

MODERN ELECTROPLATING

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7.

Copper

Copper Plating from Cyanide Baths

R. R. BAIR AND A. K. GRAHAM

Cyanide copper plating is used extensively throughout the metal finishing industry for many applications. Plating of zinc die-cast parts with cyanide copper offers the only practical method of applying a suitable undercoating for nickel and chromium deposits. The copper undercoating protects the zinc die castings from chemical attack by the acidic baths used for plating nickel; immersion deposition is thereby prevented and the nickel layer over the copper has excellent adhesion. Copper is also an important factor in contributing to improved corrosion resistance of plated zinc die-cast parts. Plating of steel parts with copper before nickel and chromium plating is also of commercial importance. When copper is applied under the proper conditions the metal distribution over irregularly shaped articles is excellent because of the good throwing power of the process. Copper deposits are readily buffed to a high finish, which reduces polishing and buffing costs on certain classes of steel parts. Another, unrelated, application involves deposition of copper as a stopoff to prevent case hardening on selected areas of ferrous metal surfaces. A high-speed cyanide copper plating process is used to produce heavy coatings of copper on steel wire for electrical use.

Excellent results are obtained by the use of high-efficiency cyanide copper baths for plating through holes in printed circuit boards. Copper from cyanide baths is also oxidized to produce antique finishes.

Before 1915, copper cyanide baths were invariably prepared by dissolving copper carbonate in alkali cyanide. The use of tartrates is mentioned in early references [1, 2], but their value apparently was not fully recognized; an exception was the combination cleaning and plating bath described by Watts [3] in 1915. Deposits from these early baths were relatively thin and were used largely as bases for oxidized and other decorative types of finishes.

There was no great demand for heavy copper deposits until the early 1930s, when zinc die castings were finding expanded use for automotive light trim and other applications. The initial effort to develop heavy copper undercoatings for nickel and chromium on zinc base die castings, as described by Castell [4] in 1934, was limited to applying thin flash deposits of copper from a cyanide bath, followed by heavier deposits from acid copper sulfate baths, which were operated at faster plating rates. This system was not satisfactory in view of the poor metal distribution obtained with the acid baths, the attack of the acid electrolyte on the die castings, and the inability to produce bright deposits from the acid copper electrolytes. Rapid advances in cyanide copper bath formulations and the utilization of level additives and special techniques for current application permitted plating of high-quality bright deposits from these baths.

Early attempts to use higher concentration copper cyanide baths which were operated at relatively low free cyanide were described by Pan [5, 6]. Deposits from these baths operated at room temperature, however, were dull and rough at a thickness of about 25 μm . Polarization of the anodes in baths containing low free cyanide also presented a problem. The use of Rochelle salt to improve anode performance in low-metal baths containing essentially no free cyanide was disclosed in 1932 by McCullough and Gilchrist [7].

The first commercially successful high-efficiency bath 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 in the range 77 to 82°C. Alkali was added to improve anode corrosion and to increase the conductivity of the bath [8]. Alkali thiocyanate was used by Wernlund [9] 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 [10]. This bath permitted deposition of smooth, bright deposits in the thickness range 25 to 50 μm . The basic formulations of the proprietary high-efficiency baths 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 baths was achieved by employing alternate plating and deplating cycles [11]. Other current manipulation techniques such as interrupted current, although not new, are being used to modify the properties of the coatings. A wide variety of addition agents has also been described in many patents. Improvements in plating speed, superior brightness, leveling, and other advantages are claimed.

FUNCTIONS OF MAJOR BATH CONSTITUENTS

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Copper cyanide baths used at present may be classified in three categories: strike, Rochelle, and high efficiency. Typical formulations are given in Table I.

COPPER CYANIDE

Copper cyanide is insoluble in water but dissolves in aqueous solutions containing alkali metal cyanides to form soluble complexes. It is generally believed that most of the metal exists in the form of the tricomplex $\text{Cu}(\text{CN})_3^{2-}$ [12, 13] although the di- and tetracomplexes are known to exist [14]. The complex salts formed with sodium or potassium cyanide are similar in composition but the potassium salts are more soluble. The use of potassium cyanide permits the use of higher current densities than that of sodium cyanide. The alkali cyanide in excess of the tricomplex salt— $\text{Na}_2\text{Cu}(\text{CN})_3$ —is termed "free cyanide." It is normally determined by titrating a sample of the bath, at or below room temperature, with silver nitrate, using potassium iodide as indicator. The concentration of the free

TABLE I. CYANIDE COPPER BATH FORMULATIONS

Bath No.	1	2	3 ^a
Bath Type	Strike, g/l	Rochelle, g/l Typical Limits	High-Efficiency, g/l Typical Limits
CuCN	15	26	75
NaCN	23	35	93
or KCN	—	—	—
Na_2CO_3	15	30	115
NaOH	—	—	—
or KOH	—	—	30
Rochelle salt	—	—	42
($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)	—	45	30–60
By analysis:			Optional
Copper	11.0	19	53
Free cyanide	6.0	6.0	10
pH	—	(12.6)	(12.2–12.8)

^aSodium and potassium cyanides and the corresponding hydroxides and carbonates may be used interchangeably in equivalent molecular amounts.

CYANIDE COPPER

Free cyanide increases at higher temperatures since lower complexes are formed and free cyanide is thereby liberated [13, 15-17].

