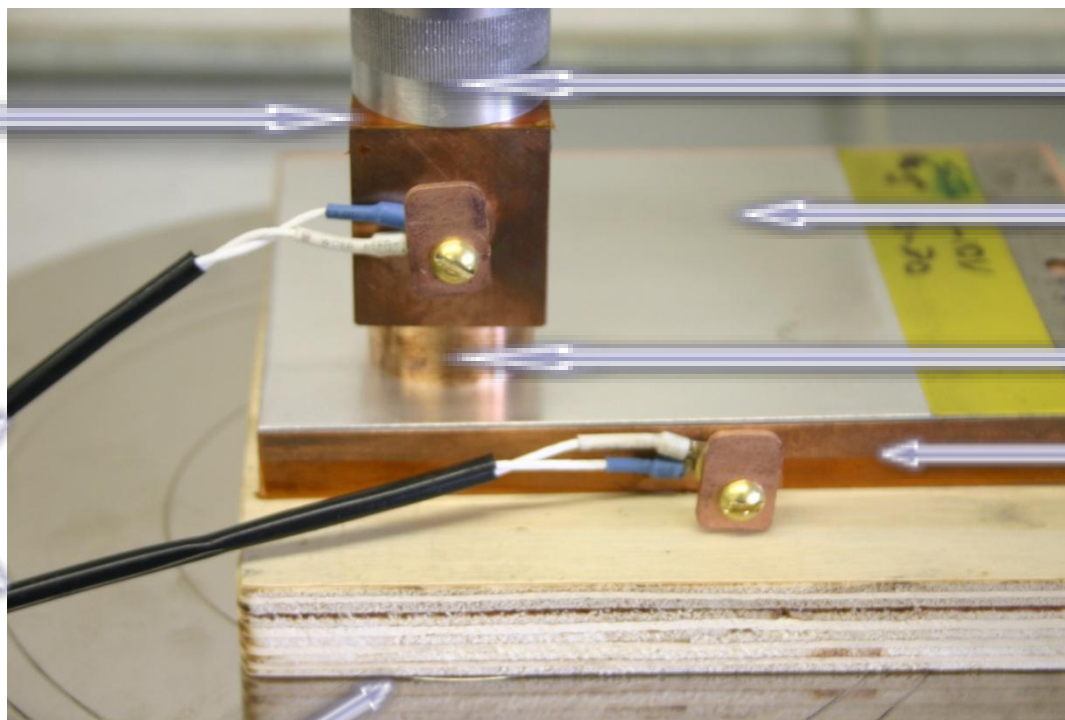
Electrical Resistance



Electrical Isolation (Kapton[®] Tape)

To 4-Wire Low Contact Resistance Meter

Electrical Isolation (plywood)



Load (200-pounds/inch²)

