Typical DC Acid Copper Electroplating Solution contains:

**Inorganic**
- Sulfuric Acid (180 - 250 g/l)
- Copper Sulfate (40 - 100 g/l)
- Hydrochloric Acid (25 - 100 mg/l)

**Organic**
- Brightener (2 - 10 mls/l)
- Leveler (5 - 15 mls/l)
- Carrier (25 - 100 mls/l)

**Water (Balance)**
Electrolyte Control

Sulfuric Acid – Virtually unconsumed...Dragout
  ➢ Titration or Specific Gravity

Copper Sulfate – Maintained by Anode Erosion
  ➢ Titration, UV/Vis

Chloride – Maintained by chemical analysis
  ➢ Titration, Ion Specific Electrode, UV/Vis
Additives – Mostly Proprietary

**Brighteners** – are plating accelerators, which act as a micro-leveler and impact grain refinement. They tend to be attracted to cathode induction zone points of higher electro-potential, temporarily packing the area and forcing copper to deposit elsewhere. As the copper deposit levels, the local point of high potential disappears and the brightener drifts away, as well as depleting (hydrolysis) to a higher level of activity.

Chemical Family - Organic Sulfides, Disulfides, Thioethers, Thiocarbamates.

**Levelers** – are strong secondary plating inhibitors, which typically co-function with Brighteners to reduce copper growth at protrusions and edges. They improve mass transfer to localized sites of lesser electro-potential or feature height.

Chemical Family – Quaternary Nitrogen Cmpd.

**Carriers** – are plating inhibitors or suppressors, they create and maintain a defined diffusion layer at the Anode (which regulate the flow of Cu+2 ions into the electrolyte and ultimately to the cathode (board surface). Carrier depletion occurs as the PEG cleaves.

Chemical Family – Polyethylene Glycol (PEG), Polyalkylene Glycol (PAG)

**Chlorides** – mild plating inhibitors, which stabilizes the Cu+1 ion that serves as an intermediate in the electro-deposition process during reduction to Cu +2. Additionally they modify adsorption properties of carrier to influence thickness distribution.

Chemical Family – Hydrochloric Acid
Hull Cell – Additive Control

- **Carbon Treated Copper Bath**
- **ASF 75, Needs Brightener**
- **ASF 90, Proper Operating Range**
CVS/CPVS – Cyclic (Pulse) Voltammetry Stripping

CVS/CPVS is an indirect bath measurement which measures the “combined” effect of the additives and by-products on the plating quality.
CVS and CPVS Instrumentation
Copper Anodes

Phosphorized: 150 – 650 ppm P
Oxygen Free Casting

Grain structure grows from surface
to the center, resulting in uniform
corrosion of the anode.

Anodes are “conditioned” when new
by developing a necessary black
CuO film – Dummying.

Balls, Nuggets, Bars.

Anode surface area and continuous bath agitation is critical.

Typical Chemical Analysis

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration, Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.0002</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.0001</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.0002</td>
</tr>
<tr>
<td>Iron</td>
<td>0.0004</td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt;0.0010</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.0001</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.0002</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.0010</td>
</tr>
<tr>
<td>Tin</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
Pattern Plating

1) Full panel Electroless Copper deposition.
2) Photoresist apply, expose with positive image artwork - majority of copper surface shielded, develop.
   a) Reduced electroplated surface.
   b) Lower current capacity required.
   c) Less copper anode bank consumption.
   d) Less copper in etchant.
3) Plate Copper, Plate Tin (Etch Resist)
   a) Adds several additional wet process baths.
4) Strip Photoresist – Potassium Carbonate
5) Etch Copper – Ammoniacal
6) Strip Tin Resist – Nitric Acid
7) Antioxidant - BTA
Panel Plating

1) Full panel Electroless Copper deposition.
2) Full panel Electrolytic Copper plated.
   a) Higher current capacity required.
   b) Significant copper anode bank erosion.
   c) Smooth, even, bright finish on panel and hole walls.
   d) Easily cleaned/prep’d for downstream processing.
3) Photoresist apply – Negative Image
4) Develop - Carbonate
5) Etch – Ammoniacal or Cupric Chloride
   a) Significant copper buildup in etch, more maintenance.
6) Strip – Potassium Hydroxide
7) Antioxidant - BTA
Contaminants – Drag in / Leach Out

Inorganics – ICP / GFAA analysis Trace Metals
- Iron (Fe)
- Calcium (Ca)
- Tin (Sn)
- Lead (Pb)
- Nickel (Ni)
- Antimony (Sb)

Organics – Hull Cell / CVS / TOC
- Cleaner/Predip surfactants (inactive)
- Resist Photo-initiators (inactive)
- Anode Bag Sizing (inactive)
- Additive breakdown products / fragmentation (active)
# Chemistry Impact / FMEA

<table>
<thead>
<tr>
<th>Defect / Failure Mode</th>
<th>Inorganic</th>
<th>Organic</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CuSO4</td>
<td>H2SO4</td>
</tr>
<tr>
<td>Burned Copper Deposit</td>
<td>Low</td>
<td>Low / High</td>
</tr>
<tr>
<td>Poor Throwing Power</td>
<td>High</td>
<td>Low</td>
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<tr>
<td>Poor Leveling</td>
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<tr>
<td>Roughness</td>
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<tr>
<td>Streaking</td>
<td></td>
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<tr>
<td>Poor response to additives</td>
<td>High</td>
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<tr>
<td>Step Plating</td>
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<tr>
<td>Grain Structure Poor</td>
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<td>Low</td>
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<tr>
<td>Anode Color Green</td>
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<tr>
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<td>Mechanical / Electrical</td>
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- Contaminant & Process Impact / FMEA

- High / Low / Filtration

- Low / High
Burnt Plating – Unbalanced CD / ASF
Even After Microetch
Plating Characteristics Impact Etch Differential
Topography Differential – SEM/BSE
Copper Topography Variations (80x)

- Burnt Copper Plating
- Transitional
- Detectable
- Bright / Leveled
Spiked Copper – Surface / Knee

Courtesy Sanmina-SCI, Owego
Spiked Copper – Hole Wall

Courtesy Sanmina-SCI, Owego
Grain Structure Failure – Blind Via

Courtesy Sanmina-SCI, Owego
Copper Chicklets – Grain Structure

Courtesy Sanmina-SCI, Owego
Cobblestones – Hole Wall

Courtesy Sanmina-SCI, Owego
Cobblestones – Hole Wall

Courtesy Sanmina-SCI, Owego
Surface Nodule – Process Debris

Courtesy Sanmina-SCI, Owego
Surface Nodule - Debris

Courtesy Sanmina-SCI, Owego
Barrel Crack / Lam Voids – 6x TS
Summary: Surface Contaminant Evaluation

Macro Level: PCB fabricator - SPC, IPC TM’s and spec’s, customer requirements, cleanliness, water quality, post process residues, solderability, visual inspection.

Micro Level: Post fab evaluations employing FTIR, Raman Spectroscopy, HPLC, SEM - EDS/Auger, IC, ICP/GFAA.

What to look for:
- Process residues (MOP, Resist Remnants, HW Salts, OSP)?
- Co-plated contaminants (inorganic / organic)?
- Hydrides, Oxides, Sulfides, Carbides, Halides?
- Gas entrapment?

What’s changed the most:
- Etch Resists (Sn vs Sn/Pb) and strip chemistry?
- High Temp OSP’s?
- DC or Pulse (Reverse and Duplex) Plating and chemistry – High aspect ratio?