Copper Plating (1909-1959)

formerly titled

Copper Plating during the Last 50 Years

by Frank Passal

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(Recompiled by J.H. Lindsay)

Although those who have spent their careers working with other metals might fervently, and understandably, disagree, copper, nickel, chromium and zinc have been the mainstays of the industry for decades. Electroplated copper in particular has served in a variety of applications, from a vital underlay in decorative automotive finishes to the most sophisticated of electronic circuitry. When the AESF (then the AES) celebrated the 50th anniversary of its founding in 1959, the June issue of *Plating* that year featured a series of articles relating the development of the important plated metals of the mid-20th century. The following article, written for the AES Golden Jubilee by Frank Passal, at the time a Research Associate at Metal & Thermit Corporation, Detroit, Michigan, relates the history of copper plating. What is striking is the astounding number of solution types from which copper was deposited.

Although the commercial application of copper plating had its origin in the early years of the nineteenth century, the most rapid progress in this field has occurred only during the last thirty years [1929-1959 — *Ed.*]. As with two of the other more important plated metals, nickel and chromium, the electroplating of copper for decorative and functional purposes began to progress most rapidly when a demand for the coating on a large scale in the automotive and other industries stimulated an intensified effort in the study of bath compositions and operating variables. Some of the motivating factors were the introduction of more rigid specifications and requirements for increased deposit thickness, higher speeds of plating and improved quality of deposits from the standpoint of luster, smoothness and freedom from porosity.

Parallel with these fundamental studies there also occurred rapid development of plating equipment such as tank linings, semi- and full-automatic conveyor systems, filtering devices, pH control instruments and DC current sources. Last but not least in improvements have been the rapid strides forward in the manufacture of purer and more consistent plating chemicals and anodes, and the utilization and development of chemical and electrochemical purification procedures.

The following report covers the most significant developments in the chemistry, technology and applications of copper plating during the last fifty years [*i.e.*, 1909-1959 — *Ed.*]. A number of acidic and alkaline plating systems will be considered, with special emphasis on the most recent developments and trends. A number of problems which still exist will be presented and discussed.

General

Although the literature on copper plating and its applications is quite extensive, there have appeared a number of excellent review articles which have served as benchmarks for a periodic evaluation of progress in this field. In 1913, Bennett's[1] review article considered a variety of acidic and alkaline copper plating formulations and operating conditions. From the number and nature of heterogeneous bath compositions and additives covered in this review it is evident that the state of the art was far from stabilized at that time. Many of the bath compositions seem rather archaic and impractical in the light of present day knowledge.

The comprehensive review article of Bandes in 1945[2] emphasized the substantial progress made in the intervening 32 years. Not only had there occurred substantial improvement in bath formulations and process conditions for the sulfuric acid bivalent copper bath and the cuprocyanide system, but several new baths had been developed which were important contributions to copper plating. These were the bivalent alkaline pyrophosphate, acid fluoborate and the alkaline organic amine baths.

The informative general review articles of Lutter[3] and Weimer[4] cover most important recent developments, particularly concerning the acid sulfate system and the alkaline cyanide and pyrophosphate systems. Baths giving deposits with improved leveling, buffing and luster characteristics are especially emphasized.

Of all the common metals which are plated, copper is perhaps the most unique from the standpoint of the variety of acid and alkaline systems from which it has been plated. The following is a partial list of anions in acidic media which have been investigated for copper plating:

a. Sulfate
b. Fluoborate[5]
c. Sulfamate[6]
d. Fluosilicate[7]
e. Alkane sulfonate[8]
f. Iodide[9]
g. Aromatic sulfonate[10]
h. Oxalate[11]
i. Formate[12]

The deposition of copper from the following alkaline systems has also been studied:

a. Cyanide
b. Thiosulfate[13]
c. Pyrophosphate[14]
d. Organic amine[15]
e. Thiocyanate[16]
f. Ethylene diamine tetra acetate (EDTA)[17]
g. Tartrate[17a]

The relatively high solubility of copper salts in acid systems, the high cathode efficiency in copper plating down to very low pH values, and the ability of copper to form a number of monovalent and bivalent complex ions in acid and alkaline media are the principal reasons why investigations have been made on such a wide variety of copper plating systems.

Of the systems which have been studied, only relatively few have reached a stage of commercial importance. These are the alkaline cyanide and pyrophosphate complex ion systems and the acid sulfate and fluoborate simple ion systems. Other types of baths have been too unstable or have been lacking in good deposit characteristics, in sufficiently wide current density range or in good anode corrosion.

In the following pages the most important acid and alkaline copper baths will be reviewed from the standpoint of bath chemistry and composition, additives, operating conditions and most important applications.

Acid systems

Sulfuric acid copper

In 1830 Professors Wagner and Jacobi, while engaged in the investigation of the Daniell Cell ($Cu/CuSO_4/ZnSO_4/Zn$), noticed a layered deposit of copper which reproduced the form of the sides of the cell vessel. The practical utilization of this observation was communicated to the Academy of Sciences in St. Petersburg by Professor Jacobi in 1838. In 1836, De la Rue,[18] while working with a form of the Daniell Cell, also noticed the surface-reproducing characteristics of electrolytically deposited copper. Other investigators such as Jordan[19] in a paper entitled "Electrotype Process," read before the Liverpool Polytechnic Society in 1839, reported similar findings.

Since these early beginnings of acid copper plating, the system has been found to have increasing widespread application in the plating industry for a variety of decorative and functional uses. In one of the large automotive organizations, it is reported, for example, that 560,000 gallons of acid copper are used for the plating of ferrous and non-ferrous basis metals prior to polishing and buffing, and to application of other decorative deposits such as nickel and chromium.

A number of review articles on this bath have appeared in the literature.[1,2,20,21] In general, the two main bath constituents are copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) and sulfuric acid. Although specific bath compositions suggested for a variety of purposes vary widely, the composition limits and operating conditions given in Table 1 are fairly representative.

A wide range in sulfuric acid concentrations will be noted. The lower concentrations, *i.e.*, below 30 g/L, seem to be most often recommended in patent literature covering the use of addition agents for brightening, grain refining, leveling and other purposes. For reasons not exactly known, the electrolyte seems to be most responsive to sulfur-containing organic additives at the lower sulfuric acid concentrations. Perhaps with the lower acid contents the additives are subject to less decomposition, and greater amounts of beneficial colloidal matter may be formed in the cathode film.