THE CYANIDE

The ratio of the free cyanide to the copper metal content in the strike and Rochelle baths is somewhat higher than in the high-efficiency baths. This is due, in part, for the lower cathode efficiency. Hydrogen is evolved simultaneously at the cathode in the strike and Rochelle baths and this evolution provides additional cleaning. Strike and Rochelle baths are also operated at a relatively high free-cyanide-to-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 baths 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 baths, but not significantly in high-efficiency baths that contain alkali and higher concentrations of the complex copper ions.

SODIUM OR POTASSIUM HYDROXIDE

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

CARBONATE

Carbonate exerts a strong buffer action at a pH of 10.8 to 11.5 in strike and Rochelle baths [15, 18] and facilitates pH control; it also reduces anode polarization in these baths. No beneficial effects of carbonate have been observed in high-efficiency baths that contain substantial amounts of caustic. Commercial high-efficiency cyanide copper baths contain an average of about 50 g/l 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 bath and hydrolysis of the cyanide are other sources of carbonates formed in the high-efficiency baths.

The oxidation of cyanide should be avoided because it increases the

STRIKE AND ROCHELLE BATHS

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cyanide consumption, causes a rapid buildup of carbonates, and complicates control of the free cyanide. Concentrations up to about 90 g/l sodium carbonate or 120 g/l potassium carbonate have no significant effect in reducing the plating speed of high-efficiency baths. If maximum plating speed is required, however, the concentrations should be controlled below these levels.

TARTRATES

Tartrates are used primarily in the low-efficiency baths. It is believed that the potassium-sodium tartrate or Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) forms temporary complexes with copper by reacting with products of electrolysis produced in the anode film. Baths containing tartrates may be operated with lower free cyanide and at higher current densities and efficiencies without impairing anode corrosion [15, 16]. 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. Baths are normally operated with about 45 g/l Rochelle salt. Wagner and Beckwith [16] claimed that the optimum concentration was about 22.5 g/l, with somewhat lower efficiencies being obtained at higher values. The substitution of sodium-potassium citrate for Rochelle salt [19] has been investigated, and several other proprietary compounds of a similar type are claimed to offer advantages.

STRIKE AND ROCHELLE BATHS

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

APPLICATIONS

Copper strike baths are used primarily for applying a thin coating of copper on zinc die castings before plating with other metals. The adherent copper coating prevents chemical attack when the die castings are subsequently plated with a heavier coating of copper from the alkaline high-efficiency baths. 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.

In addition to showing good adhesion of subsequent electrodeposits, the

copper strike from cyanide baths 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 [20, 21].

A thin copper strike is also used over zinc die castings before bright zinc plating and bright dipping to produce a commercial bright zinc finish. This eliminates the nonuniform coverage of the heterogeneous surface composition of the castings which occurs when trying to produce the finish without the copper strike.

Rochelle baths are used for plating zinc die castings and other metals when heavy coatings of copper are not required. Good deposits in the thickness range 2.5 to 7.5 μm are obtained without a copper strike. This feature—the plating of copper in one step in contrast to the two-step process of striking with copper followed by plating from high-efficiency baths—is a major factor in the continued commercial use of this type of bath.

OPERATING CONDITIONS AND BATH CHARACTERISTICS

The operating conditions of strike and Rochelle baths are given in Table 2. Strike baths are usually operated in the temperature range 40 to 60°C.

TABLE 2. OPERATING CONDITIONS FOR TYPICAL BATHS

Bath No.	1	2	3
Bath Type	Strike	Rochelle	High-Efficiency
Temperature, °C	41–60	55–70	60–80
Cathode current density, A/dm ²	1.0–3.2	1.6–6.5	1.0–11.1
Anode current density, A/dm ²	0.5–1.0	0.8–3.3	1.5–4.0
Efficiency range, Cathode, %	10–60	30–70	99+
Anode, %	95–100	50–70	99+
Ratio of anode to cathode area	3:1	2:1	3:2
Agitation			
Cathode rod	Optional	Preferred	Either or both
Air			0.75–4
Bath voltage, V	6	6	Unlimited
Limiting thickness, μm	2.5	1.3	

The cathode efficiencies are relatively low (10–60%) in the normal plating range of 1.0 to 3.2 A/dm². The bath composition and operating characteristics vary widely in actual commercial practice. Many users prefer to add 15 to 30 g/l sodium carbonate; when steel parts are plated, 15 to 30 g/l 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 baths than from strike baths. 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 bath. The average cathode efficiency is approximately 50% higher than that obtained from strike baths. The anode and cathode efficiencies vary with the temperature and degree of agitation [15]. Rochelle baths are normally operated without metal-containing addition agents, but lead has been used as a grain-refining and brightening agent [22].

Polarization phenomena in copper cyanide solutions have been extensively investigated. Graham and Read [15, 17, 18] studied the influence of bath composition, pH, and current density on anode polarization of copper and a combination of copper and iron anodes at 55°C using Rochelle baths. In general, the polarization curves exhibit two points of inflection which have been identified with the formation of copper(I) and copper(II) compounds at the anode. The effect of bath variables on these reactions was also investigated [17]. Graham and Read defined the limiting current density beyond which excessive polarization occurs for a given set of bath 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 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 baths is superior to that of high-efficiency cyanide baths. Most of the published data on throwing power are limited to current densities below 1.0 A/dm². The effect of factors influencing the throwing power of Rochelle baths 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 other factors which also influence it, as discussed later.

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 to 16 g/l. 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 baths 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 bath composition is thereby attained. The free sodium cyanide should be controlled within the range 5 to 11 g/l.

Continuous filtration of strike baths 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 baths.

Control of the pH of Rochelle baths is of major importance in obtaining the best performance. Operation within the pH range of 12.2 to 12.8 is recommended [15]. The range 12.5 to 12.8 is preferred because the bath 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 bath on zinc die castings.

