STERC Library Technical Article - June 2019

Environmental Pressure to Convert from Hexavalent to Trivalent Chromium

by
Shane Moore
Pavco, Inc.
Charlotte, NC 28273

ABSTRACT

Hexavalent chromium plating for decorative purposes has been a staple in the electroplating industry for almost 100 years. As more information regarding the toxicity of the process became available, the government began putting stringent regulations in place. These regulations started with adding fume suppressants to lower the surface tension, most of which contained PFOS, due to its ability not to breakdown in aggressive chromic acid solutions. In 2015, the government prohibited the use of PFOS as a fume suppressant due to its negative health effects, so suppliers switched to new PFAS compounds. Now PFAS compounds have come in the crosshairs, which will lead to further regulations on hexavalent chromium plating. This study will present viable trivalent chromium replacement options for the industry, which include chloride-based, sulfate-based, and barrel systems. It will review positives and negatives of each bath and compare them in regard to appearance and performance.

Overview of Regulations:

- REACH Compliance
  Registration Evaluation and Authorization of Chemicals - European directive to address production and use of chemical substances, and their impacts on human health and the environment. Administrated by ECHA (European Chemicals Agency).
- TSCA
  Toxic Substances Control Act - Inventory system in United States, similar to REACH Compliance, which categorizes chemical use according to impact on human health and the environment

Note: For both systems listed above, chemicals of very high concern must obtain authorization for use, if no other alternative is available.

- RoHS
  Restriction of Hazardous Substances - European directive to restrict the use of hazardous compounds (Hexavalent Chromium being one of them) in manufacturing of components.
- NESHAP
  National Emission Standards for Hazardous Air Pollutants - EPA directive that regulates amount of a hazardous substance known to cause health defects, that can be emitted into the environment.
- MACT
  Maximum Achievable Control Technology - NESHAP standards now based on the limits that are achievable with current technology.

- ELV
  End of Life Vehicle - European directive to recycle all components of a vehicle at its life end. Increases directive for components to be REACH and RoHS compliant.
- PEL
  Permissible Exposure Limit - Regulation implemented by OSHA, in which personnel may only be exposed to 5 $\mu g/m^3$ averaged over an 8-hour shift. Action must be taken if the exposure level reaches 2.5 $\mu g/m^3$. Previously, the limit was 52 $\mu g/m^3$. General ventilation no longer adequate to meet the increased standard, so more expensive equipment is needed in most cases to meet this limit.

The above regulations and regulatory committees have been in place for a few decades. Amendments have been made through the years that make it more and more difficult to achieve each new limit modification. Deliberation on the continued use of hexavalent chromium by current applicators has concluded that there are no current viable alternatives. As technology develops, this is becoming less and less accurate. Suppliers are developing chromium-free etch products for plating-on-plastics. Trivalent hard chromium deposits are beginning to reach the market, while decorative trivalent chromium options have been on the market for many years, and now the health and environmental impact of PFAS products are accelerating the elimination of hexavalent chromium.

Converting to Trivalent Chromium

Benefits:

- More environmentally friendly process.
    - No hazardous chromic acid.
    - PFOS and PFAS free.
    - Less chromium mist emitted equals less ventilation required.
    - Less regulatory paperwork.
- Lower overall operating costs
    - Easier/less expensive to waste treat.
    - Less electricity needed.
    - Better low current density coverage.
    - Reduced drag-out of solution (lower viscosity).

Which Trivalent Chromium electrolyte should I choose?

Sulfate-Based

PROS:

- Closest B* value (color value) to hexavalent chromium.
- Comparable hardness to Cr(VI). Higher than chloride-based Cr(III).
- Metallic impurities can be removed by ion exchange and can be carbon filtered.

CONS:

- Typically, the deposit rate is slower than Cr (VI) or chloride-based Cr (III) baths.

- Requires MMO Anodes.
    - Expensive.
    - Sensitive to chloride.
    - MMO coating deteriorates over time and must be replaced.

Chloride-Based

PROS:
- Very fast plating speed.
- Highest corrosion resistance (microporous as plated).
- Graphite Anodes (less expensive and last longer).
- Simple to operate.

