“Greening” the Chrome Plating Industry

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Outline

• The Process
  – Hexavalent Chrome

• Environmental and Health Impact
  – OSHA, FDA, Clean Water Act

• Current State
  – Environmental Measures
  – New Processes

• Future

• Implementation
The Chrome Plating Process

• Electroplating
  – Also known as electrodeposition.

• Five Key Areas of Interest for Environmental Impact
  – Equipment
  – Preparation Process
  – Process Control
  – The Solution (Electrolyte)
  – Anodes/Cathodes

Site: www.stevesplating.com/chrome_plating.htm (Retrieved 2/24/20).
The Basics

- A part is submersed into a aqueous bath.
- An electric current is supplied to the bath.
  - Positive through anode
  - Negative through cathode
- As power is supplied through the anode to the bath, the chromic acid is oxidized.
  - The process causes a loss of 6 electrons forming Cr(+6).
- At the same time the negatively charged catalyst initiates the flow of electrons causing the Cr(+6) to move towards the cathode.
- At the cathode, the Cr(+6) goes through reduction picking up electrons till a zero valence is achieved to plate only Cr.

Image Source: Swicofil AG Textile Services
Site: http://www.swicofil.com/textile_metallization.html
Retrieved (2/26/10).
Plating Equipment

• Hold Tank or Vat
  – Contains the electrolyte solution.
  – Made from a non-soluble material. Typically a PVC liner.

• Vat Heating Equipment
  – Electric submersible heater.

• Rectifier
  – Provides a constant DC current to the bath.

• Anodes
  – The contact point with the solution provide the positive current to the bath.

• Cathodes and Fixtures
  – Often combined together to hold the part and maintain the negative connection back to the rectifier.
    • Made from non-soluble materials with contact to surface of plating part. Must have contact between the part and the rectifier. Plastic coated racks are common with a lead connection to the power source.

• Pre-Cleaning
  – Plating lines will consist of pre-cleaning solutions (detergents, acid baths) as well as chemical etching baths to provide better adhesion of chromium.
Pre-Plating Process

- Soap-Detergent
  - Used for a part cleaning or scrubbing to remove dirt contaminants.
- Acid cleaning bath
  - Commonly use a sulfuric acid bath to remove contaminants.
- Alkaline dip
  - Basic solution bath for neutralizing acid.
- De-ionized water
  - Used to remove acid and sediment after pre-plating processes.
  - Often used after pre-plating (nickel) or etching processes.
- Nickel plating (common for added brightness and shine)
  - Sometimes applied as corrosion resistant layer that adds visual appeal.
- Etching
  - Chemically etching a part provides increased adhesion of plating layer.
Process Control

- DC Rectifier
  - Maintains constant current with less than 5% current break recommended

- PH, thermal control and specific gravity are all critical to the control of a hexavalent chromium bath.
  - Use of PLC interface control common in high end plating operations.

- Automated process control improves plate thickness consistency and electrolyte solution longevity.
Electrolyte Solution

- Component (1); chromium trioxide provides the chromium or metal component of the solution usually in the form of an additive salt.
- Component (2); water is added to the bath.
- The combination of the two components forms chromic acid.
- Typical concentrations range from 20-60 oz/gal of solution.

\[(1) - CrO_3 \rightarrow \text{Chromium Trioxide}\]

\[(2) - H_2O \rightarrow \text{Water}\]

\[(3) - CrO_3 + H_2O \rightarrow H_2CrO_4\]
Component (4) is the addition of a necessary Sulfate ion that acts as a catalyst to initiate the flow of current within the bath. Usually introduced in the form of sulfuric acid.

- Typical concentration of catalyst is a 100:1 ratio with respect of weight to the chromic acid.
- Ratio is adjusted to change the plating speed and throwing power.
Electrolyte Solution (cont’d)

- Multi-catalyst baths are often used in hexavalent baths.
  - Commonly have the addition of fluoride.

- Fluoride provides better substrate activation when pre-nickel platings are present.
  - Nickel plating common for its shiny, bright appearance. Applied prior to addition of a chromium layer.

- Environmental drawbacks with use of fluoride that will be discussed later.

- Application of proprietary baths with multi-catalysts has grown do to increased plating efficiency and better adhesion.

Image Source: "Chemistry, Structures & 3D Molecules @ 3Dchem.com Site: www.3dchem.com/inorganics/SiF6_2-.jpg (Retrieved 2/24/2010)."
Anodes

- Provide DC current to oxidize the solution bath.
- Non-soluble; lead-based anodes most common.
  - 7% Tin and 6% Antimony
    - Tin corrosion resistance
    - Antimony provides stiffness
- Life typically 6 months to several years.
- Use of fluoride bath restricts the use of iron anodes. Fluoride increases the dissolving rate of iron due to chemical etching, which decreases the bath life by reducing the potential for Cr(III) to convert back to Cr(VI).
  - This is caused by a reduction or loss of cations or positive charge prior to reaching the cathode.
  - Reducing the solution to Cr(3) prior to reaching the cathode is the problem.

Anodes and Cathodes

- The first reaction present when current is applied to the electrolyte is the conversion of hexavalent chromium into trivalent chromium. This is seen in reaction (1) this reaction occurs in proximity to the anode at low current.
- The Cr(VI) is reduced to chromium metal (Cr) and applied to the workpiece at the cathode. This is seen in reaction (3).
- When this reaction (3) occurs, hydrogen gas is given off at the cathode. This is seen in reaction (2).

\[
\begin{align*}
(1) & \quad Cr^{6+} \rightarrow Cr^3 \\
(2) & \quad 2H^+ \rightarrow H_2 \\
(3) & \quad Cr^{6+} \rightarrow Cr_0
\end{align*}
\]

Anodes and Cathodes

• When current is applied to the cell; the reaction at the anode is as follows. The lead anode forms lead dioxide as oxidation occurs on the surface (brown) shown in reaction (1).

• When reaction (1) occurs, the water in the electrolyte gives off primarily oxygen and some hydrogen cations.

• Finally, Cr(III) turns back to Cr(VI) in reaction (3) at the anode.

\[
\begin{align*}
(1) \quad & Pb_0 \rightarrow PbO_2 \\
(2) \quad & 2H_2O \rightarrow O_2 + 4H^+ \\
(3) \quad & Cr^{3+} \rightarrow Cr^{6+}
\end{align*}
\]
Summary of Reactions

(1) $\text{Cr}^{3+} \rightarrow \text{Cr}^3$
(2) $2\text{H}^+ \rightarrow \text{H}_2$

Simultaneous

(1) $\text{Pb}_0 \rightarrow \text{PbO}_3$
(2) $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+$

(3) $\text{Cr}^3 \rightarrow \text{Cr}^{6+}$
(3) $\text{Cr}^{6+} \rightarrow \text{Cr}_6$
Environmental and Health

• OSHA, 2/28/06
  – Can not release dust, fumes or mists from the operation.
  – 5.0 $\mu g / m^3$
    • Maximum allowable 8 hour concentration exposure. (PEL)
    • Must take air samples during working hours.
  – Results have to be presented to employees within 15 days.

• Rinse water Disposal
  – FDA and local government guidelines for permissible concentrations that are allowed into municipal sewers.
    – Rinse water may need to be deposed at proper facilities if chromium content is not removed below allowable limits.
Pre-Plating Health and Environmental Concerns

- De-ionized water baths need to be properly managed for contaminants.
  - Treated water needs to be within limits.
- Use of filtration methods are needed for proper disposal of acid bath solutions.
  - Closed loop preferred.
  - Re-circulating filtration can be combined into larger water treatment unit for all operations.

- Nickel plating
  - Respiratory Concerns
  - Dermatitis
  - PEL
    - 0.5 mg/liter- Water
    - 0.5 mg/m^3- Air
      - Exposure to humans

- Sulfuric Acid
  - Strong evidence of carcinogens.
  - Ventilation and skin contact of the top two main concerns.
  - PEL
    - 1 mg/m^3
  - Proper disposal measures needed.
The Chemical Reactions Effects on the Environment- Chrome Plating Process

• Oxygen and Hydrogen emissions at the anode and cathode.
  – Carriers for Cr(VI) or the Chromic Acid

• Provides the need for measures to eliminate airborne particles.
  – Needs proper chemical disposal.

Airborne Reduction of Chromic Acid

- Airborne emissions need to be eliminated or filtered.
  - 1\textsuperscript{st} is a suppressant chemical.
  - 2\textsuperscript{nd} is air filtration unit
- Three types of Surfactants.
  - Foaming Agent
    - Foam catches air bubbles on surface. Visual evidence through foam and easy to control.
    - Warnings needed for possibility of Hydrogen buildup in foam.
  - Wetting Agent
    - Reduces surface tension on bath.
    - Causes smaller bubbles to burst on surface and not become airborne.
  - Polypropylene Balls
    - Float on surface preventing mist from exiting the bath.
- Both suppressants are additives to the electrolyte solution.
- Air or Wet Scrubber
  - Typically used in conjunction with surfactants.
Airborne Reduction (cont’d)

- Chromic Acid Scrubbers
  - Use three mesh pads
    - Typically a series of polypropylene irrigated pads.
  - Fourth pad typically a HEPA filter/moisture elimination barrier.
  - Recycle wastewater with recirculation pump within scrubber.
  - Wastewater created
    - 15 gal/day
    - Needs to be sent for treatment.
  - Filter life 5-10 years

Image Source: (2) Tri-Mer Corporation: Chrome Scrubbers
Current Wastewater Management Techniques

• Precipitation
  – Bring a solution to separation (leaving a solid or precipitate on the bottom of solution).
  – Secondary disposal treatment needed for the precipitate or sludge.
  – Common practice.