It has been recognized for many years[22-24] that regulated additions of chloride to a sulfuric acid copper bath have some beneficial grain refining and related effects. Excessively high chloride contents, however, particularly in bright plating formulations, have pronounced deleterious effects in that deposits in low current density areas become duller, more grainy and off-color. It is very important, therefore, to carefully select copper sulfate of good quality, *i.e.*, low in chloride and other impurity contents to obtain optimum and consistent results. The water used for make-up and replenishment purposes should be low in chloride or pretreated as by ion exchange to remove chloride. Organic impurities may be removed during bath makeup by treating the copper sulfate solution (before the addition of sulfuric acid) with a slight excess of potassium permanganate at 100 to 120°F (38 to 49°C), followed by an activated carbon treatment (1.0 to 3.0 lb/100 gal; 120 to 360 g/L) and filtration.

There is a tendency in acid copper plating to obtain rough cathode deposits because of introduction into the bath of anode sludge and slime. During the last few years beneficial effects have been reported from the use of copper anodes manufactured to contain regulated amounts of additives such as phosphorus.[25,26] These additives are claimed to favor deposit smoothness by causing the formation of anode films which retard the tendency of insoluble anode dissolution products from escaping into the bath.

A great variety of additives to the baths have been recommended for grain refinement, regulation of deposit hardness, increasing leveling and luster and for obtaining other specially desired characteristics. An interesting early article by Sand[27] deals with the protective colloid type of additives and their effects on brightness, periodicity and related deposit phenomena. According to Sand, "bright copper" was observed in 1845 when "wax molds phosphorized by means of a solution of phosphorus in carbon bisulphide were put into a solution of copper sulfate to receive an electrodeposit of copper."[28] This is of interest since many of the brightening additives which have been found effective in recent years have been active sulfur-containing organic compounds related in some ways to carbon disulfide (CS_2).

A variety of additives which have been investigated are listed in Table 2. As in bright nickel plating, many of the proposed additive combinations depend on the cooperative and synergistic effects of a plurality of materials for optimum results. For example in bright

Table 1
Sulfuric acid copper concentration and operating conditions

Copper sulfate, $CuSO_4{\cdot}5H_2O$	150 to 300 g/L (20 to 40 oz/gal)
Sulfuric acid, H_2SO_4	10 to 110 g/L (1.3 to 15 oz/gal)
Temperature	20 to 50°C (70 to 120°F)
Agitation	Mechanical and air
Cathode current density	2.7 to 54 A/dm^2 (25 to 500 A/ft^2)
Anode current density	1.6 to 5.4 A/dm^2 (15 to 50 A/ft^2)

plating formulations involving the use of active sulfur-containing compounds having such reactive groups as the thiocarbonyl (=C=S), thiol (≡CSH), sulfide (=S), sulfoxide (=S=0) and disulfide (-S-S-), there is a definite tendency toward the obtaining of non-uniform, striated deposits. Auxiliary additives of the protective colloid type (such as molasses and dextrin) and surface active agents (usually of non-ionic or anionic nature) are of value in counteracting this tendency, resulting in commercially acceptable deposits.

An increasing interest has occurred within recent years in the leveling characteristics of copper and other electrodeposits. This is of special importance when copper is plated on ferrous basis metals, to be followed by polishing and buffing to hide or fill in basis metal imperfections. Recent claims have been made for better leveling deposits from the sulfuric acid system.[29] It should be kept in mind, however, that the effect of additives on leveling, hardness, buffability, ductility and other deposit characteristics may vary widely depending on the stability of the additives, their rates of decomposition, introduction of extraneous metallic and organic impurities and other factors which sometimes are difficult to control. However with the proper choice of additives and scrupulous attention to optimum operating procedure, it is possible to attain leveling and other improvements with a fair degree of consistency.

The applications of sulfuric acid copper plating are many and constantly increasing, and the following list is a partial one of the many published uses.

1. Undercoating for nickel and chromium deposits
2. Roll plating[30]
3. Wire cladding[31-33]
4. Record matrices[34]
5. Heat treatment stop-off[35]
6. Heat conductivity for cooking utensils[36]
7. Lubricant for drawing operations
8. Electroforming[37-40]
9. Barrel plating
10. Production of oxidized finishes
11. Electrotyping[41,42]

Fluoborate acid copper

An increasing interest in the fluoborate bath has occurred in recent years, particularly since a copper fluoborate liquid concentrate became commercially available. Although the fluoborate bath is much more expensive than the sulfate bath, it offers sufficient advantages, such as higher plating speed, to justify the increased cost for certain specialized applications. A number of articles[43-45] have appeared giving solution compositions, operating conditions and suggested applications. Table 3 gives recommended concentrations and operating conditions for the fluoborate bath.[5]

The applications for the fluoborate system are generally the same as for the sulfate bath. Several recent publications disclose a very large scale use of the fluoborate bath for the plating of steel telephone drop wire.[46-48] In this application at the Point Breeze Works of Western Electric Co. (Baltimore, Md.), a bath is operated which is reported to have the following composition and plating conditions:[47]

Copper	150 g/L (20 oz/gal)
Free fluoboric acid	37.5 g/L (5.0 oz/gal)
pH	below l.0
Temperature	49 to 57°C (120 to 135°F)

Fifty strands of steel wire of 0.84 mm (0.033 in.) diameter, traveling at the rate of 30.5 m/min (100 ft/min) are plated with 63.5 μm (0.0025 in.) of copper at a current density of 215 A/dm^2 (2000 A/ft^2). After copper plating, the wire is coated with thin layers of lead and brass to provide good adhesion of rubber subsequently extruded around the outside. Careful engineering and selection of materials of construction are required because of the highly corrosive nature of the fluoborate copper electrolyte.

Additives for the fluoborate bath have not been as thoroughly investigated as for the sulfate bath. Such additives as thiourea and the protective colloids have been tried with no outstanding success reported.

