Copper is the most common metal plated, exclusive of continuous strip plating and nickel [1]. The major uses of electroplated copper are plating on plastics, printed wiring boards, zinc die castings, automotive bumpers, rotogravure rolls, electrorefining, and electroforming [2]. Electroplated copper is playing a major role in the change from aluminum to copper in semiconductor interconnect technology. This materials change was heralded as a “major breakthrough” in *The New York Times* (September 22, 1997) and a “dazzling technical advance” by *Time* magazine (October 10, 1997) [2a]. It signals one of the most important changes in materials that the semiconductor industry has experienced since its creation [2b]. Copper is electrodeposited for numerous engineering and decorative applications requiring a wide range of mechanical and physical properties. The range extends from properties superior to full-hard wrought copper to properties equivalent to annealed pure copper [3].

Copper is an excellent choice for an underplate, since it often covers minor imperfections in the base metal. It is relatively inert in most plating solutions of other common metals; it has a very high plating efficiency, resulting in excellent coverage even on difficult-to-plate parts; and lastly, it is highly conductive, making it an excellent coating for printed wiring boards or as a coating on steel wire used to conduct electricity [1].

Copper deposits also act as thermal expansion barriers by absorbing the stress produced when metals with different thermal expansion coefficients undergo temperature changes, and this is particularly helpful with plastic substrates. The leveling and brightness properties of copper deposits can be further enhanced by buffing, and since copper is much softer than steel or nickel, it is easy and relatively inexpensive to buff [4].

Of the plating systems that have been studied, only relatively few have revealed a stage of commercial importance for electrodeposition of copper. These are the alkaline cyanide and pyrophosphate complex ion systems and the acid sulfate and fluoborate simple ion systems. Other types of solutions have been too unstable or lacking in good deposit characteristics over sufficiently wide current density ranges [5]. In recent years some alkaline noncyanide systems have been developed for replacing cyanide.

The areas of application of the various copper plating solutions overlap somewhat, but each has its fairly well-defined area of usefulness. Clearly, the most heavily used are the acid copper sulfate solutions. Open literature publications and patents for sulfate solutions since the 1974 edition of this book in [6] far outnumber those of all the other solutions combined. Deposits produced in cyanide solutions are typically thin (<12.5 µm) and are used as an undercoating for nickel and chromium, as a heat treatment slop-off for selective hardening of ferrous parts, or as an intermediate step prior to additional plating. For example, a copper cyanide deposit is typically a key part of the activation cycle for preparing aluminum, beryllium, and zinc die castings for plating.

Copper deposits from cyanide solutions are not generally suitable for deposition of relatively thick deposits for electroforming and similar applications. Cyanide solutions are finding less and less favor because of their toxicity and waste treatment problems and are being replaced by noncyanide solutions. Pyrophosphate solutions, once used heavily for plating through holes on printed wiring boards, have been almost completely replaced by high-throw acid sulfate solutions. Fluoborate solutions have been advertised for many years as having the capability to deposit copper at very high

---

1 Dexter D. Snyder, Part F.
current densities. However, present commercial usage of this type of solution is minimal simply because other solutions such as those with sulfate ions can do the same job and are less expensive, easier to control, and less susceptible to impurities. The chemical cost of acid fluoroborate electrolyte is approximately twice that of acid sulfate per gallon, which is one strong reason why fluoroborate copper has not gained a significant share of the through-hole plating market [7]. Continuous copper plating from fluoroborate solutions on electroless coated plastic circuits has been reported [8].

**PART A  ACID COPPER**

**2.1 HISTORY AND DEVELOPMENT**

Acid copper deposition was referred to as early as 1810 [9]. In 1831 Bessemer [10] copper plated steel castings of frogs, insects, and plants by immersion in copper sulfate solution on a zinc tray. In 1836 the Daniel cell was first used for electrodepositing copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12]. In 1839 Jacobi made Russian electrodeposition of copper [11] and a technical report was published by De la Rue [12].

In the next 70 years, progress was directed principally toward developing specific applications for acid copper electrodeposition. Most of the efforts dealt with Cu²⁺ sulfate–sulfuric acid solutions, but oxalate [14], nitrate [15], acetate [15], fluosilicate [16, 17], and Cu⁺⁺ chloride [16] solutions were also investigated.

In more recent times the following solutions have been evaluated: sulfate–oxalate–boric acid [18], sulfate–oxalate [19, 20], Cu⁺⁺ chloride [21], Cu⁺⁺ chloride–sodium thiosulfate [22], benzene disulfonic acid [23], Cu⁺⁺ iodide and bromide [24], iodide and chloride [25], fluoborate [26, 27], alkane sulfonic acid [28, 29], sulfamic acid [30, 31], Cu²⁺ formate with ammonium salts [32], phosphate–sulfate [33], fluosilicate [34], fluosilicate–silicic acid [35], Cu⁺⁺ glycolate, lactate, malate, and tartrate [36].

At the present time only the sulfate and fluoroborate solutions are commercially used. Passal reviewed the first 50 years of AES (American Electroplaters' Society) copper plating history in 1959 [5] and Van Tilburg covered the 75-year history in 1984 [11]. Other reviews of acid copper plating can be found in the literature [6, 37–41].

**2.2 APPLICATIONS**

Electrodeposition of copper from acid solutions is extensively used for electroforming, electrorefining, and electroplating. Refiners and electroformers, in particular, employ acid solutions because costs of chemicals and power are low and because the solutions are simple and easy to control. In the electrowinning and electrorefining industries, acid solutions are employed exclusively. More than 80% of the domestic production of primary copper is refined electrolytically.

Acid copper sulfate solutions are widely used for plating of printed wiring boards and for semiconductor interconnect technology. Electroformed copper articles include band instruments, heat exchangers, reflectors, and a variety of articles for military and aerospace applications. All three main types of printing processes (electrotyping, rotogravure work, and lithography) use copper and sometimes nickel and chromium [42].

Acid copper solutions containing organic brightening and leveling agents are used extensively to deposit smooth copper on rough steel and etched plastics. Zinc die castings are plated with approximately 15 μm of leveling acid copper [43, 44], before nickel and chromium plating, to eliminate buffing before plating. Because of the excellent microthrowing power of the acid copper, pits, pores, or crevices in either steel or zinc surfaces are well filled with copper, and this improves resistance to corrosion or blistering [45–47]. Acid copper deposits are one part of the sequence for decorative plating of aluminum wheels for automotive applications. In some cases the copper is buffed to add luster to the low-current-density areas of the wheel and to flow some of the copper over small pits and voids [48]. Coatings on plastics need to be bright and ductile and have the capability to expand and contract with the thermal expansion of the plastic without cracking, blistering, or peeling. Bright decorative acid copper deposits meet these requirements [4, 49].

One of the most important steps in the production of plated wire for memory use is copper plating in acid sulfate solution [50]. Many kilometers of steel wire are given a copper cyanide strike and plated with copper in acid solutions to produce a high-strength electrical cable. Thick deposits (200 μm) of copper are applied to steel rolls and then engraved for use in printing and marking papers and textiles. Stainless steel cooking vessels are copper plated in acid solutions to improve the heat diffusion characteristics of outer surfaces and avoid local hot spots. Copper plating for stopping off carburizing on selected areas is accomplished by striking in a cyanide solution followed by plating in acid solutions. Acid copper plating is sometimes used for building up worn or overmachined parts, especially when copper surfaces are desired for protection against fretting corrosion. Optical surfaces can be produced on parts by single-point diamond turning specific acid copper deposits [51–54].

Metal powders produced by deposition in acid solutions are used for making sintered compacts and pigments. The powder is deposited from dilute solutions at high temperatures, brushed off the cathodes, filtered, washed, ground into fine particles, screened, and blended for use in manufacturing.
powder compacts [55, 56]. Copper sulfate solutions have also been recommended for plating “low-density” powder compacts to fill porosity near the surface [57].

2.3 PRINCIPLES

The Cu$^{2+}$ salts in either the sulfate or the fluoborate solution are highly ionized except for small amounts of less ionized complex salts formed with certain addition agents. The addition of sulfuric acid to the sulfate solution, or fluoboric acid to the fluoborate solution, is necessary for obtaining acceptable deposits. Because of the high conductivity of commercial solutions and because anode and cathode polarizations are small, voltages required for depositing copper are less for acid than for alkaline solutions. Electrorefining plants employ the copper sulfate solution largely for this reason. Tank voltages for refining copper are frequently as low as 0.2 V for a cathode and anode current density of 1.6–2.2 A dm$^{-2}$.

Anode and cathode polarizations are nearly negligible in purified solutions used at low current densities. Even at the high cathode current density of 21.5 A dm$^{-2}$, a 6-V current source is ample when the solution is efficiently agitated. Excessive polarization of the anodes in the sulfate solution may occur when the anode current density exceeds about 5 A dm$^{-2}$. With the fluoborate solution, the anode current density can be at least 40 A dm$^{-2}$ without encountering excessive anode polarization. Anode and cathode efficiencies are nearly 100% at all practical current densities. The rate of deposition obtainable depends chiefly on the efficiency of agitation in preventing excessive polarization. Acceptable deposits were reported at a current density as high as 260 A dm$^{-2}$, equivalent to 3.63 mm h$^{-1}$ [58], with violent agitation.

The first stages of the formation of a copper deposit depend on the deposition rate, the substrate surface nature, and the deposition technique [59]. The final stage in the growth involves an equilibrium of copper electrochemically dissolving and precipitating [60]. The character of copper deposits is influenced by the concentrations of copper salts, additives, free acid, temperature, cathode current density, and the nature and degree of agitation. At potentials between −60 and −30 mV, the growth of bulk copper proceeds in cycles of nucleation, agglomeration, and crystallization.

The concentration profile of copper in an acid electrolyte has been measured in an attempt to understand the effects of the supporting electrolyte on the rate of mass transfer of Cu$^{2+}$ ion toward the cathode surface [61]. Overpotential relaxation experiments have shown that calculated mass-transfer boundary layer thicknesses increased with increasing electrode length and solution viscosity and decreased with increasing current density [62]. Impedance behavior of a copper cathode in an acid copper electrolyte has also been studied [63].

2.4 FUNCTIONS OF SOLUTION CONSTITUENTS

2.4.1 Copper and Sulfuric Acid

Cu$^{2+}$ sulfate ($\text{CuSO}_4\cdot5\text{H}_2\text{O}$) and sulfuric acid, or Cu$^{2+}$ fluoborate ($\text{Cu(BF}_4)_2$) and fluoboric acid, are the primary constituents of the sulfate and fluoborate solutions, respectively. The copper salts furnish the metal ions in solutions such as those given in Table 2.1, which contains formulations for conventional and high-throw solutions. The latter are used for plating printed wiring boards and are discussed in detail in a subsequent section. Copper can be deposited at very low cathode current densities from the acid-free aqueous solutions of the salts [64, 65], but at higher current densities the deposits from the sulfate solution are spongy and contain occluded salts. Plate characteristics are improved, solution conductivity is increased, and anode and cathode polarizations are greatly reduced when free acid is added to either solution [26, 66]. The acid also prevents the precipitation of basic salts.

The concentration of copper sulfate is not particularly critical, although the resistivity of the solution is greater when the concentration is increased [67]. Cathode polarization increases slightly at copper sulfate concentrations above 1M (250 g L$^{-1}$) [68]. A concentration of less than 60 g L$^{-1}$ copper sulfate results in a decreased cathode efficiency [69]. Changes in the concentration of copper sulfate have little

<table>
<thead>
<tr>
<th>TABLE 2.1 Formulations of Acid Copper Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Sulfate Solutions</td>
</tr>
<tr>
<td>Conventional Solutions</td>
</tr>
<tr>
<td>High-Throw Solutions</td>
</tr>
<tr>
<td>Copper sulfate, $\text{CuSO}_4\cdot5\text{H}_2\text{O}$, g L$^{-1}$</td>
</tr>
<tr>
<td>Sulfuric acid, $\text{H}_2\text{SO}_4$, g L$^{-1}$</td>
</tr>
<tr>
<td>Chloride, mg L$^{-1}$</td>
</tr>
<tr>
<td>Copper Fluoborate Solutions</td>
</tr>
<tr>
<td>Low-Concentration Solutions</td>
</tr>
<tr>
<td>High-Concentration Solutions</td>
</tr>
<tr>
<td>Copper fluoborate, $\text{Cu(BF}_4)_2$, g L$^{-1}$</td>
</tr>
<tr>
<td>Fluoboric acid, $\text{HBF}_4$, g L$^{-1}$</td>
</tr>
<tr>
<td>Boric acid, $\text{H}_3\text{BO}_3$, g L$^{-1}$</td>
</tr>
</tbody>
</table>
effect on grain size, but some grain refinement occurs as a result of increasing the sulfuric acid concentration to 1.5 \( N \) (72 g L\(^{-1}\)) [70]. When very high cathode current densities are used, a high concentration of copper sulfate, within the limits given in Table 2.1, is recommended. The solubility of copper sulfate is decreased when the sulfuric acid concentration is increased [66].

Changes in sulfuric acid concentration have more influence than changes in copper sulfate concentration on anode and cathode polarization and on solution conductivity. Cathode polarization decreases when a small amount of sulfuric acid is added to a solution of copper sulfate, reaches a minimum at about 0.4 \( M \) (38 g L\(^{-1}\)), and increases with a further increase in sulfuric acid concentration [68]. Throwing power increases dramatically in low-copper (15 g L\(^{-1}\)), high-sulfuric-acid solutions [71]. Excess sulfuric acid drastically increases the cathodic overpotential and introduces a smaller ratio of level plane of electrodeposits resulting in nodular precipitates [72]. It also drastically changes the X-ray diffraction pattern by increasing the surface overpotential and inducing three-dimensional nucleation at the higher overpotential [73]. Specific conductivity is nearly doubled when the concentration of sulfuric acid is raised from 50 to 100 g L\(^{-1}\) [74]. An additional increase in free-acid concentration to 200 g L\(^{-1}\), which is the level widely used in electrorefining, reduces the resistivity from 4.2–4.3 to 1.6–1.9 \( \mu \)Ω-cm [75].

2.4.2 Chloride

The chloride ion, in bright and high-throw acid sulfate solutions, reduces anode polarization [76] and eliminates striated deposits in high-current-density areas [40]. It is important to control the chloride ion at 60–80 ppm. Below 30 ppm, deposits will be dull, striated, coarse, and step plated. Above 120 ppm, deposits will be coarse grained and dull, and the anodes will polarize, causing plating to stop [41]. The chloride ion affects the surface appearance, structure, microhardness, crystallographic orientation, and internal stress of the deposits [77–79]. A minimal amount of chloride was essential to the ductility of deposits from two different proprietary copper plating solutions. The elongation in each case was found to rise dramatically for chloride additions in the 10-mg L\(^{-1}\) range [80].

Among the halides, Cl\(^{-}\) is the most effective over a wide range of concentrations (40–150 mg L\(^{-1}\)) in keeping stress to a null value, and this is particularly important considering the synergistic effect of Cl\(^{-}\) over some brightening additives normally used [81]. The presence of about 50 mg L\(^{-1}\) chloride is optimum for permitting an increase in microhardness without raising internal stress [82]. The chloride ion exerts no influence on throwing power [82, 83].

In the presence of Cl\(^{-}\) and additives, such as thiourea or a commercial proprietary brightener, it is suggested that in addition to CuCl surface films adsorbed Cu(I) or Cu(I) complex–Cl\(^{-}\) bridge films inhibit surface diffusion of adsorbed Cu atoms, and this becomes the rate-determining step in the deposition mechanism [84–86]. With solutions containing polyethylene glycols (PEGs), the absence or reduced quantities of chloride alters the suppression effect of PEG, adversely affecting deposit morphology. In the presence of chloride, PEG fractions inhibited currents much more strongly than in the presence of PEG alone [87].

Small amounts of chloride ion are known to have an accelerating effect on the deposition of copper. This supports the hypothesis that chloride ions act as binding sites for surfactants such as PEG to the electrode surface [88–90]. Excess chloride can produce insoluble copper chlorides at the anode surface, hindering the deposition process [91]. Although chloride ion is adsorbed on depositing copper, up to 10\(^{-3}\) M chloride ion has little effect on the current–voltage curve for acid sulfate solutions containing no brighteners or additives [92].

2.4.3 Fluoborate

Copper fluoborate is more soluble than copper sulfate. Metal ion concentration can be more than double in the fluoborate solution in comparison with a copper sulfate solution containing 50–75 g L\(^{-1}\) of sulfuric acid. If the acid concentration in the fluoborate solution is too low (pH more than 1.7), deposits are dull, dark, and brittle. Boric acid is added to stabilize the solution and prevent decomposition of copper fluoborate; this increases resistivity slightly. In a solution with a concentration of more than 15 g L\(^{-1}\) fluoboric acid or 220 g L\(^{-1}\) copper fluoborate, an increase in the concentration of either the salt or the acid lowers the resistivity.

2.5 ADDITION AGENTS

Addition agents for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density, and reducing trees are frequently added to acid copper sulfate solutions. An extensive list of additives used in acid copper plating prior to 1959 can be found in the literature [5] and in the acid copper chapter in a previous edition of this book [6]. Additives covered in patents granted in recent years are listed in Table 2.2. Materials that have been reported in recent technical literature publications include benzotriazole [84, 85, 93, 94], cadmium [95], casein [96], cobalt [97], dextrin [96], dimethylamino derivatives [98], disulfides [98, 99], 1,8-disulfonic acid [93], disodic 3,3-dithiobispropanesulfonate [100], 4,5-dithiaoctane-1,8 disulfonic acid [93], dithiothreitol [101], ethylene oxide [100], gelatin [102], glue [76, 96], gulac [76], lactose benzoylhydrazide [103], 2-mercaptoethanol [104], molasses [96], sulfonated petroleum [76], o-phenanthroline [95, 105], polyethylene...
### TABLE 2.2 Additives That Have Been Patented for Copper Plating

<table>
<thead>
<tr>
<th>Patent Reference</th>
<th>Date of Issue</th>
<th>Investigator</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.5,433,840</td>
<td>7/18/95</td>
<td>Dahms et al.</td>
<td>Polyalkylene glycol</td>
</tr>
<tr>
<td>U.S.5,417,841</td>
<td>5/23/95</td>
<td>Frisby</td>
<td>Alkoxithio and sulfonated compounds</td>
</tr>
<tr>
<td>U.S.5,328,589</td>
<td>7/12/94</td>
<td>Martin</td>
<td>Polymers comprising ether groups</td>
</tr>
<tr>
<td>U.S.5,252,196</td>
<td>10/12/93</td>
<td>Sonnenberg et al.</td>
<td>Numerous additives</td>
</tr>
<tr>
<td>U.S.5,174,886</td>
<td>12/29/92</td>
<td>King et al.</td>
<td>Polyalkylene glycols</td>
</tr>
<tr>
<td>U.S.5,151,170</td>
<td>8/29/92</td>
<td>Montgomery et al.</td>
<td>Peroxide oxidation; product of a dialkylaminothioxomethylthioalkane sulfonic acid</td>
</tr>
<tr>
<td>U.S.5,145,572</td>
<td>8/8/92</td>
<td>Hupe et al.</td>
<td>Hydroquinone or ethoxylated alkylenphols</td>
</tr>
<tr>
<td>U.S.5,068,013</td>
<td>11/26/91</td>
<td>Bernards et al.</td>
<td>Polyethylene oxides</td>
</tr>
<tr>
<td>U.S.5,051,154</td>
<td>9/24/91</td>
<td>Bernards et al.</td>
<td>Polyethylene oxides, glycols, and amines</td>
</tr>
<tr>
<td>U.S.5,024,736</td>
<td>6/18/91</td>
<td>Clauss et al.</td>
<td>Disubstituted ethane sulfonic compounds</td>
</tr>
<tr>
<td>U.S.4,990,224</td>
<td>2/5/91</td>
<td>Mahmoud</td>
<td>Urea, sodium lauryl sulfate, and tosyl or mesyl sulfonic acid</td>
</tr>
<tr>
<td>U.S.4,975,159</td>
<td>12/4/90</td>
<td>Dahms</td>
<td>Alkoxylated lactam amides</td>
</tr>
<tr>
<td>U.S.4,954,226</td>
<td>9/4/90</td>
<td>Mahmoud</td>
<td>Urea and glycerin</td>
</tr>
<tr>
<td>U.S.4,948,474</td>
<td>8/14/90</td>
<td>Miljkovic</td>
<td>Alkylarylene</td>
</tr>
<tr>
<td>U.S.4,897,165</td>
<td>1/30/90</td>
<td>Bernards et al.</td>
<td>Copper/sulfuric acid ratios</td>
</tr>
<tr>
<td>U.S.4,781,801</td>
<td>11/1/88</td>
<td>Frisby</td>
<td>Polyether surfactants + sulfurized benzene + grain refiner</td>
</tr>
<tr>
<td>U.S.4,673,467</td>
<td>6/16/87</td>
<td>Nee</td>
<td>Polyethers + mercaptouimidazole + sulfurized benzene</td>
</tr>
<tr>
<td>U.S.4,555,315</td>
<td>11/26/85</td>
<td>Barbieri et al.</td>
<td>Polyethers + organic divalent sulfur compound + tertiary alkyl amine with polyepichlorohydrin</td>
</tr>
<tr>
<td>U.S.4,551,212</td>
<td>11/5/85</td>
<td>Rao et al.</td>
<td>Phenazine dyestuffs</td>
</tr>
<tr>
<td>U.S.4,540,473</td>
<td>11/22/83</td>
<td>Bindra et al.</td>
<td>S-containing anions other than SO4</td>
</tr>
<tr>
<td>U.S.4,521,282</td>
<td>7/11/84</td>
<td>Tremmel</td>
<td>Sulfamic acid</td>
</tr>
<tr>
<td>U.S.4,430,173</td>
<td>2/7/84</td>
<td>Boudot et al.</td>
<td>Sodium salt of W-sulfo-n-propyl N,N-diethylthiocarbamate, PEG, and crystal violet</td>
</tr>
<tr>
<td>U.S.4,376,685</td>
<td>6/24/81</td>
<td>Watson</td>
<td>Alkylated polyalkyleneimine</td>
</tr>
<tr>
<td>U.S.4,347,108</td>
<td>8/31/82</td>
<td>Willis</td>
<td>Nitrogen- and sulfur-containing compounds</td>
</tr>
<tr>
<td>U.S.4,336,114</td>
<td>6/22/82</td>
<td>Mayer et al.</td>
<td>Phthalocyanine, tertiary alkyl amine with polyepichlorohydrin, polyalkyleneimine</td>
</tr>
<tr>
<td>U.S.4,334,966</td>
<td>12/2/81</td>
<td>Beach et al.</td>
<td>Polyether, mercaptouimidazole, sulfurized benzene</td>
</tr>
<tr>
<td>U.S.4,310,392</td>
<td>1/12/82</td>
<td>Kohl</td>
<td>Phenolphthalein</td>
</tr>
<tr>
<td>U.S.4,272,335</td>
<td>2/19/80</td>
<td>Combs</td>
<td>Substituted phthalocyanine radical</td>
</tr>
<tr>
<td>U.S.4,242,181</td>
<td>12/30/80</td>
<td>Malak</td>
<td>Regular coffee</td>
</tr>
<tr>
<td>U.S.4,134,803</td>
<td>1/16/79</td>
<td>Eckles et al.</td>
<td>Disulfides, sulfonic acids, and aliphatic aldehyde</td>
</tr>
<tr>
<td>U.S.4,110,176</td>
<td>8/29/78</td>
<td>Creutz et al.</td>
<td>Alkoxylated polyalkyleneimine</td>
</tr>
<tr>
<td>U.S.4,038,161</td>
<td>7/26/77</td>
<td>Eckles et al.</td>
<td>Ephalohydrins</td>
</tr>
<tr>
<td>U.S.4,036,710</td>
<td>7/19/77</td>
<td>Kardos et al.</td>
<td>Di- or triaminotriphenylmethane dyes and sulfoalkylsulfides</td>
</tr>
<tr>
<td>U.S.4,014,764</td>
<td>3/29/77</td>
<td>Kardos et al.</td>
<td>Aryl and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.4,009,087</td>
<td>2/22/77</td>
<td>Kardos et al.</td>
<td>Heteroaromatic, sulfooalkylsulfide and sulfooaryl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,996,565</td>
<td>6/29/76</td>
<td>Kardos et al.</td>
<td>Aryl amine and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,995,120</td>
<td>5/11/76</td>
<td>Kardos et al.</td>
<td>Amines and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,995,084</td>
<td>11/21/74</td>
<td>Kardos et al.</td>
<td>Aryl amine and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,995,078</td>
<td>5/11/76</td>
<td>Kardos et al.</td>
<td>Amines and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,995,079</td>
<td>11/21/76</td>
<td>Kardos et al.</td>
<td>Aryl amine and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,940,320</td>
<td>2/24/76</td>
<td>Kardos et al.</td>
<td>Aryl N-heteroaromatic and sulfoalkyl sulfide compounds</td>
</tr>
<tr>
<td>U.S.3,923,613</td>
<td>8/27/74</td>
<td>Immel</td>
<td>Urea</td>
</tr>
<tr>
<td>U.S.3,844,979</td>
<td>10/15/74</td>
<td>Arcilesi</td>
<td>Polyethers</td>
</tr>
<tr>
<td>U.S.3,804,729</td>
<td>4/16/74</td>
<td>Kardos et al.</td>
<td>Polysulfides, heterocyclic sulfur and polyether compounds</td>
</tr>
<tr>
<td>U.S.3,798,138</td>
<td>3/19/74</td>
<td>Ostrow et al.</td>
<td>2-thia- or 2-imidazolidinethiones, aldehydes, and carbon sulfur groups</td>
</tr>
<tr>
<td>U.S.3,778,354</td>
<td>12/11/73</td>
<td>Toledo</td>
<td>Cobalt</td>
</tr>
</tbody>
</table>

(continued)
ether [106], polyethylene glycol [87, 107, 108], polyethylene imine [107], polyarylamine, polypropylene ether [109, 110], propylene oxide [100], sugar [96], thiacarbamoyl-thio-alkane sulfonates [111], and thiourea [76, 81, 84, 85, 96, 112–114]. Chloride, which can also be considered an additive, is discussed in Section 2.4.2.

Many of the present-day, commercially available additives contain three components designated as carrier, leveler, and brightener. Reid [115] reports that “Carriers are typically polyalkylene glycol type polymers with a molecular weight around 2000, levelers are typically alkane surfactants containing sulfonic acids and amine or amine functionalities, and brighteners are typically propanol sulfonic acids which are derivatized with surface active groups containing pendant sulfur atoms.”

The use of a particular additive must be evaluated for each application because undesirable characteristics can then be avoided. For example, many of the addition agents proposed result in embrittlement of the plate. Deposition potentials are generally higher when addition agents are added. Cathode polarization is greatly increased by adding gelatin (0.2 g L⁻¹) [70, 116] or glue [68, 117]. These additions result in grain refinement, but this is chiefly unidirectional because the structure remains columnar and becomes more fibrous [70]. Gelatin additions to the sulfate solution introduce porosity, organic inclusions [64, 118], or both.

Phenolsulfonic acid is used in the electrotyping industry, but results with it depend on the sulfonation and purification procedures [119]. Deposits become harder and smoother after a solution has been electrolyzed or dummied for a short

<table>
<thead>
<tr>
<th>Patent Reference</th>
<th>Date of Issue</th>
<th>Investigator</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.3,775,265</td>
<td>8/25/70</td>
<td>Bharucha</td>
<td>Amines for plating on Al</td>
</tr>
<tr>
<td>U.S.3,775,264</td>
<td>3/9/72</td>
<td>Bharucha</td>
<td>Amine and ammonia for plating on aluminum</td>
</tr>
<tr>
<td>U.S.3,770,598</td>
<td>11/6/73</td>
<td>Creutz</td>
<td>Polyethyleneimine</td>
</tr>
<tr>
<td>U.S.3,770,597</td>
<td>3/16/71</td>
<td>Tixier</td>
<td>Formaldehyde and thiourea</td>
</tr>
<tr>
<td>U.S.3,769,179</td>
<td>1/19/72</td>
<td>DuRose</td>
<td>High-acid, low-copper + grain refiners</td>
</tr>
<tr>
<td>U.S.3,682,788</td>
<td>8/8/72</td>
<td>Kardos et al.</td>
<td>Polysulfides, thiourea, and polyethers</td>
</tr>
<tr>
<td>U.S.3,767,539</td>
<td>10/23/73</td>
<td>Clauss et al.</td>
<td>Selenium compounds</td>
</tr>
<tr>
<td>U.S.3,751,289</td>
<td>8/7/73</td>
<td>Arcilesi</td>
<td>Polyethers</td>
</tr>
<tr>
<td>U.S.3,743,584</td>
<td>7/3/73</td>
<td>Clauss et al.</td>
<td>Polymeric phenazonium compounds</td>
</tr>
<tr>
<td>U.S.3,732,151</td>
<td>5/8/73</td>
<td>Abbott</td>
<td>Triaryl methane and sulfurized sulfonated aromatics</td>
</tr>
<tr>
<td>U.S.3,725,220</td>
<td>4/3/73</td>
<td>Kessler et al.</td>
<td>Sulfonium compounds</td>
</tr>
</tbody>
</table>

**Pyrophosphate Copper**

- **U.S.3,100,517** 3/31/92 Starinshak et al. Plating of wire with insoluble anodes
- **U.S.3,928,148** 12/23/75 Lerner Pyro + cyanide
- **U.S.3,784,454** 1/8/74 Lyde Mercaptothiazoles, aliphatic dicarboxylic acids, and hydroxyethyl cellulose
- **U.S.3,729,393** 4/24/73 Lyde Mercaptothiazoles, thiazoles, or pyrimidines + alkaryl-sulfonic acids
- **U.S.3,775,268** 12/30/71 Fino et al. Lead
- **U.S.3,674,660** 7/14/72 Lyde Iminodiacetic, cinamic, aliphatic, carboxylic acids, and hydroxyethylcellulose

**Cyanide Copper**

- **U.S.3,790,451** 2/5/74 Weisenberger et al. Acetylenic alcohol + complexing agent + hydroxy acid

**Cyanide-Free Copper**

- **U.S.4,933,051** 6/12/90 Kline Organophosphonates
- **U.S.4,521,282** 6/4/85 Tremmel Sulfamic acid
- **U.S.4,469,569** 9/4/84 Tomaszewski et al. pH 7.5–10.5 + a Cu-soluble anode and a ferrite-insoluble anode
- **U.S.4,462,874** 7/31/84 Tomaszewski et al. pH 6–10.5 + a Cu-soluble anode and a Ni–Fe alloy–insoluble anode
- **U.S.3,898,286** 10/7/73 McCoy Copper, tin, lead, and glucoheptonic acid
- **U.S.3,928,147** 10/7/73 Kowalski Phosphonates for zinc die castings
- **U.S.3,833,486** 3/26/73 Nobel et al. Phosphonates
- **U.S.3,706,635** 11/15/71 Kowalski Phosphonates
- **U.S.3,706,634** 11/15/71 Kowalski Phosphonates
- **U.S.3,475,293** 10/28/69 Haynes et al. Phosphonates
time following an addition of phenol or phenolsulfonic acid [120].

The smoothing and grain-refining tendencies of addition agents are sometimes associated with the formation of complex ions with copper or of colloids at or near the cathode interface. Gelatin or glycine, for example, forms complex ions with copper [121–123] and also exists in colloidal form [124]. Particles of colloids arising from additions of selenious and arsenic oxides have been observed by ultra-microscopic examination to concentrate at the cathode [125].

Nodulation prevention in refineries is of high priority, and it is the major concern in overall cathode quality [114]. Nodulation is suppressed by proper selection of solution operating conditions but, most important, by proper choice of addition agents. In most refineries operating presently, addition agents consist of animal glue, thiourea, chloride ion, and sometimes a sulfonated hydrocarbon. It has recently been shown that thiourea, which is added to give a smooth copper surface, can initiate nodulation, and this effect is always associated with a large increase in overpotential, >100 mV [114].

2.6 OPERATING CONDITIONS

2.6.1 Temperature

Temperatures may vary from 18 to 60°C; however, a temperature between 32 and 43°C is common, since it can be maintained economically with little or no heating or cooling. An increase in the temperature results in a higher conductivity and reduced anode and cathode polarization [70]. A temperature below 30°C is recommended for plating bright copper in acid solutions to maintain good leveling power. These solutions are customarily agitated with air.

2.6.2 Current Density/Agitation

An increase in current density in either the sulfate or the fluoborate solution results in increased cathode polarization (but not to the extent noted for many other solutions). Cathode films become more depleted in Cu(II) ion and more concentrated in sulfate ion when the current density is increased [126]. Clear evidence has been reported of grain refinement produced by increasing the current density [127–130]. For example, an increase in current density from 1 to 7 A dm⁻² reduced grain size by about one-third [130].

Current density and agitation must be balanced in order to obtain deposits having the desired properties. For producing electrotypes, cathode current densities of 16–22 A dm⁻² are generally employed when using the sulfate solution agitated with air. Fast-moving, endless wire can be plated at 50 A dm⁻² [131]. Still higher current densities are used when sufficient agitation can be supplied. When movement of the work is impractical or when air agitation fails to provide good mixing at all significant surfaces, the current density is usually kept at 3.7–5.4 A dm⁻². It is claimed that higher current densities are practical with the fluoborate solution when agitation is the same as for the sulfate solution [26, 27].

2.6.3 Ultrasonic Agitation

Although results with ultrasonic agitation have shown some improvements, practical applications are still limited to surface cleaning processes [132, 133]. Researchers have shown that ultrasonic agitation can result in an increase in limiting current density and current efficiency and a decrease in concentration polarization in acid sulfate solutions [134, 135] as well as pyrophosphate [134] and ethylene-diaminetetraacetic acid (EDTA) solutions [136]. It can also increase the hardness of deposits. This change is believed to be due to a substantial reduction in porosity and to work hardening caused by the repeated impacts of electrolyte jets on the surface of the deposit during the collapse of cavities at high intensities of 13 kHz [137, 138]. Ultrasonic agitation is dependent on the location of the transducer in the plating tank.

2.6.4 Other Forms of Agitation

A reciprocating paddle cell has been used to deposit coatings of uniform thickness on large surface areas [139]. The paddle is a pair of confronting, separated triangular blocks aligned parallel to the cathode and was designed in this manner to provide uniform laminar flow. Mass-transfer characteristics of the paddle cell, which induces a nearly periodic flow, have been evaluated for acid copper solutions. Of importance are the paddle length scales and spatial location of the cathode relative to the paddle stroke boundary [140]. Also the paddle height above the cathode significantly affects deposition uniformity [141].

2.6.5 Filtration and Purification

Filtration requirements depend on the dirt load of air, any dirt brought in by the work, and the amount of detached anode sludge particles. If the cathodes are steel and if they are incompletely protected with a copper or nickel strike, particles that become detached from immersion deposits will also contribute to the filtration requirements. Although it is possible to maintain acceptably smooth deposits with only occasional batch filtration, continuous filtration is usually preferred. Cellulosic filter aids are satisfactory, but siliceous filter aids should be avoided when the fluoborate solution is filtered; filter papers are satisfactory.

Potassium permanganate is often added to solutions used for plating of printed wiring boards to oxidize contaminants to species that are more easily removed by carbon treatment. Manganese, which accumulates in the solutions as a result of
this procedure, exerts a detrimental effect on deposit tensile properties and interferes with cyclic voltammetric stripping analysis for the additive. Use of hydrogen peroxide at slightly elevated temperatures produces comparable purification results without the disadvantages associated with the use of permanganate [142].

Up to the early to mid-1980s many of the bright leveling acid copper processes contained some hazardous organic additives. By contrast, acid copper processes available today can produce the same leveling and fine-grained amorphous deposits as older processes, but without the concern for the safety of workers and the environment due to the additives. Waste treatment is easily accomplished by increasing the pH to about 9 to precipitate the copper. Once the precipitated copper is filtered out, the remaining solution does not contain any controlled material [4].

2.6.6 Equipment

Steel tanks with rubber or plastic are preferred for large acid copper solutions, but glass fiber-reinforced plastic tanks are used for small volumes of solution. Lining materials that are generally suitable for either the sulfate or the fluoborate solution are properly formulated natural hard rubber, neoprene rubber, polyethylene, or plasticized vinyl chloride polymers. Air lines can be made of hard rubber or polymerized vinylidene chloride. Special grades of carbon pipe and tubing make efficient heat exchangers or cooling coils. Lead is, however, satisfactory in the sulfate solution and is less expensive. Rubber or rubber-lined filters are used for continuous filtration, but stainless steel is satisfactory for short periods.

Graphite is recommended for use as a heat exchanger for copper fluoborate solutions [143]. For further details, see [144].

2.6.7 Anodes

Rolled and cast bars and electrolytic copper sheets have been employed as anodes in sulfate and fluoborate solutions. Another choice is high-purity, oxygen-free anodes, which are commercially available in several shapes and sizes. The benefit of oxygen-free anodes is that anode sludge is decreased [145]. On the other hand, the tenacity of the anode film is improved, and the number of particles that become detached from anode surfaces in air-agitated solutions is decreased by adding 0.02–0.04% phosphorus to cast copper [146, 147]. The films on phosphorized copper anodes are responsible for the slight polarization of about 0.5 V [145]. Rolled copper anodes containing at least 0.004% phosphorus are customarily recommended by the vendors of brighteners for plating bright copper in copper sulfate solutions. Chunks of polarized copper are frequently used in acid copper plating of printed wiring boards to minimize sludge formation and to produce better anode corrosion. The black film formed on copper anodes containing phosphorus contains Cu⁺, chlorine and phosphorus and is envisioned to be a porouslike CuCl-like matrix that is laden with aqueous copper sulfate solution. The beneficial effect of phosphorus in copper anodes is to inhibit disproportionation of Cu⁺ [148].

Anode film particles often become detached from the anodes. Air agitation promotes the detachment, causing some particles to be dissolved by the free acid. If the work is racked so that cathode shelves lie in a horizontal plane, particles will settle out on these areas and roughen the plate. In such cases the anode sludge can sometimes be decreased and the deposits made smoother by raising the solution temperature or increasing the acid concentration. Fine copper particles can be prevented from reaching the cathode by bagging anodes with woven Dynel or polypropylene. To allow good mixing of the solution adjacent to the anodes, bags can be made in the form of envelopes, enclosing several anodes placed edgewise to the cathodes.

To avoid excessive polarization at any anode in the copper sulfate solution, the anode current density should not be more than about 5 A dm⁻² in unagitated solutions. With vigorous agitation, the limiting anode current density is more than 17 A dm⁻². The anode current density in an unagitated fluoborate solution can be as high as 40 A dm⁻², and with air agitation, it can be increased to 55 A dm⁻².

Small amounts of silver, sulfur, lead, tin, nickel, and other elements are common impurities in rolled, cast, and electrolytic copper [145]. Silver as an impurity in the anodes employed in sulfate and fluoborate solutions is of much less consequence than it is in cyanide solutions. Oxygen-free high-conductivity and electrolytic copper were found to have a lower impurity content than rolled or ordinary cast anodes. Two batches of high-purity anodes with average grain sizes of 10 and 0.01 mm performed similarly [145]. The anodic behavior of copper anodes containing arsenic or antimony as impurities has been investigated for electrorefining operations [149]. Lead containing 3% tin and 3% antimony has been proposed as an insoluble anode for facilitating the plating of printing rolls [150]. An insoluble anode that has been used in copper electrowinning was made of an alloy of copper, silicon, iron, and lead [69]. Graphite is the only electrically conductive material known to be insoluble as an anode in the fluoborate solution. When used as an anode, graphite produces a sludge of finely divided carbon particles. Recent reviews on anode reactions can be found in [151–154].

2.6.8 Specifications

Information on standards, specifications, and recommended uses for copper plating can be found in [39, 155].
2.7 EFFECTS OF IMPURITIES IN PLATING SOLUTIONS

Acid copper solutions are more tolerant of ionic impurities than many other plating solutions. Many metallic ions introduced regularly by carryover with the work, by dissolution of impurities in the anode, or by dissolution of the basis metal (e.g., iron, nickel, or zinc) can be expected to accumulate in the solution because conditions are usually not satisfied for effecting codeposition of such metallic impurities (nickel, cobalt, zinc, iron) with copper. For example, less than 2 ppm nickel was codeposited with copper in a sulfate solution containing 15 g L\(^{-1}\) nickel [156].

Nickel and iron reduce the conductivity of the sulfate solution to the same degree as an equivalent increase in copper. The deposition potentials of arsenic and antimony are apparently near that of copper in the sulfate solution, since codeposition was reported to occur [157]. Arsenic and antimony in concentrations of 10–80 g L\(^{-1}\) and 0.02–0.1 g L\(^{-1}\), respectively, embrittled deposits and roughened surfaces. Addition of gelatin or tannin, however, effectively inhibited codeposition of these impurities and prevented roughness and embrittlement caused by them. Antimony readily codeposits with copper, but only small amounts of arsenic could be detected [158]. Bismuth, like arsenic and antimony, caused granular deposits [159]. Antimony and bismuth are believed to form insoluble complex compounds with arsenate [160].

Small concentrations of alkali metal and alkaline earth salts were found to smooth copper deposits [16]. Tin salts were also reported to smooth deposits and were, at one time, purposely added to the sulfate solution for this reason [15]. Lead is completely precipitated as partly sulfate and partly silver. If silver is a contaminant, a small amount will be codeposited with copper. A high current density favors the codeposition of silver [156]. Silver chloride caused pitting in semibright copper plate [161].

Nitrites are reduced to ammonia at the cathode in copper sulfate solutions [162]. A reduction product of the sulfate ion, which is said to have a grain-coarsening effect, can be removed by heating the solution and adding an oxidizing agent [163], but oxidizing agents such as hydrogen peroxide or potassium permanganate are said to reduce throwing power [161].

In the fluoborate solution, lead is the only metallic impurity known to interfere with the deposition of ductile plates; it can be precipitated by adding sulfuric acid. Besides lead, metals like silver, gold, arsenic, and antimony might be codeposited with copper, but the effects of such impurities are not known.

Organic impurities originating from decomposition of addition agents or leaching of elastomeric tank linings sometimes embrittle deposits, but they can be removed by treating the solution with an appropriate activated carbon followed by filtration. Treatment with activated carbon is desirable when a new solution is being prepared—especially the fluoborate solution, which may be contaminated with impurities leached from rubber shipping drums.

2.8 ANALYTICAL METHODS

The concentration of copper sulfate or copper fluoborate can be approximated by specific gravity measurements, but the contribution of sulfuric acid to the specific gravity of the sulfate solution must be taken into account [164]. The acid concentration of fluoborate solutions is controlled by measuring pH using colorimetric pH papers. Analytical methods for determining copper and sulfate concentration are described by Langford [165], who also presents procedures for determining copper and fluoboric acid concentration. Methods for determining trace amounts of lead [166], nickel [167], chromium [168], and chloride [77, 169] have been reported.

The concentration of addition agents is controlled by many techniques: empirical methods, such as evaluating the appearance of deposits on special bent or sloping cathodes immersed in beaker samples of the plating solution, Hull cell tests [170–172], and a variety of sophisticated analytical procedures.

Tench and Ogden and their colleagues pioneered in the use of cyclic voltammetry stripping (CVS) [173–177]. They were also instrumental in using CVS with copper pyrophosphate solutions; this is covered later in this chapter. Others who have used CVS with acid copper solutions can be found in [111, 112, 178–183]. One difficulty with CVS stems from the tendency of most acid copper solutions to “age” during operation by forming additive by-products [183]. Therefore a standard curve of stripping charge versus additive concentration for a fresh solution cannot be used for an aged one. Tench and White [184] modified the technique to step the electrode potential over a range to include plating, stripping, cleaning, and equilibration and called this technique cyclic pulse voltammetric stripping (CPVS). These researchers and others reported that CPVS was highly effective in mitigating the effects of additive breakdown products and other contaminants [181, 183–185].

Other methods that have been used with acid copper solutions include chromatography [102, 186], ion chromatography [180], high-performance liquid chromatography [180, 187–190], differential pulse polarography [191], and spectrophotometry [192–194]. Kanazawa et al. [195] used a quartz crystal microbalance to measure efficiency of an acid copper solution, and Mansfeld [196] developed a copper plating solution unit that operates by monitoring the polarization of a copper cathode at a constant applied direct current (dc). This unit is used to detect the presence of excess amounts of organic contaminant in the solutions, and it has worked well in production situations. Another technique for
testing the influence of additives is a modified rotating-cone electrode, which is recommended because of reproducible and controlled mass-transfer performance at fixed rotation speeds [197]. Troubleshooting has been covered by Mohler [198] and Rudolph [199].

### 2.9 PROPERTIES AND STRUCTURE

Copper is electrodeposited for numerous engineering and decorative applications requiring a wide range of mechanical and physical properties. This range extends from properties superior to full-hard wrought copper to properties equivalent of annealed pure copper and is summarized in Table 2.3. This subject is extremely broad, and no attempt will be made to provide comprehensive coverage on the matter since there already exists a number of excellent reviews on the topic. The best source is Safranek’s book on the properties of electrodeposits [3]. An extensive research project sponsored by the American Electroplaters and Surface Finishers Society showed that the mechanical properties of electroplated copper varied widely depending on factors such as solution composition, current density, temperature, impurities, and addition agents [200–202].

The grain structures of copper deposits usually correspond to one of four types, shown in Figure 2.1. Deposits from the sulfate solutions containing no addition agents are columnar (Fig. 2.1a). Additions of gelatin, phenolsulfonic acid, and many other agents cause the fibrous structure shown in Figure 2.1b. Such copper usually is 15–20% harder than columnar copper. The fine-grained deposit in Figure 2.1c is characteristic of copper deposited in copper cyanide solutions at high temperatures (70–80°C), copper pyrophosphate solutions, copper sulfate solutions containing tri-isopropylamine or other amines, and copper sulfate solutions containing popularly used brighteners. The banded copper in Figure 2.1d is characteristic of copper deposited with periodic current reversal from cyanide solutions containing brighteners. Copper is deposited from the sulfate solution as face-centered-cubic (fcc) crystals that are randomly oriented [203] unless deposited at less than 1.5 A dm⁻², when the basis metal can exert an influence on the structure so that crystals in the basis metal and plate are oriented similarly [204].

Grain continuity from the basis metal into sulfate copper deposits has been detected by many investigators [129, 205, 206]. Thus the structure of the deposit is often influenced by that of the basis metal. The basis metal structure was reproduced in the copper plate when the copper substrate was cleaned and immersed in an acid solution before plating [207, 208] but was not reproduced when the basis metal was cleaned but not dipped in acid solution before plating [208]. The grain size of the substrate appeared to influence the reproduction of the basis metal structure in the copper deposit [208]. The structure of copper, electrodeposited from sulfate solutions, was not influenced by dislocations such as etch pits in the substrate surface, unless the etch pits contained oxides or sulfides [209]. Oxide and sulfide particles in the surface layer of the substrate behaved as nucleation sites.

Tensile strength, in general, is inversely proportional to the square root of the grain diameter, as shown in Figure 2.2 for a variety of copper deposits and wrought copper [210]. Loss of tensile properties such as reduced elongation and tensile strength of electrodeposited copper has been noted by many researchers. It affects copper in a number of applications: printed wiring boards that exhibit cracking in deposits as a result of soldering operations, optics parts for physics experiments that require high-temperature stability of the copper to maintain precise stability during usage, and shaped charge parts which undergo deformation at very high strain rates. It is postulated that segregation at grain boundaries is driven by a reduction in grain boundary interfacial energy which, in turn, leads to a reduction in the grain boundary cohesive strength [211–213].

---

**TABLE 2.3 Ranges of Properties of Copper Electrodeposits**

<table>
<thead>
<tr>
<th>Outstanding Characteristic</th>
<th>Tensile Strength</th>
<th>Elongation, % (2 in.)</th>
<th>Internal Stressa</th>
<th>Hardness (VHN200), kg mm⁻²</th>
<th>Electrical Resistivity, μΩ-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>High strength</td>
<td>45–63</td>
<td>64–90</td>
<td>4–18</td>
<td>−4.2 or 3.6 to 5.5</td>
<td>131–159</td>
</tr>
<tr>
<td>Hardness</td>
<td>3.5–55</td>
<td>5–79</td>
<td>0–10</td>
<td>−4.2 or 3.5</td>
<td>193–350</td>
</tr>
<tr>
<td>Low electrical resistivity</td>
<td>18–27</td>
<td>26–38</td>
<td>15–41</td>
<td>−0.5–1.6</td>
<td>48–64</td>
</tr>
<tr>
<td>Near-zero stress</td>
<td>14–23</td>
<td>20–33</td>
<td>8–24</td>
<td>−0.08–0.06</td>
<td>56–57</td>
</tr>
<tr>
<td>Good leveling</td>
<td>36</td>
<td>51</td>
<td>14–19</td>
<td>2.0</td>
<td>128–137</td>
</tr>
<tr>
<td>Thermal stabilityb</td>
<td>22.5–30</td>
<td>32–43</td>
<td>26–39</td>
<td>0.5–2.9</td>
<td>55–106</td>
</tr>
</tbody>
</table>

Source: From Safranek [3]. Reprinted with permission of the American Electroplaters and Surface Finishers Society, Orlando, FL.

a Negative values indicate a compressive stress.

b Deposits that changed <0.02% in length after heating to 400°C.
Zakraysek [214–217] observed a thermally induced ductile–brittle transition in electrodeposited copper with embrittlement occurring as a result of fracture along grain boundaries. Lin and Sheppard [218] noted an embrittlement effect when electroplated copper having a columnar grain structure was tensile tested at temperatures between 150 and 300°C. The effect was also strain rate dependent at the lower temperature. This was not noted for deposits annealed without straining at the same temperatures and then tested at room temperature. The behavior is believed to be associated with inhibition of grain growth and grain boundary weakening, possibly as the result of vacancy effects at the grain boundaries resulting from chloride in the deposit [218].

The surface mobilities of vacancies in copper can be increased by as much as four orders of magnitude by the presence of monolayers of adsorbed halides [219]; chloride surface contamination can induce cracking in copper by the vacancy mechanism at temperatures as low as 200°C [220]. Since small quantities of chloride are used in acid copper sulfate solutions, some chloride can be incorporated in the deposit [218]. Thin copper chloride crystals have been epitaxially absorbed onto copper single crystals from a sulfate solution containing only 7 ppm chloride [221].

Others noted poor performance of electrodeposited copper in shaped-charge applications [211, 222]. In these cases, strain rates were very high (10⁴ and higher) compared to rates around 10⁻³ for typical tensile tests. Despite the radical difference in deformation history, Lassila [211] postulates that the fundamental material characteristic of high-temperature embrittlement is the primary cause of the poor performance. The presence of segregated impurities is believed to be the primary cause of brittle fracture and participation. Support of this hypothesis was provided by Sole and Szendrei [223], who electroformed shaped-charge liners that exhibited good performance by using additive-free acid
of these techniques, see [229–235].

Merchant [224, 225] characterized thermal response of electrodeposited copper by monitoring changes in microstructure, tensile strength, elongation, and microhardness following 30 min isothermal annealing at temperatures between 23 and 400°C. By judicious control of additives to the electrolyte, considerable enhancements of strength and hardness were obtained. The annealing gradually removed embrittlement with the removal rate dependent on the time/temperature parameters of the thermal exposure [225]. Embrittlement at 180°C with increasing deposit thickness was attributed to developing low-density regions in the morphological boundaries [226]. Others who have investigated thermal response of acid copper coatings can be found in [227, 228].

2.10 CURRENT MODULATION TECHNIQUES

Current modulation techniques such as periodic reverse, pulse plating, and asymmetric alternating current plating have been used to improve deposit properties. For overviews of these techniques, see [229–235].

With periodic reverse (PR) plating, parts are plated in a conventional manner for a selected time and are then deplated for a shorter period by reversing the current. Malone [236] used PR plating to enhance the uniformity and grain structure regardless of deposit thickness. A current density of about 5 A dm⁻² and a PR cycle with a cathodic-to-anodic ratio of 2:1 in a solution containing no additives provided consistent mechanical properties and excellent thermal stability. Wan [237] observed that the hardness of deposits increased when PR or pulse plating were used instead of dc.

Pulsed-current techniques involve application of a forward current for a certain time interval with a short, high-energy reverse pulse periodically interposed. The main difference between dc and pulsed current is that with dc plating only voltage (or current) can be controlled, while with pulse plating three parameters—on-time, off-time, and peak current density—can be varied independently [238]. These variables are believed by many to create a mass transport situation, an electrocrystallization condition, and adsorption and desorption phenomena which are not otherwise possible [229, 238, 239].

In acid copper deposition, pulsed current has been used for improvement of mechanical and physical properties of deposits [210, 234, 240]. Benefits include finer grain structure [210, 241–245], increased hardness [237, 246, 247], reduced stress [248], reduced surface roughness [238, 249, 250], reduced porosity [246], and improved leveling [251, 252] and throwing power [253]. Use of pulsed reversed current in acid copper sulfate solutions containing a combination of polyethers, sulfopropyl sulfides, and chloride ions can provide enhanced throwing power because of a change in the polarization characteristics of the electrolyte [239, 254]. Enhanced throwing power was not obtained when single additives were present. Best results were obtained with an anodic–cathodic ratio of 3:1 and a cathodic–anodic ratio of 20:1 [254]. Macrothrowing power was poor for pulse plating [251].

Benefits claimed for printed wiring board plating include improving the through-hole distribution of solutions used for plating printed wiring boards [238, 254–259], a reduction in average plating time by 30–50% [259], a reduction in average track height of 50% [259], and a finer grained, more ductile deposit with less stress [248]. Holmbom and Jacobsson [260] observed that by pulse plating at high frequencies (above 1 kHz) through-hole plating uniformity was improved compared with that of dc deposits. At lower current frequencies, the uniformity was worse than that of dc plating. Deposits prepared by periodic reverse plating exhibited a similar uniformity to pulse-plated deposits. However, appearance was completely dull due to loss of brighteners which were desorbed during the reversal part of the plating cycle. In addition, chlorine evolution occurred at the cathodes during the reversed pulses. A computer model that predicts the effect of pulse plating copper in small holes was developed by Ng et al. [253]. Leisner et al. [261] investigated throwing power under pulsed-current conditions in an attempt to optimize through-hole plating. However, as subsequently mentioned in the section on printed wiring boards [262], although many claims have been made for pulse plating, no manufacturing process based on this technology other than that described by Engelhaupt [258] has been reported.

Deposits produced by using pulse plating to selectively deposit copper (spot plating) were brighter and contained larger crystallites than those applied by using direct current [263]. Puippe and Ibl [245] noted that an increase in off time was accompanied by an increase in grain size, similar to the way this system reacts with dc. For optics applications, a dendritic crystal structure is deposited using a bipolar pulse plating technique. This surface is then oxidized to provide a highly antireflective surface [264]. Wan et al. [265] reported that pulse time exerted the greatest effect on current efficiency, and Popov et al. [266] showed that the effective current density is dependent not only on values of the effective overpotential but also on the ratio of pulse-to-pause duration and on the frequency of the input pulsating potential. Rudder [267] compared pulse plating of acid copper against cyanide copper and found that the leveling and thickness performance of the pulse-plated cyanide copper was better than that of acid copper.

Reverse pulse plating was investigated by a number of researchers. White and Galasco [268] obtained surface
distributions on variably spaced, 50-µm-wide lines and deposit properties typical for dc by employing reverse pulsed current in additive-free solutions. Current efficiency for reverse pulse plating was lower than that for pulse plating or for dc plating [269]. Mann [270] noted that, when using high reversal frequencies, plating speed, throwing power, and surface quality were improved in comparison with dc plating. By combining pulse current and pulse reverse current, Zhou et al. [271] developed an additive-free solution that produced deposits comparable to commercial additive solutions. A benefit claimed for this approach is that waste disposal cost can be greatly reduced compared to the current process due to the possible in-process recycling of rinse water and plating solution in the additive-free solution.

Morphological changes in copper deposits caused by use of superimposed alternating current (ac) were correlated with reduction in grain size and smooth deposits. Hexagonal pyramidal growth obtained with dc on the [111] copper plane transformed to layers, triangular pyramids, and polycrystalline deposits under the influence of superimposed ac [272].

Additional information on pulse plating with acid copper solutions can be found in the literature [273–276]. Pulsed-current techniques have been used by researchers at Battelle; this is discussed in more detail in Section 2.15.

2.11 PLATING ON STEEL, ZINC, PLASTICS, AND ALUMINUM

Historically, buffed acid copper deposits have been widely used as an undercoat for nickel–chromium deposits. The development of reliable processes capable of producing fully bright, ductile, high leveling deposits that did not require buffing served to promote even wider use of acid copper solutions [277].

The fact that copper is much cheaper than nickel suggests that it might be considered an economical replacement for a large proportion of the total thickness of electroplated coatings. However, an equal thickness of copper undercoat is not comparable with nickel. It has been proved fairly conclusively that inferior corrosion resistance results when part of the bright nickel layer in a bright nickel plus decorative chromium coating is replaced by an equal thickness of copper [278].

