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The Hexavalent Chromium Challenge

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Restricted Substance - Hexavalent Chromium

- **Common Oxidation States of Chromium (Cr)**
  - Cr(0): Chromium metal - Not restricted
  - Cr(III): Trivalent chromium - Not restricted
  - Cr(VI): Hexavalent chromium – Restricted

    (Known Carcinogen, Mutagen, Respiratory and Skin Irritant)
  - For Analytical Testing
    - Total Cr or Presence of Cr – relativity simple
    - Cr(VI) in a mixed valence matrix – more complex

Hexavalent Chromium in Electronic Products

- **Sources of Cr(VI) in Electronic Products**
  - **Polymeric Matrix:**
    - Pigments in Plastics
  - **Metallic Matrix: (major source in electronic products)**
    - **Chromate Conversion Coatings** on
      - Chassis (galvanized steel frames)
      - Fasteners (screws, nuts, bolts, etc.)
      - Metal Components (heatsinks)

Replacing Hex Chrome Coatings

- **Chromate Conversion Coatings (CCC)**
  - Cr(VI) converts to Cr(III) during the coating process
  - Some Cr(VI) is incorporated into the coating
- **Properties**
  - Excellent corrosion resistance and “self-healing” ability
  - Good conductivity/Electromagnetic Compatibility (EMC)
  - Good paint adhesion
  - Relatively low cost
- **No direct substitute with equal benefits (may also require modification to mechanical design, EMC materials/gasketing designs to compensate)**

Can We Switch Completely Away from Chromium?

- **In some applications, trivalent chromate coating is the only alternative**
- **Sourcing Issues:**
  - North America and Europe lack a commercially viable supply of non-chromium based alternatives
- **Accurate Cr(VI) Test Methods are needed to:**
  - Distinguish trivalent chrome coating from hex chrome coating until the industry is fully switched over
  - Confirmation testing when switching to lower cost geography
  - Random teardown or validation testing

Current Challenges in Hexavalent Chromium Testing on Chromate Conversion Coating

Current Cr(VI) Testing Methodologies

- **ISO 3613 is the basis for many current methods**

  GMW 3034 (US auto); JIS 8625 (Japan); IEC CD ver. 2;

  ZVO-0102-QUA-02 and ZVO-0101-UV-05e (Germany)

  - With various modifications to testing window and detection limits

- **These methods are based on mass Cr(VI) per surface area (industry standard), not per coating weight – there are no easy ways to relate results back to the RoHS Pass/Fail limit of mass per coating weight**

- **Challenge #1: Measuring Coating Weight Accurately**
  - Coating weight decrease with time due to dehydration
  - ISO 3892 – result accuracy not certain, and also involves the use of sodium cyanide

Colored Chromate vs. Colorless Chromate

- **Testing of Colored Chromate vs. Colorless Chromate**

  - Testing Colored Chromate coating is usually not a problem – enough Cr(VI) for boiling water extraction; but need to be careful with spot test since the color changes can be very subtle and misidentified as a negative test

  - Testing for Colorless Chromate coating is a challenge! Sometimes, inconclusive results between methods are obtained

IEC Inter-laboratory Study

Sample	Spot Test	Water Extraction	XPS (% Cr(VI) /total Cr peak)	Total Cr by ICP ug/cm^2
HGS	+	+	25%	29.64
HAA	+	+	30%	17.88
LGS	-	-	20%	8.23
LAA	-	-	24%	1.58

HGS = yellow CCC on galvanized steel
LGS = Clear CCC on galvanized steel
XPS data obtained from a study conducted by HP

HGS = yellow CCC on Al alloy
LGS = Clear CCC on Al alloy

- Spot Test and Water Extraction indicate no Cr(VI) for LGS and LAA
- XPS results indicate there is Cr(VI) in LGS and LAA, perhaps in excess of the RoHS limit
- Since there is no easy way to relate these results to the RoHS “per coating weight” – how would we know for sure if LGS and LAA is indeed RoHS compliant??