Other acid copper systems

Such systems as the alkane sulfonate,[8,49] the formate[12] and the sulfonate[6] have been studied, but none of these seems to have achieved commercial importance. Tests made with the formate system for the production of Ballard shells (0.15 mm; 6 mil) indicated possibilities for obtaining higher limiting current densities than for the sulfate bath. However, the deposits were not quite as ductile as desired and under the operating conditions used enough formic acid was evolved to constitute a health hazard without adequate ventilation.

Recently two systems have been proposed[50,51] for use in the direct deposition of copper on aluminum and its alloys. One of these systems[50] comprises a bath within the pH range of 5.0 and 6.5 containing bivalent copper, pyrophosphate, oxalate and ammonia or tertiary amines. The other system,[51] which has a pH below 4, contains bivalent copper, nitrate, citrate, sulfate and fluoride. Claims are made that these two baths dissolve the superficial oxide film on the aluminum, thus permitting intimate bonding of copper to the aluminum.

Alkaline systems

Pyrophosphate complex system

Although it has been known for over a hundred years that the divalent copper-pyrophosphate complex anion is highly soluble and stable, and could be utilized for copper plating in alkaline media, only during the last twenty years has this type of bath achieved commercial importance. A number of patents[52,53] and review articles[2,4,54-56] have appeared disclosing bath formulations, operating conditions and applications.

A number of interesting articles have recently appeared on the chemistry of the pyrophosphate copper complexes.[57,60-63] Walters and Aaron[61] determined that within the pH range of 5.0 to 10 there is evidence of the presence of 1:2 and 1:1 complexes of metal to pyrophosphate, and that 2:1 and 4:1 complexes may exist in very dilute solutions. Within the pH range generally used for copper plating from the pyrophosphate complex, *i.e.*, 7.0 to 9.5, the predominant complex seems to be the 1:2 complex $Cu(P_2O_7)_2^{-6}$. Interestingly, zinc also seems to form the 1:2 complex within this pH range, and this information is used to calculate the "free" pyrophosphate content when zinc is a bath impurity, *i.e.*, the theoretical P_2O_7 to copper and zinc concentration by weight is assumed to be close to 5.5, and any excess P_2O_7 is assumed to be "free" pyrophosphate. The latest recommended concentration limits, bath constituents and operating conditions are given in Table 4.

For plating on ferrous basis metals a cyanide or pyrophosphate copper strike must be used before entering the above plating bath, to attain good adhesion. The latter strike contains 10 g/L (1.33 oz/gal) of copper and 250 g/L (33.4 oz/gal) P_2O_7 (ratio of P_2O_7/Cu = 25) plus 10 g/L (1.33 oz/gal) of an organic complexing agent. This strike bath is generally operated at a pH of about 9.0, at room temperature and 0.4 to 1.1 A/dm^2 (4.0 to 10 amp/ft^2).

Table 2
Additives that have been investigated for acid copper plating

Patent Reference	Date of Issue	Investigator or Company	Additives
U.S. 2,392,289	12/18/1945	Beaver	Subst. thiourea + wetting agent + dextrin
U.S. 2,424,887	07/29/1947	Henricks	Reaction product of C_6H_6 + a sulfurizing agent
U.S. 2,462,870	03/01/1949	Keller	Thiourea + molasses
U.S. 2,475,974	07/12/1949	Max	Triethanolamine
U.S. 2,482,354	09/20/1949	Max	Tri-isopropanolamine
U.S. 2,489,538	11/29/1949	Phillips, *et al.*	A cyanamide or dicyanamide
U.S. 2,563,360	08/07/1951	Phillips, *et al.*	A thiourea + wetting agent
U.S. 2,602,774	07/08/1952	Beaver	A thiourea + chloride
U.S. 2,663,684	12/22/1953	Pierce	Mercaptobenzothiazoles
U.S. 2,696,467	12/07/1954	Overcash, *et al.*	Thiourea + lignosulfonates
U.S. 2,700,019	01/18/1955	Jernstedt	A thiohydantoin + organic carboxylate + P.R.
U.S. 2,700,020	01/18/1955	Pierce	Mercaptobenzimidazoles
U.S. 2,707,166	04/26/1955	Brown, *et al.*	Safranine dyes
U.S. 2,707,167	04/26/1955	Hoover	Safranine dyes
U.S. 2,733,198	01/31/1956	Nobel, *et al.*	Amino thiazole or aminothiazoline + aldehyde condensation products
U.S. 2,738,318	03/13/1956	Fellows, *et al.*	Safranine dyes + thioureas
U.S. 2,742,412	04/17/1956	Cransberg, *et al.*	A thiourea + glycerol, glycol, or glycol ethers
U.S. 2,742,413	04/17/1956	Cransberg, *et al.*	A thiourea + urotropine, pyridine or morpholine
U.S. 2,758,076	08/07/1956	Passal	2-mercaptobenzimidazoles + thioureas
U.S. 2,762,762	09/11/1956	Donahue	Chloride control in electroforming
U.S. 2,798,040	07/02/1957	Pye	Acrylamide polymers
U.S. 2,799,634	07/16/1957	Woehrle	A subst. thiohydantoin + a dithiocarbamate + dextrose
U.S. 2,805,193	09/03/1957	Beaver	Thiazine dyes
U.S. 2,805,194	09/03/1957	Beaver, *et al.*	Triphenylmethane dyes
U.S. 2,830,014	04/08/1958	Gundel	Organic sulfonic acids
U.S. 2,837,472	06/03/1958	Gundel	Organic sulfonic acids
U.S. 2,840,518	06/24/1958	Condon, *et al.*	Protein autolysate or enzymes + a thiourea
U.S. 2,842,488	07/08/1958	Strauss	tertiaryamines + sulfonic acids
U.S. 2,853,443	09/23/1958	Harrover	alkylolamine + a thiohydantoin condensation product
U.S. 2,871,173	01/27/1959	Castellano	*o+p* substituted meta amino benzene sulfonates
DBP 837,029	—	Gen. Motors Corp	Substituted thioureas, thiocarbazides, thioamides
DBP 863,159	—	Dehydag	Organic disulfimides
DBP 888,493	—	Dehydag	Esters of sulfthio or trithio carbonic acid
DBP 924,489	—	Deutche Gold Und Silber	Condensation products of acrolein etc. and nitrogen compounds + poly glycolesters + alkali xanthates
DBP 932,709	—	Dr. W. Kampschulte	Acetylenic alcohols + thiophenols
DBP 933,843	—	Dr. Hesse + Cie	Polyvinylamines or polyvinylpyrrolidone
DBP 940,860	—	N.V. Metallic	Thiourea + nitrogen heterocyclics
DBP 962,129	—	N.V. Metallic	Thioureas + polyhydroxy alcohols
DAS 1,000,204	—	Dehydag	Substituted nitrogen heterocyclics
DAS 1,004,009	—	Dehydag	Substituted aromatic sulfonates
DAS 1,007,592	—	Dehydag	Substituted thioureas or dithiocarbamates
DAS 1,011,242	—	Dehydag	Organic sulfonates + polyacrylic or polymethacrylic acids
Aust.	—	Pfanhauser	Colloids + thiourea + Ni or Co salts
French	—	Houdaille-Hershey	Para tolyl sulfides, sulfoxides, disulfides or disulfoxides
French	—	Dehydag	Substituted aromatic sulfonates
French	—	Dehydag	Thioalkane sulfonic acids