The pH of Rochelle copper baths 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 sulfite-sulfuric 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 caustic soda. The buffer curve (Figure 1) may be used to adjust to other pH values.

The buffer curve in Figure 1 is also very useful when colorimetric pH measurements are employed [23]. The approximate amounts of caustic soda or concentrated sulfuric acid required to change the pH of a Rochelle cyanide copper bath can be determined. If acid additions are necessary, the acid should be diluted with about two parts by volume of water and then added through a tube with the exit end located well below the surface of the bath while vigorous stirring is maintained.

Controlling the free cyanide concentration of Rochelle baths within the range of 4 to 9 g/l is also very important. Excessive anode polarization is encountered at very low free cyanide, and the quality of the deposits is also

HIGH-EFFICIENCY CYANIDE COPPER BATHS

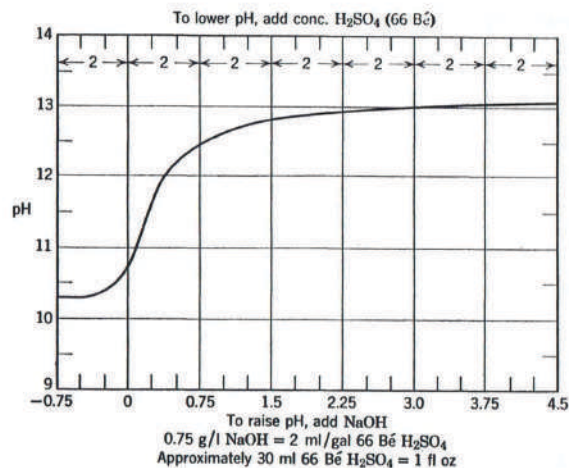


Fig. 1 Buffer curve for Rochelle copper plating bath.

adversely affected. Operating with a significantly higher free cyanide concentration than recommended results in lower cathode efficiencies and the production of dull deposits which are difficult to buff.

HIGH-EFFICIENCY CYANIDE COPPER BATHS

Baths that are formulated and operated under conditions which 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 baths.

APPLICATIONS

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

Tests have led to the development of additional data on corrosion resistance of plated coatings over steel and zinc die castings. Developments

in decorative plating were summarized by Sample [24] particularly with reference to earlier results of exposure test programs conducted by ASTM Committee B08. It was concluded that an all-nickel basis plate under chromium offers better protection over steel than a comparable thickness of copper-nickel. The thickness of the nickel coating was the principal factor responsible for the protective value of the decorative coating system. Other findings [25], however, have shown that copper deposits from proprietary high-efficiency cyanide baths may offer good protection as an undercoat for selected sulfur-free and sulfur-bearing duplex nickel coatings plus chromium. The selection of duplex nickel coatings with microporous or microcracked chromium has permitted the use of substantial thicknesses of the less costly copper. The combination has contributed to the improved performance of many automotive parts. There are good indications that the characteristics of the copper deposits have a profound effect on the overall corrosion resistance of copper-nickel-chromium coatings on steel.

There are wide differences of opinion on the ideal coating system for protecting zinc die castings. The total thickness specification of the composite copper-nickel-chromium coatings has been increasing in recent years. A total thickness of 50 μm is now specified in some cases for plated automotive zinc die castings which are subjected to severe exposure conditions. The relative thicknesses of copper and nickel vary considerably throughout the industry; the thickness of copper normally varies from about 7.5 to 20 μm .

Copper is also plated from high-efficiency baths 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 bath, and type of surface finish on the steel. Commercial experience has shown that the newer proprietary high-efficiency cyanide copper plating processes produce coatings which are superior for this application; this may be attributed to their reduced porosity.

The use of high-efficiency cyanide copper baths to plate steel wire with a heavy coating of copper is expanding rapidly in the United States and in foreign countries [26]. The wire is shaped and plated in the form of a spiral or helix as it passes through a plating unit described by Kenmore and Manson [27]. A typical 20-m plating tank will contain approximately 3000 m of wire. Concentric anodes are located inside as well as outside the wire coil. The thickness of the coating is regulated by varying the number of turns of wire in the plating tank and by adjusting the current and the speed of the wire. Plated wire comes off the line at speeds up to 18 m/min. High current density (about 10 A/dm^2) is achieved by using potassium-formulated baths containing a high metal content and proprietary addition agents [28]. Good agitation throughout the solution is also an important factor.

The copper-plated wire is used in electrical transmission and in applications requiring good corrosion resistance. Electrical conductivity wire is normally plated to such a thickness that the copper is approximately 10 to 40% by weight of the total. The thickness on 6.3-mm-diameter wire, for example, is approximately 127 to 510 μm . This thickness is very uniform and does not vary by more than 1% of the wire diameter. The adhesion is excellent. The wire is readily drawn to smaller diameters by passing it through a die.

Early efforts to use high-efficiency cyanide electrolytes for plating the phenolic printed circuit boards were unsuccessful because leaching of phenol or other organics contaminated the baths. The fiberglass-reinforced epoxy resin type of printed circuit boards are inert to the electrolytes and the high-efficiency cyanide copper electrolytes are being used to produce excellent through-hole plating.

A bright cyanide copper bath using various organic brighteners is of interest [50].

OPERATING CONDITIONS AND BATH CHARACTERISTICS

High-efficiency cyanide baths are normally operated in the temperature range 60 to 80°C (see Table 2), 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 bath temperature can restrict the performance of the bath as regards 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 2 to 5.5 A/dm^2 , whereas wire is plated from high metal baths at current densities as high as 11 A/dm^2 . Maximum plating speeds are achieved with potassium-formulated baths containing high metal and operated with vigorous solution circulation. The baths 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.