In terms of corrosion performance, copper underlayers are generally not detrimental when there is adequate thicknesses of double-layer nickel. Under microdiscontinuous chromium and double-layer nickel, copper layers are neither detrimental nor beneficial. In essence, the nickel and chromium layers are so protective that parts are obsolete before the copper would even start to corrode [279]. These general characteristics have been confirmed in panel exposure programs involving steel, zinc, plastics, and aluminum [280–281]. Jonkind [282] compared various processes for Cu–Ni–Cr plating of aluminum bumper bar stock (Alloy X-7046) with Ni–Cr-plated steel bumpers. The aluminum-plated parts showed at least equal corrosion test results with the steel-plated parts in CASS, neutral salt spray, and atmospheric tests.

Acid copper deposits are used over a cyanide copper strike for plating zinc die castings [283]. The ductility of copper deposits is one of the most important parameters in the coating of plastics [284]. It is suggested that elongation should be at least 15% [285]. Typical bright copper solutions for plating on plastics contain around 60 g L⁻¹ copper and 60 g L⁻¹ sulfuric acid. Lower copper concentrations (10–20 g L⁻¹) and higher contents of sulfuric acid (200 g L⁻¹) are also used because of their excellent leveling capability and throwing power [284]. A high-throw acid copper strike is very effective in improving quality by increasing the copper thickness in low-current-density areas while also reducing cost and waste treatment requirements when compared to a nickel or pyrophosphate copper strike [49].

2.12 PLATING OF PRINTED WIRING BOARDS

When printed conductors are used on both sides of a printed wiring board, electrical connections between the two sides of the board are most reliably made via plated through holes in the board. Because copper is widely used as the base conductor metal in a printed circuit, it is natural that copper also be used for plating the through holes. A historical summary of the evolution of acid sulfate copper-plating processes and their benefits as they relate to printed wiring board market needs is presented in Table 2.4.

The precise technical requirements of electronic products and the demands of environmental safety compliance have been the driving forces exerting major influence on plating practices [41]. The preferred plating process is acid copper sulfate with organic additives. Copper pyrophosphate deposits, once the standard of the industry, have been almost entirely replaced by acid copper, except for some military and special applications [41, 262].

The success of the acid copper sulfate solutions is attributed to their good throwing power, ease of control, good mechanical and physical properties, and favorable properties regarding waste disposal and treatment compared to pyrophosphate and cyanide solutions. The major factors that affect throwing power, the ability of a plating solution to produce a relatively uniform distribution of metal upon a cathode of irregular shape, are cathode polarization, cathode efficiency, and solution conductivity. Rothschild [71] compared throwing power for a variety of copper plating solutions by using a Haring cell [286]. This work, summarized in Table 2.5, clearly shows the benefit obtained with the low
copper–high acid formulations which have become the standard of the industry for plating printed wiring boards. Some chloride is also essential in these solutions; this is discussed in Section 2.4.2. Turner [287] and Walker and Cook [82] obtained results similar to those of Rothschild [71], namely through-hole plating ability improved with decreasing copper concentration and increasing acid content. A noncyanide formulation provided even better throwing power than the low copper–high acid formulation.

Fundamental studies on through-hole electroplating [288] and a thorough review of plating into through holes and blind holes were published by Yung et al. [262]. A mathematical model for through-hole plating was developed by Hazlebeck and Talbot [289]. Kessler and Alkire outlined procedures for investigating complex electrochemical phenomena appearing during plating of printed wiring boards [290] and developed a model for predicting copper thickness distribution on multilayer printed wiring board through holes [291]. References [292–295] provide additional information on plating high-aspect-ratio holes.

Innovative agitation schemes such as jet plating for high-speed plating (>10 A dm$^{-2}$) of printed wiring boards have been implemented in production lines [262, 288, 296, 297]. Other techniques that have been used include high-speed additives [41], vibratory agitation [298], and forced solution flooding [299]. Deposit distribution on a printed wiring board was not improved when ultrasonic agitation was compared with mechanical agitation [300]. Hewlett-Packard utilized a conveyorized impingement-agitated plating system where copper plating was done at 7.5 A dm$^{-2}$, which is at least twice the current density usually used for plating printed wiring boards. The significant agitation in the process was accomplished by use of hydraulic injection. Agitation via panel motion or entrained air bubbles was insignificant [301].

Most additive systems for acid copper sulfate solutions used for plating printed wiring boards are based on some combination of a polymer surfactant of a high molecular weight such as PEG, which apparently inhibits copper deposition by forming an adsorbed film on the cathode that mediates transport of species from the solution, and a sulfur-containing and/or nitrogen-containing organic species such as disulfide or organic sulfonate, which induces leveling [80]. Some single-blend additives can be comprised of three components: (1) carrier agent, (2) leveling agent, and (3) ductility agent. Carrier agents are the primary grain refiners and impart brightness to the deposit. Leveling agents level out drilling imperfections in plated through holes and also prevent fault planes and foldovers in multilayer board plating. Ductility agents create the equiaxed grain structure that is best suited to withstand thermal shocks [178, 302].

In a study of eight commercial acid copper solutions, all yielded sufficiently ductile deposits for multilayer circuit board applications, but some of the solutions exhibited a relatively strong dependence on solution agitation [303]. In one production situation, a 40% annual savings was realized by operating a solution with additives at 6.4 A dm$^{-2}$ versus 3.2 A dm$^{-2}$ [178]. In additive-free solutions, increased levels of agitation improved deposit quality dramatically up to the point of eliminating ion concentration gradients causing mass transport–limited plating conditions. With additives, the plating solutions were considerably less sensitive to changes in plating parameters such as the current density.

**TABLE 2.4 Historical Summary of Acid Copper Evolution Related to Printed Wiring Plating**

<table>
<thead>
<tr>
<th>Year</th>
<th>Innovation</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970</td>
<td>Original high-throw process</td>
<td>Improved throwing power when compared to conventionally used pyrophosphate copper</td>
</tr>
<tr>
<td>1973</td>
<td>Ductile high-throw process</td>
<td>Improved ductility agents to consistently pass thermal shock testing</td>
</tr>
<tr>
<td>1976</td>
<td>Process for high-aspect-ratio MLB</td>
<td>Improved ductility for MLBs with high aspect ratios</td>
</tr>
<tr>
<td>1979</td>
<td>High temperature and high throw</td>
<td>Improved distribution without need for chillers</td>
</tr>
<tr>
<td>1983</td>
<td>Increased current density with high throw (4.3–6.5 A dm$^{-2}$)</td>
<td>Improved productivity and lower operational cost</td>
</tr>
<tr>
<td>1984</td>
<td>Process control/additive analysis</td>
<td>Elimination of subjective readings and lower operational costs</td>
</tr>
<tr>
<td>1984</td>
<td>High current density and high throw (10.8 A dm$^{-2}$)</td>
<td>Improved productivity and lower operational cost</td>
</tr>
</tbody>
</table>

*Source: From Mayer and Barbieri [178].*

**TABLE 2.5 Values of Throwing Power (Haring Cell 11:1 Ratio)**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Throwing Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional acid sulfate copper$^a$</td>
<td>14</td>
</tr>
<tr>
<td>Conventional acid fluoborate copper$^b$</td>
<td>14</td>
</tr>
<tr>
<td>Cyanide copper</td>
<td>50</td>
</tr>
<tr>
<td>Low copper–high fluoboric acid copper$^c$</td>
<td>58</td>
</tr>
<tr>
<td>Pyrophosphate copper</td>
<td>62</td>
</tr>
<tr>
<td>Low copper–high sulfuric acid copper$^d$</td>
<td>87</td>
</tr>
<tr>
<td>Alkaline noncyanide copper$^e$</td>
<td>95</td>
</tr>
</tbody>
</table>

*Sources: From Rothschild [71]. Ratio from (H. E. Haring and W. Blum, Trans. Am. Electrochem. Soc., 44, 313 (1923). $a$ Copper, 48 g L$^{-1}$; sulfuric acid, 75 g L$^{-1}$. $b$ Copper, 120 g L$^{-1}$; fluoboric acid, 30 g L$^{-1}$. $c$ Copper, 15 g L$^{-1}$; fluoboric acid, 340 g L$^{-1}$. $d$ Copper, 15 g L$^{-1}$; sulfuric acid, 210 g L$^{-1}$; 30 mg L$^{-1}$ chloride. $e$ From L. C. Tomaszewski and R. A. Tremmel, Proc. AESF SUR/FIN 85, Session D, Detroit, MI (1985).*
and level of agitation [304]. Byle and Bratin [305] also studied the effects of additives.

Yung et al. [288] utilized a gap cell, which provided accurate nondestructive profile measurements without tedious cross sectioning to show that agitation, which is necessary inside the holes to replenish the plating solution, is also necessary to provide a certain amount of agitation on the surface of the board.

Pulsed-current techniques (discussed in detail in Section 1.10 on current modulation techniques) are claimed to offer benefits for plating of printed wiring boards. However, aside from Engelhaupt [258], no other manufacturing process based on this technology has been reported [262].

Nonuniform copper plating on printed wiring boards may be attributed to nonuniform anode currents due to high contact resistances between anode hooks and anode rods. Turner [306] developed an anode hook design to make a stable low-resistance contact by clamping the hook to the anode rod. Use of titanium for the hook and rod resulted in a low-maintenance-contact system.

Optimizing the performance of a plating process does not need to involve extensive, tedious testing. The traditional approach of examining one variable at a time while holding all others constant not only requires repeated tedious experiments but also allows bias error in each measurement [307]. Use of factorial, screening, response-surface designs, or Taguchi techniques allows for accurate solutions from a minimum of test runs [308]. Any of these approaches in studying the effects of many variables is highly recommended for both research and production activities.

Barringer and Carano [309] used the Taguchi technique to optimize the leveling of an acid copper plating solution for printed wiring boards. The effects of temperature, leveler (one component included in the addition agent), and ratio of sulfuric acid to copper metal were investigated. The best leveling was obtained at the low temperature, increasing the ratio of sulfuric acid to copper resulted in some slight improvement of leveling, and additions of leveler produced no improvements. Taguchi techniques were applied by Wan and McCaskie [307] to elucidate the relative importance of various process parameters on dendrite formation in an acid copper system. Chloride and arsenic concentrations were two critical factors that affected dendritic growth, while lead and temperature exerted little effect. Elbs and Rasmussen [310] utilized Taguchi techniques for optimizing the current efficiency of a cyanide copper solution.

An important requirement of copper deposits is that they have sufficient strength to withstand subsequent soldering of the circuits. During this operation, high forces are generated by differential expansion of the board material (usually epoxy glass) and the copper. Therefore the copper must be either strong enough to contain and deform the epoxy glass or have sufficient elongation to be stretched without fracture [311]. With the proper additives, fine-grained deposits with tensile strengths around 345 MPa and a minimum elongation of 10% are routinely produced [41].

Most of the studies on the ductility of copper deposits for printed circuit boards (PCBs) have been done under a uniaxial stress state. However, the stress state of electrodeposited copper in through holes of a PCB is definitely biaxial. Therefore Ye et al. [312] correlated cathodic overpotential, solution composition, and aging with characteristics such as crystallographic texture, roughness, and ductility. Copper foils with a low [220] preferred crystallographic orientation and a smooth surface were obtained when deposition was done at 87–113 mV cathodic overpotential from solutions with a low chloride content (<40 ppm). Highest ductilities were achieved under these plating conditions.

Kang et al. [313] studied surface morphologies of foils with different textures. Increasing solution temperature and decreasing current density changed the texture from (111) to (110). The mechanical properties at elevated temperature of a proprietary formulation for multilayer board plating were evaluated in detail by Fox [314]. The deposit was found to exhibit adequate localized ductility, although, as is generally the case for electroplated copper, its final elongation after fracture was lower than that for wrought, annealed copper. Merchant reported on the defect structure, isothermal anneal kinetics, and thermal response of electrodeposited copper [224, 225, 315, 316].

2.13 PATTERNED ELECTRODEPOSITION FOR MICROELECTRONICS

Computers, microprocessors, and other microelectronic devices could not exist without the technology of depositing thin metal or alloy films with fine lithographic patterns [317]. Romankiw et al. [318–321] have demonstrated the capabilities of resist patterned electroplating for the past two decades. Dukovic [317] suggests that there are three trends that appear to be propelling patterned electrodeposition into a phase of major expansion. First, high-speed machines require the high conductivity of copper, and acid copper plating is simple and capable of reaching high rates. Second, the pattern replication powers of electrodeposition are ideally suited to the level of miniaturization required for wiring structures. Third, demands for cost reduction have increased the importance of reducing the capital and operating expenses associated with metal deposition processes, and it is therefore likely that electroplated copper thin film, which is important today, will continue to play a central role in the future.

IBM researchers have successfully implemented copper electroplating technology for the fabrication of chip interconnect structures [2a, 2b, 321a]. The process, termed damascene copper electroplating, meets the challenges of filling trenches and vias with copper without creating a void or
seam. Under proper conditions, electroplating inside trenches occurs preferentially in the bottom, leading to void-free deposits, a phenomenon referred to as superfilling. Proprietary additives are used in the plating solution to produce the superfilling properties.

Electrodeposited bonding bumps are indispensable microconnectors for high-density interconnection in recent microelectronics applications. The bumps generally have mushroom shape and are deposited onto dot-shaped cavities of several 10–200 μm in diameter formed by photoresist. Kondo et al. [322] discussed the shape evolution of copper bumps, and Dukovic [323] developed a two-dimensional numerical computation of tertiary current distribution.

High-speed selective jet electroplating has also been used to produce deposits in a selective manner without the need for masking [324]. The principle is that a nonsubmersed, free-standing electrolyte jet impinges onto a substrate and deposition occurs within the impingement region, with little or no deposition occurring in the surrounding areas. Booking [324] determined the effects of temperature, velocity, and concentration during high-speed selective jet plating in an acid copper sulfate solution without additives.

The development of laser-enhanced electroplating processes offers a promising technique for high-speed and maskless selective plating and/or as a repair and engineering design change scheme for microcircuits [300, 325–328]. For this, temperature is used to modify the position of the equilibrium potential in a localized region so that electrodeposition is driven by the potential difference between this region and the nonirradiated regions. Use of a focused argon laser beam (488 nm) in an acid copper solution provided plating rates as high as 25 μm s⁻¹ [300]. Bindra et al. [327, 328] discussed the mechanism of laser-enhanced acid copper plating and Paatsch et al. [329] reported on laser-induced deposition of copper on p-type silicon. It was demonstrated that the increase in the plating rate under laser illumination results principally from photoinduced heating of the electrode surface [328].

### 2.14 ELECTROFORMING

Copper finds extensive use in electroforming [330, 331]. Acid sulfate with periodic reversal of current [236, 332], acid sulfate with oxygen reduction additive, and pyrophosphate solutions provide excellent properties for aerospace applications [236]. However, although acceptable properties are attainable via pyrophosphate deposition, very little electroforming is done with these solutions. Electroforming with acid copper or nickel is used as one of the primary methods of fabricating the outer shells of regeneratively cooled thrust chambers for advanced design rockets and other applications.

Typically the process involves filling machined (or etched) channels with wax, making the wax conductive with silver powder, plating thick copper to seal over the channels, and then removing the wax. Some thrust chamber requirements for copper require that the deposits retain useful mechanical properties and metallurgical structure at temperatures up to 400°C. The electroformed copper deposits often contain some oxygen, and this can be deleterious at high temperatures because hydrogen can combine with the oxygen and produce water.

With the high temperatures involved, steam pressure generated by the reaction often exceeds the strength of the copper and causes plastic deformation and/or tearing, frequently manifesting itself by grain boundary cracking or cavities [333, 334]. This problem is avoided by using an oxygen control additive such as sugar [335, 336] or potassium aluminum sulfate [337].

All of the pentoses are suitable for use in the copper sulfate solution, such as xylose, arabinose, ribose, and lyxose. These materials act as oxygen scavengers in the solution by picking up oxygen and thereby preventing the anodes from being oxidized [172]. Table 2.6 includes the gas and carbon content of a variety of copper deposits and clearly shows the high purity attainable with an oxygen control additive such as d-xylose [338].

Farmer et al. [339], in evaluating copper for a physics accelerator application, noted that copper deposited from acid sulfate solution containing one set of proprietary additives was unstable during heat treatment and exhibited void formation around 450°C. By contrast, another acid copper solution with different proprietary additives formed no voids when heated at 1000°C. Deposits from a cyanide solution and an acid copper solution containing d-xylose also showed no void formation after heating at 1000°C, giving further proof that deposits with low carbon and gas contents (Table 2.6) are stable at high temperatures.

Electroformed targets for a 14-MeV neutron source facility did not require the high-temperature stability just discussed. However, they did require a deposit elongation around 20% because of a forming operation after plating. This was

<table>
<thead>
<tr>
<th>Plating Solution</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low copper–high acid proprietary</td>
<td>50</td>
<td>11</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>d-Xylose</td>
<td>12</td>
<td>1</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Pyrophosphate proprietary</td>
<td>21</td>
<td>6</td>
<td>140</td>
<td>17</td>
</tr>
<tr>
<td>High copper–low acid proprietary</td>
<td>190</td>
<td>14</td>
<td>50</td>
<td>9</td>
</tr>
<tr>
<td>Cyanide</td>
<td>NA</td>
<td>3</td>
<td>53</td>
<td>6</td>
</tr>
<tr>
<td>OFHC (wrought)</td>
<td>90</td>
<td>4</td>
<td>50</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

*Source: From Dini [338].

*Trademark: American Metal Climax, Inc.

*Oxygen control additive.
obtained by using a medium-copper (150 g L\(^{-1}\) copper sulfate), high-acid (188 g L\(^{-1}\) sulfuric acid) formulation [340].

Copper deposits usually contain small amounts of other impurities besides oxygen, and these can affect properties such as electrical resistivity [3]. Hydrogen is present in different bound states in the deposits and the total amount of hydrogen is often five to six orders of magnitude larger than the equilibrium solubility of hydrogen at room temperature [341]. It is most likely that the hydrogen is bound to crystal lattice defects such as vacancies and dislocations or adsorbed at the grain boundaries or present in microvoids. Deposits obtained at low current densities contain a larger amount of hydrogen than those obtained at high current densities.

Hydrogen is evolved from the deposits as a function of temperature with the major amount being eliminated at temperatures around 450°C [341]. Sulfate (0.071–0.099 wt %) and sulfide (0.040–0.069 wt %) have been found in deposits from acid copper solutions. These impurities decreased with the increase in plating temperature, with the increase in acidity of the plating solution, and with the addition of 0.1 g L\(^{-1}\) gelatin [342].

Strongly enhanced ductility (up to 40%) and reflectivity were achieved in the presence of dimethylamino derivatives [98]. The ductility of the coatings in contrast to the tensile strength appeared to be correlated to the amounts of codeposited carbon and sulfur. An elongation of 15% and low stress were obtained from solutions containing polypropylene ether. These deposits were essentially sulfur free, with carbon and nitrogen contents of about 0.015 to 0.003 and 0.001 wt % [110]. A high-throw acid copper solution has been used with glue and phenol sulfonic acid for electroforming of bellows [343].