Table 3
Fluoborate acid copper concentration limits and operating conditions

Copper fluoborate	224 to 448 g/L (30 to 60 oz/gal)
Baumé at 27°C (80°F)	21 to 39°
pH (colorimetric)	0.3 to 1.4
Temperature	27 to 77°C (80 to170°F)
Cathode current density	8.1 to 37.7 A/dm^2 (75 to 350 A/ft^2)
Agitation	Mechanical and air

For zinc and its alloys a preliminary cyanide copper strike is recommended before plating in the pyrophosphate bath. In normal operation the P_2O_7 slowly hydrolyzes according to the following reaction:

$$P_2O_7^{-4} + H_2O = 2HPO_4^{-2}$$

Although the HPO_4^{-2} ion does not have any complexing action, it does aid anode corrosion and has a very definite buffering action as illustrated by the curve in Fig. 1.

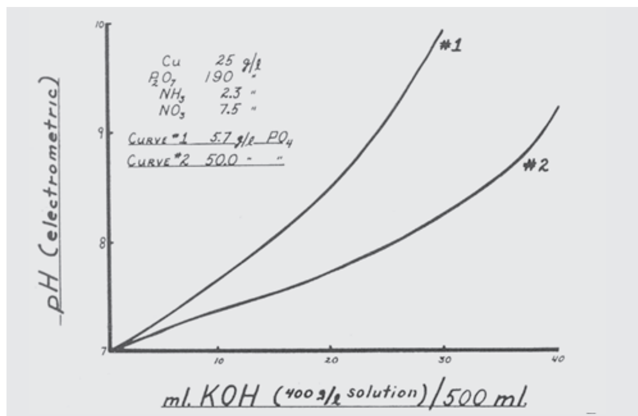


Figure 1—Buffering effect of orthophosphate (PO_4^{-2}) concentration in the pyrophosphate plating solution.

The NO_2^- radical increases the limiting current density by acting as a hydrogen acceptor according to the following probable reaction:

$$NO_2^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$$

The cyanide which may be introduced from the cyanide copper strike acts as a detrimental impurity, and residual traces left on the surface being plated will often result in a tendency towards initially blotchy and non-uniform deposits. This tendency may be minimized by the use of a brief cathodic treatment in a solution of potassium pyrophosphate before entering the plating bath proper. Residual traces of CuCN formed by hydrolysis of the cupro-cyanide complex are believed to be either removed by the gassing action or reduced to metallic copper.

Table 4
Pyrophosphate alkaline copper concentration limits and operating conditions

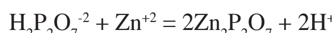
Copper	22.5 to 30 g/L (3.0 to 4.0 oz/gal)
P_2O_7	170 to 210 g/L (23 to 28 oz/gal)
Wt. ratio P_2O_7:Cu	7.0 to 8.5
NO_3^-	7.5 to 15 g/L (1.0 to 2.0 oz/gal)
NH_3	0.5 to 2.0 g/L (0.07 to 0.27 oz/gal)
pH	8.0 to 8.5
Temperature	38 to 60°C (100 to 140°F)
Cathode current density	1.1 to 7.5 A/dm^2 (10 to 70 A/ft^2)
Agitation	Mechanical and air

Certain organic impurities and cyanide are harmful but can normally be corrected by one of the following purification treatments:

1. Activated carbon treatment [2.4 to 6.0 g/L (2.0 to 5.0 lb/100 gal); 54°C (130°F); 4 to 8 hr].
2. Potassium permanganate [0.1 to 0.2 g/L (0.75 to 1.50 oz/gal)] followed by activated carbon treatment.
3. Hydrogen peroxide 30% (0.5 to 2.0 pt/100 gal) followed by activated carbon treatment or the addition of a slight excess of sodium hypophosphite to destroy residual traces of H_2O_2 or complexes thereof.

Recently certain aromatic nitrogen heterocyclic thiols have been developed which in controlled concentrations may brighten the deposits, make the deposits more uniform in grain size, give a degree of leveling and improve buffability.[58,59] For control, occasional analyses for copper, pyrophosphate and ammonia, and pH adjustment with KOH or with $H_4P_2O_7$ or HNO_3, will suffice to keep the bath in good operating condition.

The P_2O_7 content of .the bath can be determined by taking advantage of the following reaction:



$$H_2P_2O_7^{-2} + Zn^{+2} = 2Zn_2P_2O_7 + 2H^+$$

The released hydrogen ion is a measure of the P_2O_7 content and is determined by titration with standard alkali.[55] Another convenient procedure is one by which $P_2O_7^{-4}$ and PO_4^{-3} are determined colorimetrically using the Molybdate-Vanadate color forming reagent. The total phosphorus content as PO_4 is determined after the acid hydrolysis of P_2O_7. From this total PO_4 content is subtracted the initial PO_4 content, also determined colorimetrically, and the difference is calculated as P_2O_7.