The anode current density may vary from 1.5 to 4 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 [29]. 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 optimum performance. In addition to increasing the plating rate, vigorous circulation is effective in minimizing pitting caused by hydrogen bubbles clinging to the surface of the parts being plated. Circulation is accomplished commercially by pumping the electrolyte or by air agitation.

Many patents have been issued covering metallic and organic addition agents for use in cyanide copper baths, as described in a review by Passal [30]. Lead and selenium compounds are apparently being used extensively in high-efficiency baths; they function as brighteners. Selenium is also effective in increasing the permissible bright cathode current density plating range. High-efficiency baths are inherently sensitive to organic contamination, which can cause pitting and dulling of deposits. Surface-active agents are used in most of the commercial baths. Betaines [10] and other proprietary additives are effective in lowering the surface tension and in sequestering organic contamination. See references 31 to 40 for patented bright cyanide copper plating compositions.

The plating characteristics of some of the high-efficiency baths can be improved by utilizing current manipulation techniques. Parts are plated in the conventional manner for a selected time and are then deplated for a shorter period by reversing the current. This technique is referred to as periodic current reversal plating (PR). Direct (plating) cycles of 2 to 40 sec with 1/2- to 10-sec reverse (deplating) cycles are described by Jernstedt [11]. Longer cycles, in excess of 60 sec direct with reverse cycles in excess of 12, are disclosed by Wernlund [41]. Current interruption cycles are also used. For example, zinc die castings are frequently plated using a 10-sec plating cycle followed by interrupting the current for 1 sec and then repeating the cycle. The use of current interruption cycles frequently will give excellent deposit brightness from bright plating baths which are contaminated sufficiently that acceptable deposits cannot be produced by the use of continuous direct current.

One of the major 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. This is illustrated by the cross section photomicrographs shown in Figure 2. The degree of leveling obtained with current reversal is substantial, as shown by comparing the contour of the surface of the steel and the surface of the copper plate. The polish marks on the steel surface which has a surface finish of 0.64 to 0.76 μm (rms), for example, can be leveled to values of 0.15 to 2 μm (rms) by plating 25 μm copper from a high-efficiency bath containing proprietary leveling agents. The leveling obtained with current interruption is less than with current

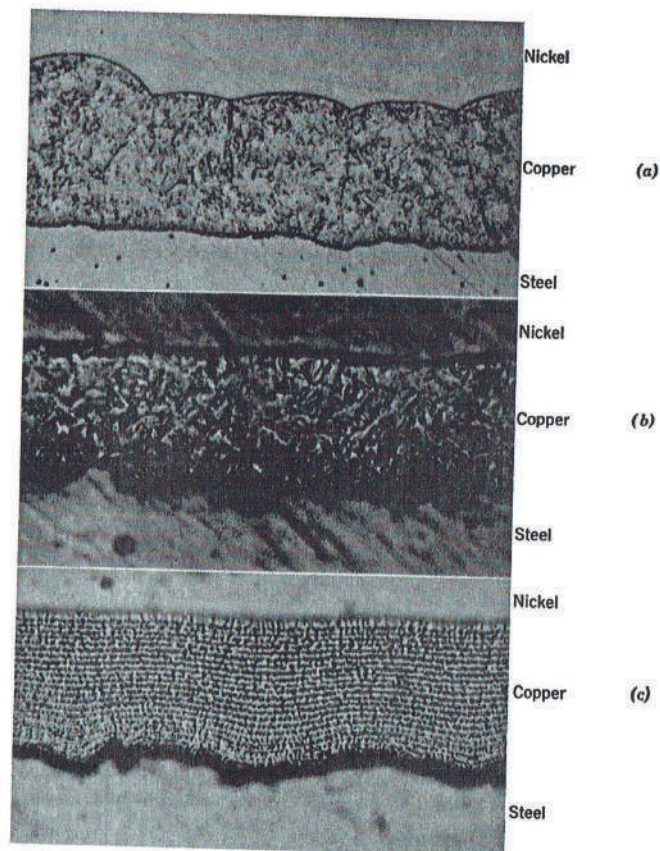


Fig. 2 (a) Continuous direct-current copper deposit showing typical columnar structure. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etchant. 750 $\times$. (b) Interrupted direct-current copper deposit with random structure. Cycle used was 10-sec plate followed by a 1-sec interruption. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etchant. 750 $\times$. (c) Periodic current reversal plating of copper showing typical laminar structure. Cycle used was 60-sec plate followed by 20 sec of reversed polarity. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etchant. 750 $\times$.

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 deplated. As an example a 60/20 PR cycle has only a 50% net deposition rate if the current applied is the same on the plate and deplate cycles. The use of PR has not had broad acceptance because of this factor.

High-efficiency baths that operate at 100% cathode efficiency would normally be expected to have poor throwing power. The metal distribution on parts plated in high-efficiency baths 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 baths have good throwing power because the cathode efficiency decreases with increase in current density.

MAINTENANCE AND CONTROL

High-quality copper deposits can be produced consistently from the high-efficiency baths by following good plating practice. Analytical methods are available for determining the concentrations of the normal bath components [42]. 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.

The composition of the baths in commercial operation varies widely. The copper metal content of the average bath is maintained at about 45 to 55 g/l. Baths used for plating steel wire or rod, however, are usually maintained at a metal concentration of 60 to 90 g/l. The free sodium cyanide is normally maintained in the range 10 to 20 g/l. The free cyanide can be lower when the metal content is low. Baths 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 baths has been described [43]. These are operated under conditions to give high current efficiencies. The fact that the ratio of anode to cathode areas must be greater than 4:1 to maintain bath stability is considered a possible disadvantage.