Panel

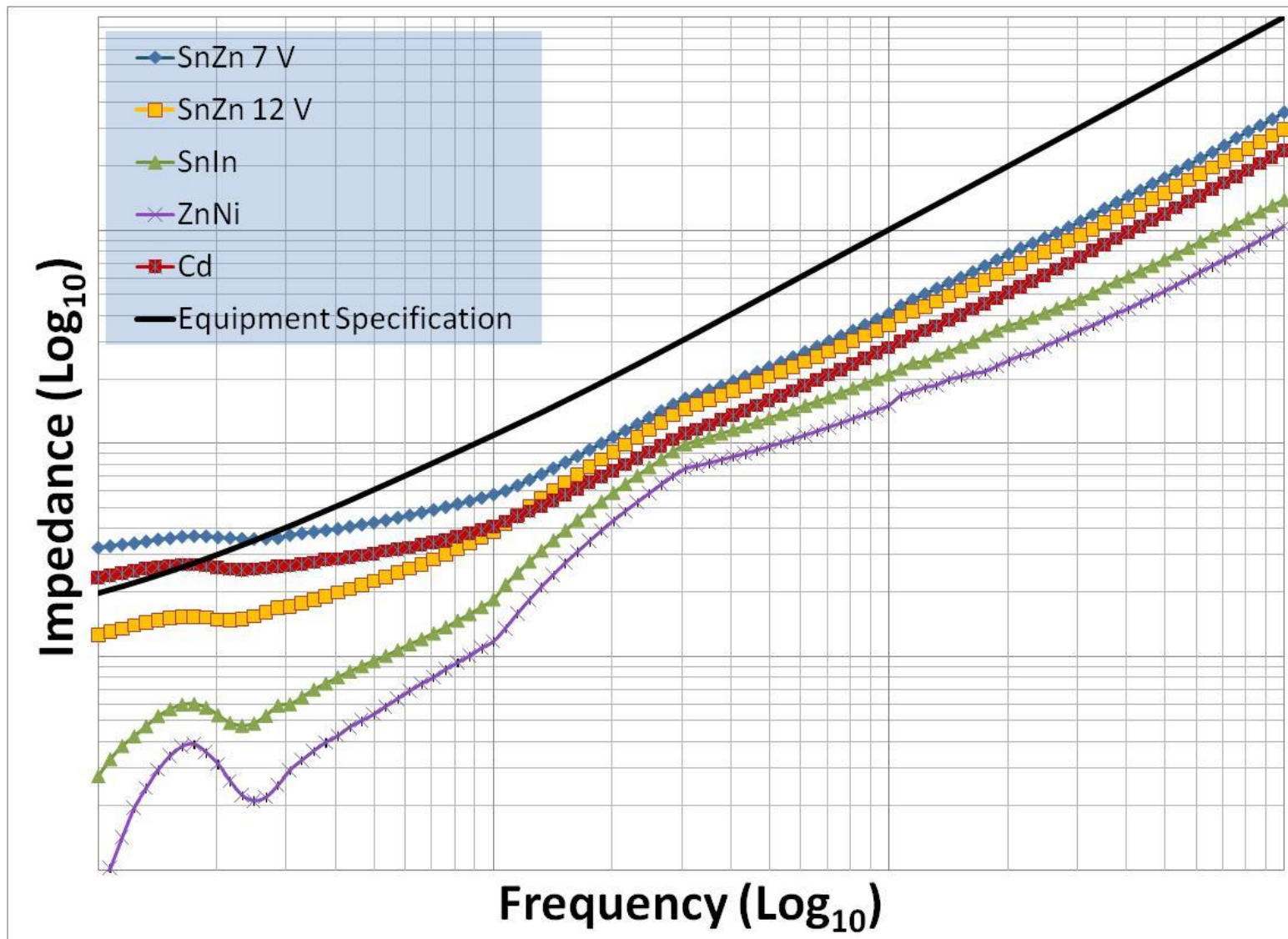
Upper Electrode (1-inch² Area)

Lower Electrode (= Panel Area)