The pyrophosphate copper system has numerous applications such as the following:

1. Undercoating for nickel and chromium
2. Nitriding and carburizing stop-off
3. Roll plating
4. Printed circuit plating
5. Plating on plastics
6. Plating on aluminum
7. Electroforming
8. Lubricant for deep drawing operations

Of particular advantage for many applications is the approximate neutrality of the electrolyte. The deposits are especially dense and fine-grained.[60] Some parts plated with copper from a pyrophosphate bath as a stop-off for selective hardening are illustrated in Fig. 2. Figure 3 shows the application of copper from this system as a lubricant for the deep drawings of steel shell casings. Figure 4 illustrates a thick copper deposit from this system which is extraordinarily smooth and free of nodules. In Fig. 5 there is illustrated an electroformed part of 1.2-mm ($^{3}/_{64}$-in.) wall thickness, which has electroformed into it four 9.5-mm ($^{3}/_{8}$-in.) long posts by plating through four holes of approximately 2.4-mm ($^{3}/_{32}$-in.) inside diameter.

Figure 2—Steel parts plated in pyrophosphate copper bath for selective hardening.

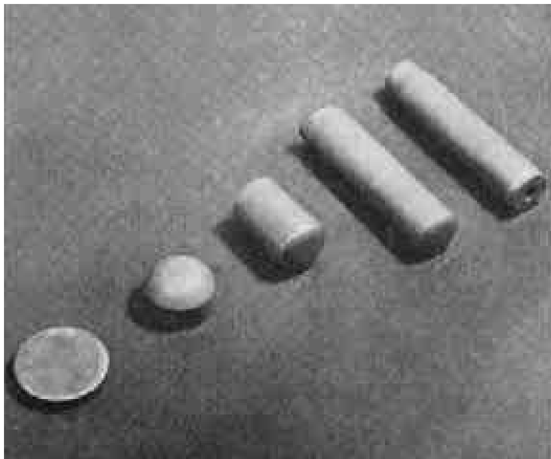


Figure 3—Application of pyrophosphate copper as a deep drawing lubricant starting with a copper plated slug.

Figure 4—Part plated with 0.50-cm (3/16-in.) thick copper in a pyrophosphate bath.

Figure 5—Part electroformed in a pyrophosphate bath.

Monovalent cyanide complex system

The plating of copper from a cyanide complex dates back to the early years of the nineteenth century. In 1840, G.R. and H. Elkington obtained a patent[63a] on the plating of iron with copper, silver or gold from a cyanide electrolyte, based on work of J. Wright. Wright is believed to have obtained the idea from a memoir of the famous chemist C.W. Scheele entitled "De Materia Tingente Coerulei Berolinensis" (1783) in which it was disclosed that copper has appreciable solubility in a cyanide containing solution.

Since monovalent eopper in the presence of excess cyanide anion may form a number of possible cuprocyanide complex anions, a number of studies have been made to determine which species predominate as a function of (a) copper to cyanide ratio, (b) copper and cyanide concentrations, (c) excess cyanide concentration, (d) temperature, (e) pH, (f) ionic strength and other variables. In a recent article[64] the equilibrium conditions attained have been studied by infrared spectrophotometry. Table 5 summarizes the findings.

The following equilibrium constants (K) based on activities were calculated for a temperature of 29°C (84°F):

$$Cu(CN)_4^{-3} = Cu(CN)_3^{-2} + CN^- \qquad K_{4,3}^{a} = 0.026 \pm 0.002$$

$$Cu(CN)_3^{-2} = Cu(CN)_2^{-} + CN^- \qquad K_{3,2}^{a} = 4.2\times10^{-5} \pm 0.66\times10^{-5}$$

In another article[65] the stability constants of cuprocyanide complexes were studied by ultraviolet spectrophotometry in an investigation that involved the study of plating solutions. The change in the composition of cuprocyanide solutions with increasing concentrations of added cyanide ion was studied. The results reported for very dilute solutions agreed well with those from infrared measurements at much higher concentrations.[64,66] The hydrolysis of cyanide to cyanate and ammonium formate were discussed by Deltombe and Pourbaix[67] and Marsh and Martin.[68] Simpson and Waind[65] discussed the preparation of pure cuprous cyanide for their ultraviolet spectrophotometric investigation.

The classical concept of the deposition of metal from a complex ion is that the ion dissociates to give a low concentration of simple metal cations which are then reduced to metal at the cathode. More recently[69,70] the theory has been proposed that deposition proceeds directly from the complex anion and fairly substantiative evidence for this theory has been put forth.

Up to about 1914, cuprocyanide plating baths were generally prepared by dissolving a variety of divalent copper salts in solutions containing an excess of alkali metal cyanide.[1] This proce-

Table 5
Equilibrium data for the cuprocyanide system

Equilbrium	K, mol/L (activities)	Free Energy of Formation, F_f, kcal/mol
$\frac{[Cu^+][CN^-]^2}{[Cu(CN)_2^-]}$	1×10^{-24}	$Cu(CN)_2^- = 58.5$
$\frac{[Cu^+][CN^-]^3}{[Cu(CN)_3^{-2}]}$	2.6×10^{-29}	$Cu(CN)_3^{-2} = 91.8$
$\frac{[Cu^+][CN^-]^4}{[Cu(CN)_2^{-3}]}$	5×10^{-31}	$Cu(CN)_4^{-3} = 129.0$

dure, made necessary by the unavailability of cuprous cyanide, was somewhat wasteful, since some of the cyanide was oxidized according to the following reactions involving the use of cupric carbonate as the divalent copper salt:[71]

$$2CuCO_3 + 8NaCN = 2Na_2Cu(CN)_3 + 2Na_2CO_3 + (CN)_2$$

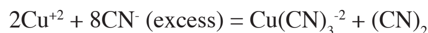
$$(CN)_2 + 2NaOH = NaCNO + NaCN + H_2O$$

According to the above reaction one-eighth of the original sodium cyanide is oxidized to cyanate. The intermediate cupric cyanide, a greenish yellow precipitate, decomposes into cyanogen and cuprous cyanide the latter of which dissolves in excess NaCN to form the cuprocyanide complex anion. In modern plating practice cuprous cyanide is generally used for bath preparation.

