Duplex Nickel and Trivalent Chromium:
Technology Update and Market Interest

Presented By: Jeff Boehmer
Columbia Chemical Company
What Drives Technology?

- Government Regulations
  - EPA / EU / OSHA
- OEM’s / Customers
- Suppliers
What Drives Technology?

Government Regulations

ELV Recycling

Environmental Stewardship

WEEE

ROHS compliant
What Drives Technology?

Environmental Protection Agency

1994 – EPA launched The Common Sense Initiative

The program set out to find “cleaner, cheaper and smarter” ways of reducing pollution and recommending changes to environmental management in six key industrial sectors, including metal finishing.

1997 – National Metal Finishing Environmental R&D Plan

Plan set priorities for pollution prevention and innovative technologies. High priorities on reducing or eliminating emissions of hexavalent chromium, cyanide, chlorinated solvents and cadmium.

Successes include biodegradable degreasers, pollution prevention and control technology for chromium electroplating, powder coating, and zero discharge........
What Drives Technology?

Environmental Protection Agency

2015 – On July 21, 2015 the U.S. Court of Appeals for the DC Circuit denied NASF’s objection, claiming that the EPA has misapplied the requirements of the Clean Air Act, and upheld the final rule.

What does this mean for Decorative Chromium Plating?

Hexavalent Chromium

• Maintain lower surface tension
• Maintain lower emission limits
• Eliminate the use of PFOS fume suppressants

Evaluate and approve Trivalent Chromium Technology
What Drives Technology?

OEM’s / Customers

- Create, support and direct U.S. cooperative research and development to advance automotive technologies.
- Be responsive to the needs of our environment and society and include the appropriate public and private stakeholders.
- Focused on developing materials and processes that enable high volume production of vehicles when compared to today’s vehicles are:
  - Half the Mass
  - As Affordable
  - More Recyclable
  - Of Equal or Better Quality and Durability
What Drives Technology?

Closer look at the ‘BIG 3’

Technology Approvals

Approval of products to help guarantee desired results

- **Pro**: OEM gains confidence that the desired results will be achieved by all suppliers, worldwide.

- **Con**: Limit metal finisher on processing choices (until more chemistries are approved)

This methodology has enlisted the help of chemical and material suppliers to aid in monitoring metal finisher’s process control. OEM’s are approving more supplier’s products and processes to add proven options, along with continued evaluation of new generation technologies.
What Drives Technology?

Suppliers

- Technological Advancements
  - Bringing the ‘next BIG thing to market’........First!
- Improvements to existing products
- Products to align with industry changes
- Price Competitive
- Create products that align with Company’s Core Values

Customers
- What are they asking for? What are they looking for?
Duplex Nickel
Technology Update

SEMI-BRIGHT NICKEL

• Increase leveling properties to reduce the workload of the Bright Nickel

• Quantitatively measure leveling for increased process control and condition of plating bath

• Improve deposit structure

BRIGHT NICKEL

• Increase leveling properties and brightness (Index baths)

• New Generation non-Index Bright nickel
  – High leveling
  – Excellent brightness
  – Superior ductility
Problem Challenge
Decorative Plating - Leveling Quantification

Nickel plating leveling was difficult to quantitate

- Hull cell panels were typically hand scratched.
- Pre-scratched panels were not consistent with surface roughness.

Outcome

- Source hull cell panels for consistent surface roughness
- Quantify surface roughness using profilometer
Semi Bright Nickel
Roughness Measurements
ASTM D7127 - 13

- Nickel plating smooths rough surfaces
- Profilometer permits documentation of roughness changes
- Surface roughness determined by average of peaks and valleys
Process for Determination of Level Package

- Identify leveler package
  - Which package is appropriate for your current density requirements

- Determine package concentration
  - More is not necessarily better

- Component formulation for greatest leveling
Effect of Current Density on Leveling

- Component formulation for optimum performance

Final Component Formulation Ratio
- Performance at 50%/50%
- Strongest throwing power
- Best roughness improvement

<table>
<thead>
<tr>
<th>Component</th>
<th>B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance at 50%/50%</td>
<td>Strongest throwing power</td>
</tr>
</tbody>
</table>
Advantage
Decorative Plating - Leveling Quantification

![Bar chart showing roughness improvement (%) at different current densities (ASF) for Product A and Product B.](image)
Advantage
Decorative Nickel Plating

Additional attributes measured during the R&D process include:

- Stress
- Ductility
- STEP
- Surface Tension
- Consumption Rates
- Overall Appearance

How can this work for me?
APPLICATION

Brightener Level-Trending

Bright Nickel Leveling Reduction Indicating Treatment

- Initial Leveling
- Leveling after 1 year

Bar chart showing roughness improvement (%). The x-axis represents current density (ASF) with values 80, 40, 20, and 8. The y-axis represents roughness improvement. The bars are colored blue and green, indicating initial leveling and leveling after 1 year, respectively.
APPLICATION

Feasibility of Treatments

Bright Nickel
Carbon Treatment

Roughness Improvement (%)

<table>
<thead>
<tr>
<th>Current Density (ASF)</th>
<th>After Carbon Treatment</th>
<th>Before Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>
Summary

• Quantitate leveling to help the customer know the leveling performance of the solution.
  – Fingerprint the bath performance.
  – Allows the customer to know quickly if they has a solution problem or substrate problem

• Utilize a measurable attribute to determine the ‘health’ of the nickel plating baths
  – Don’t have to rely on expensive equipment to determine breakdown products (HPLC, IC)