Test set-up follows MIL-DTL-81706

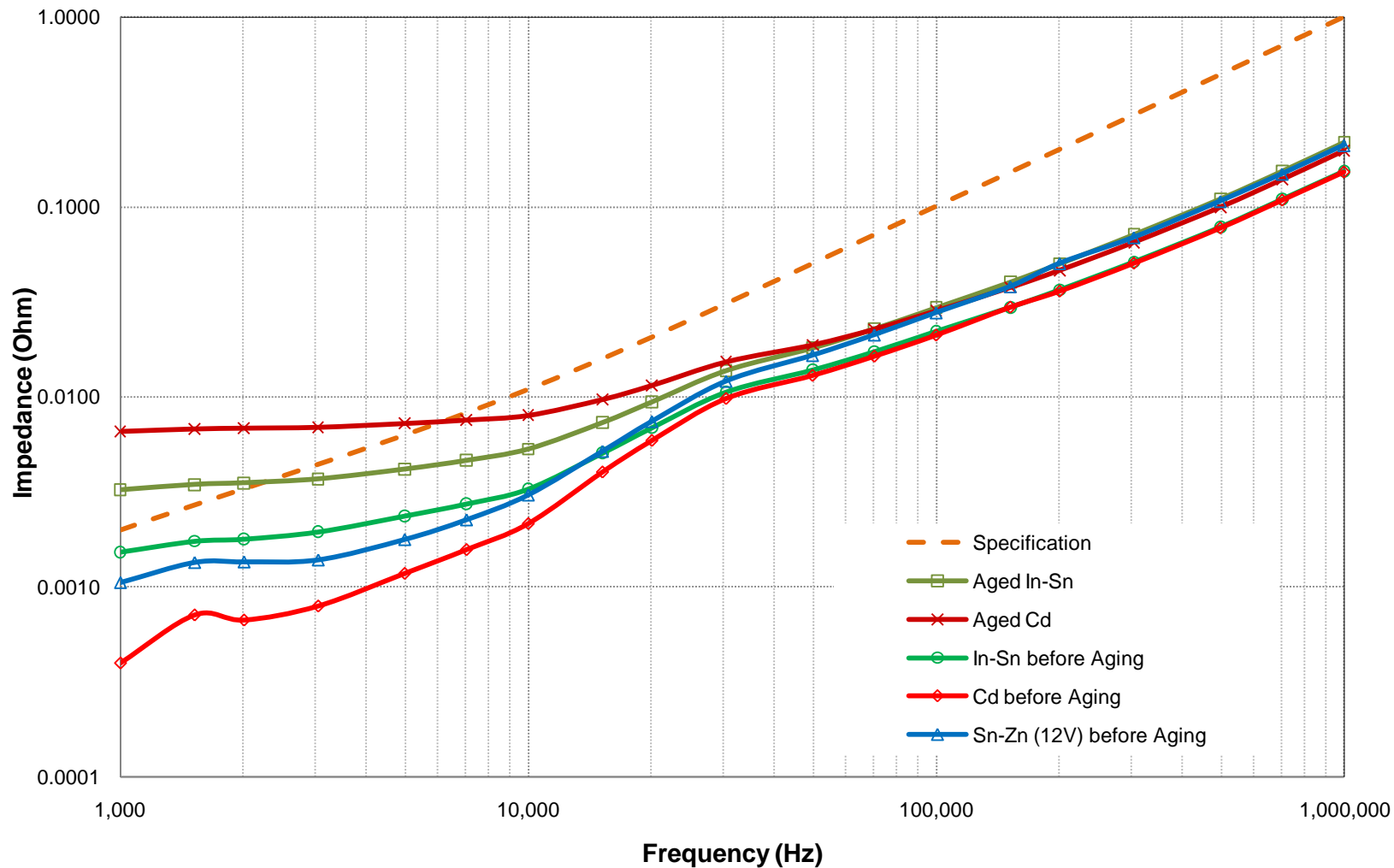


Electrical Resistance Results, Round 1





Electrical Resistance, Round 2, Aged Panels



Temperature Cycling

Table 6. Temperature Cycling Conditions for Each Test Cycle

Step Number	Temperature Condition	Temperature Range (°F)	Time (minute)
1	Cold	-70 to -65	120
2	Ambient	+72 to +87	5
3	Hot	+175 to +178	120
4	Ambient	+87 to +72	5