Good cleaning and thorough rinsing of the parts before plating are very important, since high-efficiency baths are sensitive to organic contamina-

tion, 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 baths 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 of 30% hydrogen peroxide to the bath 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 baths reduces the bright current density range and produces grainy deposits. Carbonate should be removed if the concentration exceeds about 90 g/l sodium carbonate or 118 g/l potassium carbonate. It can be precipitated by adding calcium hydroxide (hydrated lime). Excess sodium carbonate may also be crystallized out of sodium-formulated plating baths by cooling the solution to about -30°C . This procedure is unsuitable for baths maintained solely with potassium salts because of the greater solubility of potassium carbonate at all temperatures.

Crain and others [44] discuss the causes of carbonate buildup in cyanide copper plating solutions and control procedures, including a patented method applicable to both sodium and potassium baths.

Chromate is harmful in the high-efficiency baths even when present in very low concentrations (5–10 ppm). Its action is similar to that observed in other cyanide copper plating baths: It produces dull, nonuniform deposits. In low concentrations it produces blotchy deposits at low current densities; 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 ethylenediaminetetraacetic acid type. Although chelating agents of this type do not function as reducing agents, the chromate is probably reduced to a chromium(III) compound by the copper(I) ion in the presence of the chelating agent. The mechanism of the reaction is not fully understood. Reducing agents such as sugar derivatives and sodium stannite are also used [45]. In the absence of Rochelle salt, the reduced chromium will gradually precipitate and is removed by filtration.

Too high a concentration of zinc is objectionable because it 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 to 2.25 g/l. Excessive buildup of zinc in high-efficiency baths can be avoided by removing die castings which fall off the 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 to 0.5 A/dm². Small amounts of sodium thiocyanate are effective in sequestering excessive zinc.

For a discussion of impurities in copper cyanide plating solutions, including their effects on the deposit and methods for their removal, see reference 46.

ANODES

Cast ball, cast elliptical, or electrolytic copper sheet anodes are generally used with strike and Rochelle baths. Steel anodes are sometimes used in conjunction with copper in a low-efficiency bath such as a strike to safeguard against excessive polarization [15, 17] and as a means of controlling the metal content. Copper compounds formed at the anode are soluble in these baths when the anodes are operated below the critical current density [17]. Excessive current densities usually cause polarization of the anodes by formation of an insulating film.

Copper anodes substantially free of oxide inclusions are recommended for high-efficiency cyanide baths. 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 and is therefore not recommended for high-efficiency baths. Crystal structure of the copper is also an important factor in anode corrosion. A large crystal structure, in general, is preferred. Several types of good-quality copper anodes which reportedly are produced by melting, extrusion, or casting under an inert atmosphere are available.

MATERIALS OF CONSTRUCTION

Commercial experience has shown that rubber-lined steel plating tanks are more satisfactory than plain steel for high-efficiency cyanide copper plating baths. The rubber linings should be evaluated for contamination which may be introduced through leaching of the rubber since all types of linings are not suitable. When unlined steel tanks are used it is difficult to avoid stray currents, which may lead to nonuniform current distribution. Copper will frequently plate on the cathodic surfaces of the steel tank in a nonadherent form with the net result of producing roughness on the plated parts. The stray currents produce anodic areas on the tank walls; under certain conditions this may lead to corrosion of the equipment.

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 which may be generated in the heat exchanger are thereby

REFERENCES

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 may contaminate some types of high-efficiency processes.

TESTS OF DEPOSITS

A method of determining the stress in copper deposits has been reported by Graham and Lloyd [47], who showed that the stress increased with increase in current density and with the addition of 2 to 75 ppm of lead to the bath. The stress decreased as the temperature and copper content of the bath increased. The addition of potassium thiocyanate (15 g/l) produced an expansive stress instead of the contractile stress usually observed. Its magnitude varied from 1100 kg/cm² (tensile) to 350 kg/cm² (compressive).

The thickness of copper has been determined by a variety of methods. The Aminco-Brenner Magne-Gage is useful as a rapid nondestructive test for copper deposits over iron or steel [48]. The Hull-Strausser test [49] is a destructive one in which the copper is dissolved in an acidic ferric chloride solution containing antimony. An accuracy of about $\pm 10\%$ is claimed in the thickness range 0.25 to 15 μm . "Electronic" thickness test equipment has been developed which operates by anodically deplating a small area of the specimen. The time required to dissolve the plate on the test spot is proportional to the thickness of the deposit. An accuracy of plus or minus a few percent is claimed with this type of test. The precision is substantially better than that obtained by cross sectioning and determining thickness by the microscopic method, particularly for thicknesses of less than 13 μm . For details of these and other methods see Chapter 30.

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Acid Copper Electroplating and Electroforming

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HISTORY AND DEVELOPMENT

Acid copper deposition was referred to as early as 1810 [1]. It is said that Bessemer plated small castings in 1833 [2]. A technical report by De la Rue appeared in 1836 [3] and the first patent for making electrotypes was granted to Jacobi in 1840 [4]. Smee discussed commercial copper plating processes in 1843 [1]. During the next 70 years progress was directed principally toward developing specific applications for acid copper electrodeposition. Publications during this period were reviewed by Bennett [5]. Most of these references deal with copper(II) sulfate-sulfuric acid baths, but oxalate [6], nitrate [7], acetate [7], fluosilicate [8, 9], and copper(I) chloride [8] solutions are also mentioned.