A number of reviews of cyanide copper plating have appeared from time to time giving bath compositions, operating conditions and applications.[1,2,20,72-76] In the early days of cyanide copper plating relatively thin deposits of copper were applied from baths having low metal contents and operated at low temperatures, as compared to present day practice. The baths tended to have low cathode current efficiency and the deposits were generally used as an undercoating for subsequent deposits from acid copper or nickel baths.

In the early 1930s, higher metal contents and operating temperatures were investigated by Pan[77] and others. Graham and Read[78] in 1937 and 1938 published the results of a comprehensive study of the cyanide copper plating system and the beneficial effects on anode corrosion and cathode deposits of additions of Rochelle salt. Wagner and Beckwith also published in 1938 a study of effects of Rochelle salt additions.[79]

The beneficial effects of Rochelle salt and substitutes and improvements over this compound which are sold today as proprietary additives, are perhaps due to the complexing and solubilizing action these materials have on divalent copper. When anode current densities reach values where appreciable polarization sets in, a dark film of cupric oxide is formed, which tends to grow in thickness and insulate the anode. In the presence of chelating or complexing additives this film tends to dissolve and the resulting cupric complex anions diffuse into the body of the solution where the copper is reduced to the monovalent state according to the following reaction:


$$2Cu^{+2} + 8CN^- \text{ (excess)} = Cu(CN)_3^{-2} + (CN)_2$$

$$(CN)_2 + 2OH^- = CNO^- + CN^- + H_2O$$

Further important developments in cyanide copper plating were along the lines of improving the cathode efficiency and increasing limiting current densities by proper choice of bath concentrations and operating conditions. Higher copper contents and temperatures, and potassium salts or mixtures of potassium and sodium salts, were investigated together with effects of controlled free cyanide contents. An excellent review of the development of these higher speed baths was published by Oplinger in 1939.[80] In this investigation the beneficial effects of additions of the thiocyanate anion as a major bath constituent[81] and of cationic surface active agents[82] were discovered.

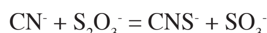
Most of the baths used in large scale cyanide copper plating today are based on the principles developed by Oplinger and his co-workers, and employing a variety of proprietary additives. Some of the more recent contributions and improvements to cyanide copper plating technology are listed in the following:

1. Use of periodic current reversal[83] and periodic current interruption
2. Diaphragming[84,85] and bagging of anodes
3. Use of improved anodes such as OFHC[86]
4. Development of proprietary additives as improvements over Rochelle salt
5. Development of materials for reducing hexavalent chromium such as sodium hydrosulfite,[87] stannous chloride and proprietary materials
6. Improvement in manufacture of cyanides to minimize sulfide and other impurity contents
7. Development of additives and operating conditions to improve leveling characteristics
8. Development of additives to oxidize sulfide and similar impurities[88]

Although bath and operating conditions may vary over wide limits depending on requirements, the concentration limits and operating conditions given in Tables 6, 7 and 8 for the copper strike, Rochelle salt and high speed type baths are representative of modern practice.

Many types of additives have been investigated for cyanide copper plating for such purposes as grain refining, increasing brightness and leveling. The system seems to be responsive to additions of organic compounds having active sulfur groups and/or containing metalloids such as selenium or tellurium; organic amines or their reaction products with active sulfur containing compounds; inorganic compounds containing such metals as selenium, tellurium, lead, thallium, antimony, arsenic; and organic nitrogen and sulfur heterocyclic compounds.

One of the early additives used in cyanide copper plating for purposes of grain refinement and increasing deposit luster was "hypo" or sodium thiosulfate ($Na_2S_2O_3$). The beneficial effects of this additive may have been due to the formation of the thiocyanate anion[89-91] according to the following reaction:


$$CN^- + S_2O_3^- = CNS^- + SO_3^-$$

Nietzel and Desesa[89] outline a spectrophotometric method for determination of thiocyanate ion by measuring the adsorption of the ferric thiocyanate complex in nitric acid media. This procedure could be developed as a method for estimation of thiocyanate as a major bath ingredient or to study the fate of thiosulfate and other active sulfur-containing additives. A list of brightening and other purpose additives are given in Table 9 which have been reported in the literature during 1929-1959.

The plating of copper from cyanide systems has widespread applications such as its use as an undercoating for nickel and chromium, as a heat treatment stop-off for selective hardening of ferrous parts, or as a strike and cleaning step prior to application of coatings from other baths. Copper deposits from cyanide baths are not generally suitable for deposition of relatively thick deposits for electroforming and similar purposes. A tendency exists for such deposits to develop excessive roughness and noduling, and to be high in hardness and difficult to machine. It is possible, however, to build up fairly thick, perfectly smooth deposits with proper choice of additives and with special precautions to avoid introduction into the bath of anode particles.

To counteract the tendency toward deposit roughness in the cyanide system, strict attention must be given to adequate filtration, preferably with separation of anode and cathode compartments, by diaphragming or bagging. A good filter aid mixture recommended by a division of one of the large automotive companies is a mixture of equal parts by volume of Filterbestos and a cellulosic type filter aid.

For bagging of anodes, which seems to be a recent trend, cotton bags of regulated weave and porosity must be used to minimize a tendency toward anode polarization. When bags are used the anode current density should be kept below 1.1 A/dm^2 (10 A/ft^2) and Rochelle salt or proprietary Rochelle salt substitutes can be added to decrease anode polarization. One large automotive installation has found that the bags must be removed and cleaned every four weeks and 70% of the bags replaced, to avoid serious anode polarization effects.

To increase plating speed, to give more uniform deposit luster and grain size and to increase tolerance toward contaminants, periodic reversal and interruption of current are used extensively, particularly the latter. Air agitation is used in many installations, and wetting and anti-pitting agents are available which are low foaming in nature and which may also act as brighteners and increase tolerance toward contaminants.

A variety of wetting and anti-pitting agents have been used in the cyanide system such as cationic substituted betaines and quaternary ammonium derivatives. Recently there has been a trend toward use of non-ionics such as polyoxyethylene ethers, anionics such as the polymeric methylene-bis-naphthalene sulfonates, or anionic-cationic bi-functional materials. The different types of wetting agents have varying degrees of compatibility with impurities which may be introduced into the bath. Many of these incompatibilities may result in loss of deposit luster, serious deposit blotchiness and non-uniformity, striations, pitting and other effects. The proper choice of wetting agents and anti-pitters must be made on the basis of careful study of possible contaminants.