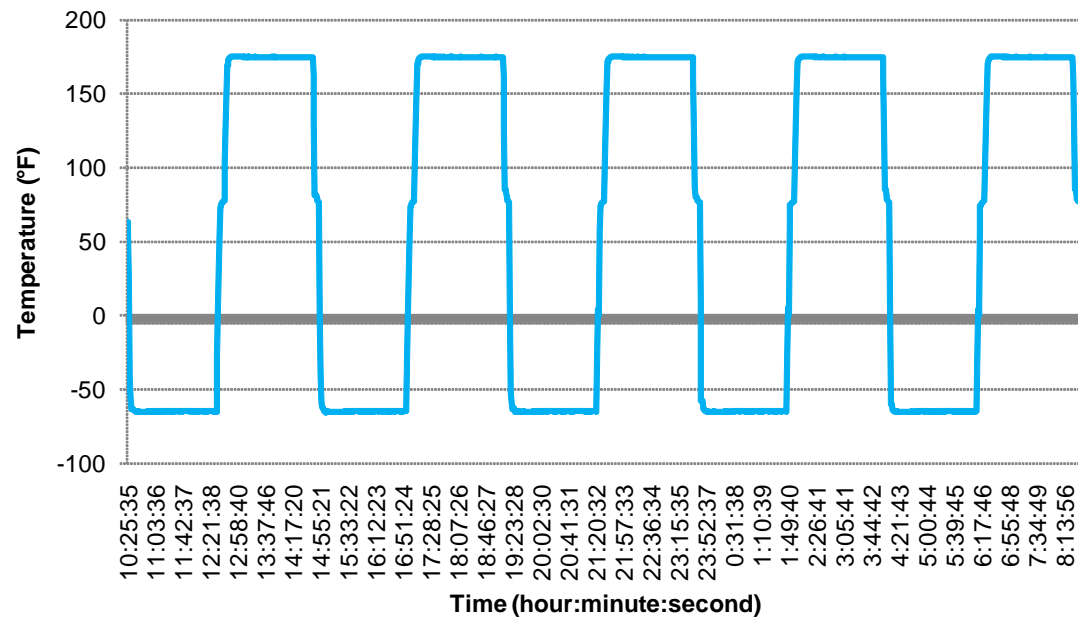
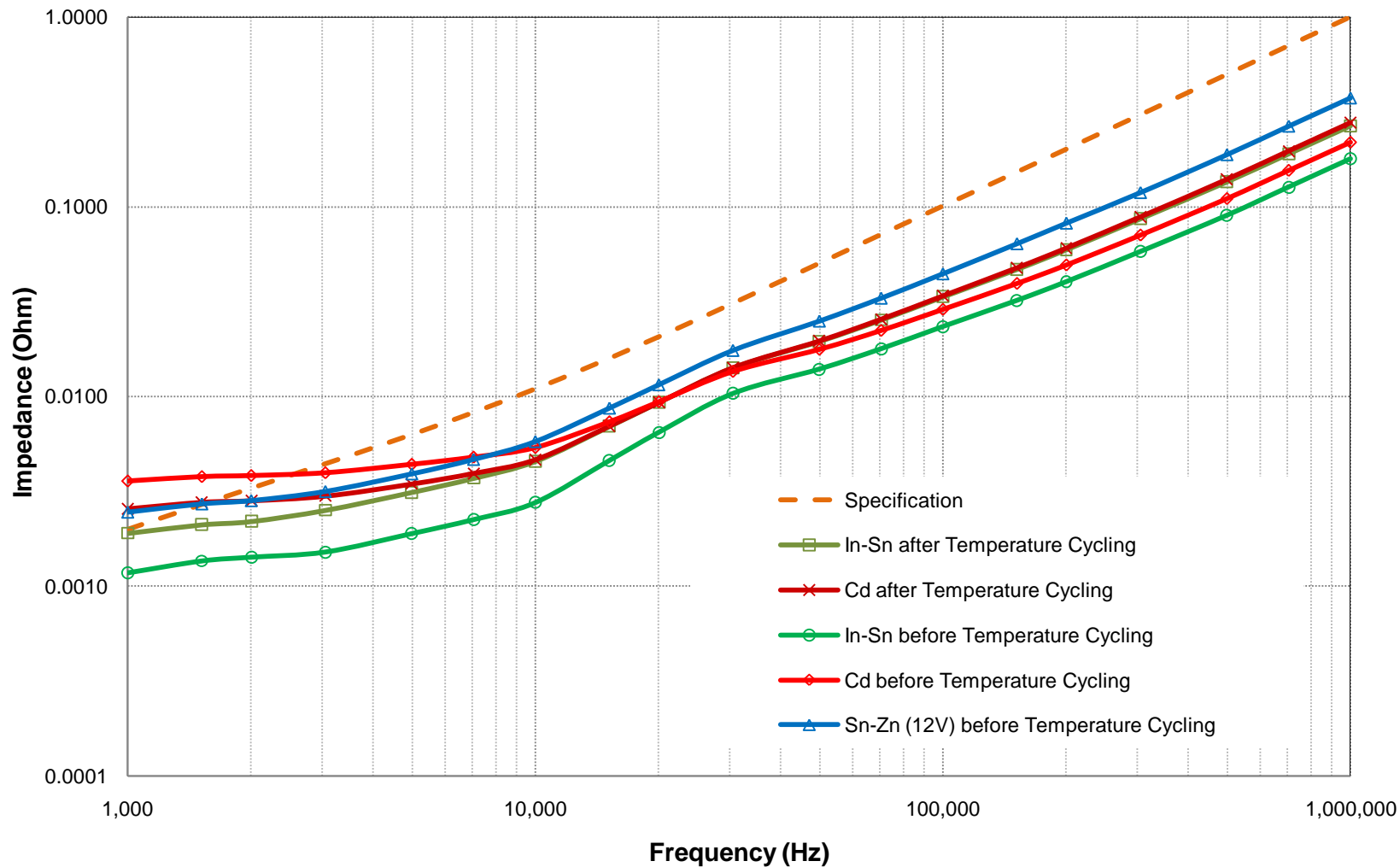


Figure 1. Variation of Temperature with Time for Temperature Cycling Test



Electrical Resistance, Round 2, Temperature Cycling



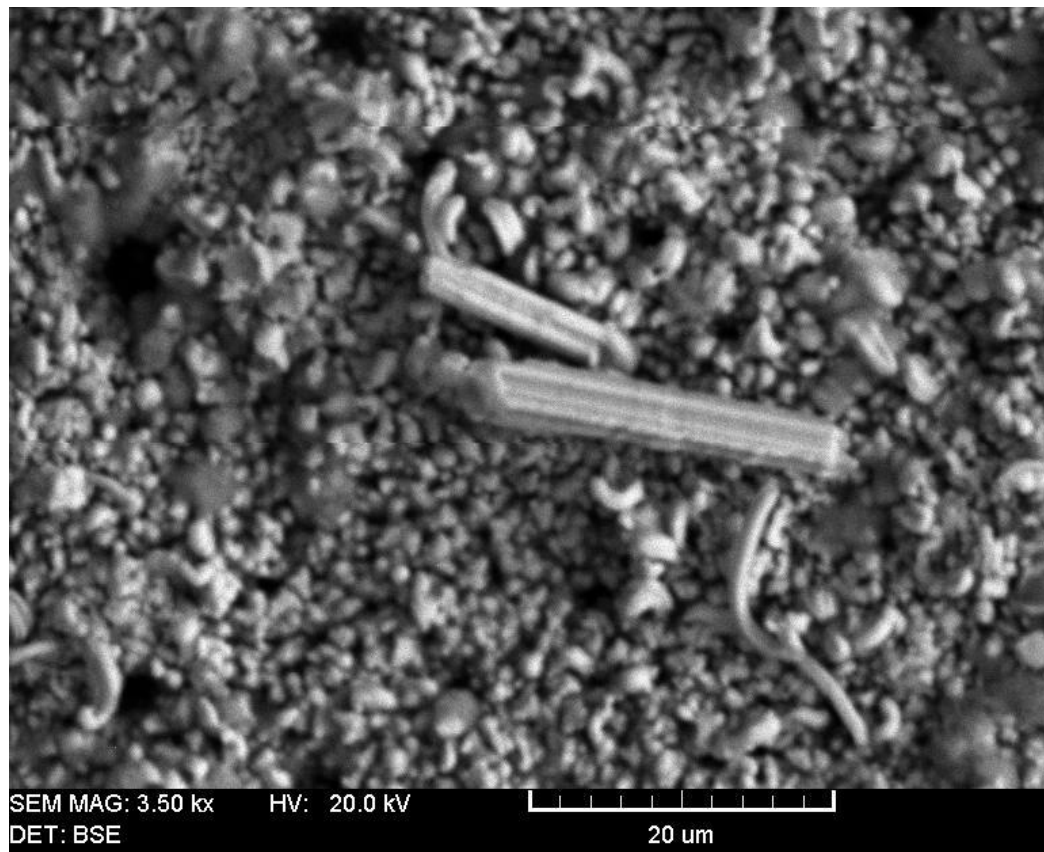


Whisker Growth



One panel of tin-zinc alloy plated panels (at 12-volts processing) produced whiskers within 1,000 hours of exposure at 131°F and 85% Relative Humidity.

All other panels passed under ambient test conditions.



Tin whiskers on tin-zinc alloy plating. All other tin-zinc, tin-indium and zinc-nickel alloy plated panels had passed within 1,000 hours of testing.



Whisker Growth Tests Results



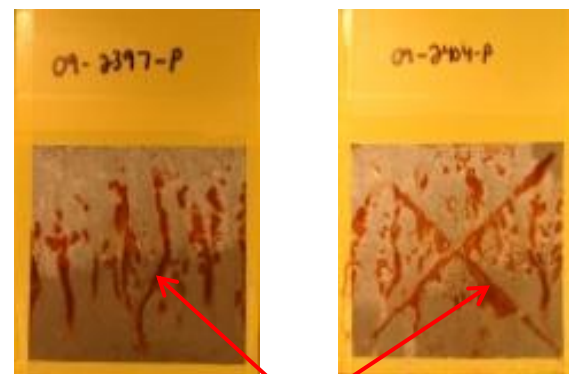
Whisker Observation				
Panel Type	Baseline	1000 hr	2000 hr	3000 hr
Cd, 85 °F 60%	No	No	No	No
Cd, 130 °F 85%	No	No	No	No
ZnNi, 85 °F 60%	No	No	No	No
ZnNi, 130 °F 85%	No	No	No	No
SnZn 12v 85 °F 60%	No	No	No	No
SnZn 12v 130 °F 85%	No	Yes	Yes	Yes
InSn 7030 85 °F 60%	No	No	No	No
InSn 7030 130 °F 85%	No	No	Yes	Yes



Corrosion Resistance



- **Testing per ASTM B 117**
 - 6 panels per coating