• Determine feasibility of treatments
  – What is the best treatment to increase leveling … cost effective method
COMPARISON OF DECORATIVE HEXAVALENT CHROMIUM PLATING vs TRIVALENT CHROMIUM PLATING
# REQUIREMENTS OF FINAL RULING

## LOWER EMISSION LIMITS

<table>
<thead>
<tr>
<th>Plating Process</th>
<th>New Limits</th>
<th>Previous Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decorative Chromium</td>
<td>0.007 mg/dscm</td>
<td>0.010 mg/dscm</td>
</tr>
<tr>
<td>Chromic acid Anodizing</td>
<td>0.007 mg/dscm</td>
<td>0.010 mg/dscm</td>
</tr>
<tr>
<td>Small Hard Chrome</td>
<td>0.015 mg/dscm</td>
<td>0.030 mg/dscm</td>
</tr>
<tr>
<td>Large hard Chrome</td>
<td>0.011 mg/dscm</td>
<td>0.015 mg/dscm</td>
</tr>
<tr>
<td>New Sources (All)</td>
<td>0.006 mg/dscm</td>
<td>0.015 mg/dscm</td>
</tr>
</tbody>
</table>
REALITY of REGULATIONS

Even though the EPA stated that non-PFOS-based fume suppressants demonstrated they could lower the surface tension, they have not demonstrated the ability to reduce chromium emissions.

Lower Emission Limits combined with non-PFOS-based fume suppressants may cause many installations to use HEPA filters.
How does this affect our Industry?

• Facilities must demonstrate compliance to the new emission limits and implement control/work practices as necessary.

• Existing Hexavalent chromium platers will need to upgrade their air handling equipment or switch to alternative trivalent chromium plating technologies.

• Serious interest of OEM’s and Agencies evaluating and approving Decorative Trivalent Chromium
  — Automotive, AIAG, USCAR
How can I succeed?

1) Understand the methods needed within your shop to successfully achieve the new standards, including cost impact.

2) Education in new technologies as they become available, specifically trivalent chrome plating.

3) Understanding the cost savings of operating a trivalent chromium plating bath.

4) Understanding the overall benefits of trivalent chrome plating.
# Operational Advantages

<table>
<thead>
<tr>
<th>Trivalent Chromium</th>
<th>Hexavalent Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Burning / Whitewash</td>
<td>Lower cost per amp-hr</td>
</tr>
<tr>
<td>Improved Thickness Distribution</td>
<td>Tolerant to Impurities</td>
</tr>
<tr>
<td>Tolerant to Current Interruption</td>
<td>Self Passivation</td>
</tr>
<tr>
<td>Microporous as plated</td>
<td></td>
</tr>
<tr>
<td>Improved Covering Power</td>
<td></td>
</tr>
<tr>
<td>Filming of anodes not necessary</td>
<td></td>
</tr>
<tr>
<td>No Pb in plating system</td>
<td></td>
</tr>
</tbody>
</table>
# Waste Treatment Requirements

1 gallon (3.785 Liters) of Solution

<table>
<thead>
<tr>
<th>Trivalent Chromium</th>
<th>Hexavalent Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 g/L chrome metal</td>
<td>120 g/L chromium</td>
</tr>
<tr>
<td>0.17 kg calcium hydroxide</td>
<td>1.36 kg sodium bisulfite</td>
</tr>
<tr>
<td><strong>0.43 kg solids</strong></td>
<td><strong>0.73 kg sulfuric acid</strong></td>
</tr>
<tr>
<td></td>
<td><strong>1.0 kg calcium hydroxide</strong></td>
</tr>
<tr>
<td></td>
<td><strong>2.8 kg solids</strong></td>
</tr>
</tbody>
</table>

**1 Step Processing**       **3 Step Processing**
### EHS- Environmental, Health and Safety Advantages

<table>
<thead>
<tr>
<th>Trivalent Chromium</th>
<th>Hexavalent Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non- carcinogenic</td>
<td></td>
</tr>
<tr>
<td>Anodes last indefinitely</td>
<td></td>
</tr>
<tr>
<td>No Lead compounds for disposal</td>
<td></td>
</tr>
<tr>
<td>Easy air pollution requirements</td>
<td></td>
</tr>
<tr>
<td>No Sludge (Barium Sulfate)</td>
<td></td>
</tr>
</tbody>
</table>
TriCOL DÉCOR
Color Advantage

BYK-Gardner Color/Gloss
• Measures color in metal deposits according to Lab color scale
• Determines gloss at surfaces and deposits
White Trivalent Chromium Color Evolution

- Initial Trivalent Chromium L=76
- Leading Competitor L=79.08
- TriCOL Décor L=79.43
- Hexavalent Chromium L=82.3
Influence of Formulation Components on Cr Thickness and Position

Thickness versus chromium concentration
Influence of Formulation Components on Cr Thickness and Position

Thickness versus Conductivity salt concentration
Influence of Formulation Components on Cr Thickness and Position

Wetting agents versus surface morphology
Comparison of Thickness

Hexavalent

Trivalent

Cr Depth

Current Density (ASF)

Bottom of Panel (cm)
Comparison of Thickness

Hexavalent

Trivalent
Why is Automotive looking at Trivalent chromium?
• Increased warranty claims due to use of CaCl in specific markets. (Russian Mud)

• EU End-of-Life Vehicle Directive

• 30+ years experience with exterior use in Heavy Truck market
Benefits by converting to Trivalent Chromium

- New Opportunities, including Automotive
- Reduction in Waste Water Treatment Chemistries
- Reduction in Hazardous Waste Generation
- Increased Production
- Reduced Scrap rates
- Enhanced worker safety
- Green Marketing
THANK YOU