Challenges in Developing Test Method for Colorless CCC

- **Challenge #2: Measuring Cr(VI) Accurately**
  - Cr(VI) level changes with time and storage conditions
  - Cr(III)/Cr(VI) conversion - no appropriate metallic matrix standards or reference materials to ensure the method itself did not induce conversion
  - Matrix interference
  - Economical

Challenges in Developing Test Method for Colorless CCC

- **Potential Metallic Matrix Reference Materials by X-ray Absorption Spectroscopy (XAS)**

  Lytle *et al. Corros. Sci.* 1995; **37**:349

  collaboration between Boeing and Stanford Synchrotron Radiation Lab

Table 1. Compilation of XAS results at Cr-sites in Alodine treated 2024 and 7075 aluminum

Sample	Time (min)	Salt spray	Hex Cr frac		Edge jump		Surface (N, R)				Total (N, R)			
			Surface	Total	Surface	Total	N_4	R_4 (Å)	N_6	R_6 (Å)	N_4	R_4 (Å)	N_6	R_6 (Å)
7075#1	1	No	0.22	0.24	0.36	0.49	—	—	—	—	—	—	—	—
7075#11	1	No	0.22	0.21	0.21	0.50	0.80	1.69	4.75	2.02	1.38	1.70	3.94	1.99
7075#6	1	No	0.21	0.22	0.26	0.51	1.42	1.69	3.88	1.98	—	—	—	—
7075#6	1	Yes	0.07	0.07	0.22	0.44	0.77	1.78	4.85	2.00	—	—	—	—
7075#15	1	Yes	0.14	0.14	0.22	0.32	—	—	—	—	—	—	—	—
7075#8	3	No	0.25	0.26	0.25	0.90	—	—	—	—	—	—	—	—
7075#13	3	No	0.24	0.24	0.33	0.83	1.20	1.70	4.20	2.01	1.27	1.70	4.10	2.02
7075#3	3	Yes	0.24	0.26	0.27	0.88	1.45	1.67	3.83	1.97	1.52	1.69	3.73	1.98
2024#49	1	Yes	0.15	0.16	0.22	0.29	0.92	1.67	4.62	1.97	1.55	1.66	3.69	1.94
2024#P1-1	1	Yes	0.07	0.08	0.28	0.34	0.80	1.79	4.81	1.99	—	—	—	—
2024#FT1-1	1	Yes	0.24	0.27	0.29	0.54	—	—	—	—	—	—	—	—
2024#PM-1	1	Yes	0.20	0.20	0.24	0.35	—	—	—	—	—	—	—	—
2024#F1-1	1	Yes	0.25	0.27	0.27	0.40	—	—	—	—	—	—	—	—
2024#4	3	No	0.22	0.24	0.26	0.42	1.40	1.72	3.89	2.00	1.04	1.68	4.45	2.01
2024#7	3	No	0.21	0.22	0.26	0.40	1.33	1.74	4.01	2.01	1.43	1.70	3.86	1.99
2024#10	3	No	0.21	0.24	0.28	0.39	—	—	—	—	—	—	—	—
2024#6	3	Yes	0.18	0.19	0.24	0.37	1.03	1.87	4.46	2.03	1.32	1.70	4.02	1.98
2024#P3-1	3	Yes	0.16	0.20	0.27	0.83	—	—	—	—	—	—	—	—

Time—immersion time in Alodine 1200S bath.
Salt spray—exposure to standard salt spray (ASTM B117-90) for 168 h.
Hex Cr frac.—fraction of hexavalent Cr (±10%) determined using XANES.
Edge jump—relative amount of Cr present (±5%) for a given mode (electron yield or fluorescence).
Surface—top ~700–1200 Å sampled using electron yield mode.
Total—Surface layer plus underlying bulk region to ~24 μm sampled using fluorescent yield mode. Note that Cr was present only in the Alodine layer.
N_4, R_4—coordination number (±25%) and bond length (±0.03 Å) of Cr in four-fold site determined by EXAFS.
N_6, R_6—coordination number (±25%) and bond length (±0.01 Å) of Cr in six-fold site determined by EXAFS.

Structure and chemistry of a chromium-conversion surface layer on aluminum

Potential Metallic Reference

- **Once metallic matrix references are generated, they can be used to:**
  - Evaluate methods and determine method detection limits
    - Spot Test and Water Extraction vs. XPS
  - Develop economical testing methods
    - Raman Spectroscopy

      Kikuchi *et al.* Analytical Sciences (Rapid Communications), March 2005, vol. 21

Conclusion

- **There is a strong need in the US Electronic Industry to accurately and reliably determine RoHS compliancy in anti-corrosion protection coatings, from material qualification, random teardown test, to prevention of accidental "mix-ups"**

- **If EU can be persuaded to adopt the well established industry unit of "Cr(VI) mass per surface area" rather than per coating weight, it will eliminate the need to develop a new, accurate and environmental friendly method for coating weight determination. Eliminating the need for a coating weight test also means additional saving to the US industry!**

- **NIST and US Government support in developing a set of metallic matrix reference materials and validating existing methods are crucial to the US industry in terms of RoHS Hexavalent Chromium testing and compliancy**

- **X-ray Absorption Spectroscopy of various types of Chromate Conversion Coating may lead to a set of potential reference materials; thereby, enabling method evaluation and development of economical testing methods**

IBM Team

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