Developing Standardized Testing for Trivalent Chrome Thickness

ASTM INTERNATIONAL

B08 Test Methods

Workgroup AC574 - WK74450_B568-98(2014)

ASTM B08.10 Committee on Test Methods for Metallic and Inorganic Coatings

Mark Schario, Committee Chairman

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TOPICS

- **Overview of Initiative**
- Review of Test Methods & Variables
- Initial Round Testing & Summary: Thickness Comparison
- Initial Round Testing & Summary: Alloy Composition
- Next Steps

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Overview of Initiative

Contributing factors: Industry shift to trichrome, alloy properties

Objective: USCAR/ASTM

- To identify best practices for thickness determination of trivalent chromium deposits in decorative applications.
- Based on testing, modify existing ASTM Standards or create new standard(s) to meet the needs of decorative electroplating on multiple substrates.
- Additional information such as variables in electrolyte composition and current density will be useful for engineering and OEMs in their individual or manufacturer specifications.

ASTM STANDARDS AFFECTED

TEST METHODS

- ASTM-B-568 X-ray
- ASTM-B-504 Coulometric
- ASTM-B-556 Thin Chromium

PLATING STANDARDS

- ASTM-B-456 Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium
- ASTM-B-604 Decorative Electroplated Coatings of Copper Plus Nickel Plus Chromium on Plastics

Decorative Plating Layers- Hexavalent Chromium

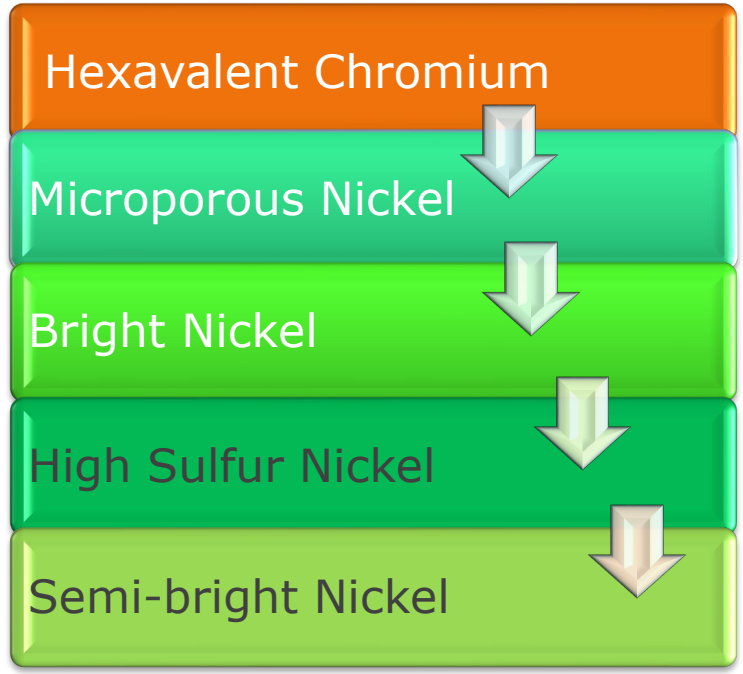
Chromium provides hard passive layer and white color

Microporous nickel provides porosity and prevents undercutting of the chromium layer

Sulfur containing Bright Nickel acts as the sacrificial layer

High sulfur nickel is anodic to bright and semi-bright layer

Semi-bright nickel layer prevents corrosion to substrate



Decorative Plating Layers- Trivalent Chromium

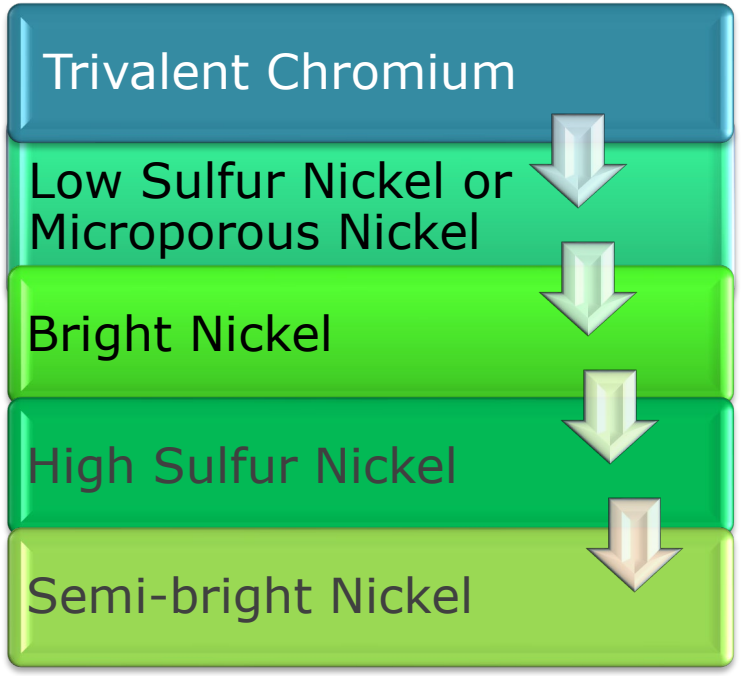
Chromium provides hard passive layer, white color and microporosity

Low Sulfur Strike prevents undercutting of the chromium layer

Sulfur containing Bright Nickel acts as the sacrificial layer

High sulfur nickel is anodic to bright and semi-bright layer

Semi-bright nickel layer prevents corrosion to substrate



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Sample Preparation

1. Test Specimens: All specimens were prepared by plating a steel hull cell with a uniform bright nickel layer, rinsing, then applying the chromium layer to provide different current densities. All samples were plated in same hull cell with air agitation.

2. Hull cells were first tested by X-RAY (ASTM-B-568), then tested in same spot with coulometric test.

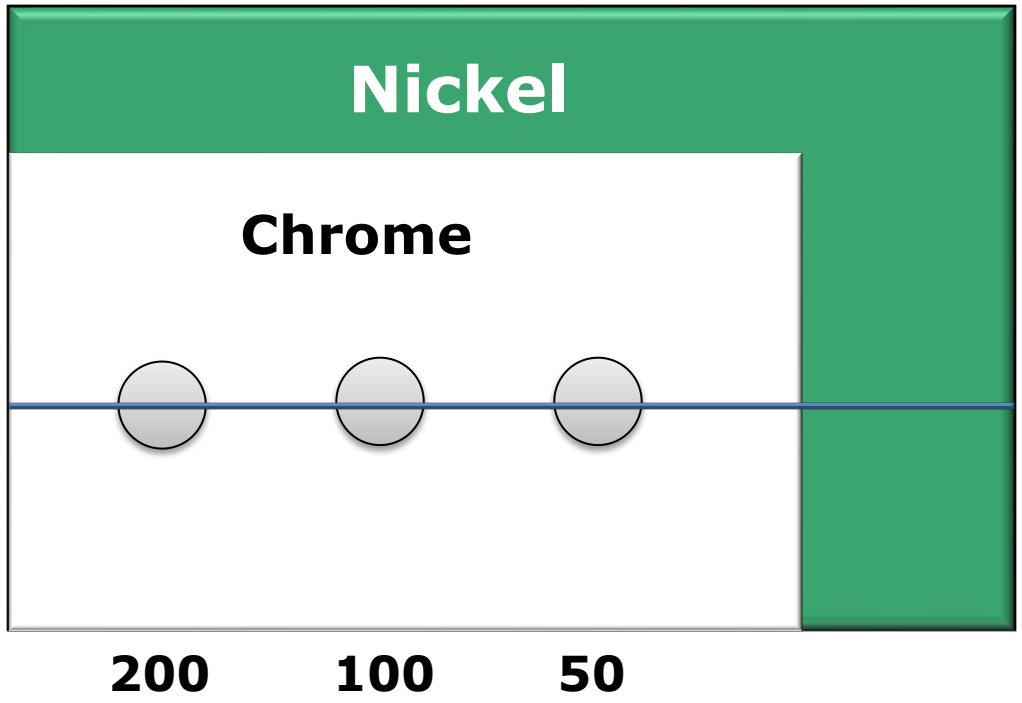
3. The hull cell panels were then cut down the center of the dissolved area so SEM measurement could be made directly adjacent to the already tested area. Samples were then polished and examined using the SEM for final thickness measurement.