 - 4 x 6 panels
 - Both scribed and unscribed panels evaluated
- **Testing Results**
 - Cd – 3000 hrs, scribed and unscribed
 - SnZn – 24 hrs, scribed and unscribed
 - InSn – unscribed, 192 hours
 - ZniNi – did not pass bend adhesion and did not proceed to this test



Red Rust

SnZn, 24 hrs exposure



Corrosion Chart



Test		Cd Coatalyte #312	Sn-Zn 12 V LDC-5030	In-Sn LDC 4901/5001
	Unscribed ²	3 (0.61 ± 0.06)	0 (0.53 ± 0.02)	1 (0.37 ± 0.02)
Electrochemical Properties (ASTM G 3)	OCP (V)	-0.78	NSS ⁹	-0.69
Via EIS Method 1	Corr Rate (mpy)	32.3 ± 29.3	5.4 ± 6.6	1.3 ± 0.02
Via EIS Method 2	Corr Rate (mpy)	32.1 ± 28.7	7.0 ± 7.0	1.5 ± 0.01
Via cathodic polarization (neutral buffer)	Corr Rate (mpy)	2.5 ± 0.07	69 ± 71	0.52 ± 0.11
Via Tafel measurements of cathodic polarization (DHS)	Corr Rate (mpy)	4.0 ± 3.8		0.31 ± 0.24
Via Tafel measurements of anodic polarization (DHS)	Corr Rate (mpy)	73 ± 104		0.60 ± 0.18
Pitting	Number	None	None	None
Crevice Corrosion	Level	Mostly Severe	Mostly Severe	None to Moderate



