Beauty and the Beast

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Beauty and the Beast
A Comparison of Trivalent and Hexavalent Black Chromium Plating Processes

“The Beauty”
Chromium Sulfate-based Trivalent Black Chromium

“The Beast”
Chromium Trioxide-based Hexavalent Black Chromium
Background:

• Hexavalent black chromium commercially available for over 50 years.
• Patents date back to 1952
• Gilbert and Buhman [1]
  – Developed process using chromic anhydride and acetic acid.
  – Artillery parts, rifle parts, and military equipment's at Rock Island Arsenal.
• Westinghouse Electric, Kewanee Oil (current day Atotech USA) were other pioneers to develop hexavalent black [2,3]
Background:

• Trivalent black chromium patents date back to the early 1970s.

• Initial trivalent chromium patent: Gyllenspentz and Renton of Albright and Wilson [4-6]
  – Utilization of trivalent chromium with formate, acetate, bromide, and ammonia.

• Robert Tremmel [5-7]
  – Utilization of thiazole compounds.
<table>
<thead>
<tr>
<th>Electrolyte metal component</th>
<th>Trivalent Black Chromium</th>
<th>Hexavalent Black Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloride</td>
<td>Sulfate</td>
</tr>
<tr>
<td></td>
<td>Chromium Chloride</td>
<td>Chromium Sulfate</td>
</tr>
<tr>
<td>pH</td>
<td>2–3</td>
<td>3.2 – 3.8</td>
</tr>
<tr>
<td>Temperature, F</td>
<td>70 – 120</td>
<td>120 - 140</td>
</tr>
<tr>
<td>Cathode Current Density, A/ft²</td>
<td>70 -150</td>
<td>70 - 150</td>
</tr>
<tr>
<td>Anode-Cathode Ratio</td>
<td>2:1</td>
<td>2:1</td>
</tr>
<tr>
<td>Anode material</td>
<td>Carbon</td>
<td>Precious metal coated titanium</td>
</tr>
<tr>
<td>Rectifier voltage</td>
<td>Up to 12</td>
<td>Up to 12</td>
</tr>
<tr>
<td>Agitation</td>
<td>Mild air</td>
<td>Mild air</td>
</tr>
<tr>
<td>Maximum deposit thickness, microns</td>
<td>&gt;1 μm</td>
<td>0.3 μm</td>
</tr>
<tr>
<td>Deposition rate, μm/min</td>
<td>0.15 – 0.25</td>
<td>0.02 – 0.03</td>
</tr>
</tbody>
</table>

Source: [3]
Operational Comparison

Trivalent Black
- Good throwing power
- Good covering power (similar to Watts nickel)
- Multiple chemical constituents need to be balanced for optimum black

Hexavalent Black
- Poor throwing power
- Poor covering power (similar to bright hexavalent chromium)
  - May need auxiliary anodes to obtain good part coverage
- Fewer chemical components to balance
Plating Rack Fixturing

Trivalent Black chromium

Hexavalent Black chromium

Integrated plating rack showing auxiliary anode for obtaining uniform coating thickness on a diecasting

Courtesy of Associated Rack
How Black is Black?

Color can be measured with a colorimeter using LAB values for color and lightness.

Gloss meters can also be used to measure reflectivity.

Black can be a very specific term...
Color
<table>
<thead>
<tr>
<th>Commercial Product</th>
<th>Supplier</th>
<th>L</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichromium Graphite</td>
<td>Atotech</td>
<td>68</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Dark Twilight</td>
<td>MacDermid Enthone</td>
<td>81</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Econo-chromium BK</td>
<td>Atotech</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Econo-chromium BL plus oil</td>
<td>Atotech</td>
<td>33</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Trimar Eclipse</td>
<td>MacDermid Enthone</td>
<td>50</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Trichromium Graphite</td>
<td>MacDermid Enthone</td>
<td>67</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Tristar 700 (chloride)</td>
<td>Coventya</td>
<td>54</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Tristar 720 (Sulfate)</td>
<td>Coventya</td>
<td>54</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Tricol Blackjack</td>
<td>Colombia Chemical</td>
<td>54</td>
<td>0.1</td>
<td>4</td>
</tr>
</tbody>
</table>
Hex and Trivalent Black chromium
Surface Scan
Hexavalent Black chromium
Surface Scan
Trivalent Black chromium
Deposit Structure