4. Two separate sample were retained in the same area for a surface measurement of composition, and finally sent out to Anton Parr for the Calotest, a destructive test method.

HULL CELL PANEL DIAGRAM

Tests Performed:

- X-Ray
- Coulometric
- SEM
- Calotest (Pending)



Trivalent Solutions:

White Chloride

Black Chloride 7.5 ml/L

Black Chloride 17 ml/L

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Thickness Test Methods

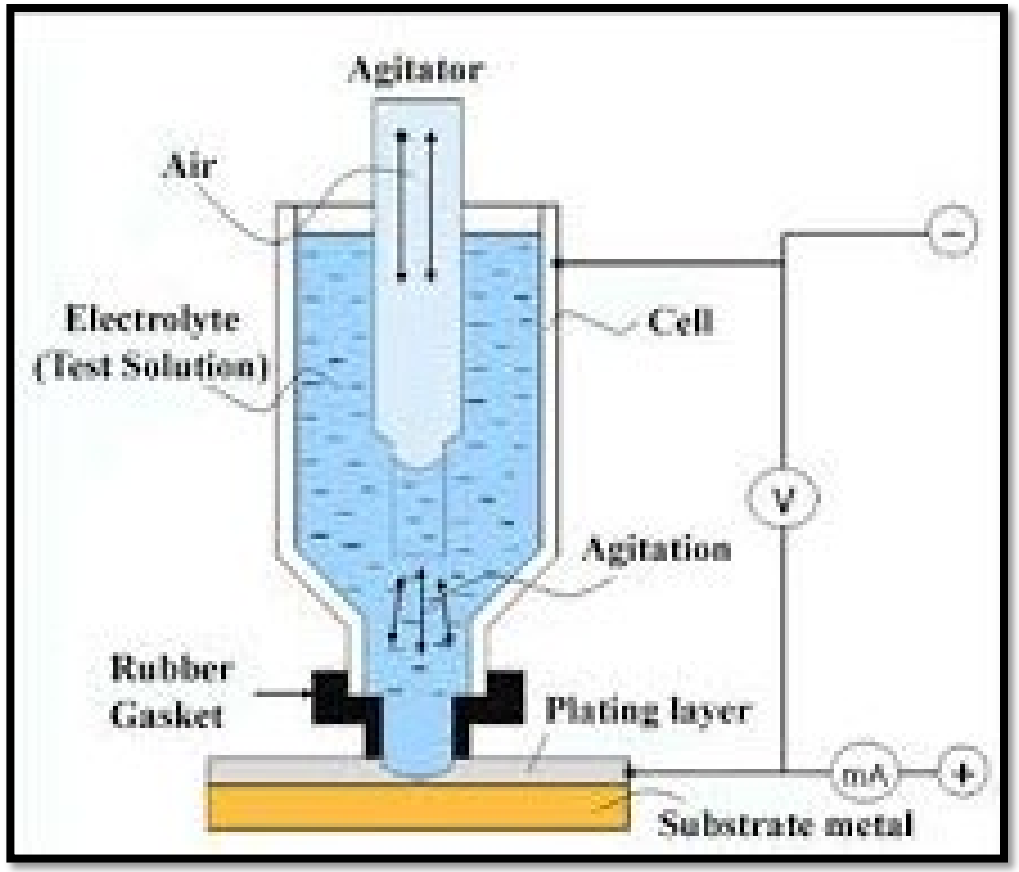
- **ASTM-B-504** Measurement of Thickness of Metallic Coatings by the Coulometric Method
  - This is a destructive test that dissolves the chromium layer. This is the most common test method in industry.
- **ASTM-B-568** Measurement of Coating thickness by X-Ray Spectrometry
  - This is a non-destructive test that measures the thickness.
- **ASTM-B-748** Cross section by Scanning Electron Microscope
- **Calotest** This is a destructive test that wears through the chromium layer, then measures the thickness by the width in relation to the diameter of the wear ball.

ASTM-B-504 Coulometric

Measurement of Thickness of Metallic Coatings by the Coulometric Method

This is a destructive test that dissolves the chromium layer.

Most common test method in the industry.