Electrochemical Properties (Open Circuit Potential)



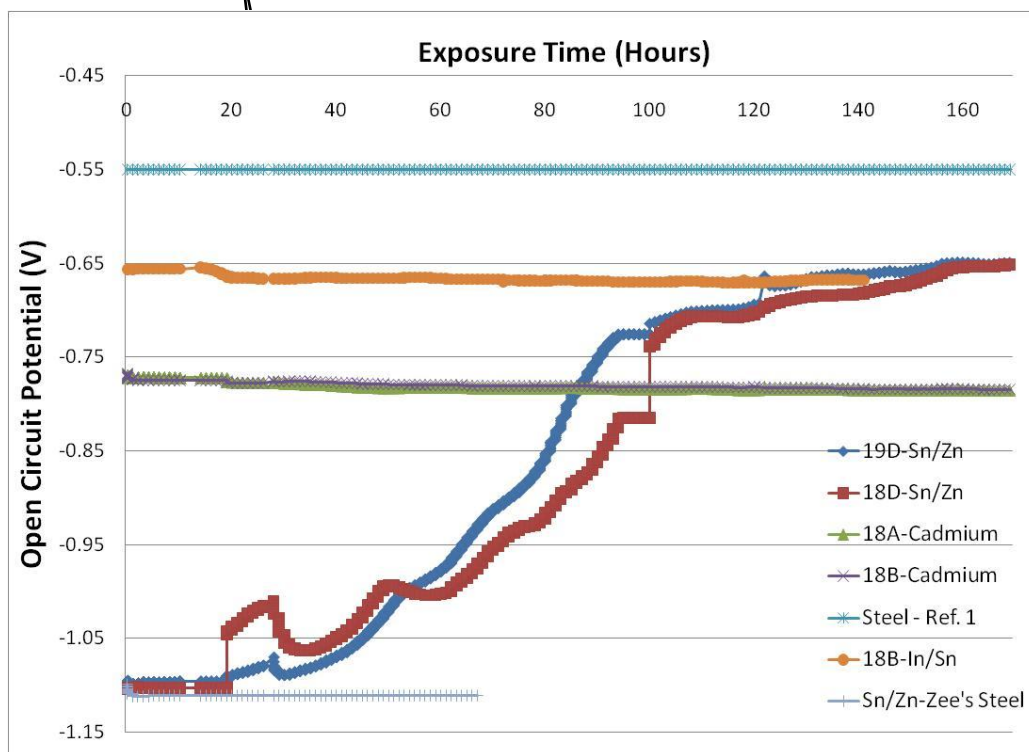
In-Sn coatings immersion exposure to the neutral solution of $\text{Na}_2\text{SO}_4 + \text{H}_3\text{BO}_3$

**Test Cells
per Samples**

Thermocouples



Multiplex 16 Samples



**Samples
vacuum
storage**



**Test Cell
for Samples**

Open Circuit Potential Preliminary Results



Summary



- Mission Essential Need to replacement Cadmium coating on DoD weapon system with “greener” / safer alternative(s)
- Replacement needs to be sacrificial to mild steel, and electrically conductive throughout its service – this limits the options.
- Round 1 and Round 2 tests are complete
- No candidate performed as well as the cadmium on the corrosion resistance tests
- InSn performed better than the cadmium in the electrical resistance tests
- Currently looking at other alternatives.

Back Up Slides



Background



- Cd has been a good coating for this weapon system.
 - Some of the mild steel component mating surfaces are electroplated with Cd
 - Prevent corrosion
 - Sacrificial to prevent formation of oxides of mild steel
 - Galvanic couple with aluminum alloys and stainless steel
 - Ensure a high electrical conductivity and sufficient grounding path during its service life
 - Provide the ability to withstand harsh weapon system environments
- Cd coating / repair process by brush plating that references SAE-AMS-QQ-P-416