Several other acid baths were reported from 1930 to 1960, including sulfate-oxalate-boric acid [10], sulfate-oxalate [11, 12], copper(I) chloride [13], copper(I) chloride-sodium thiosulfate [14], benzene disulfonic acid [15], copper(I) iodide and bromide [16], fluoborate [17, 18], alkane sulfonic acid [19, 20], sulfamic acid [21, 22], copper (II) formate with ammonium salts [23], phosphate-sulfate [24], and fluosilicate-silicic acid [25] solutions. Copper(II) glycolate, lactate, malate, and tartrate baths were examined in 1966 [26]. At present, only the sulfate and fluoborate baths are commercially prominent.

APPLICATIONS

Electrodeposition of copper from acid baths is extensively used for electroforming, electrorefining, manufacture of copper powder, and electroplating. Refiners and electroformers, in particular, employ acid solutions because costs of chemicals and power are low and because the baths are simple and easy to control. Electroformed copper articles are produced in several important fields of industry, including electrotypes, phonograph records, band instruments, heat exchangers, and reflectors. More than 2700 metric tons of copper anodes are consumed annually in making electrotypes valued at about \$100,000,000. Modern methods of electrotype molding differ greatly from the procedures of the early forties. Developments have been announced concerning the electroforming of complex shapes with reentrant angles, which cannot be made by other methods, for radar, aircraft, and other industries.

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 of copper (200 μm) are applied to steel rolls and then engraved for use in printing and marking paper and textiles. Stainless steel cooking vessels are copper plated in acid baths 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 bath 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.

Metal powders produced by deposition in acid baths 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 [27, 28].

Acid copper baths containing organic brightening and leveling agents are used extensively to deposit smooth copper on rough steel, etched plastics, and unbuffed zinc die castings. For example, several million bumpers, initially given a strike in a copper cyanide or nickel plating bath, are plated yearly with about 25 μm of acid copper before nickel and chromium [29, 30]. Many die castings are plated with approximately 15 μm of leveling acid copper [31, 32], 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, which improves resistance to corrosion or blistering [33-35]. Copper sulfate baths have also been recommended for plating "low-density" powder compacts, to fill porosity near the surface [36].

In the electrowinning and electrorefining industries acid baths are employed exclusively. More than 80% of the domestic production of primary copper is refined electrolytically.

PRINCIPLES

The copper(II) (Cu^{2+}) salts in either the sulfate or the fluoborate bath 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 bath, 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 baths. Electrorefining plants employ the copper sulfate bath 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 to 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 bath may occur when the anode current density exceeds about 5 A/dm^2 . With the fluoborate bath, the anode current density can be at least 40 A/dm^2 without encountering excessive anode polarization.

Because of the low cathode polarization, the acid baths do not have as good throwing power as alkaline solutions. The plate distribution closely approximates the primary current distribution; the deviation was found to be 10.8% or less for the sulfate bath [37]. This disadvantage is largely overcome in electroforming practice by appropriate current shields.

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/hr [38], with violent agitation.

The character of copper deposits is influenced by the concentrations of copper salts and of free acid, the temperature, the cathode current density, and the nature and degree of agitation. Dense deposits with good surface smoothness up to a thickness of 500 μm or more can be produced without addition agents. To brighten or harden the plate, one or more of several addition agents can be utilized, as discussed later.

FUNCTIONS OF BATH CONSTITUENTS

PRIMARY CONSTITUENTS

Copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sulfuric acid, or copper(II) fluoborate [$\text{Cu}(\text{BF}_4)_2$] and fluoboric acid, are the primary constituents of the sulfate and fluoborate baths, respectively. The copper salts furnish the metal ions in solutions such as those given in Table 1. Copper can be deposited at very low cathode current densities from the acid-free aqueous solutions of the salts [39, 40], but at higher current densities the deposits from the sulfate bath 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 [41, 17]. 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 [42]. Cathode polarization increases slightly at copper sulfate concentrations above 1 M (250 g/l) [43]. A concentration of less than 60 g/l copper sulfate results in a decreased cathode efficiency [44]. When very high cathode current densities are used, a high concentration of copper sulfate, within the

ACID COPPER

TABLE 1. FORMULATIONS OF COMMERCIAL ACID COPPER BATHS

Copper Sulfate Solutions ^a	"Average" Concentration	Concentration Limits
Copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, g/l	188	150-250
Sulfuric acid, H_2SO_4 , g/l	74	45-110
Specific gravity, at 25°C	1.165	1.115-1.21
Resistivity, at 21°C [45], ohm-cm	4.2-4.3	
Copper Fluoborate Solutions ^b	Low Concentration	High Concentration
Copper fluoborate, $\text{Cu}(\text{BF}_4)_2$, g/l	224	448
Fluoboric acid, HBF_4 , g/l	15	30
Boric acid, H_3BO_3 , g/l	15	30
pH (colorimetric)	1.2-1.7	0.2-0.6
Specific gravity, at 27°C	1.17-1.18	1.135-1.36
Resistivity, at 27°C [17], ohm-cm	7.3	

^aFrom 30 to 100 ppm of chloride ions is required for typical bright copper plating baths.

^bCopper fluoborate baths are prepared by diluting a concentrated solution containing 45% $\text{Cu}(\text{BF}_4)_2$ and adjusting the pH with either fluoboric acid or copper carbonate. The concentrate contains boric acid.

limits given in Table 1, is recommended. The solubility of copper sulfate is decreased when the sulfuric acid concentration is increased [41].