Trivalent Black
• Amorphous
• Glass-like
• Deposit can get cloudy at higher thicknesses

Hexavalent Black
• Crystalline
• 50% chromium oxide / 50% chromium
• As-plated deposit can be non-uniform
• Post-treatment with waxes and oils can enhance the color and reflectivity
TEM micrograph of trivalent black chromium coating

Transmission Electron Microscopy – Showing structure and morphology
Environmental Health and Safety

• Chromium (VI)
  – Toxicity is much greater
  – Classified as carcinogen
  – OSHA’s Permissible Exposure Limit (PEL) for Cr (VI) is 5μg/m³
  – Respirator and skin protection required
  – Use of ventilation, scrubber system, push air.

• Chromium (III)
  – Less toxic
  – No data on the carcinogenic potential
  – OSHA’s Permissible Exposure Limit (PEL) for Cr (III) is 500 μg/m³
  – Skin protection required
  – With use of wetter, the system is regulated similar to nickels.
Waste Water Treatment

• Hexavalent chromium significant WWT concern
• WWT process 3-step
  1. Reduce Cr(VI) to Cr (III) (w/sodium meta bisulfite) at low pH
  2. Raise pH 9-10 to form chromium hydroxide
  3. Precipitate and filter
• Trivalent chromium similar without first step
• Trivalent chromium also decreases chance of hexavalent chromium discharge
Black chromium Applications:

• Motorcycle
• Automotive
• Consumer/Medical
• Industrial
• Solar Panels
Motorcycle Applications

Get the Look – BLACKED OUT!

www.arlingtonplating.com
Surfin 2019
Black Chromium Muffler Pipes

Photo courtesy of Calchromium
Black Chromium Muffler Tips

Photo Courtesy of Polaris Industries
Motorcycle Applications

Harley Davidson Black chromium Master Cylinder

www.arlingtonplating.com
Surfin 2019
Motorcycle Applications

Harley Davidson Brake Pedal
Automotive Applications

“Cadillac adds black chromium package to spark CTS and ATS sales”
Automotive Applications

Honda Accord Black chromium Grille Accent
Automotive Rear Garnish

Honda Accord Rear Garnish
Automotive Applications

Black chromium rear exhaust bezel – Honda Accord

www.arlingtonplating.com
Surfin 2019
Automotive Wheel Rims
Automotive Paddle Shifter

Cadillac ATS or CTS Magnesium Paddle Shifters
Automotive Exhaust Tips

Jones Dual Oval Exhaust Tip

Lexus GX460 Exhaust Tip
Consumer/Medical Applications

Ray Ban Sunglass Frames

Welch Allyn Otoscope

Photo’s courtesy of Anoplate Corporation
Industrial Applications – Black chromium

Linear motion guides

Color Uniformity Wear Protection
Solar Applications – Black chromium

Black chromium absorbs and retains thermal energy

Olymco Plating
Alternatives to black chromium:

- Black Anodizing
- Black Electroless Nickel
- Vapor Phase Deposition (PVD)
- Black Powder Coat
- Black Paint
- Black Oxide
- Black Chromate on Zinc
- Moly Black Electrolytic Nickel
Summary

• The black color is more prominent today on motorcycles and automotive exterior trim
• Hexavalent black will provide the deepest black finish
• Hexavalent black will have the same OSHA exposure, operational, and environmental concerns as Hexavalent bright chromium
• New Trivalent blacks are darker and the color can be controlled with additives and filtration
• Trivalent blacks will operate similar to a watts nickel process with less environmental, health and safety concerns
Thank you!

Questions?
Sources: