Hexavalent Chromium: Use, Toxicology and Restrictions

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What is Chromium?

- Naturally occurring metallic element found in rocks, soil, plants and volcanic dust
- Exists primarily in mineral form, chromite, FeCr$_2$O$_4$
- Chromite is the main constituent in chrome ore, and the only commercial source of Cr
Exists in several oxidation (valence) states

- Inorganic
  - Trivalent ($\text{Cr}^{+3}$)
  - Hexavalent ($\text{Cr}^{+6}$)
- Organic
- Elemental (Metallic ($\text{Cr}^0$))
Industrial Uses of Cr

- **Metallic (Cr⁰)**
  - Metal Cr
  - Does not occur naturally
  - Used for making steel
  - Chrome plating

- **Trivalent (Cr⁺³)**
  - Most stable form
  - Used in leather tanning, dyes, paint pigments, brick lining in furnaces

- **Hexavalent (Cr⁺⁶)**
  - Occurs in a range of compounds
  - Used in Chrome plating (CrO₃)
  - Wood preserving
  - Conversion coatings
Properties of Different States

- **Metallic (Cr\(^0\))**
  - Does not occur naturally
  - Not toxic

- **Trivalent (Cr\(^{+3}\))**
  - Insoluble
  - Essential micro-nutrient (helps convert sugar, protein, & fat)
  - Somewhat toxic

- **Hexavalent (Cr\(^{+6}\))**
  - Soluble, readily absorbed
  - Structurally similar to phosphate ("Trojan horse")
  - Converted to V-IV-III in cells
  - Highly toxic
Chromium in the environment

- Cr enters the air, water and soil in the III and VI forms
- In air, Cr compounds exist as fine dust that settles
- Strongly binds to soil, so doesn’t reach groundwater
- Does not bioaccumulate in fish
Toxicological Responses

Acute Responses:
- Ulceration of nasal septum
- Allergic dermatitis (can be very severe)
- Asthma
- Permanent eye damage

Chronic Responses:
- Cell injury: interferes with cellular respiration
- Ingestion can cause stomach, liver, kidney damage
- Lung cancer
- Teratogenic: probable, little data
Toxicological Responses
Erin Brockovich Factor

- PG&E used Cr(VI) for anti-corrosion
- Private wells contaminated
- $333m settlement
- Controversial – health risks through drinking water uncertain
Regulation of Cr (VI)

- Primary contaminant in ½ of Superfund sites
- CalEPA – Toxicity review committee study of drinking water (2001) inconclusive
- MCL for drinking water is 50 ppb
- Real threat is inhalation exposure
Inhalation Exposure to Cr(VI)

Sources of Cr emissions:

- Oil and coal combustion
- Cement plants
- Chrome plating production
  - Avg conc: 10-30 μg/m³ with ventilation
  - 120 μg/m³ w/o ventilation
- Stainless steel production and welding
  - 1500 μg/m³

(PEL: 100 μg/m³, REL is 1 μg/m³)
Hex Chrome Under ELV

- Total limit @ 2.0 grams/vehicle for Cr+6 for corrosion protection purposes only
  - Originally exempt only until June 2003 (automobile Model Year 2005)
  - Annex II exemptions allow hex chrome used in Corrosion Preventative Coatings until January 1, 2007
  - Limited thereafter to 0.1% (w/w) per homogenous material
    **NOT intentionally introduced**

- Currently there is no standard test method

Most OEMs banning Cr+6 completely
Hex Chrome Under ELV

- Applies to chromate conversion coating for zinc and zinc alloy parts
  - Deliberately leave Cr+6 on the parts
  - Fasteners, tubing, brackets, etc. (1000s of parts)
  - Most common: yellow chromate
- Not affected:
  - Chrome plating = metallic chrome (0-valence chrome)

http://www.nidi.org/index.cfm/ci_id/10179.htm
Hex Chrome Under ELV

- To do business in Europe, automakers must follow the ELV directive.
- Impossible to have one spec for Europe and another for the rest of the world

one universal specification is required
Hex-free is still in its infancy
Chromate Conversion Coatings

COATING FEATURES
- Protection of sacrificial zinc (or zinc alloy) layer
- Excellent corrosion resistance
- Friction properties – organic coating adhere well
- Self-healing
- Wide range of colors possible (clear, blue-bright, iridescent, golden yellow, olive drab, matte black and bronze)
- Solderability
- Constant conductivity
Alternative Systems

Traditional Cr (VI) Coating System

- Lubricant
- Cr(VI) Chromate
- Electroplated Zn
- Substrate

ELV Compliant Coating System

- Lubricant
- Sealer or electrocoat
- Cr(III) or non-chromium
- Electroplated Zn or Zn alloy
- Substrate
Hex-free alternatives

1. Trivalent Chromate

- Most commercially acceptable alternative at lowest cost
- Suitable or superior corrosion resistance

- Not self-healing
- Growing realization all chromate to be phased out in time

2. Non-Chromium Passivations
   (organic films, inorganic salts, oxides, organimetalllics)

- Non-chromate

- Individual adoption seems unlikely
- Similar corrosion resistance as Cr+6 not possible yet

You the guy who just made a seven-coordinate compound of chromium III...

Well we've got a MESSAGE for ya....

Chromium III doesn't LIKE being seven-coordinate...

LATE THAT NIGHT, PROFESSOR ROBINSON'S LABORATORY WAS OVERRUN BY HOSTILE ELEMENTS.