Metal Finishing Process

Barrel method electroplating
Metal Finishing Objectives

- List key chemicals associated with metal finishing
- Describe basic metal finishing processes
- Describe electroplating process details
- List major modes of release to the environment
- Identify analytical methods useful for detecting metal finishing contaminants in the environment
Process Overview

- Billion of dollars per year
- Tens of thousands of businesses
- Both large and small businesses, from steel rolling mills and automotive manufacturing to "mom and pop" job shops

Zinc-plated screws “galvanized”

Gold-plated jewelry clasps
Process Overview

- Metal surface preparation
- Surface protection and / or decoration
- Focus on electroplating
  (Barrel method)
Metal Finishing Process Video
Metal Finishing Process Video
## Key Chemicals

### Solvents
- Benzene
- TCE
- etc.

### Coatings
- Cadmium
- Chromium
- Cyanide
- etc.

### Acids and Bases
- HCL
- Caustic
## Key Chemicals

<table>
<thead>
<tr>
<th>Solvents</th>
<th>2005 ATSDR Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>6</td>
</tr>
<tr>
<td>TCE</td>
<td>16</td>
</tr>
<tr>
<td>etc.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coatings</th>
<th>2005ATSDR Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>8</td>
</tr>
<tr>
<td>Chromium</td>
<td>18, 77</td>
</tr>
<tr>
<td>Cyanide</td>
<td>28</td>
</tr>
<tr>
<td>etc.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acids and Bases</th>
<th>2005 ATSDR Rank</th>
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<tbody>
<tr>
<td>HCL</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Caustic</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>
Specialty Electronic Parts - Rack Method

Cu, In, Ga, Se sequentially electroplated onto solar panels
Standard Process Schematic

UNFINISHED METAL PRODUCTS

CYANIDE, METAL SALTS, SOLVENTS, BASES, ACIDS

NEUTRALIZED SALTS, METALS, SOLVENTS, EMULSIONS

SOLVENT VAPORS

FINISHED METAL

RECYCLED SOLVENTS

METAL SLUDGE, SCALE
Process Details - Metal Surface Preparation

• Physical modification
  – De-scale, cut, shape, smooth

• Surface oil removal
  – Wipe, dip, vapor degrease

• Final cleaning
  – Detergent, acid, base, anodic, cathodic, ultrasonic
TYPICAL VAPOR DEGREASER

- Condensing coils and cooling jacket
- Solvent level
- Vapor line
- Freeboard
- Boiling solvent
- Heaters
Process Details – Cleaning / Degreasing

Solvents that are most used:

- Trichloroethylene
- 1,1,1-Trichloroethane
- Methylene chloride
- Tetrachloroethylene (Perchloroethylene)
<table>
<thead>
<tr>
<th>Organic coatings</th>
<th>Inorganic / metal coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent based</td>
<td>Physical deposition</td>
</tr>
<tr>
<td>Water based</td>
<td>Chemical deposition</td>
</tr>
<tr>
<td>100% solids</td>
<td>Electrochemical methods</td>
</tr>
</tbody>
</table>
Process Details – Chemical Conversion Coating

- Conditions surface for painting or coating

- Uses chromates, phosphates, phosphoric acid, and hexavalent chromium
• Electrochemical process

• Converts surface metal to insoluble oxide

• Uses chromic, sulfuric, or boric acids

Chromic Acid  Anodizing vat
Process Details - Electroplating Process

- Electrochemical process
- Acid, alkaline, or neutral pH
- Uses metal salts, cyanides, brighteners, solid metal anodes
  - Cyanides keep metal ions in solution
  - Brighteners make surface more reflective

Fiber drums of ZnCN concentrate in abandoned plating shop
Process Details - Electroplating Process

Source: adapted from EPA 1995

Waste water Discharge
Process Details - Electroplating Process

Source: adapted from EPA 1995
Plating vat for Chrome Plating
## Process Details - Common Electroplating Bath Compositions

<table>
<thead>
<tr>
<th>Bath Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass and bronze</td>
<td>Copper cyanide, zinc cyanide, sodium cyanide, sodium carbonate, ammonia, Rochelle salt</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromic acid, sulfuric acid</td>
</tr>
<tr>
<td>Cadmium cyanide</td>
<td>Cadmium cyanide, cadmium oxide, sodium cyanide, sodium hydroxide</td>
</tr>
<tr>
<td>Cadmium fluoroborate</td>
<td>Cadmium fluoroborate, fluoroboric acid, boric acid, ammonium fluoroborate, licorice</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn metal, sodium hydroxide, sodium cyanide (some non-CN baths too)</td>
</tr>
</tbody>
</table>

Source: EPA 1990
Modes of Release

- Air emissions
  - Solvent vapors
  - Acid mists

- Water releases
  - Rinse water
  - Spent plating bath treatment
  - Washdown liquids
Metal Finishing Process Video
Modes of Release

- Soil
  - Washdown liquids
  - Solvent spills

- Groundwater
  - Hexavalent chromium (more mobile)
  - Chlorinated solvents (DNAPL)
Modes of Release

• Solid and hazardous wastes
  – TCLP metals (D006, D007, etc.)
  – Wastewater (F006)
  – Spent plating baths (F007, F008, F009)
  – Quenching baths, etc. (F010, F012, F019)
Analytical Considerations

• Laboratory methods
  – Metals: AA, ICP
  – Solvents: GC/MS

• Field analytical methods
  – Hazard Categorization
  – Metals: XRF
  – Solvents: Portable GC, Portable GC/MS
  – CN gas: Real time instruments, Draeger
Summary

• Mostly small businesses with limited environmental control programs

• Use a wide variety of chemicals:
  – Organic solvents
  – Metals, metal salts, and cyanide
  – Corrosives

• Metal finishing wastes can affect all four media: soil, surface water and sediment, air, and groundwater