• Ion-exchange
  – Exchange of ions.
  – Commercially available.
  – Relatively expensive

• Reverse Osmosis (RO)
  – Expensive filters.
  – Excessive waste water during filtration method.

• Adsorption
  – Use of activated carbon or other adsorption methods.
    • Secondary chemicals necessary to increase efficiency when working with inorganic waste.
  – Secondary treatment may also be needed.
    • Relatively inexpensive.

Image Source: Carbon Resources
Site: http://www.carbonresources.com/activated-carbon-2.html
Retrieved (2/24/10).
Wastewater Management

- Closed-Loop systems are ideal.
  - Auxiliary tanks used to bring used solution up to quality, useable solution.
- Trivalent chromium turned back to hexavalent through low current electrodeposition.
- All other unusable solution treated.

Image Source: Steves Plating Corporation, "Chrome Plating" (2010).
Site: www.stevesplating.com/chrome_plating.htm (Retrieved 2/24/20).
Wastewater Treatment

• Ion Exchange Systems
  – Metal ions exchanged for hydrogen and sodium ions.
    • The resin kicks the sodium and hydrogen ions away to except the metal ions.

• In the case of Cr(VI)
  – Ionic level brought down to Cr(III) prior to ion exchange
    • Introduction of acid to the waste solution will further reduce the Cr(VI) to Cr(III)
Ionic Exchange (cont’d)

• Regenerant
  – The metal pulled out of the wastewater encapsulated into the resin.

• Regenerant Recycling Options
  – Evaporation.
  – Precipitation.
  – Electrowinning.
  – Disposing to secondary recycling facilities.

• Electrowinning
  – Plating the removed metal onto cathode plates for disposal.

• Further DI/RO (De-Ionized/Reverse Osmosis) treatments may be needed for municipal sewer return to reach proper TDS (total dissolved solids) levels.

• Also ppm levels need to be achieved (Cr).
Future Remediation Processes

• Photocatalytic
  – The use of photocatalysts have grown in the air filtration industry.
    • Other industries draw to the possibilities.

• Biofiltration
Photocatalysis

- Use of $TiO_2$ with citric acid creates electron-hole pairs that generate free radicals.
- The free radicals breakdown the metal ions and release by-products in return (carbon dioxide and water).
Biofiltration

- Removal of heavy metals using bacteria, algae, yeast and fungi.
  - Dead or alive in some instances.
- Current investigation is high in area of biofiltration due to the economic benefits and sustainability.
  - Current methods of filtration are very expensive with questionable sustainability.

Image Source: University of Arizona- Department of Agriculture
Site: http://ag.arizona.edu/azaqua/extension/Classroom/Filtrationpage.htm
Retrieved (2/26/10).
Future Processes

- Trivalent chromium
- HVOF spray coatings
- PVD coatings

Site: www.stellite.co.uk/tabid/76/Default.aspx (Retrieved 2/24/10).

Site: http://www.pvd-coatings.co.uk/coating-machine.htm (Retrieved 2/24/10).
Trivalent Chromium

- Trivalent chromium has been used for many years in the decorative industry.
- Major hurdle has been the ability to increase the plating thickness while still maintaining the bath sustainability.

- A few companies have developed proprietary solutions with the incorporation of ligands and complexants to increase the sustainability.
  - Still has not been widely proven to eliminate the neutralization of the bath which inhibits the baths production sustainability.
HVOF Coatings

• High Velocity Oxy-Fuel (HVOF)
  – High pressure, dry coating using the combustion of a fuel (hydrogen, butane, etc.).
  – Powder is deposited at high pressure and velocity in melted form.
    • Aerospace and DoD are investigating the use of HVOF, heavily.

• The coating has promising end-of-life removal potential.
  – The electrolytic removal method is chemically benign.

Image Source: University of Toronto, Center for Advanced Coating Technologies (2010).
PVD Coatings

• Uses a physical process of evaporation or vaporization of a material.
  – Carried out under a vacuum condition.
  – Solid material is bombarded with high energy.
  • This energy vaporizes the material on the atomic level.
• The vaporized coating is transported and may entail a series of reactions onto the workpiece surface.
  – Deposition occurs to the workpiece
• Coatings are currently developed to be as hard as chrome. Some including chromium for a similar visual appeal.
  – Process is expensive.
Implementation

• Assessment of partners current operations.
  – Create an outline of areas to investigate.

• Review available technology for implementation to their operations.
  – Trivalent chrome process
  – Ion exchange
  – Suppressant solutions
  – HVOF

• Assess Application
  – Do new technologies fit with Ottawa’s product line?
  – Cost effective.

• Work collaboratively with partner to develop a plan of action.

• Start conducting cost analysis breakdowns vs. environmental benefits.
  – Provide implementation plans to partner for evaluation.

• Implement small scale studies/research if applicable.
  – Possibilities include:
    • Biofiltration
    • Photocatalytics
    • Ion-Exchange, etc.

• Energy Analysis of Operations
Thank You

• Questions?