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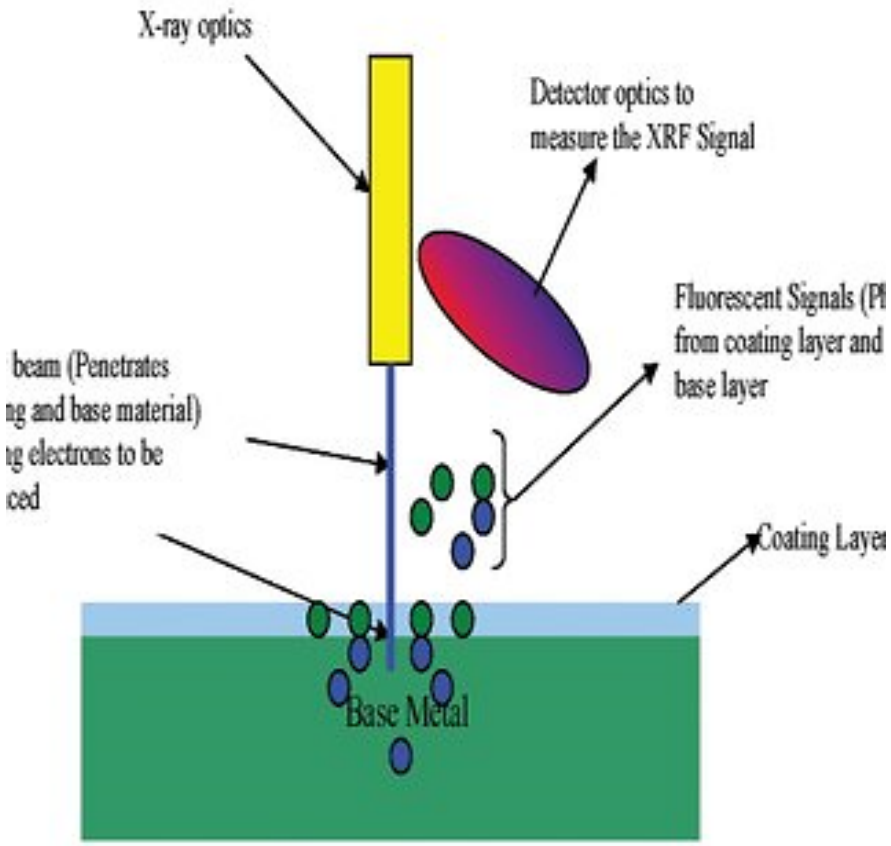
ASTM-B-568 X-Ray

Measurement of Coating thickness by X-Ray Spectrometry

This is a non-destructive test that measures the thickness.



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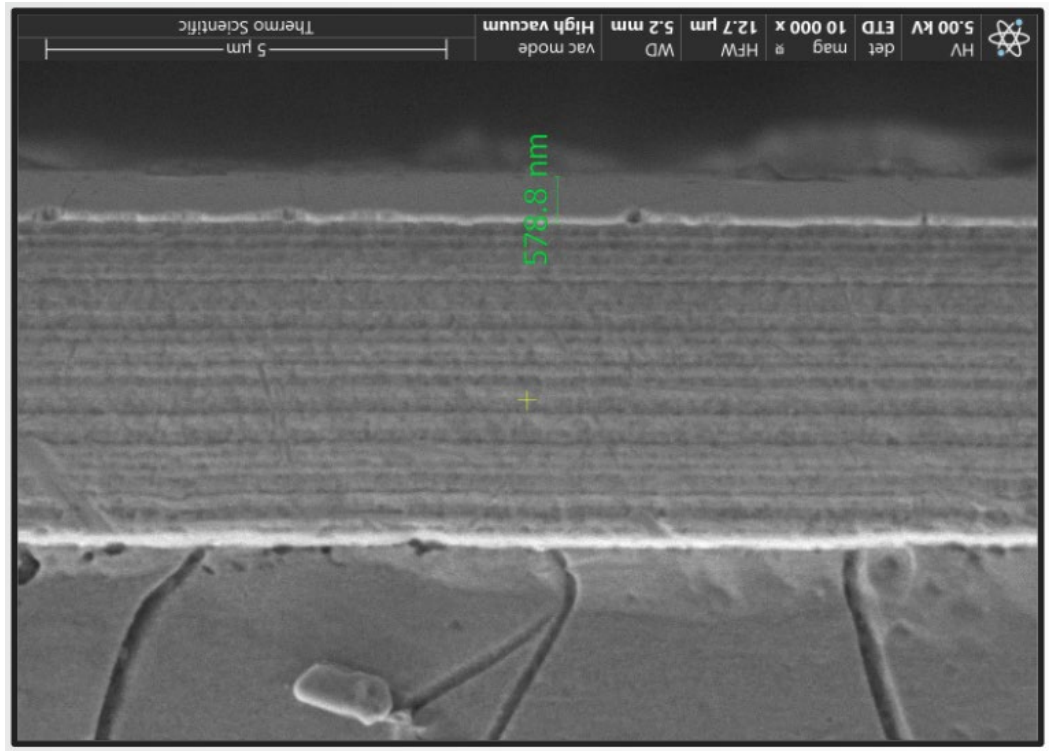
ASTM-B-748 Cross Section by SEM