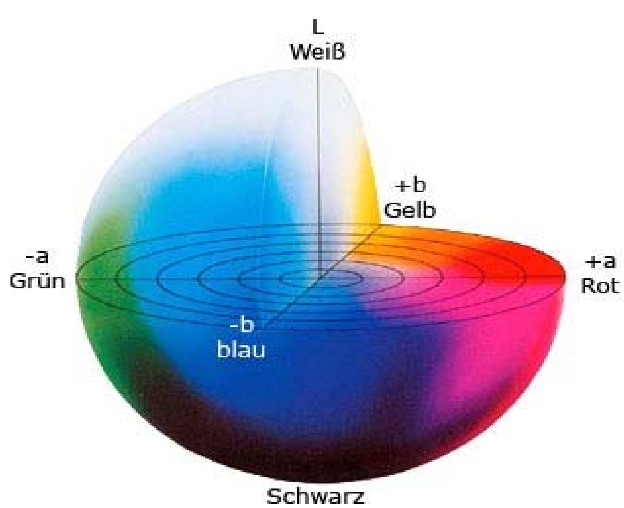
CONS:
- Color isn't as close to hexavalent chromium (higher B* value).
- Slightly softer deposit compared to hexavalent and sulfate-based, but still acceptable in most applications.

Trivalent Chromium for Barrel Applications

Advantages:
- Reduced labor costs (10% compared to rack).
- Better LCD coverage compared to rack plating.
- Improved thickness distribution.
- No rack marks.
- Better corrosion protection to non-chrome alternatives.
- Simple to operate.

Dark Trivalent Chromium

There has been an increase in market demand for a dark trivalent chromium deposit. Most suppliers in the decorative industry have this option. Some systems are built from sulfate-based technology and some are chloride based. These dark deposits usually have an "L" value range of 50-60.



Characteristics Explained

L*a*b Color Value

- The "*L*" value is a measure of how white vs dark the appearance. The higher the *L* value, the whiter the deposit. Conversely, the lower the *L* value, the darker the deposit.

- The “a” value is a measure of how green vs. red the appearance. .These values are typically of no value when evaluating chromium deposits.
- The “b” value is a measure of how blue vs. yellow the deposit. The higher the b value, the more yellow the deposit. The lower the b value, the bluer the deposit.

The table below shows typical color values according to the chromium electrolyte:

Process	L	b*
Hexavalent chromium (rack)	82 - 84	-1.0 to -1.4
Chloride Trivalent chromium (rack)	78 - 80	1.0 to 2.0
Sulfate Trivalent chromium (rack)	80 - 84	-0.3 to -1.0
Barrel chromium – Sulfate Trivalent chromium	78 - 82	1.0 to 2.0

*The above measurements were analyzed by colorimeter. In most cases, it is very difficult to see the color variation, especially with an untrained eye.

The color of trivalent chromium deposits can be influenced by:

- **Metallic contamination:** This is the most prominent variable that will affect the color of the deposit. Typical contaminants are copper, nickel, zinc and iron. Unless these are removed, either by electrolysis or ion exchange, the deposit can appear darker and/or more yellow, depending on the contaminant.
- **Additive control:** Maintaining the additives at their optimum concentrations, according to supplier recommendations, is very important in maintaining color. Most additives are dosed based on amp-hours, so if these addition systems are maintained, a consistent appearance will be achieved.
- **pH:** The pH of trivalent chromium systems is well buffered, but must be analyzed and adjusted as needed to maintain consistent color, and low current density coverage.

Hardness

The table below shows average harness values of chromium deposits. Although the chloride-based and barrel trivalent chromium deposits are not quite as hard as the sulfate-based trivalent chromium or hexavalent chromium, their hardness values meet most requirements, so this is usually not an issue.

Process	Hardness (Vickers)
Sulfate-Based Trivalent Chromium	1188
Hexavalent Chromium	1018
Chloride-Based Trivalent Chromium	807
Trivalent Chromium for Barrel Applications	750

Summary

As trivalent chromium technology continues to develop, motives for using hexavalent chromium will eventually be eliminated. After viable options for the use of hexavalent chromium have been proven, sunset dates for banning its use will no longer be postponed and a permanent ban will be put in place. Fortunately, the advanced trivalent chromium technology on the market today will facilitate these conversions from hexavalent to trivalent chromium.

Shane Moore is an International Technical Service Engineer and leads the Decorative Team for Pavco in Charlotte, NC.