Although not electroforming, very thick deposits (around 5000 μm) were produced on the outer surface rotor of a 300-MVA superconducting generator. This was done in acid sulfate solution with a proprietary brightener. Deposit properties were yield strength around 210 MPa, elongation 15%, and high electrical conductivity at cryogenic temperatures [344]. Radio-frequency quadrupole accelerator components up to 4 m long were plated with 250 μm copper in an acid sulfate solution containing a brightener system [345].

### 2.15 HIGH-SPEED ELECTROPLATING

A current density of 300 A dm\(^{-2}\) or more is practical for depositing most metals if the solution flow rate is in the range of 1.0–1.2 m s\(^{-1}\), depending on the topography of the surface, the solution viscosity, and other factors [346]. High current densities for achieving fast rates have been used in both copper sulfate and copper fluoborate solutions. Large variations in the copper and sulfuric acid concentrations had no significant effect on the appearance of deposits from the sulfate solution. The tensile strength of copper deposited with turbulent flow in a sulfate solution increased from 350 to 450 MPa as the current density was raised from 100 to 300 A dm\(^{-2}\), which increased the deposition rate from 25 to 75 μm min\(^{-1}\). High-speed copper deposited in a fluoborate solution exhibited a lower tensile strength, 280 to 350 MPa over the range of 100–300 A dm\(^{-2}\). However, all of these values are higher than those reported for copper deposited at conventional rates.

High-speed copper plating has been developed for commercial applications such as electroforming of flexible printed circuits [347], in-mold plating of polymeric materials [348], and plating of round bars [349]. A process for electroforming copper circuit paths on a reusable metal substrate and transferring the circuitry to a flexible polymeric surface coated with adhesive has been advanced to production. The copper circuit paths are electroformed at rates up to 50 μm min\(^{-1}\) using fast-rate electrodeposition technology. The process does not generate spent etching solutions or plating rinse water and costs can be 70–80% of those associated with the conventional etched-circuit process for high-volume production. Another benefit is that high-speed deposition conserves equipment and floor space [348].

A combination of high-speed plating with pulsed current (fast-rate, interrupted current, FRIC) allows for deposition of copper with different structures at rates of 50 μm min\(^{-1}\) or higher [350]. By controlling the frequency and/or duty cycle with the high-speed deposition rate, it is possible to tailor the deposit structure to suit the application. For example, with applications that need structural strength particularly at corners, the FRIC technique at high frequency would be used to promote growth of mainly polycrystalline copper which would be equally strong in all directions. By contrast, for applications such as wire coatings that require maximum electrical conductivity, columnar structures produced at moderate frequency are preferred [350].

For agitation of the electrolyte, forced circulation across the cathode by pumping electrolyte is most commonly used, although ultrasonic agitation and gas sparging have also been investigated [351]. When plating wire and strip using direct current, the deposition rate can be increased by intensifying the electrolyte flow, by optimizing the gap between the cathode and anode, and by the use of high-performance electrical contacts [352].

### 2.16 DIAMOND TURNING

Diamond-turning surface finishing uses single-point diamond tools on a precision lathe under precisely controlled machine and environmental conditions. Diamond tools are used when it is necessary to machine the smoothest possible surface texture. When the surface to be cut is one of the preferred diamond-turnable materials such as copper,
Electroless nickel, or aluminum, surface textures as smooth as 1 nm can be obtained. Coatings offer significant advantages for diamond-turning applications inasmuch as they can be applied to lightweight substrates such as aluminum or beryllium, and copper coatings produced in acid sulfate solutions have been used in many applications. A number of 1.3-m-diameter molybdenum parts required form accuracy of approximately 250 Å, and this was obtained by coating the parts with 0.3–0.45 mm of copper prior to diamond turning [52]. A physical vapor deposition process was used to provide an initial, thin (6-µm) adherent copper layer, and this was followed by thick plating in an acid copper solution containing proprietary additives. An important requirement for these parts, as well as for many other diamond-turning applications, is long-term microstructural stability. If the deposit undergoes recrystallization after machining, the precise surface finish is degraded. Copper deposits have been shown to markedly soften after storage at room temperature for 30 days [353]. For example, copper mirror surfaces for the Antares laser system changed over a six-month period due to recrystallization [51]. The problem was eliminated by employing a low-temperature heat treatment (1 h at 250°C). This same treatment provided stability for the proprietary copper used for the 1.3-m-diameter molybdenum parts mentioned earlier [52].

Rao and Trager [354] reported that copper for diamond turning should have a grain size from about 200 to 500 Å and a hardness from about 250 to 320 Knoop (15-g load). An additive comprising a mixture of phenazine dyestuffs in the combination from about 30 to 40% by weight of a Janus Green B–type dyestuff and from about 70 to 60% by weight of Safranine T provided these properties.

By judicious choice of plating operating conditions, such as current density, pH, solution composition, and additive concentration, it is possible to deposit coatings that are in a stress-free state. A plot of current density versus stress was used to define conditions for depositing 1-mm-thick copper with zero stress on glass substrates and on pyrex optics. This deposit was capable of withstanding single-point diamond turning to provide an optical surface and was able to withstand heating at 250°C for 4 h without degradation of the metal–glass bond [53].

Occasionally, a phenomenon referred to as black spots has been obtained. These are small, localized defects noted on electroplated copper after single-point diamond turning. Analysis of these spots has revealed oxides, sulfates, and chlorides, materials which are components of the plating solution [355, 356]. It is speculated that the most likely cause of these defects is a void or pit exposed by the diamond-cutting tool. In an effort to eliminate these minuscule pits Dini et al. [356] evaluated plating under reduced pressure (around 100 torr). Copper deposits produced under these conditions exhibited finer and denser grain structure and a reduced surface roughness.

2.17 MISCELLANEOUS

2.17.1 Magnetics

Effects of magnetic fields on electroplating of copper were investigated by Takeo et al. [357], who noted a reduction in energy required for deposition with increasing magnetic field as a consequence of reduced concentration overpotential. Changes in structure and hardness were also noted as the applied magnetic field strength was increased. Ismail and Fahidy [358] studied the effect of uniform magnetic fields on the morphological properties of fine-mesh metal screen deposits. Popov et al. [359] provided some correlation between dendritic growth and copper powder formation.

2.17.2 Striations

Occasionally spiral patterns (striations) that follow the streamlines of the fluid are obtained during electrodeposition of copper, zinc, and silver [360]. This is accompanied by small or negative polarization resistance and is typically observed only below a certain current density. The range of current density depends on the electrolyte and its concentration. Studies with rotating hemispherical electrodes (RHEs) revealed no striations in the deposition of copper from sulfate solution unless a certain amount of gelatin was added. With increasing additions of gelatin (10–20 ppm), the polarization curve became progressively steeper, vertical, and finally S shaped while shifting to a more negative potential [360]. Spiral patterns were also observed in acid copper sulfate solutions containing PEGs and chloride [89].

2.17.3 Underpotential Deposition

Underpotential deposition (UPD) involves formation of up to a monolayer of atoms on foreign substrates at potentials that are more positive than the potential of the reversible deposition in the same solution, that is, before bulk deposition can occur. The fact that UPD exists means that the chemical potential of adatoms deposited at the underpotentials is different from that of the corresponding bulk metal. The adatoms are more strongly bound to the surface of the foreign substrate than to the surface of its own species [361, 362]. The likelihood that UPD plays an important role in electroplating processes has long been recognized [363]. An example wherein UPD plays an important role is in the electroplating of gold where ions of metal (or semimetal) serve as brightening agents for gold plated from cyanide and noncyanide solutions. Gold deposition proceeds in the region of UPD of the foreign metals, which are incorporated only at trace levels in the deposit. These foreign metals act as brighteners because of their strong influence on the nucleation process [363]. With copper, it has been demonstrated that the UPD of Pb or Sn on copper can be used to produce electroplated Cu–Pb and Cu–Sn alloys, with small amounts
of alloyed Pb and Sn. This is done in acid solutions that do not contain complexants. These alloys are of interest as possible on-chip wiring for very large scale integration where the content of alloying agent must be kept small in order to maintain a low resistivity [363]. Some other studies on UPD include Cu on Au [364] and Cu and Ag on Pt [365].

PART B
CYANIDE COPPER*

2.18 HISTORY AND DEVELOPMENT

Before 1915 copper cyanide solutions were invariably prepared by dissolving copper carbonate in alkali cyanide. The use of tartrates is mentioned in early references [366, 367], but their value apparently was not fully recognized. An exception was the combination cleaning and plating solution described by Watts [368] in 1915. Deposits from these early solutions were relatively thin and were used largely as bases for oxidized and other decorative types of finishes.

The first commercially successful high-efficiency solution was introduced in 1938. It was used extensively throughout the automotive industry in subsequent years for plating zinc die castings as well as steel parts. High rates of deposition were achieved by operating at temperatures around 80°C. Alkali was added to improve anode corrosion and to increase the conductivity of the solution [369]. Alkali thiocyanate was used by Wernlund [370] in 1941 to brighten the deposits. Successful commercialization of the process required the use of specific surface-active agents to sequester organic contaminants and prevent pitting [371]. This solution permitted deposition of smooth, bright deposits in the thickness range of 25–50 μm. The basic formulations of the proprietary high-efficiency solutions now in commercial operation are similar to these, except that thiocyanate and other active sulfur-containing constituents are not recommended in the new processes.

The next major advance in high-efficiency cyanide copper solutions was introduced in 1938. It was used extensively throughout the automotive industry in subsequent years for plating zinc die castings as well as steel parts. High rates of deposition were achieved by operating at temperatures around 80°C. Alkali was added to improve anode corrosion and to increase the conductivity of the solution [369]. Alkali thiocyanate was used by Wernlund [370] in 1941 to brighten the deposits. Successful commercialization of the process required the use of specific surface-active agents to sequester organic contaminants and prevent pitting [371]. This solution permitted deposition of smooth, bright deposits in the thickness range of 25–50 μm. The basic formulations of the proprietary high-efficiency solutions now in commercial operation are similar to these, except that thiocyanate and other active sulfur-containing constituents are not recommended in the new processes.

The next major advance in high-efficiency cyanide copper solutions was achieved by employing periodic reverse plating cycles [372]. Other current manipulation techniques such as interrupted current are occasionally used to modify the properties of the coatings. A wide variety of addition agents have been developed; this is covered in Section 2.22. Reviews of cyanide copper plating can be found in [373–379].

2.19 APPLICATIONS

Cyanide copper plating is used throughout the metal-finishing industry for many applications, although not as extensively today as in the 1970s because of environmental issues. Horner [380] estimates that present usage is less than 50% of that in the 1970s. Possible site contamination, worker safety considerations, and high waste treatment and reporting costs are some drawbacks [381].

Applications include as an undercoat for other deposits to protect basis metal or promote adhesion; for surface improvement in buffing, soldering, lubricity, rotogravure, printing rolls, and decorative plating of zinc die castings [382–385]; in plating of steel parts with copper before nickel and chromium plating [384, 385]; as a stopoff to prevent case hardening on selected areas of ferrous metal surfaces; and in plating of coinage [386, 387]. A high-speed cyanide copper plating process is used to produce heavy coatings of copper on steel wire for electrical use. For noncorrosive environments, aluminum is often plated with copper cyanide after zincating. This is followed by a decorative nickel–chromium coating [388].

2.20 FUNCTIONS OF MAJOR SOLUTION CONSTITUENTS

2.20.1 Copper Cyanide

Typical formulations for cyanide solutions are given in Table 2.7. Copper cyanide is insoluble in water but dissolves in aqueous solutions containing alkali metal cyanides to form four stable soluble complexes and free species in water: CuCN, [Cu(CN)₂]⁻, [Cu(CN)₃]²⁻, [Cu(CN)₄]³⁻, and Cu⁺ and CN⁻. In all four oxidation complexes, the oxidation number of copper is +1. A model of copper discharge from cyanide electrolyte was developed by Dudek and Fedkiw [389].

Deposition occurs from the Cu(CN)₃⁻ and Cu(CN)₄⁻ complexes [390]. Cuprous cyanide complexes shift the copper deposition potential to more negative values which avoid displacement deposition on less noble substrates. The predominant copper cyanide species discharged in copper strike plating is proposed to be Cu(CN)₃⁻; although Cu(CN)₄⁻ is at a higher concentration, it is not as electroactive. These kinetics give rise to the inherent good “macroscopic throwing power” observed in the cyanide solution [391]. Additional information on kinetics can be found in [392].

The Taguchi method was used to evaluate a number of parameters in a copper cyanide solution. An increase in copper concentration and a decrease in potassium cyanide resulted in good current efficiency over a wide current density range. Hydroxide and carbonate concentration were of secondary importance [393].

2.20.2 Free Cyanide

The alkali cyanide in excess of the tricomplex salt Na₂[Cu(CN)₃] is termed free cyanide. The ratio of the free
cyanide to the copper metal content in the strike and Rochelle solutions is somewhat higher than in the high-efficiency solutions. This accounts, in part, for the lower cathode efficiency. Hydrogen is simultaneously liberated at the cathode in the strike and Rochelle solutions, and this hydrogen evolution provides additional cleaning. Strike and Rochelle solutions are also operated at a relatively high free cyanide–metal ratio in order to produce the desired type of deposit. The excellent adhesion of strike deposits can be attributed largely to the high free cyanide combined with low metal, which minimizes any tendency to form nonadherent immersion deposits. Free cyanide is essential in all cyanide copper plating solutions in order to obtain good corrosion of the copper anodes. If it is too low, the anodes polarize and become coated with an insulating film. Free cyanide contributes to conductivity in strike and Rochelle solutions, but not significantly in high-efficiency solutions that contain alkali and higher concentrations of the complex copper ions. The concentration of the free cyanide increases at higher temperatures, since lower complexes are formed and free cyanide is thereby liberated [390]. Free cyanide is normally determined by titrating a sample of the solution with silver nitrate at or below room temperature using potassium iodide as an indicator.

### 2.20.3 Sodium or Potassium Hydroxide

Sodium or potassium hydroxide is added to high-efficiency solutions primarily to provide good electrical conductivity and to improve throwing power. Alkali is also essential in these solutions for good anode corrosion. The brightness of the deposits from high-efficiency solutions is also influenced by the alkali metal hydroxide. Usually only small amounts of caustic are added to strike or Rochelle solutions for adjusting or maintaining the pH within the proper range. Many users of high-efficiency cyanide copper solutions base their formulations on sodium cyanide to complex the cyanide copper and add potassium hydroxide as a means of introducing the potassium ion.

### 2.21 COMPARISON OF SODIUM AND POTASSIUM FORMULATIONS

The complex salts formed with sodium or potassium cyanide are similar in composition, but the potassium salts are more soluble. Horner [394] compared the throwing power and efficiencies of sodium and potassium formulations and the effects of free cyanide, carbonate content, and other factors. He concluded that potassium salts offered no advantage for cathode efficiency over sodium salts but did show improved throwing power. Hatherley et al. [387] reported that sodium and potassium formulations each possess various advantages and disadvantages. Conductivity is higher in potassium solutions, especially at high concentrations of carbonate. Cathode polarization curves also favor potassium formulations over sodium. By contrast, sodium solutions exhibit less of a risk of anode passivation. Juhos et al. [395] also found that sodium formulations favored the anode reactions. Hatherley et al. [387] suggest that commercial considerations might be used to specify optimum carbonate level where the advantage of high conductivity has to be set against reduced cathode efficiency.

#### 2.21.1 Carbonate

Carbonate exerts a strong buffer action at a pH of 10.8–11.5 in strike and Rochelle solutions [396, 397] and facilitates pH control. It also reduces anode polarization in these solutions.
No beneficial effects of carbonate have been observed in high-efficiency solutions that contain substantial amounts of caustic. Commercial high-efficiency cyanide copper solutions contain an average of about 50 g L\(^{-1}\) sodium carbonate. It is formed by oxidation of the cyanide radical at the surface of polarized anodes or insoluble anodic metal surfaces. Absorption of carbon dioxide from the air by the caustic alkali in the solution and hydrolysis of the cyanide are other sources of carbonates formed in the high-efficiency solutions.

The oxidation of cyanide should be avoided because it increases the cyanide consumption, causes a rapid buildup of carbonates, and complicates control of free cyanide. Concentrations up to about 90 g L\(^{-1}\) sodium carbonate or 120 g L\(^{-1}\) potassium carbonate have no significant effect in reducing the plating speed of high-efficiency solutions. If maximum plating speed is required, however, the concentrations should be controlled below these levels.

### 2.21.2 Tartrates

Tartrates are used primarily in the low-efficiency solutions. It is believed that the potassium–sodium tartrate or Rochelle salt (KNaC\(_4\)H\(_{6}\)O\(_6\)·4H\(_2\)O) forms temporary complexes with copper by reacting with products of electrolysis produced in the anode film. Solutions containing tartrates may be operated with lower free cyanide and at higher current densities and efficiencies without impairing anode corrosion [396, 398]. Obtaining better quality deposits by the use of Rochelle salt is associated in part with the formation of complex salts which are probably present in the cathode film. Solutions are normally operated with about 45 g L\(^{-1}\) Rochelle salt. Wagner and Beckwith [398] claimed that the optimum concentration was about 22.5 g L\(^{-1}\), with somewhat lower efficiencies being obtained at higher values.

The substitution of sodium–potassium citrate for Rochelle salt [399] has been investigated and several other proprietary compounds of a similar type are claimed to offer advantages.

### 2.22 ADDITION AGENTS

Additives for cyanide copper systems include compounds having active sulfur groups and/or containing metalloids such as selenium or tellurium. Other agents that have worked are organic amines or their reaction products with active sulfur-containing compounds; inorganic compounds containing metals such as selenium, tellurium, lead, thallium, antimony, and arsenic; nitrogen and sulfur heterocyclic compounds; and unsaturated alcohols, saccharin, and PEG. An extensive listing of additives used in acid and cyanide copper prior to 1959 can be found in [374] and more recent information in [400–411]. Of interest are data from Table 2.2 in the section on acid copper plating which lists only one U.S. patent for cyanide copper plating since the mid-1970s compared to over 60 for acid copper.

### 2.23 SOLUTION TYPES: STRIKE AND ROCHELLE SOLUTIONS

Copper cyanide solutions may be classified in three categories: strike, Rochelle, and high efficiency. Strike solutions are used extensively to apply relatively thin coatings of copper as an undercoating for other metals. Rochelle solutions, in general, are not as sensitive to contamination as the high-efficiency solutions and are used in applications where an intermediate thickness of copper is applied. Deposits from these solutions vary from dull to semibright; the brightness or luster is not of major importance for most applications.

Copper strike solutions are used for applying a thin coating of copper on aluminum and zinc die castings before plating with other metals [384]. The adherent copper coating prevents chemical attack when these substrates are subsequently plated with heavier coatings from other solutions. The thickness of strike deposits normally varies from about 0.5 to 1 μm, although it may sometimes be as high as 2.5 μm. The heavier strike deposits must be used when the subsequent plating operation is from an acid electrolyte. For instance, the copper strike deposit on zinc die castings must be three to five times as heavy for subsequent acid copper plating as compared with cyanide copper plating.