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CALOTEST

This is a destructive test.

A spherical ball wears through the coating.

The width of coating is then measured and combined with the diameter of the ball to yield a thickness value.

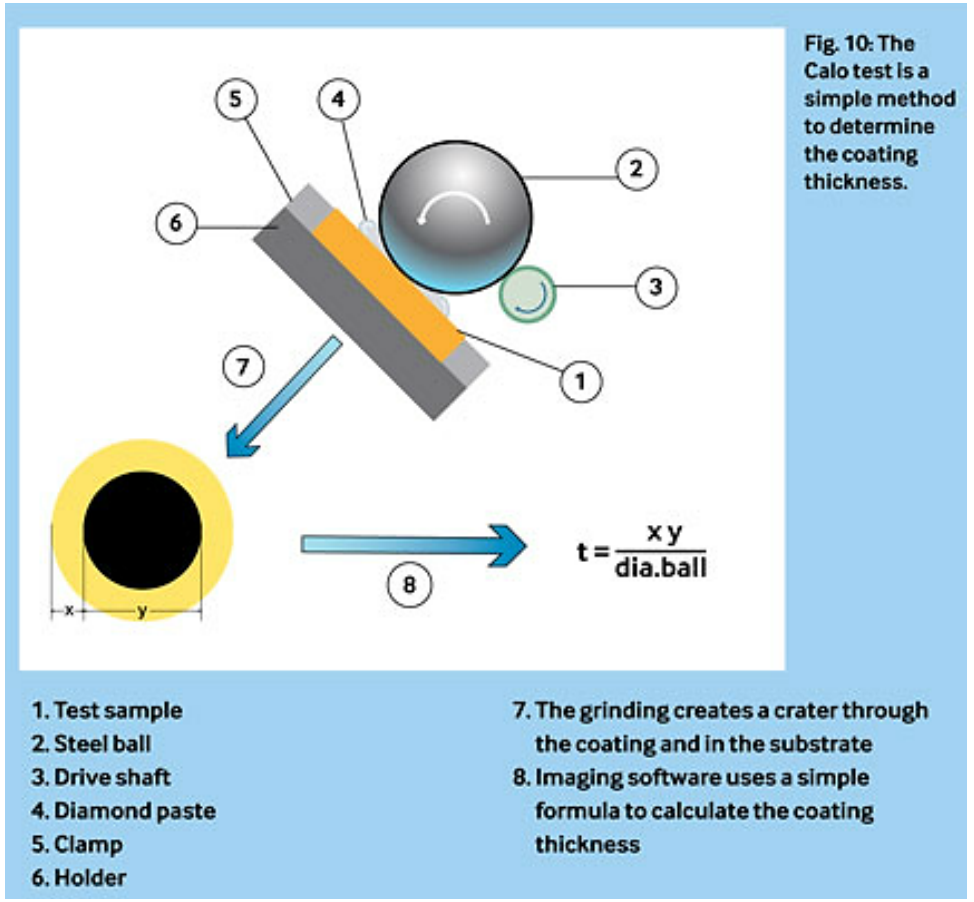

Fig. 10: The Calo test is a simple method to determine the coating thickness.