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate concentration such as 60 g/l of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is combined with 80 g/l of sulfuric acid, 30 mg/l of hydrochloric acid, and appropriate brighteners. Analogously, copper fluoborate solutions containing 56 g/l of $\text{Cu}(\text{BF}_4)_2$, 160 g/l of fluoboric acid and brighteners are also regarded as "high-throw" baths for through-hole plating. Air agitation is used for both types of solutions.

Copper fluoborate is more soluble than copper sulfate. Metal ion concentration can be more than double in the fluoborate bath in comparison with a copper sulfate solution containing 50 to 75 g/l of sulfuric acid.

Changes in sulfuric acid concentration have more influence than changes in copper sulfate concentration on solution conductivity and anode and cathode polarization. For example, specific conductivity is nearly doubled when the concentration of sulfuric acid is raised from 50 to 100 g/l [46]. An

additional increase in free acid concentration to 200 g/l, which is the level widely used in electrorefining, reduces the resistivity from 4.2-4.3 to 1.6-1.9 ohm-cm [47]. 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), and increases with a further increase in sulfuric acid concentration [43]. Changes in the concentration of copper sulfate have little effect on grain size, but some grain refinement was detected as a result of increasing the sulfuric acid concentration to 1.5 N (72 g/l) [48].

If the acid concentration in the fluoborate bath is too low (pH more than 1.7), deposits are dull, dark, and brittle. Boric acid is added to stabilize the bath and prevent decomposition of copper fluoborate; this increases resistivity slightly. In a bath with concentration of more than 15 g/l fluoboric acid or 220 g/l copper fluoborate, an increase in the concentration of either the salt or the acid lowers the resistivity.

ADDITION AGENTS

Addition agents for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density, and reducing trees are frequently added to the acid copper sulfate bath, but the use of a particular addition 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) [48, 49] or glue [43, 50]. These additions result in grain refinement, but this is chiefly unidirectional, because the structure remains columnar and becomes more fibrous [48]. Gelatin additions to the sulfate bath introduce porosity, organic inclusions [39, 51, 52], or both.

The effects of glycine, one of the amino acids formed by the hydrolysis of gelatin, are similar to the effects of gelatin [53]. Cystine and methionine, like gelatin, are cathode-polarizing agents [54]. On the other hand, dicarboxylic amino acids appeared more effective than monocarboxylic [55].

Phenolsulfonic acid is used in the electrotyping industry, but results with it depend on the sulfonation and purification procedures [56]. Deposits become harder and smoother after a bath has been electrolyzed or dummied for a short time following an addition of phenol or phenolsulfonic acid [57].

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 [58-60] and also exists in colloidal form [61]. Particles of colloids arising from additions of selenious and arsenic oxides have been observed by ultramicroscopic examination to concentrate at the cathode [62].

With 0.14 to 0.42 mg/l selenious oxide and 0.0065 to 0.13 mg/l arsenious oxide, grain structure was refined, surfaces were smoothed, and density was improved. Nevertheless, the ability of a colloidal or ionic addition agent to improve the deposit cannot be conclusively predicted in advance on the basis of a general knowledge of its ionic or colloidal behavior in electrolytes. Thus, in a copper(II) nitrate bath colloidal addition agents were effective as cathode polarizers, but did not always result in surface smoothing or grain refining [63].

Brightening Agents. Thiourea additions brighten copper deposited from acid sulfate baths. A 1951 patent disclosed the use of 0.002 to 0.005 g/l [64]. An appreciable grain-refining effect was reported for a concentration of 0.003 g/l or more [65]. The grain-refining and brightening effects of thiourea are attributed to its adsorption in copper deposits and the resulting effect on crystal nucleation [66].

Sulfide ions created when thiourea decomposes reduce the ductility of copper deposits [67-69]. Combined with dextrin [62, 70, 71], molasses [72-74], lignosulfonates [75], mercaptobenzimidazoles [76], naphthalene sulfonic acid [77-79], or tribenzylamine [80] and other organic agents [71], small concentrations of thiourea were once employed for brightening purposes, but have been largely superseded by better brighteners that have little or no harmful effect on ductility.

Sulfonated acetylthiourea or sulfonated aryl and alkyl substitution products of acetylthiourea were developed for bright copper plating from acid baths [81]. Another process utilized the sulfonation products of sulfurized aromatic compounds prepared by the reaction of toluene with sulfur chloride or thionyl chloride in the presence of anhydrous aluminum chloride and sulfuric acid [82, 83]. Acetyl cyanamide was proposed as a brightener for either the sulfate or the fluoborate bath [84]. Several complex amines were patented as brightening agents in 1958 [85-87]. In 1959, a patent disclosed a combination of thiohydantoin (a thiourea derivative) and a multiringed aromatic amine [88]. A substituted amino benzene sulfonic acid was disclosed in another patent for brightening copper deposited from the copper sulfate bath [89]. Polyacrylamides [90, 91], the reaction products of aminothiozole [92], acrylamines with a high molecular weight [93], tertiary amines [87], thiocarbamates [94, 95], thiocarboxylic acid amides [96], tetrahydropyranil amides [97], homopolymers of 1,3-dioxolane [98], and a combination of phenol polyglycols and thiosemicarbazones [99] are also included among the brightening agents patented since 1955.

Some of these brightening agents also induce leveling. For example, a surface finish of 0.46 μm (rms) can be smoothed to only 0.18 μm with 12.5 μm of good leveling bright copper or to only 0.1 μm with 25 μm [32]. Such

OPERATING CONDITIONS

processes deposit copper with a leveling power much higher than that of bright nickel deposits.