The bond strength between electroless nickel and a variety of aluminum alloys is higher when a copper strike is used [412]. Besides showing good adhesion of subsequent electrodeposits, the copper strike from cyanide solutions is an additional cleaning operation. Furthermore, a thin copper strike (1.3 μm) under lead coatings over steel has shown improved protective value in atmospheric exposure tests compared to lead coatings alone [413, 414]. Aluminum parts can be plated in a barrel if the free cyanide in the copper strike is high enough (15–20 g L\(^{-1}\)) to prevent displacement of copper on zinc [415]. A good review of copper cyanide striking is provided by Mohler [416].

### 2.24 OPERATING CONDITIONS AND SOLUTION CHARACTERISTICS

The operating conditions of strike and Rochelle solutions are given in Table 2.8. Strike solutions are usually operated in the temperature range of 40–60 °C. The cathode efficiencies are relatively low (10–60%) in the normal plating range of 1.0–3.2 A dm\(^{-2}\). The solution composition and operating characteristics vary widely in actual commercial practice. Many users prefer to add 15–30 g L\(^{-1}\) sodium carbonate. When steel parts are plated, 15–30 g L\(^{-1}\) sodium hydroxide may be added to improve the conductivity. Rochelle salt, or its equivalent, is sometimes used to improve anode and cathode characteristics.

Because of the higher cathode efficiency, heavier deposits can be more practically produced from Rochelle solutions.
than from strike solutions. These plating characteristics are achieved by operating at higher temperatures, controlled pH, and higher metal concentration and adding substantial amounts of Rochelle salt to the solution. The average cathode efficiency is approximately 50% higher than that obtained from strike solutions. The anode and cathode efficiencies vary with the temperature and degree of agitation [396]. Rochelle solutions are normally operated without metal-containing addition agents, but lead had been used as a grain refining and brightening agent [417].

Polarization phenomena in copper cyanide solutions have been extensively investigated [387, 390, 396, 418, 419]. Hatherley and co-workers [387] reported that potassium- and sodium-based solutions may both be operated at close to 100% cathode efficiencies but potassium solutions can sustain efficient copper deposition to a higher maximum current than can sodium. They also noted that increasing free cyanide diminishes the limited current density that can be sustained at maximum efficiency, and this relationship is linear for both sodium and potassium solutions. An increase in the carbonate or hydroxide content is also associated with a reduction in the maximum current for efficient copper deposition. Last, the efficiency of solutions cannot be restored by precipitation of carbonate with lime, nor by any of the other chemical agents that have been proposed in the past [387, 390].

Graham and Read [396, 418, 419] defined the limiting current density beyond which excessive polarization occurs for a given set of solution variables. Excessive polarization causes insulation of the anodes and usually necessitates their removal for cleaning. Variations in metal content and free cyanide have little effect on the limiting current density. If the carbonate content is too high, the copper may act as an insoluble anode without exhibiting excessive polarization.

Reducing the pH from 12.8 to as low as 10.3 does not greatly alter the limiting current density. The presence of tartrates does not overcome the tendency of the anodes to polarize excessively, but the allowable current density is raised when both carbonate and tartrate are present. If insoluble iron anodes are used along with copper anodes, higher anode current densities may be used because the iron anodes depolarize the copper.

The throwing power of Rochelle solutions is superior to that of high-efficiency cyanide solutions. Most of the published data on throwing power are limited to current densities below 1.0 A dm⁻². The factors influencing the throwing power of Rochelle solutions when operated at more practical current densities and temperatures may be quite different. The greatest single factor contributing to good throwing power and metal distribution appears to be associated with a decrease in cathode efficiency with increasing current density. High efficiencies, in general, contribute to poor throwing power, but there are also other factors, as discussed later.

### 2.25 MAINTENANCE AND CONTROL

Copper strike solutions in commercial use vary in metal content but are usually maintained at a copper metal concentration of about 10–16 g L⁻¹. The metal content increases during operation because the copper anode efficiency is higher than the cathode efficiency. It is common practice to use a combination of steel and copper anodes in the strike solutions to obtain an overall anode efficiency equal to the average cathode efficiency. The control of the critical free sodium cyanide is simplified, and a more stable solution composition is thereby attained. The free sodium cyanide should be controlled within the range of 6–11 g L⁻¹.

Continuous filtration of the strike solutions through activated carbon is recommended for the best results. This prevents particle roughness on the shelf areas of the plated parts and minimizes drag in of organic contamination into subsequent plating solutions.

Control of the pH of Rochelle solutions is important for obtaining the best performance. Operation within the pH range of 12.2–12.8 is recommended [396]. The range 12.5–12.8 is preferred because the solution is buffered in this range by the carbonate. Operation at a pH in excess of 12.9 should be avoided, owing to decreased anode efficiencies and chemical attack of the solution on zinc die castings.

The pH of Rochelle copper solutions can be determined by a pH meter, by colorimetric methods, or by titrating with hydrochloric or sulfuric acid. The first two methods are rapid and simple; the titration method, however, has the advantage of indicating directly the approximate excess of caustic above the sulfo-orange sodium carbonate endpoint. The pH at the sodium carbonate buffer point is approximately 11.5; it can be raised to 12.7 by the addition of 0.75 g L⁻¹ caustic soda.
Controlling the free-cyanide concentration of Rochelle solutions within the range of 4–9 g L$^{-1}$ is also important. Excessive anode polarization is encountered at very low free cyanide and the quality of the deposits is also adversely affected. Operating with a significantly higher free-cyanide concentration than recommended results in lower cathode efficiencies and in the production of dull deposits that are difficult to buff.

### 2.26 HIGH-EFFICIENCY CYANIDE COPPER SOLUTIONS

Solutions that are formulated and operated under conditions that give essentially 100% anode and cathode efficiencies are classified in this category. The rates of deposition are appreciably higher than can be obtained from strike or Rochelle solutions.

Many of the high-efficiency cyanide copper solutions are used for plating of automotive bright trim parts. As pointed out earlier, Rochelle solutions may be used for plating zinc die castings. Most installations, however, use high-efficiency solutions in order to obtain the required thickness relatively quickly. The brightness of deposits from the high-efficiency solutions is also an important factor.

Copper is also plated from high-efficiency solutions on selected surfaces of ferrous metal parts to prevent carbon penetration during case hardening. Thickness requirements vary from 13 to 25 μm, depending on the type of carburizing medium used, time of treatment in the carburizing solution, and type of surface finish on the steel. Another use of high-efficiency solutions is the plating of steel wire with a heavy coating of copper [420–422]. Part-to-part spread in deposit thickness for barrel plating is considerably less for alkaline solutions (cyanide, pyrophosphate, and amine) than for acid solutions (sulfate and fluoborate) [423].

### 2.27 OPERATING CONDITIONS AND SOLUTION CHARACTERISTICS

High-efficiency cyanide solutions are normally operated in the temperature range of 60–80°C (see Table 2.8), with the higher temperature preferred for maximum plating speed. Many of the high-efficiency electrolytes are operated at temperatures as low as 60°C to fit specific needs and equipment. It is emphasized that a reduction in solution temperature can restrict the width of bright plating range and maximum usable current densities. The cathode current density range in commercial practice varies from about 1 to 11 A dm$^{-2}$, depending on the contour of the parts being plated. Automotive parts are generally plated at current densities in the range of 2–5.5 A dm$^{-2}$, whereas wire is plated from high-metal solutions at current densities as high as 11 A dm$^{-1}$. Maximum plating speeds are achieved with potassium formulated solutions containing high metal and operated with vigorous solution circulation. The solutions must be operated at substantially 100% cathode efficiency in order to produce good-quality deposits and to avoid hydrogen evolution at the cathode, which produces dull, burned deposits.

These high-efficiency solutions would normally be expected to have poor throwing power. However, metal distribution on plated parts is better than would be predicted from the efficiency factor alone. One reason for this is that the high concentration of salts, particularly alkali, and high operating temperatures greatly improve the conductivity and reduce the difference in current density on protruding and recessed areas. Rochelle salt solutions have good throwing power because the cathode efficiency decreases with increase in current density.

The anode current densities may vary from 1.5 to 5 A dm$^{-2}$. The anode efficiency under these conditions is essentially 100%. At very low anode current densities (0.2–0.6 A dm$^{-2}$), particles of copper may be formed or generated at the anode surface through intercrystalline corrosion. The particles settle on shelf areas of the parts and produce serious roughness. Certain types of proprietary organic addition agents are claimed to play an important role in improving anode corrosion [424]. They apparently form a thin organic film over the anode surface and thereby promote smooth anode corrosion and minimize any tendency to generate copper particles.

Solution circulation or movement of the electrolyte is also important in obtaining performance. In addition to increasing the plating rate, vigorous circulation is effective in minimizing pitting caused by hydrogen bubbles clinging to the surface of parts being plated. Circulation is accomplished commercially by pumping the electrolyte or by air agitation.

The plating characteristics of some of the high-efficiency solutions can be improved by utilizing current manipulation techniques (discussed in more detail in Section 2.10). Parts are plated in the conventional manner for a selected lime and are then deplated for a shorter period by reversing the current. This technique is referred to as PR current plating. Direct plating cycles of 2–40 s with 0.5–10 s reverse (deplating) cycles were described by Jernstedt [372]. Longer cycles, in excess of 60 s direct with reverse cycles in excess of 12 s, were disclosed by Wernlund [425]. Ismail [426] reported that surface roughness increased with frequency and amplitude of the PR current used. Increasing the solution temperature led to brighter surfaces up to 50°C, and a PR ratio of 2 gave the best surface brightness. The PR plate was brighter and had a higher corrosion resistance than the corresponding dc plated deposits. A number of production applications utilizing PR plating are discussed in [427].

Current interruption cycles are also used. For example, zinc die castings are frequently plated using a 10-s plating cycle followed by interrupting the current for 1 s and then repeating the cycle. This approach can provide excellent
deposit brightness from bright plating solutions which are contaminated sufficiently that acceptable deposits cannot be produced by use of continuous direct current.

One of the advantages gained by employing periodic current reversal or interrupted cycles is leveling. The degree of leveling obtained is greatest with PR, particularly with relatively long reversal cycles. Deposits so plated show a laminar structure, whereas those plated with conventional direct current are columnar. The leveling obtained with current interruption is less than with current reversal, but it is adequate for covering minor surface marks such as buffing wheel lap marks on zinc die castings. The uniformity of distribution of the copper on irregularly shaped parts is also improved when current reversal is used. It prevents excessive buildup of metal on high-current-density areas and yields significant savings in anode consumption.

The choice between periodic current reversal and current interruption greatly favors the latter. Periodic reversal has a low net rate of deposition because on the reversal the copper is being depleted. As an example, a 60/20 PR cycle has only a 50% net deposition rate if the current applied is the same for the plate and deplete cycles. The use of PR plating has not had broad acceptance because of this factor. Rudder [428] compared pulse plating of cyanide copper versus acid copper and found that the leveling and thickness performance of the pulse-plated cyanide copper was better than that of the acid copper.

2.28 MAINTENANCE AND CONTROL

High-quality copper deposits can be produced consistently from the high-efficiency solutions by following good plating practice. Analytical methods are available for determining the concentrations of the normal solution components [429–433]. Methods are also available for determining contaminants such as carbonates, ferrocyanide, and zinc. The Hull cell is used extensively for detecting organic contamination, controlling addition agents, and determining the effectiveness of various purification treatments [434–436].

The composition of the solutions in commercial operations varies widely. The copper metal content of the average solution is maintained at about 45–55 g L$^{-1}$. Solutions used for plating steel wire or rod, however, are usually maintained at a metal concentration of 60–90 g L$^{-1}$. The free-sodium cyanide is normally maintained in the range 10–20 g L$^{-1}$. The free cyanide can be lower when the metal content is low. Solutions containing high metal usually require a slight increase in free cyanide for optimum plating performance. An interesting exception to the usual composition and operating conditions for so-called stable copper cyanide plating solutions has been described by Dingley [437], who operated solutions under conditions to give high current efficiencies. Anode-to-cathode areas had to be greater than 4:1 to maintain solution stability.

Good cleaning and thorough rinsing of the parts before plating are very important, since high-efficiency solutions are sensitive to organic contamination, which produces dull deposits and sometimes pitting. Continuous carbon treatment of the copper strike is recommended as a precaution in minimizing drag-in of organic contaminants. The high-efficiency solutions are normally purified continuously by passing them through a filter packed with activated carbon. A periodic batch treatment with activated carbon may be required if excessive amounts of contaminants are present. The effectiveness of the purification can, in some cases, be improved by adding about 1 mL L$^{-1}$ of 30% hydrogen peroxide to the solution before adding the carbon. The peroxide can be added safely by first diluting it with 15 parts of water. Its effectiveness is attributed largely to its ability to convert some types of organic contaminants to a less soluble form by oxidation.

Excessive carbonate in high-efficiency solutions reduces the bright current density range and produces grainy deposits. Carbonate should be removed if the concentration exceeds about 90 g L$^{-1}$ sodium carbonate or 118 g L$^{-1}$ potassium carbonate. It can be precipitated by adding calcium hydroxide (hydrated lime). Excess sodium carbonate may also be crystallized out of sodium formulated plating solutions by cooling the solutions to about $-30^\circ$C. This procedure is unsuitable for solutions maintained solely with potassium salts because of the greater solubility of potassium carbonate at all temperatures. Crain and others [438] discuss the causes of carbonate buildup in cyanide copper plating solutions and control procedures, including a patented method applicable to both sodium and potassium solutions.

Chromate is harmful in the high-efficiency solutions even when present in very low concentrations (5–10 ppm). Its action is similar to that observed in other cyanide copper-plating solutions in that it produces dull, nonuniform deposits. In low concentrations it produces blotchy deposits at low current densities and this condition is extended to higher current densities as the concentration of chromate increases. Adverse effects of chromate can be eliminated by adding a chelating agent of the EDTA type. Although chelating agents of this type do not function as reducing agents, the chromate is probably reduced to a Cr$^{3+}$ compound by the Cu$^{1+}$ ion in the presence of the chelating agent. Reducing agents such as sugar derivatives and sodium stannite are also used [439]. In the absence of Rochelle salt, the reduced chromium will gradually precipitate and is removed by filtration.

Hexavalent chromium in just a few ppm can cause dullness, blistering, skip plating, and reduced cathode efficiency. It also gives rise to a reduced bond strength between the copper deposit and steel substrate [440]. Proprietary compounds are available that reduce the hexavalent chromium to the trivalent state without any side effects.

Zinc, which contributes to step plating in low-current-density areas, codeposits with the copper to form brass deposits which are somewhat brittle. The brassy appearance
of the deposits can be detected when zinc concentrations are as low as 1.5–2.25 g L\(^{-1}\). Excessive buildup of zinc in high-efficiency solutions can be avoided by removing die castings that fall off racks into the plating solution and by applying an adequate thickness of copper in the strike before the higher speed copper plating. If the zinc builds up to an objectionable concentration, the excess can be removed by dummy electrolysis using an average cathode current density of 0.3–0.5 A dm\(^{-2}\). Small amounts of sodium thiocyanate are effective in sequestering excessive zinc.

Iron contamination comes from salts, water, drag-in, and attack of steel in the cyanide solution. The iron can be complexed into a stable ferrocyanide salt that does not codeposit but does accumulate in the solution. If the iron level gets too high, the anode efficiency is lowered, thus causing carbonate buildup.

For a discussion of impurities in copper cyanide plating solutions, including their effects on the deposits and methods for their removal, see [382, 441, 442]. Horner [382] is an excellent source on troubleshooting of copper cyanide solutions.

### 2.29 ANODES

Cast ball, cast elliptical, or electrolytic copper sheet anodes are generally used with strike solutions. Steel anodes are sometimes used in conjunction with copper in a low-efficiency solution such as a strike to safeguard against excessive anode polarization and as a means of controlling the metal content [396, 418]. Copper compounds formed at the anode are soluble in these solutions when the anodes are operated below the critical current density [418]. Excessive current densities usually cause polarization of the anodes by formation of an insulating film. Cast, rolled, or oxygen-free high-purity copper anodes are preferred for Rochelle and high-efficiency solutions.

Copper anodes for high-efficiency solutions should be substantially free of oxide inclusions. Copper oxide particles produce serious roughness on the plated parts because copper oxide is readily reduced to particles of copper at the cathode. Electrolytic sheet copper contains substantial amounts of oxide and other occlusions; it is therefore not recommended for high-efficiency solutions. Crystal structure of the copper is also an important factor in anode corrosion. A large grain structure, in general, is preferred. Several types of good-quality copper anodes produced by melting, extrusion, or casting under an inert atmosphere are available.

### 2.30 MATERIALS OF CONSTRUCTION

Rubber or polyvinylchloride (PVC)–lined steel plating tanks are more satisfactory than plain steel for high-efficiency cyanide copper plating solutions. Polypropylene tanks with adequate reinforcing may also be used, provided that the operating temperature is not excessive [378]. Leaching should be done on any new tanks or equipment coming in contact with the plating solution. This removes any material that may leach into the plating solution and cause poor-quality deposits.

Unlined steel tanks are also widely used. However, under certain adverse conditions the steel may become susceptible to corrosion from the electrolyte. Increasing the alkalinity of the solution by adding hydroxide and raising the free-cyanide content serve to protect the steel and prevent its dissolution [382, 443].

The most satisfactory method of heating the electrolyte is to circulate it through an external heat exchanger and return it to the plating tank through a filter. Particles that may be generated in the heat exchanger are thereby removed. Brass or bronze fittings of any type are not recommended, since they are chemically attacked by the electrolyte. Lead-containing equipment parts must also be avoided, since lead can contaminate some types of high-efficiency processes.

### 2.31 ENVIRONMENTAL

Copper cyanide processes are relatively easy to operate and produce excellent deposits; however, they use extremely dangerous solutions and therefore must be monitored carefully because of the potential of poisoning the workers and the environment. Accidental spills of acid into the cyanide tank or cyanide spilled into a sewer system can result in a very dangerous condition. Cyanide’s waste treatment must also be very carefully conducted in a separate tank under closely controlled conditions [444]. Cyanide-bearing solutions require oxidation of the cyanide with an oxidizing agent such as chlorine or hypochlorite, followed by precipitation of the heavy metals [378]. While it is unlikely to happen on a frequent basis, if the cyanide copper solution ever requires disposal, the cost is prohibitive compared to alkaline non-cyanide copper [445].

### 2.32 STRUCTURE AND PROPERTIES

The best source for property data is Safranek’s [446] treatise on properties of electrodeposits. Another comprehensive reference is that of Lamb et al. [447, 448], who provide data on Young’s modulus, fatigue strength, effects of cold rolling and annealing on mechanical properties, tensile and elongation data for temperatures from –78 to 325°C, thermal expansivity, texture analysis, and gas content for solutions containing no addition agents. The following paragraph summarizes information that appeared in Safranek’s book; very little has appeared on properties of cyanide deposits since publication of his book [446]:

The most satisfactory method of heating the electrolyte is to circulate it through an external heat exchanger and return it to the plating tank through a filter. Particles that may be generated in the heat exchanger are thereby removed. Brass or bronze fittings of any type are not recommended, since they are chemically attacked by the electrolyte. Lead-containing equipment parts must also be avoided, since lead can contaminate some types of high-efficiency processes.
Copper plated from cyanide solutions is highly embrittling to high-strength steel substrates because of the inefficiency of the solutions and the fact that cyanide solutions are highly conducive to hydrogen entry into steel [449]. For waveguide applications, copper deposited from a cyanide solution formed no voids during heat treatment to 1000°C [450].