1. Test sample
2. Steel ball
3. Drive shaft
4. Diamond paste
5. Clamp
6. Holder
7. The grinding creates a crater through the coating and in the substrate
8. Imaging software uses a simple formula to calculate the coating thickness

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THICKNESS COMPARISON

White Trivalent Chromium

Chloride Based

Thickness measurements in microns

Cr Type	Amp per ft^2	X-Ray	Coulometric	SEM	Calotest	Factor X-ray to SEM
White	200	0.205	0.203	0.335	pending	1.63
	100	0.307	0.279	0.54/0.56	pending	1.75
	50	0.078	0.076	0.11	pending	1.41

THICKNESS COMPARISON

Black Trivalent Chromium

Chloride Based

Low Concentration Blackening Agent

Thickness measurements in microns

Cr Type	Amp per ft^2	X-Ray	Coulometric	SEM	Calotest	Factor X-ray to SEM
Black **7.5 ml/L**	200	0.128	0.127	0.202	pending	1.56
	100	0.137	0.178	0.241	pending	1.75
	50	0.032	0.051	0.060	pending	1.87

THICKNESS COMPARISON

Black Trivalent Chromium

Chloride Based

Medium Concentration Blackening Agent

Thickness measurements in microns

Cr Type	Amp per ft^2	X-Ray	Coulometric	SEM	Calotest	Factor X-ray to SEM
Black **17 ml/L**	200	0.085	0.102	0.255	pending	3
	100	0.098	0.127	0.330	pending	3.4
	50	0.033	0.051	0.141	pending	4.27

THICKNESS COMPARISON

Trivalent Chromium

Comparison of Factor X-Ray to SEM

Chloride Based

Factor X-ray to SEM White	Factor X-ray to SEM Black 7.5 ml/L	Factor X-ray to SEM Black 17 ml/L
1.63	1.56	3
1.75	1.75	3.4
1.41	1.87	4.27

Summary – Thickness Comparison

1) Initial SEM measurements yielded higher thickness values than x-ray and Coulometric testing.

2) Black trivalent electrodeposits yield an even greater disparity than white trivalent chromium electrodeposits.

3) Suppliers should provide factor when using x-ray or coulometric testing to provide applicators guidance on actual plating thickness.

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ALLOY COMPOSITION

White Trivalent Chromium
Chloride Based
Surface Shot - EDX

Sample Code	% C	% O	% Cr	% Fe	% Ni	Total %
White C 100 ASF	2.71	1.83	91.99	3.47		100.00
	2.66	2.05	92.21	3.09		100.01
	2.62	1.64	93.83	1.90		99.99

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ALLOY COMPOSITION

Trivalent Systems
Black Chloride 7.5ml/L
Surface Shot - EDX

Sample Code	% C	% O	% S	% K	% Cr	% Fe	% Ni	Total %
Black **7.5 ml/L** 100 ASF	3.41	4.74	11.73	0.98	68.13	7.49	3.52	100.00
	3.58	4.63	11.66	0.93	67.31	7.59	4.30	100.00
	3.04	4.85	11.86	0.96	67.62	7.39	4.27	99.99

ALLOY COMPOSITION

Trivalent Systems
Black Chloride 17ml/L
Surface Shot - EDX

Sample Code	% C	% O	% S	% K	% Cr	% Fe	% Ni	Total %
Black **17 ml/L** 100 ASF	5.15	4.44	11.00	1.04	60.23	6.26	11.89	100.01
	5.15	4.89	11.00	1.27	59.96	6.47	11.25	99.99
	5.32	4.90	11.08	1.28	59.28	6.35	11.78	99.99

Summary – Alloy Composition

1) Measurement of the alloy was affected by penetration through the chromium layer into the nickel layer. The decorative chromium thickness is too thin for this method. Thicker coatings will be needed to get accurate elemental composition information.

2) Further testing using EDX will require thickness >0.5 microns.

Next Steps

- Anton Parr is checking thickness as an optional destructive test method. Additional companies are being researched for this test.
- Based on the differences identified, we are setting up a round robin test phase, recruiting labs who can provide necessary thickness testing on known samples.
- Surveyed group to determine participants capabilities to assist.
- Plating large panels for distribution once round robin testing labs are identified.
- Upcoming B08.10 workgroup meeting in November.

Thank You…

Questions?

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