Since cyanide copper deposits generally have low micro-throwing power, they generally do not have much hiding power or ability to cover basis metal defects. It has been observed in plant practice that modifications of the copper strike, either by suitable additions or by proper choice of operating variables and composition, will result in very dull, reddish deposits which improve the hiding power of subsequent relatively thick copper deposits.

Several of the newer proprietary copper plating processes have claimed substantial improvements in leveling characteristics which should aid in bridging basis metal defects.

Table 6
Cyanide copper strike: concentration limits and operating conditions

CuCN	15.0 to 30.0 g/L (2.0 to 4.0 oz/gal)
Free KCN or NaCN	7.5 to 15.0 g/L (1.0 to 2.0 oz/gal)
KOH or NaOH	0.0 to 15.0 g/L (0.0 to 2.0 oz/gal)
K_2CO_3 or Na_2CO_3	0.0 to 45.0 g/L (0.0 to 6.0 oz/gal)
Rochelle salt*	15.0 to 45.0 g/L (2.0 to 6.0 oz/gal)
Temperature	20 to 60°C (70 to 140°F)
Cathode current density	0.5 to 5.4 A/dm^2 (5 to 50 A/ft^2)
Cathode current efficiency	20 to 50%

*or Rochelle salt substitute according to vendor recommendations

Table 7
Rochelle salt type bath: concentration limits and operating conditions

CuCN	20.0 to 45.0 g/L (2.5 to 6.0 oz/gal)
Free KCN or NaCN	3.8 to 15.0 g/L (0.5 to 2.0 oz/gal)
K_2CO_3 or Na_2CO_3	15.0 to 60.0 g/L (2.0 to 8.0 oz/gal)
Rochelle salt*	30.0 to 60.0 g/L (4.0 to 8.0 oz/gal)
pH colorimetric	12 to 13
Temperature	50 to 70°C (120 to 160°F)
Cathode current density	1.1 to 6.4 A/dm^2 (10 to 60 A/ft^2)
Cathode current efficiency	30 to 80%
Agitation	Mechanical and air

*or Rochelle salt substitute according to vendor recommendations

Table 8
High speed type bath: concentration limits and operating conditions

CuCN	45.0 to 90.0 g/L (6.0 to 12.0 oz/gal)
Free KCN or NaCN	5.5 to 18.5 g/L (0.75 to 2.5 oz/gal)
KOH or NaOH	15.0 to 38.0 g/L (2.0 to 5.0 oz/gal)
K_2CO_3 or Na_2CO_3	30.0 to 75.0 g/L (4.0 to 10.0 oz/gal)
Rochelle salt*	0.0 to 45.0 g/L (0.0 to 6.0 oz/gal)
Temperature	60 to 82°C (140 to 180°F)
Agitation	Mechanical or air
Current cycles	Periodic interruption or reversal
Anode current density	0.5 to 4.3 A/dm^2 (5 to 40 A/ft^2)
Cathode current density	0.5 to 10.8 A/dm^2 (5 to 100 A/ft^2)

*or Rochelle salt substitute according to vendor recommendations

Table 9

Additives that have been investigated for cyanide copper plating

Patent Reference	Date of Issue	Investigator or Company	Additives
U.S. 1,863,869	06/21/1952	McCullough, *et al.*	Tartrates and citrates
U.S. 2,065,082	12/22/1936	Lewis	Aluminum plus citrate
U.S. 2,129,264	09/06/1938	Downing, *et al.*	Quaternary ammonium compounds
U.S. 2,164,924	07/04/1939	Hull	Calcium to remove carbonate
U.S. 2,255,057	09/09/1941	Holt	Betaines as anti-pitting agents
U.S. 2,287,654	06/23/1942	Wernlund	Sulfocyanides + carbohydrates
APC 351,241	05/18/1943	Weiner	Inorganic selenium and tellurium compounds
U.S. 2,347,448	04/25/1944	Wernlund	Sulfocyanide
U.S. 2,471,918	05/31/1949	Willson	Acylthiophenes
U.S. 2,495,668	01/24/1950	Willson	Mercapto alcohols, glycols, carboxylic acid or alcohol sulfide
U.S. 2,541,700	02/13/1951	Holt	Quaternary ammonium compounds as anti-pitters
U.S. 2,582,233	01/15/1952	Chester, *et al.*	Sulfided polyamines
U.S. 2,609,339	09/02/1952	Passal	Rhodanine and derivatives
U.S. 2,612,469	09/30/1952	Reisinger	Reaction products of anthranilic acid + hydrogen sulfide + triethanolamine
U.S. 2,636,850	04/28/1953	Jernstedt	Zinc + thiocyanate + PR
U.S. 2,677,653	05/04/1954	Chester, *et al.*	coke oven by-product
U.S. 2,677,653	05/04/1954	Chester, *et al.*	Dithiobiuret
U.S. 2,690,997	10/05/1954	Jernstedt	Lithium to give increased speed
U.S. 2,694,677	11/16/1954	Ostrow	Selenium (-2) + aldehyde polyamine condensation products
U.S. 2,732,336	01/24/1956	Ostrow	Selenium + lead or antimony + polyamines
U.S. 2,737,485	03/06/1956	Overcash	Selenium + zinc + quaternary amine + tartrate
U.S. 2,770,587	11/13/1956	Ostrow	Selenium (-2) compounds
U.S. 2,771,411	11/20/1956	Chester, *et al.*	Coke oven by-products
U.S. 2,771,412	11/20/1956	Chester, *et al.*	Coke oven by-products
U.S. 2,773,022	12/04/1956	Turner	Alkyl dithio carbamates of Cd, Co, Ni, Zn
U.S. 2,774,728	12/18/1956	Wernlund	Antimony + thiocyanate + methylene bis naphthalene sulfonates
U.S. 2,778,788	01/22/1957	France	Mo, Pb, Sn, Cd + wetting agent mixture
U.S. 2,783,194	02/26/1957	Nobel, *et al.*	Iodates to oxidize sulfide
U.S. 2,785,117	03/12/1957	Ceresa, *et al.*	Lithium for improved speed
U.S. 2,787,590	04/02/1957	Rinker	Barium metallic cyanide for carbonate precipitation
U.S. 2,809,929	10/15/1957	Ostrow	Anode containing Ni, Co, Fe
U.S. 2,813,066	11/12/1957	Ostrow	Alkylpolyamines to complex metallic impurities
U.S. 2,814,590	11/26/1957	Portzer	Selenium chelates with amines
U.S. 2,825,684	03/04/1958	Wernlund	Inorganic selenium compounds + Cd, Bi or Ag.
U.S. 2,838,448	06/10/1958	France	Arsenic, zinc + amines
U.S. 2;841,542	07/01/1958	Manquen	Tellurium + salts of organic acids
U.S. 2,848,394	08/19/1958	Foulke, *et al.*	Titanium coordination compounds
U.S. 2,854,389	09/30/1958	Boelter, *et al.*	Copper selenide-methylene bis naphthalene sulfonate
U.S. 2,858,257	10/28/1958	Ceresa, *et al.*	Removal of carbonate with calcium
U.S. 2,859,159	11/04/1958	Wernlund	Antimony + Zn, As, Co, Fe or Cd
U.S. 2,861,928	11/25/1958	Ceresa, *et al.*	Removal of carbonate with calcium
U.S. 2,861,929	11/25/1958	Martin, *et al.*	Selenate or selenites + methylene bis maphthalene sulfonates
U.S. 2,862,861	12/02/1958	Moy	Thio substituted 6 member nitrogen heterocyclics
U.S. 2,873,234	02/10/1959	Passal	Selenium bis dithiocarbamates