### PART C  ALKALINE NONCYANIDE COPPER

Alkaline noncyanide copper plating solutions have found increasing popularity since the mid-1980s because of environmental issues. The cost of using and disposing of cyanides and associated environmental concerns have led to efforts to replace cyanides. Besides the obvious plus of elimination of cyanide from the wastewater stream, these new solutions are safe to work with and are easily waste treated with lime in the same treatment process used for nickel, acid copper, and acids [451]. Other benefits include faster barrel plating speed, lower sludge volume generation because of lower metal concentrations, simplified wastewater treatment, no trouble with carbonate buildup, and lower Occupational Safety and Health Administration (OSHA) safety concerns. Disadvantages include higher operating costs, difficulty in using the process on zinc die castings, greater sensitivity to impurities, and a chemistry more difficult to control [451]. Copper concentration limits and operating conditions for alkaline noncyanide solutions are summarized in Table 2.9.

Typically the throwing power of the noncyanide solutions is very good, as can be seen from Table 2.5. An alkaline noncyanide solution provided even better throwing power than the high-throw acid copper formulation used for plating printed wiring boards. Since the noncyanide processes use cupric copper ions while the cyanide processes contain monovalent copper, the latter provide for faster plating at the same current density. However, the noncyanide processes can operate at higher current densities, thus yielding faster plating overall [452]. Most noncyanide processes use air agitation, while at least one (phosphonate) uses a purification cell, with proprietary anodes to prevent buildup of too much cuprous copper [453]. The noncyanide processes require excellent cleaning prior to plating and are not as tolerant of poor cleaning practices as cyanide processes. However, adhesion can be as good as that obtained with cyanide. For example, excellent results have been reported for aluminum prepared for plating by substituting a pyrophosphate strike for cyanide [454, 455]. Similar good results were obtained with 1018 steel and cast iron. The deposits have good mechanical properties, including higher ductility than cyanide deposits, as well as outstanding metal distribution and very good tolerance to common impurities [456]. Safranek and Miller [457, 458] reported that a cyanide strike can be replaced with a pyrophosphate strike if ultrasonic agitation is used during the striking process. Applications where the copper deposit is used as a heat treat masking barrier prior to carburizing, nitriding, or through hardening have proved successful [459, 460]. A number of proprietary formulations are available and these are based on a variety of chelating ligands, most commonly carboxylic acids, amines, and phosphonates [460–463]. Table 2.2 on acid copper plating lists a number of U.S. patents. Nonproprietary formulations that have been evaluated include solutions containing amine–ammonia [464], chloride [465], citrate [465, 466], EDTA [467, 468], glycerolate [469], phosphate [470], pyrophosphate [454, 455, 471], tartrate [472, 473], and triethanolamine [474].

<table>
<thead>
<tr>
<th>Constituent or Condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper metal (g L⁻¹)</td>
<td>5–14</td>
</tr>
<tr>
<td>PH</td>
<td>9–10.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>38–65</td>
</tr>
<tr>
<td>Cathode current density (A dm⁻²)</td>
<td>0.5–3.0</td>
</tr>
<tr>
<td>Tank voltage</td>
<td>2–12</td>
</tr>
<tr>
<td>Anode–cathode ratio</td>
<td>1.5:1</td>
</tr>
<tr>
<td>Copper anodes</td>
<td>OFHC or EFT</td>
</tr>
<tr>
<td></td>
<td>110 copper</td>
</tr>
</tbody>
</table>

### PART D  PYROPHOSPHATE COPPER*

2.33 HISTORY AND DEVELOPMENT

The earliest published reference to copper pyrophosphate deposition was by Roseleur in 1847 [475]. In 1883 Gutensohn [476] was granted a patent for copper pyrophosphate plating on a number of substrates. Others associated with the early state of the art included Brand [477], Delval [478],

Royer [479], and Regelsberger [480]. Pioneering work by Stareck [481, 482] led to the development of a commercial copper pyrophosphate in 1941. The same year Coyle [483] described the main aspects of the process. Reviews of copper pyrophosphate plating can be found in [484–490].

2.34 APPLICATIONS

Pyrophosphate copper is used in the production of electroformed objects such as waveguides, paint spray masks [491], helical antennae [492], heat exchangers [493], molds for making toys [491, 494], and hard, high-strength [495], wear-resistant [496] deposits. Pyrophosphate deposits are also used on steel [491, 497, 498] and aluminum parts [499–504], and in some cases, they serve as a replacement for cyanide deposits [505, 506]. Other applications include plating zinc die castings [507, 508] before bright nickel and chromium plating, as a lubricant for wire deep drawing operations [485, 491], as a stopoff on steel for selective hardening operations such as nitriding and carburizing [485, 509–512], in roll plating [485], in minimizing hydrogen embrittlement [513, 514], and in the manufacture of plated steel cord for radial tires and high-pressure plastic pipes [515, 516]. Pyrophosphate solutions are also used for plating through holes on printed wiring boards, although in most cases this application has been replaced by high-throw acid copper sulfate formulations [490, 517–519]. Use of pyrophosphate processes for automotive decorative plating has been completely eliminated for many years [520]. Pyrophosphate solutions have been used for plating on plastics; however, these solutions are considerably more expensive to make up than high-throw acid copper formulations [521].

2.35 BASIC CHEMISTRY

The copper pyrophosphate plating solution contains copper pyrophosphate (Cu3P2O7·3H2O), either potassium pyrophosphate (K3P2O7) or the corresponding sodium salt (Na3P2O7), nitrate (NO3), and ammonia (NH3). The pyrophosphate salts react in aqueous solution to form alkaline complex anions, the major complex Cu3P2O7 2− and also Cu3P2O7 4−. The solution is of intermediate stability [522]. Between pH values of 7 and 11, the stability of the complex anion is evidenced by the slow but sure hydrolysis of (P2O7)4− to (PO4)3−. At pH values above 11, Cu(OH)2 precipitates; at pH values noticeably below 7 either CuH2P2O7 or CuH2P2O6 precipitates. Acidification below pH 7 converts the (P2O7)4− to either (H2P2O7)2− or (HPO4)2− and thus destroys the complex anion [523]. Additional information on the chemistry of copper pyrophosphate complexes may be found in [486–488, 524–534].

**TABLE 2.10 Optimum Range of Solution Constituents**

<table>
<thead>
<tr>
<th>Analytical Constituent</th>
<th>Composition (g L−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper, Cu2+</td>
<td>22–38</td>
</tr>
<tr>
<td>Pyrophosphate, (P2O7)4−</td>
<td>150–250</td>
</tr>
<tr>
<td>Nitrate, NO3−</td>
<td>5–10</td>
</tr>
<tr>
<td>Ammonia, NH3</td>
<td>1–3</td>
</tr>
<tr>
<td>Orthophosphate, (HPO4)2−</td>
<td>No greater than 113</td>
</tr>
<tr>
<td>Organic additives</td>
<td>As required</td>
</tr>
</tbody>
</table>

2.36 CONSTITUENTS

2.36.1 Copper and Pyrophosphate

Typical formulations are included in Table 2.10. The copper and pyrophosphate contents of the plating solution are critical in terms of the ratio of one to the other. To promote anode corrosion and to increase electrical conductivity, the solution must contain excess complexing compound. Although either may be used, potassium pyrophosphate is preferred over the sodium salt because it is more soluble, and a potassium solution has a higher electrical conductivity because of the higher mobility of potassium ions.

2.36.2 Nitrate

The presence of a nitrate results in a higher maximum current density because, especially at current densities above 3.2 A dm−2, the nitrate ion reduces cathode polarization by acting as a hydrogen acceptor according to the equation [485]

\[ \text{NO}_3^- + 10\text{H}^+ + 8e^- = \text{NH}_4^+ + 3\text{H}_2\text{O} \]

As the solution is used extensively, reduction of the nitrate ion also leads to a buildup of nitrite [535].

2.36.3 Ammonia

A small amount of ammonia is used to produce more uniform and lustrous deposits and to improve anode corrosion. Excess ammonia can cause cuprous oxide to form and this can hinder adhesion [522].

Because ammonia evaporates from the plating solution, it is usually added daily in quantities either dependent on the size of the tank, for example, 140 g of ammonium hydroxide per square meter of exposed surface per day [536], or as determined by chemical analysis of the solution. In some installations, gaseous ammonia is used [537]. Kojima [538] disclosed that ammonia consumption increased with increasing temperature, pH, agitation, and ammonia content in the solution, while current had little effect on consumption.

2.36.4 Orthophosphate

Orthophosphate formed by the hydrolysis of pyrophosphate is beneficial in that it promotes anode corrosion and acts as
a buffer. At all concentrations it affects the properties of the plating solutions and deposits. Increasing orthophosphate concentration decreases the throwing power and efficiency of the solution and causes a reduction in the ductility of deposits [539].

Low pH (less than 7), increasing P$_2$O$_7$ concentration, high P$_2$O$_7$–Cu ratio, high temperatures (greater than 60°C) in the plating solution or heat exchanger, or local overheating will cause orthophosphate to build up. Orthophosphate cannot be removed chemically from a pyrophosphate solution. The concentration can be reduced only by either discarding the solution altogether or by diluting and rebuilding it.

2.36.5 Additives

Additives have more of an influence on deposit properties than any other plating variable, as will be shown in the section on properties and structure. When used at controlled, limited concentrations, organic additives refine the grain structure, provide desired tensile and ductility properties, impart leveling characteristics to the plating solution, and act as brighteners. However, decomposition products from an excessive additive concentration can cause brittle copper deposits.

Thus, for optimum quality deposits, no more additive should be added to a solution than is necessary to replace losses by consumption.

Organic additives covered in the patent literature as brighteners include mercaptothiadiazoles [540–550], mercaptothiazoles [551–556], mercaptobenzimidazole [557], and pyrimidines [555, 558, 559]. Other organic and inorganic materials, such as glycerol [560, 561], triethanolamine [560, 561], trioxylutaric acid [525, 562], diphenylamine sulfonic acid [561], naphthalene disulfonic acid [563], gelatin, bakers yeast, casein, glycoll [564], hydroxyethylcellulose [565], sodium selenite [525, 559], sodium sulfite [560, 561], Rochelle salt, sodium thiosulfate, potassium bromide [561], and the chlorides of As, Bi, Fe, Cr, Sn, Zn, Cd, Pb [482, 563], and alkali metals have been used as brighteners. Additions of small amounts of lead are reported to improve plating properties [566, 567]. Organic acids such as oxalic, lactic, tartaric, malic, and citric or their ammonium or alkali salts also produce some brightening [482].

2.36.6 Operating Conditions

A copper pyrophosphate plating solution may be operated over a relatively wide range of conditions. The optimum range, similar to that given by Couch and Stareck [568], is shown in Table 2.11.

2.36.7 Pyrophosphate–Copper Ratio

The copper pyrophosphate solution is analyzed for both copper and pyrophosphate, and it is therefore convenient to describe the solution in terms of the ratio between these constituents. For optimum plating, the weight ratio of pyrophosphate to copper should be kept in the range 7:1–8:1.

Ratios of 8.5:1 or higher promote formation of orthophosphate and thereby decrease the bright plating range. Operation with a ratio of less than 7:1 tends to produce a rough-surfaced plate and renders the solution unstable.

2.36.8 pH

The optimum solution pH is in the range of 8–9. As discussed earlier, a pH outside this range results in hydrolysis of pyrophosphate to orthophosphate or the formation of precipitates. Also, if the pH is too high, both anode corrosion and operating current density range decrease. Radin [569] states that a pyrophosphate solution will operate acceptably even at pH values as high as 9.3 provided the copper concentration exceeds 26 g/L. When a solution is operated at this high pH, the tendency toward roughness can be eliminated by increasing the P$_2$O$_7$–Cu ratio. In practice, a pH of 7–9 is easily maintained because at this pH both anode and cathode efficiencies are virtually 100%. Clearly, there is no chemical breakdown of the constituents, and the solution is highly buffered. When adjustments must be made, pyrophosphoric acid is used for lowering pH and potassium hydroxide for raising it.

2.36.9 Temperature

The solution is usually operated between 50 and 60°C. Temperatures greater than 60°C can lead to rapid formation of orthophosphate.

2.36.10 Current Density

Cathode current density is a function of the temperature and agitation of the plating solution. However, under standard operating conditions, a current density of 1–9 A dm$^{-2}$ is appropriate. The anode current density is fairly critical, and it should be kept between 2 and 4 A dm$^{-2}$. At too high an anode current density, an insoluble oxide tends to form. The operating current density range may be increased by

<table>
<thead>
<tr>
<th>TABLE 2.11 Optimum Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_7$–Cu ratio</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>Cathode current density, A dm$^{-2}$</td>
</tr>
<tr>
<td>Anode and cathode efficiency, %</td>
</tr>
<tr>
<td>Anode–cathode ratio</td>
</tr>
<tr>
<td>Agitation</td>
</tr>
</tbody>
</table>
ultrasonics, by current interruption or reversal, and by increased metal concentration.

2.36.11 Agitation

Copper pyrophosphate solutions are among those that must be most vigorously agitated. Without sufficient agitation, a brownish deposit is obtained, and the operating current density range is drastically lowered. A solution can be continuously agitated by either one or a combination of three methods: air, mechanical movement of the cathode, or ultrasonics. When air agitation is used, the air should be supplied by a low-pressure blower because compressed air can contain oil.

Gurylev et al. [570] claimed that ultrasonic agitation reduces anode and cathode polarization and permits a 4–4.5 times increase in the deposition rate over that obtained with intensive mechanical agitation. The combination of ultrasonics and periodic reverse current increased current efficiency and allowable anode current density. Rutter et al. [571] reported that the use of ultrasonics resulted in improved adhesion and a denser deposit. Safranek and Miller [507, 508] and others who have plated over zinc die castings showed that ultrasonic agitation of copper pyrophosphate solutions displaced air or hydrogen from blind pockets and resulted in more uniform deposits than could be obtained with copper cyanide strikes. Uspenskii and Schluger [572] investigated pH variations in an ultrasonic field and Trofinov and Galushko [573] polarization characteristics. Trofinov [574] concluded that metal distribution from a copper pyrophosphate electrolyte could not be influenced much by an ultrasonic field. Vasudevan et al. [575] reported an improvement in both anodic and cathodic current efficiencies under ultrasonic agitation but no change in hardness of the deposit.

2.36.12 Equipment

The equipment—a tank, heater, and filter—is similar to that used for bright nickel plating. A steel tank coated with rubber, Koroseal (Trademark: B. F. Goodrich Co.), PVC, or a plastisol is suitable, although rubber linings should be leached before use with a dilute solution of potassium hydroxide to remove all alkali soluble matter that can contaminate the plating solution. For heating the solution, either steam heating coils or electric immersion heaters made of stainless steel or Duriron may be used. Continuous filtration helps prevent rough deposits. The filter should be constructed of stainless steel, rubber, or PVC-lined steel or cast iron.

2.36.13 Anodes

OFHC anodes are the best available; however, electrolytic sheet and rolled electrolytic copper anodes are also satisfactory. Cast anodes of good purity can also be used, but they should be free of impurities such as lead, nickel, silver, and tin because these tend to promote deposit roughness. Anode bags are not usually used; they are not needed and can restrict circulation of the plating solution around the anode and cause polarization. Anodes can be left in the solution when it is not being used since they do not dissolve in the absence of applied current.

2.37 MAINTENANCE AND CONTROL

2.37.1 Analysis

For the analytical determination of copper, pyrophosphate, and orthophosphate, the simplest procedure is that of Konishi [576], where all three constituents are determined by titration with EDTA. Copper can also be determined electrochemically [577] or by titration by the iodine–thiosulfate method [577–579], pyrophosphate by titration with standard alkali [577–579], and orthophosphate gravimetrically [578, 579] or colorimetrically [580]. Ammonia is analyzed by distillation and adsorption in standard acid [577, 579] or by cyclic voltammetric stripping (CVS) [581]. Tench and Ogden and their circle of researchers have pioneered in the use of CVS, particularly for controlling additives and contaminants in copper plating solutions for printed wiring board production. Their work with pyrophosphate solutions is covered in references [542–549] and reviewed in detail in [582]. Tam and co-workers [534, 535] also used CVS to study the effects of all constituents on cathodic and anodic reactions.

2.37.2 Impurities and Purification

Cyanide, oil, lead, decomposition products of the organic additives, residues from photoresists and solvents used in circuit development, epoxy laminate residues, excess orthophosphate, and substances leached from plating tanks are the impurities most often encountered in a copper pyrophosphate plating solution. These impurities cause streaked, dull deposits and also lower the effective current density range. Precautionary methods will prevent these materials from entering the solution. Thorough rinsing, when copper cyanide striking is used, will prevent cyanide contamination; a clean air line for solution agitation will prevent oil contamination; and avoiding the use of lead coils, lining, fittings, or filters will prevent lead contamination.

Cyanide, which can be detected by a copper benzidine test [583], can be removed by treatment with either 1.25 mL L\(^{-1}\) of 30% H\(_2\)O\(_2\) or 0.1–0.2 g L\(^{-1}\) potassium permanganate followed by treatment with activated carbon. The tendency toward streaked, nonuniform pyrophosphate deposits due to residual traces of cyanide left on the surface after copper cyanide striking can be minimized by brief cathodic treatment in a solution of potassium pyrophosphate before it is placed
in the plating solution. Oil can be removed by treating the solution with 2.5–6 g L\(^{-1}\) of activated carbon at 55°C for 4–8 h. Low-current-density electrolysis will remove lead.

Copper pyrophosphate solutions are quite tolerant of metallic contamination because many metals besides copper form complexes with the pyrophosphate ion and remain in solution. For example, no harmful effects have been reported from zinc which may be introduced when the solution is used to plate zinc die castings. It has been recommended, however, that a high P\(_2\)O\(_7\)/Cu ratio (preferably 7.5:1) be maintained under this circumstance so as to allow some excess pyrophosphate for complexing with the contaminant. Phosphorus included in the deposit was reported to influence external appearance, microhardness, and microstructure [584]. Iron and lead can alter deposit morphology and concentrations below 200 and 1000 ppm, respectively, are recommended [516]. Chloride ion, which is known to affect anode reactions, can be tolerated at concentrations lower than 0.1 M with vigorous agitation of the solution [515].

Organic contaminants, besides reducing deposit ductility and strength, can also cause loss of throwing power and irregular deposition. The contamination can come from decomposition products from organic additives, air agitation, leaching of photoresists, and the carbon used for removing contaminants. Rothschild et al. [585] provide an excellent review on carbon treating of pyrophosphate solutions for keeping them free of organic contaminants and recommend the use of Hull cell tests to determine the effectiveness of treatment. In some cases an activated carbon treatment alone is not sufficient purification. To ensure removal of the decomposition products, it is best to carbon treat the solution, H\(_2\)O\(_2\) treat, and then carbon treat again. The carbon should be plating grade and sulfur free.

Cyclic voltammetric stripping analysis is an excellent means for detecting a wide range of contaminants in addition to organic additives in pyrophosphate solutions. Excellent correlation has been obtained between the measured contaminant level and plating problems normally attributed to solution contamination such as poor solder adhesion and low deposit ductility [542, 544, 545, 548].