Alternate Anode Arrangement



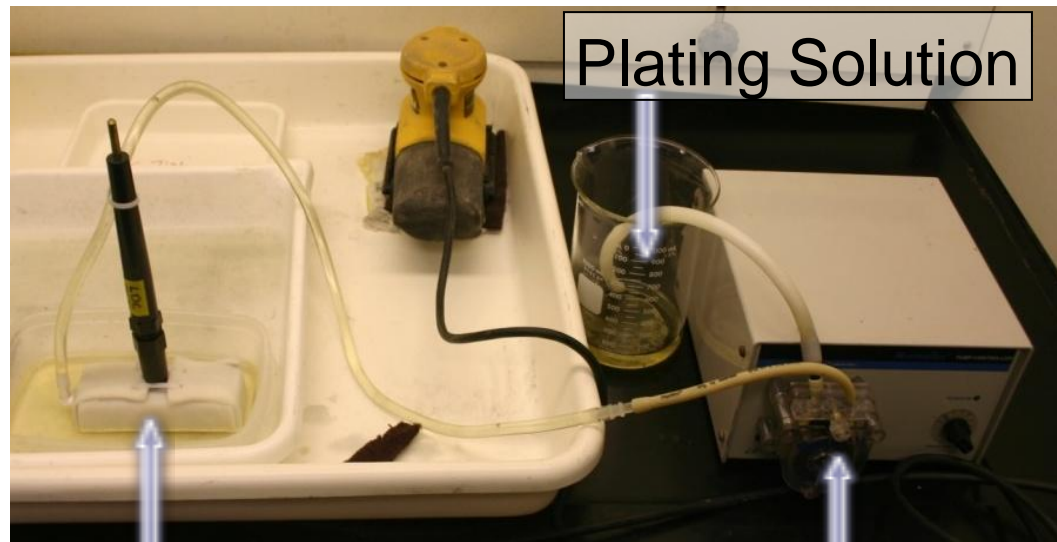
Anode Machined for Metered Chemical
(either graphite [shown] or plastic for dimensionally stable)

Cathode



Test Panel

Sleeved Anode



Plating Solution

Chemical Metering Pump

Meter chemical to anode, through its sleeve, and onto the part



Cd Spot Repair (Brush) Plating



Procedure:

1. Remove soils/corrosion from plated surfaces
2. Activate the substrate and undamaged Cd
3. Brush plate Cd onto the activated areas:
 - Wrap sacrificial Cd anode in an absorbent sleeve
 - Keep the anode sleeve wet with plating solution
 - Apply a steady, uniform anode motion on the part
 - Use a constant voltage until the target ampere-hour is reached
4. Inspect the Cd plating quality



Alternatives (Alts.) per QQ-P-416



1. Aluminum
2. Cadmium-titanium
3. Zinc
4. Lead
5. Zinc-cadmium
6. Nickel
7. Zinc-nickel
8. Nickel-cadmium
9. Tin
10. Tin-cadmium
11. Tin-nickel
12. Tin-zinc
13. Acrylic
14. Epoxy
15. Fluorocarbons
16. Nylon
17. Polyester
18. Polyurethane



Caveats of Indium Alloys



1. Low temperature eutectic:
 - The tin-indium system eutectic is 244°F at ~48.3 weight % tin
 - The cadmium-indium-tin system eutectic is ~199°F
 - Good for a solder
2. Greater hardness than both Cd and indium:
 - Less deformable on the mating surfaces
 - Potentially reduces the contact between these surfaces and electrical conduction
3. Relatively expensive; therefore, conduct a review of its cost/benefit to adopt indium alloy plating



Indium Alloy Brush Plating



- Start at 6 volts, adjust for target current density
 - Nominal average of 2.5 amperes/square inch
- Manage the process resistive heat, which raises the temperature of the anode and a thin panel
 - Use a thicker, $\frac{1}{8}$ - to $\frac{1}{4}$ -inch thick panel
 - Convert the anode to platinum wire instead of graphite
 - Feed the plating solution through the anode to cool it
- Use a soft anode sleeve material



Indium alloy plating