Table 9

Additives that have been investigated for cyanide copper plating (continued)

U.S. 2,873,235	02/10/1959	Passal	Tellurium bis dithiocarbamates
Aust. 187,767	—	Langbein-Pfanhauser	Betanaphtol + metanitrobenzoic acid + saccharin
Aust. 195,204	—	Langbein-Pfanhauser	Thallium compounds
Can. 401,287	—	Hull	Methoxy phenyl aldehydes + Al, Ti or other metals
Can. 401,288	—	Hull	Oxyheterocyclic compounds + Al, Ti or other metals
Can. 562,949	—	Ceresa, *et al.*	Plating from lithium cupro cyanide
DBP 874,100	—	Gunter Muschenig	Acetylene derivatives
DBP 879,048	—	Deutche Gold und Silber	Selenium and/or tellurium compounds + organic acids
DBP 895,686	—	Kampschulte	Alkali formaldehyde sulfoxylate + unsaturated alcohols
DBP 924,489	—	Deutche Gold und Silber	Condensation products of acrolein etc. + nitrogen compounds + polyglycol esters + alkali xanthates
DBP 924,490	—	Schering AG	Oxyethyl ethers + acetylenic alcohols
DBP 933,843	—	Dr. Hesse + Cie	Polyvinylamine or polyvinylpyrrolidone
Fr. 1,055,127	—	Zinc et Alliages	Furfural + coumarin + piperazine
Fr. 1,097,166	—	Dehydag	Organic aliphatic sulfonates

The future of copper plating

Copper plating has become an important integral part of the electrochemical industry and its future should be one of continued improvement and expanding application. Some general improvements which may be considered for the future are the following:

1. Development of more stable and easily controllable additives
2. Development of more convenient and economical waste disposal treatments
3. Development of improved purification treatments to remove contaminants (chemical precipitation, selective ion exchange, etc.)
4. Development of alkaline type baths with better and more consistent leveling

Because of the nature of the electrolyte the cyanide copper system, particularly the modem bright and semi-bright formulations, may at times give operational difficulties which are not too thoroughly understood and which at times are not easy to correct. Most of these difficulties are due to traces or higher concentrations of extraneous impurities, or to additive decomposition products. In contrast to nickel plating, where a variety of chemical precipitation, oxidation, reduction and electrochemical purification treatments are available, the cyanide system is lacking in ease of handling of contamination problems. One of the most difficult and persistent problems in the modern high speed baths is low current density "step-plate," which manifests itself usually in low current density areas as off-color deposits with a pronounced tendency toward formation of striations or deposits which in adjacent areas build up in thickness at unequal rates. This "step-plate" phenomenon, which may involve selective or preferential adsorption of organic or inorganic matter, is not too well understood and warrants further study and investigation.

It has also been observed with the high speed cyanide systems that improper balance of bath constituents and certain additives and their decomposition products at times will result in dome-shaped, friable, dark reddish-brown, scattered nodules which do not seem to be connected with shelf-roughness or anode particle effects. These nodular growths, which fortunately are only visible after plating of unusual deposit thicknesses, may in thinner deposits account for general overall slight roughness which at times is troublesome, and certainly is not conducive to a finished plated article having good corrosion resistance.

Many new applications for copper plating are possible. For example, with the present popularity of "duplex" coatings for imparting improved corrosion resistance, it is not inconceivable that a combination of copper deposits from different types of bath, and having different metallurgical structure, chemical purity and reactivity, might substantially improve corrosion resistance. Another application of copper plating which has been recently considered is its use as a stop-off for the "chemical milling" of aluminum. Since copper also acts as a barrier for hydrogen penetration, it can act in thin films to prevent or minimize hydrogen embrittlement of a basis metal, *i.e.*, embrittlement of nickel deposits or ferrous basis metals by chromium plating.

For the benefit of the electroplating industry it is hoped that the next fifty years will be as productive in copper plating improvement and application as the last.

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About the Author

Frank Passal received a B.S. in chemistry in 1934 from the University of Pennsylvania where he attended on a four-year Charles Ellis Scholarship. In August 1934 he joined the staff of United Chromium, Inc. in Waterbury, Conn., and was transferred to the company's research laboratories in Detroit in 1941. He was made Assistant Director of Research in 1950. After integration of United Chromium with Metal & Thermit Corp. in 1955, he received his title of Research Associate. He is a member of the AES, The Electrochemical Society, and Sigma Xi. His research activities have been involved in the development of pyrophosphate, acid, cyanide copper; SRHS chromium; bright nickel; alkaline and acid zinc; and other plating baths. He has developed analytical and other control methods for plating baths and is the inventor and co-inventor of numerous patents in the field of plating.

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