Waste pyrophosphate solutions are difficult to treat because of ammonia in the solutions and also the complexes that are formed [586]. Wastes require low-pH hydrolysis to orthophosphate followed by precipitation of the heavy metals [488].

2.38 STRUCTURE AND PROPERTIES

The best source for property data is Safranek’s treatise on properties of electrodeposits [587]. Another comprehensive reference is that of Lamb et al. [588], who provide data on Young’s modulus, fatigue strength, effects of cold rolling and annealing on mechanical properties, tensile and elongation data for temperatures from −78 to 325°C, thermal expansion, texture analysis, and gas content for solutions containing no addition agents.

Copper pyrophosphate deposits show tensile strength variations from 27 to 70 kg mm\(^{-2}\); yield strengths from 14 to 36 kg mm\(^{-2}\), hardness from 83 to 250 kg mm\(^{-2}\), and elongations from 1 to 39%. Several investigators have related these variables to solution content and operating variables with additive concentration being the most important variable [495, 547, 589–595].

Optimum ductility has been obtained by using solutions free of organic additives [588]. In some cases, continuous filtration is also used [589, 596]. High-purity, high-quality deposits have been produced on internal walls of colliders in beam tubes by using multistage purification and pulsed reverse current in solutions with no additives [597, 598].

A comparison of recrystallization temperature for electrodeposited pyrophosphate copper and wrought copper with various degrees of cold work suggests that the electrodeposited copper exhibits behavior expected of 100% cold-worked material [592]. Malone [599] reported that pyrophosphate copper electrolites were capable of producing deposits with excellent mechanical properties. However, he cautioned that the pyrophosphate electrolite is very difficult to control and maintain in comparison with the acid sulfate solution, and producing deposits consistently within a specific range may prove difficult unless the electroplater has considerable experience with the pyrophosphate solution and the many peculiarities associated with it. The influence of pH, temperature, agitation, and current density on throwing power and efficiency can be found in [600].

2.39 PLATING OF PRINTED WIRING BOARDS

The 1974 edition of this book [484] devoted a section to this topic in the chapter on copper pyrophosphate. Around the time of publication of that volume, high-throwing-power acid copper sulfate solutions were developed [601]. Today these solutions are used instead of pyrophosphate for most printed wiring board applications, except in some military and special applications [490]. It is estimated that greater than 95% of all printed wiring boards today are plated in acid copper sulfate solutions [518]; this is discussed in more detail in Section 2.12. A good review of present practice with pyrophosphate plating of printed wiring boards can be found in [490].

PART E COPPER COMPOSITES

Present-day structural materials have two major shortcomings: loss of strength at elevated temperatures and relatively
low elastic moduli [602]. One way to solve these problems is in strengthening materials by incorporating high-strength and high-modulus particles, fibers, or continuous filaments in a metal matrix. The major disadvantages of present methods (internal oxidation, powder metallurgy, high-pressure bonding, and infiltration) in producing dispersion-strengthened and fiber-reinforced composites are the high process temperatures and pressures required. Degradation of the fibers due to handling and difficulties encountered in machining the finished composite structure are also concerns.

A less common method of producing these composites is electrodeposition. There is no requirement in electrodeposition for high temperatures that can damage the fibers. The strengthening of electrodeposits can be accomplished by the encapsulation of inert particles (whiskers), or filaments during plating to produce high-performance coatings [602–604]. Two terms commonly used to refer to use of electrodeposition to produce composite materials are composite plating and electrocomposites. Electrodeposition of copper and nickel are the two plating processes most commonly used to produce composites; copper will be covered in this section. Reviews on composite plating can be found in [602–610].

Copper composite materials have typically been produced in sulfate solutions, although acid fluoroborate and alkaline cyanide solutions have also been used. Particles that have been codeposited with copper include alumina, barium sulfate, borides, carbides, carborundum, corundum, graphite, molybdenum disulfide, polystyrene, phosphorus, polytetrafluoroethylene (PTFE), quartz, titania, tungsten disulfide, molybdenum disulfide, phosphorus, polytetrafluoroethylene (PTFE), quartz, titania, tungsten disulfide, molybdenum disulfide, phosphorus, polytetrafluoroethylene (PTFE), quartz, titania, tungsten disulfide, and zirconium oxide. Mechanical or ultrasonic agitation was required to uniformly disperse the particles, which ranged from 50 to 200 g L⁻¹ in the solution.

A variety of techniques can be used for codeposition of particles. Namely occlusion plating particles are allowed to codeposit on the cathode surface while some intermittent vigorous mechanical stirring of the plating solution is applied [609], sediment codeposition particles are allowed to sediment on a flat cathode as electrolysis proceeds and are only occasionally agitated [611–614], and composite plating particles are deposited on a vertical cathode [609]. Particles are kept in suspension by either mechanical or chemical means. Suspension by mechanical means is accomplished by use of a vibrating perforated bottom plate or by the use of air agitation. Suspension by chemical means typically requires the addition of appropriate surfactants to the plating solution.

The optimum conditions for preparing particle suspensions and codepositing a designated volume fraction of uniformly dispersed inert particles have not been firmly established. Most of the literature data have been derived empirically. Particle diameters have ranged from 0.02 to 100 μm. Quantities dispersed in solution have varied from 50 to 200 g L⁻¹ [604]. Wetting agents, monovalent cations and aliphatic amines absorbed on particle surfaces, promoted encapsulation and improved dispersion [609, 615, 616]. Particle encapsulation was less during operation of a copper sulfate solution, in comparison with the amounts reported for codeposition in cyanide solutions [604, 609, 615–617].

2.40 ALUMINA

The copper–alumina system has been investigated by many researchers [604, 605, 607, 618–641]. Both α-alumina (0.3–1.0 μm) and rutile titania (0.3 μm) were readily co-deposited with copper in an acid solution, but γ-alumina (0.2 μm) and anatase titania were not. Calcining (20 h at 1125°C) promoted the codeposition of γ-alumina particles in copper [618]. This effectively transformed the surface of γ particles into an α structure, as verified by X-ray studies. Lakshminarayanan et al. [619–621] concluded that α- and γ-alumina could be codeposited provided that the plating solution was free of chloride. By contrast, Roos et al. [622] reported that both γ- and α-alumina could be codeposited in an acid sulfate solution with or without the presence of chloride ions in the solution. However, under identical conditions, much smaller quantities of γ-alumina were codeposited as compared with α-alumina.

With pulsed or periodically reversed current, increasing the current density increased the alumina content of copper [623, 624]. Ultrasonic agitation reduced agglomeration, improved particle distribution, and improved the strength retention of copper–alumina composites [625].

2.41 PROPERTIES

Lakshminarayanan et al. [620] reported that codeposition of 1.2%, by volume, of 0.03 μm γ-alumina increased the yield and ultimate tensile strengths of copper from 97 and 197 MPa to 128 and 246 MPa, respectively, while elongation was reduced from 32 to 20%. An increase in the alumina content to 2.4% increased the yield and tensile strengths to 217 and 345, respectively, while the elongation was 15% [620]. A fairly high yield strength of 50 MPa was retained after the copper–alumina composites were annealed at 420°C. Stankovic and Gojo [641] noted that tensile strength increased to about 290 MPa with increasing alumina particle content. Further increases in the particle content did not affect the tensile strength significantly. As regards electrical resistivity, a 2.2% alumina composite exhibited a moderate increase over pure copper (1.86 vs. 1.72 μΩ·cm) [620].

Abrasive wear was reduced 83–85% by codepositing 5.5 or 7.3% of carborundum particles [642]. Based on friction measurements, copper–graphite composites appeared to be the best self-lubricating coating when compared with composites containing molybdenum disulfide or PTFE particles [643]. Silicon carbide codeposited particles provided
a high hardness which was retained up to 900°C. Abrasion and oxidation resistance also improved as a result of inclusion of silicon carbide [605]. A summary on property data can be found in reference [606].

2.42 MECHANISM

A two-step mechanism was proposed by Guglielmi [644] in which the combined effect of adsorption and electrophoretic attraction is held responsible for the encapsulation of particulate matter in a growing electrodeposited layer. The validity of Guglielmi’s model has been verified for different codeposition systems, including copper with alumina from acidic sulfate solutions, with and without the addition of thallium. However, Guglielmi’s model does not allow prediction of the manner in which process parameters such as size, type, and pretreatment of the particles, composition, temperature, and pH of the plating solution affect the electrolytic codeposition [609].

Foster and Kariapper [627] proposed a mathematical model in 1974 that could describe the effect of hydrodynamics on codeposition, but only a limited amount of quantitative work has been done to prove its validity. Snaith and Groves [645–647] also reported on mechanisms.

In 1987 Celis et al. [639] proposed a model that contains measurable parameters so that the prediction of the amount of codeposited particles for a given system becomes feasible. As described, “This mathematical model is developed on the basis of two fundamental postulates related to the mechanism of codeposition, namely: 1—an adsorbed layer of ionic species is created around particles at the time these particles are added to the plating solution or pretreated in ionic solutions and 2—the reduction of some of these adsorbed ionic species is required for the incorporation of particles in the metallic matrix” [639].

Figure 2.3 shows that the particle has to proceed through five stages: (1) the adsorption of ionic species upon the particle, (2) the movement of the particle by convection toward the hydrodynamic boundary layer at the cathode, (3) the diffusion of the particle through the diffusion double layer, (4) the adsorption of the particle with its adsorbed ionic cloud at the cathode surface, and (5) the reduction of some adsorbed ionic species by which the particle becomes irreversibly incorporated in the metal matrix. The model has been demonstrated to be valid for the codeposition of alumina particles with copper from acid copper sulfate plating solutions [609, 639].

2.43 CONTINUOUS FIBER-REINFORCED COMPOSITES

Acid copper solutions have been used in fabricating fiber-reinforcing metal composites. In these processes, simple salt solutions work satisfactorily, whereas highly complexed solutions such as cyanide do not [648]. Continuous, unidirectional filament-reinforced electrocomposites that have been produced include 25 μm tungsten in copper and 100 μm boron in copper [604]. A composite containing 40% volume of tungsten filaments, produced by continuously winding tungsten wire on the cathode during copper deposition, exhibited a tensile strength of 1325 MPa [649].

Graphite–copper composite panels have been fabricated by weaving copper-coated graphite fibers into a fabric and then consolidating by hot pressing. This offers a potential technique for low-cost processing of metal matrix composite electronic heat sinks [650]. Carbon fibers are continuously coated with copper in a pyrophosphate–HEDP (hydroxyethylidene diphosphonic acid) electrolyte [651].

PART F
COPPER PLATING IN MICROELECTRONICS

New applications are opening up for copper conductors in microelectronics, microelectromechanical systems (MEMSs), and nanotechnology [652]. Incorporating material into three-dimensional geometries is a strength of electrodeposition. A major success has been the replacement of aluminum and its alloys by copper for ultra-large-scale integration (ULSI) interconnects [653]. The deep reservoir of copper plating knowledge has enabled a natural and rapid emergence of process technology. Implementation of copper
results in a 40% lower wire resistance, 20–30% anticipated boost in chip performance, improvements in wire reliability, and 10–15% lower chip cost.

Moore’s law for microelectronics states that the density of elements on integrated circuits will increase steadily as predictable process improvements are implemented. As stated today, the number of transistors that can be placed on an integrated circuit with commercial processes doubles approximately every three years. As feature size reached submicrometer level, the drawbacks of aluminum interconnects became apparent, notably the high electrical resistance. The microelectronics industry identified copper as a likely interconnect replacement material and began to incorporate this change in plans such as the SEMATECH Roadmap [653].

SEMATECH creates its Roadmap with targets such as the required half-pitch of dynamic random-access memory (DRAM) designs. As feature size on ULSI devices decreases, this minimum size requirement decreases. The industry is currently operating at the 45-nm SEMATECH Roadmap node. When a new feature size node becomes the norm, major changes and investment are required for new microfabrication facilities. Programs are in progress to prepare for the coming shift to the 32-nm node. And a further shift to the 22-nm minimum-size node is projected within six to eight years.

In 1998, IBM announced its successful development of copper electroplating technology for fabrication of chip interconnect structures [654, 655]. The challenge was to fill trenches and vias within the silicon chip without creating voids or seams and without degrading the circuit materials and patterns. IBM found that it could fill submicrometer-size features completely, that is, without voids, if the plating solution contained an appropriate mixture of additives. They termed this phenomenon “superfilling” and named the process “damascene copper,” after the classic art form of metal inlay. The silicon substrate is first configured with its trenches and vias. Then an insulating coating is applied followed by a seed layer of copper. At this point, copper metal is added by electrodeposition to fill the trenches and the vias, completing the interconnect pattern. Finally, excess over plated copper is removed from the wafer surface. Filling of trenches only is termed single damascene, and simultaneous filling of trenches and vias is termed dual damascene.

It was understood that success with superconformal feature filling depended heavily on the additive mix, and their relative diffusion/adsorption characteristics, in the plating solution. Copper electrodeposition had been well studied, so there was a solid base from which to build and refine the process. Other tools were also available, such as controlled agitation and pulse reversal deposition. Projections based only on today’s technology for depositing seed layers and for damascene filling indicate that copper superconformal filling will be the preferred practice down to at least the 22-nm node on the SEMATECH Roadmap [656].

Understanding of the phenomena operating was incomplete during the early development of the copper damascene process [657]. A National Institute for Standards and Technology (NIST) group determined that the superconformal filling of trenches and vias by electrodeposited copper involved competitive interaction between additive species that accelerate and inhibit deposition. The accelerator adsorbs on the cavity wall and, as electrodeposition proceeds, the feature diameter generally decreases. Current understanding suggests that the surface density of accelerator increases with decreasing feature diameter, leading to an increase in deposition. This occurs as the base of trenches and vias, becoming the basis for bottom-up filling. Normally, in the absence of additives, a cavity in a surface would be capped with overgrowing deposit, trapping a microcavity—a situation that must be avoided with ULSI fabrication.

Additives and basic ingredients of acidic copper plating solutions fall into one of the following categories:

- Copper sulfate provides the source of copper ions.
- Sulfuric acid gives conductivity and induces soluble anode corrosion.
- Chloride is synergistic with organic additives in the brightening and leveling.
- The brightener, or accelerator, typically contains low-molecular-weight sulfur and a second atom of high polarity and/or ionic character. Its function is to refine the grain structure in normal copper electrodeposition. Typical brighteners include thiourea, disulfides, thiocarbamates, and thiocarboxylic acid amides.
- Inhibitors convert an unevenly distributed stationary cathode diffusion layer into a more evenly distributed layer and reduce the variation in copper deposit thickness across the surface. Examples include high-molecular-weight polyether compounds, surfactants, and polyoxyalkylene glycols.
- The polar leveler slows down the charge transfer of copper ions to copper metal, thus slowing the plating rate in those areas considered high current density.

NIST developed a quantitative process model on this basis—curvature-enhanced accelerator coverage (CEAC)—that has guided development [658]. The basic idea is that (a) the growth velocity of the infilling copper is proportional to the local accelerator, or catalyst, coverage, and (b) the catalyst remains segregated at the metal–electrolyte interface during metal deposition. This leads to catalyst enrichment on advancing concave surfaces and catalyst dilution on advancing convex surfaces. The result is the desired bottom-up filling of submicrometer features in the integrated circuit. The NIST group validated the CEAC model with an archetypical additive package of chloride, PEG, and a sulfide such as 3-mercapto-1-propanesulfonate (MPSA) or
[Na₂(SO₃(CH₃)₂)₂] (SPS). In acidified copper sulfate solution, inhibition is provided by interaction between PEG–C1 and the copper surface. Acceleration is associated with the competitive adsorption of the sulfide or its derivatives.

Damascene copper has the tendency to form bumps above filled features, termed overshoot. The NIST group recently reported on using a cationic surfactant additive to inhibit this undesirable copper overplate [659]. The surfactant is included at a level that permits the desired SPS-derived bottom-up filling but quenches the SPS mechanism as filling is completed. NIST has published an extensive coverage of the nature and modeling of superconformal film growth [660].

As damascene processing is used for ULSI designs with ever-smaller features, the copper grain size becomes a factor. Pulse current and periodic pulse reverse current tend to give improved distribution of copper on high-aspect-ratio surfaces when compared to direct current plating. And copper grain size tends to decrease with increasing pulse frequency [661].

Vereecken and IBM colleagues have shed more light on the mechanism by which damascene additives interact with the cuprous and cupric ions to create the balance of acceleration and inhibition [662]. Kim and NIST colleagues also applied electroanalytical methods to probe the mechanism [663]. They conclude that inhibiting additives limit access of cupric ions to the copper surface. They further determined that cationic surfactant additives deactivate SPS (sulfur-containing) accelerator additive by tying up the anionic group. The combined process can be optimized to enable superfilling to be sustained while simultaneously attenuating overfill bump formation.

As of 2004, over 200 damascene electroplating systems were in use in semiconductor fabrication worldwide [664]. Wafers are typically held face down in the electrolyte and rotated during electrodeposition. Superconformal filling of via holes and trenches and production of void-free vias and lines is largely dependent on the action of organic additives in solution. The organic additive concentrations must be kept within a process window. IBM accomplishes this with a combination of monitoring and makeup of solution. They consider analysis by cyclic voltammetry analysis to be one option for tracking bath composition [665]. Organic additives added to copper electroplating baths typically include suppressor (polymers such as PEGs), accelerators (sulfur-containing compounds), and levelers (secondary suppressors). Organic components are consumed during the actual damascene processing step. Innovators continue to identify chemistries and added surface treatments to suppress void formation and reduce stress in the filled features and vias [666, 667].

The IBM announcement [654, 655] included an initial model to guide future process development and control. NIST developed further insights on bump suppressions using its CEAC model [668]. And the Alkire University of Illinois group has contributed a series of improvements to the algorithms and computation methods [669–673].

Electrochemical phenomena such as copper damascene are embraced as a challenge of current nanotechnology research because their behavior results from linked interactions spanning many length scales. At one extreme is the molecular scale of adsorbed additives and copper nanostructures. At the other extreme is the macroscale of the silicon wafer and its features. Multiscale simulation has become a priority for all fields of science and engineering [668, 669]. As a result of increased investment and sharing, computing power and algorithms are becoming ever more powerful. The improvement in scientific understanding and modeling capability will continue. Computing is no longer an issue. The research focus is on developing improved models and algorithms, which can come from related fields as well as electrochemical science and engineering.

REFERENCES

2a. P. C. Andricacos, Interface, 7, 23 (Spring 1998).
2b. P. C. Andricacos, Interface, 8, 32 (Spring 1998).
REFERENCES

ELECTRODEPOSITION OF COPPER

96. J. B. Mohler, Met. Finish., 85, 121 (June 1987).
115. J. Reid, PC Fab, 10, 65 (Nov. 1987).
REFERENCES

159. H. Bovet, Pro-metal, 7 (43), 452 (1955); Translation 3738, H. Butcher, Altadena, CA.
166. E. J. Serfass, W. S. Levine, and M. H. Perry, Plating, 37, 166 (1950).
190. J. D. Reid, in Proc. AESF SVR/FIN 90, Session H, Boston, AESF, Kissimmee, FL, July 1990.
ELECTRODEPOSITION OF COPPER


586. F. Altmyer, private communication, Apr. 1996.