Toxics Use Reduction Institute

Advances in Metal Finishing: Hexavalent Chromium and Alternatives

Liz Harriman - TURI

TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

Cr(+6) in Surface Finishing Session Overview

- Introduction
- Cr(+6) or Cr(VI) Environmental and Health Effects
- Drivers for Change
- Uses in Surface Finishing
- Alternatives
- Case Study: Coating Systems, Inc.
- Discussion

Chromium and Compounds

- Cr(0) – metal, alloys
- Cr(+3) – trivalent, most stable
- Cr(+6) – hexavalent, less stable, more toxic
  - Typ. as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_2^{-7}$) anions
- Other valence states rare, less stable

Cr(+6) Health Effects

- Lungs and respiratory system
  - Known human lung carcinogen via inhalation (IARC Group 1)
  - Ulcerations and perforations of nasal septum; chronic bronchitis, pneumonia, decreased pulmonary function, irritant
  - Asthmagen (causes asthma) – *both Cr(+3) and Cr(+6)*
- Dermal/Skin
  - Contact dermititis, “chrome ulcers” in broken skin
- Ingestion
  - 2008 NTP 2 yr animal study showed evidence of carcinogenicity in small intestine; report not final
  - Large doses or chronic exposure can cause kidney damage

Cr(+6) Environmental Effects

- Cr(+6) and Cr(+3) in environment:
  - Cr+3 relatively insoluble in water; low mobility in soils
  - Cr+6 highly soluble in water, highly mobile
  - Presence of manganese oxide can oxidize Cr(+3) to Cr(+6)
  - Alkaline conditions and low iron favor Cr(+6)
  - Presence of high iron and high organics favors Cr(+3)
- Public health concerns over Cr(+6) in drinking water
- Cr(+6) higher aquatic toxicity than Cr(+3)
  - Cr(+6) more toxic to freshwater biota than marine, more toxic in comparatively soft and acidic waters, and to younger organisms
- Cf(+6) Eco-toxicity related to strong oxidizing action of chromates

Occupational Exposure Limits

- OSHA PEL = 5 µg/m^3 8 hr TWA
  - OSHA action level 2.5 µg/m^3
  - OSHA PEL = 25 µg/m^3 for large aircraft painting
- NIOSH REL = 1 µg/m^3 10-hr TWA
  - NIOSH Draft Criteria Document Update Sept 2008 proposes lowering REL to 0.2 µg/m^3
- OSHA requires employers to notify their workers of all hexavalent chromium exposures as of June 15, 2010 (not just when PEL exceeded)

Drivers for Cr(+6) TUR

- TURA potential HHS designation for Cr(+6) compounds
  - Administrative Council voted in April to
    - separate chromium compounds category
    - designate Cr(+6) compounds as Higher Hazard Substances
  - Policy Analysis available
- EU: ELV, RoHS
  - Eliminates most uses of Cr+6 in finished products
- EPA – HAPs NESHAP
  - 2004 major sources
    - Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks
  - July 2008 smaller area sources
    - Plating and Polishing Industry

Drivers for Cr(+6) TUR

- DOD April 8, 2009 memorandum, "Minimizing the Use of Hexavalent Chromium (Cr^{6+})"
- ASETSDefense [Advanced Surface Engineering Technologies for a Sustainable Defense]
  - *facilitates the implementation of new, environmentally friendly technologies for surface engineering (coatings and surface treatments), via database and information on the status of approvals and implementation of alternative technologies.*
- DOD funding R&D on alternatives and test methods for expedited qualification

ASETSDefense Launches Surface Engineering Database

This relational database provides background documents and detailed engineering data for making informed decisions on the use of clean alternative coatings and surface treatments. Products and processes that have been validated, authorized, implemented, or evaluated in service are included. Refer to Database tab.

MAIN MENU

- Home
- Surface Engineering Database
- Clean Alternative Information
- ASETSDefense Workshops
- DoD Policies
- Team Work Spaces
- Tools
- Assistance
- Links
- Contact ASETSDefense

Chromate Conversion Alternatives

Current Usage

Chromate conversion coatings and chromated sealers are used to create a self-healing conversion coating on Al and Mg alloys that is resistant to corrosion. They are also used for sealing electroplated and anodized coatings. These treatments are typically used prior to painting and finishing, since they generally improve adhesion of paints and sealants.

Typical Applications	Typical Chromate Conversion Coatings	Specifications
• Aircraft skins • Al frames for aircraft and vehicles • Mg gearboxes • Corrosion-resistant coatings (Cd, Al, ZnNi, etc.) • Anodize sealing • Fasteners and electrical connectors (Zn or Cd plated) • Wash primer for steels, armor	• Conversion and sealing coatings for Al (e.g., Alodine, Iridite, etc.) • Conversion and sealing coatings for Mg (e.g., Dow 7, 17, 19, HAE anodize)	• MIL-DTL-81706 • MIL-C-5541 • MIL-M-45202 • AMS 3171 • TO 1-1-8 • MIL-A-8625 • MIL-C-3171 • MIL-C-17711 • MIL-M-45202 • DOD-P-15328 • QQ-P-416

ESOH Issues

Cr^{6+} (CrVI, hexavalent chromium) is a known carcinogen that is strongly regulated under

- EPA Clean Air Act rules
- OSHA Occupational Exposure to Hexavalent Chromium (Cr^{6+} PEL is currently $5\mu gm^{-3}$)
- European rules (RoHS, WEEE, ELV)

Hexavalent Chromium Resources

- DOD April 8, 2009 memo, "Minimizing the Use of Hexavalent Chromium (Cr^{6+}),"
  - http://www.asetsdefense.org/documents/DOD Policy Memo on Hex Chrome.pdf
- DOD ASETSDefense—Advanced Surface Engineering Technologies for a Sustainable Defense, database and topic hub
  - http://www.asetsdefense.org/
- DOD Dec. 2010 Conference session: Minimizing Hexavalent Chromium Use in DoD Operations
  - http://symposium.serdp-estcp.org/Technical-Sessions/2B
- OSHA hexavalent chromium page
  - https://www.osha.gov/SLTC/hexavalentchromium/index.html

Hexavalent Chromium Resources (cont)

- EPA Sep 2010 draft IRIS Toxicological Review of Hexavalent Chromium
  - http://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid=221433
- NIOSH Draft Criteria Document Update: Occupational Exposure to Hexavalent Chromium, Sept 2008
  - http://www.cdc.gov/niosh/topics/hexchrom/