OPERATING CONDITIONS

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 [48]. Decreasing the temperature from 35 to 15°C brought about a considerable grain refinement in plates deposited at 3 A/dm² [48]. A temperature below 30°C is recommended for plating bright copper in acid baths to maintain good leveling power. These solutions are customarily agitated with air.

Current density and agitation must be balanced in order to obtain deposits having the desired properties. For producing electrotypes, cathode current densities of 16 to 22 A/dm² are generally employed when using the sulfate bath agitated with air. Fast-moving, endless wire can be plated at 50 A/dm² [100]. Still higher current densities are used when sufficient agitation can be supplied. Impinging of jets of electrolyte on the surface of the cathodes is said to permit a current density of 215 A/dm². 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 to 5.4 A/dm². It is claimed that higher current densities are practical with the fluoborate bath when agitation is the same as for the sulfate bath [17, 18]. Acceptable deposits 25 μm thick were obtained without agitation at 38 A/dm².

In either the sulfate or the fluoborate bath, an increase in current density results in increased cathode polarization (but not to the extent noted for many other solutions). Cathode films become more depleted in copper(II) ion and more concentrated in sulfate ion when the current density is increased [101]. Clear evidence has been reported of grain refinement produced by increasing the current density [102-104]. An increase in current density from 1 to 7 A/dm² reduced grain size to about one-third [105]. It was reported that high current densities resulted in grain refinement but promoted nodules and tree growth [48].

Periodic current reversal is patented for promoting leveling in copper plate deposited from copper sulfate baths containing 15 g/l zinc or cadmium [106]. A recommended PR cycle includes 2 sec plating and 0.4 sec deplating at 11 and 16 A/dm², respectively. Directing ultrasonic waves with a frequency of 1000 kHz and an acoustical intensity of 100 w/cm² to the cathode resulted in a colloidal suspension of copper instead of an adherent deposit [107].

MAINTENANCE AND CONTROL

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 bath must be taken into account. The acid concentration of fluoborate baths is controlled by measuring pH, using colorimetric pH papers.

The concentration of addition agents is usually controlled by empirical methods, such as evaluating the appearance of deposits on special bent or sloping cathodes immersed in beaker samples of the plating solution. An analytical method based on a bromination reaction [57] was developed for determining the concentration of phenol or phenolsulfonic acid.

Filtration requirements depend on the dirt load of the 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.

EFFECTS OF IMPURITIES

Acid copper baths 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 (for example, iron, nickel, or zinc) can be expected to accumulate in the bath, 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 bath containing 15 g/l nickel [108].

Nickel and iron reduce the conductivity of the sulfate bath to the same degree as an equivalent increase in copper [109]. The deposition potentials of arsenic and antimony are apparently near that of copper in the sulfate bath, since codeposition was reported to occur [110]. Arsenic and antimony in concentrations of 10 to 80 g/l and 0.02 to 0.1 g/l, respectively, embrittled deposits and roughened surfaces. Additions 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 [111]. Bismuth, like arsenic and antimony, caused granular deposits [112].

Antimony and bismuth are believed to form insoluble complex compounds with arsenate [113].

Small concentrations of alkali metal and alkaline earth salts were found to smooth copper deposits [8]. Tin salts were also reported to smooth deposits and were, at one time, purposely added to the sulfate bath for this reason [8]. Lead is completely precipitated as sulfate, and silver partly. If silver is a contaminant, a small amount will be codeposited with copper. A high current density favors the codeposition of silver [108]. Silver chloride caused pitting in semibright copper plate [114].

Between 2 and 35 mg/l chloride is added in the form of hydrochloric acid to electrefining solutions to precipitate silver and avoid "sandy" deposits [113]. From 30 to 100 mg/l of chloride is recommended for bright copper plating with many modern brighteners.

Nitrates were reduced to ammonia at the cathode in copper sulfate baths [115]. A reduction product of the sulfate ion, which is said to have a grain-coarsening effect, can be removed by heating the bath and adding an oxidizing agent [65], but oxidizing agents such as hydrogen peroxide or potassium permanganate are said to reduce throwing power [114].

In the fluoborate bath, 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 can be removed by treating the solution with an appropriate activated carbon, followed by filtration. α -Naphthylamine was identified as an injurious contaminant leached from certain rubber tank linings [116]. As little as 10 mg/l α -naphthylamine caused an irregular pattern of uneven copper plate having ridges and valleys. Treatment with activated carbon is desirable when a new bath is being prepared—especially the fluoborate bath, which may be contaminated with impurities leached from rubber shipping drums. An instance has been reported of embrittlement traceable to impurities leached from wood tanks [117].

ANALYTICAL METHODS

Methods for determining copper and sulfate concentrations and a method for determining iron and aluminum in copper sulfate baths are described by Langford [118], who also presents procedures for determining copper and fluoboric acid concentration. Methods for determining trace amounts of lead [119], nickel [120], chromium [121], and chloride [123] have been reported.

Copper anodes in sulfate and fluoborate baths usually become coated with films containing finely divided copper and copper oxide particles. A copper oxide film is believed to cause intergranular corrosion, which promotes disintegration of surface layers into fine copper particles [112]. Some, however, have attributed the films to copper particles formed by the disproportionation of copper(I) ion to copper(II) ion and metal [123]. The films on the anodes in the sulfate bath also contain insoluble impurities such as arsenic, selenium, tellurium, lead, and silver.

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 bath temperature or increasing the acid concentration. In one series of tests, less copper was found in anode films formed in fluoborate baths than in those from sulfate baths [17].

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.

Rolled and cast bars and electrolytic copper sheets have been employed as anodes in sulfate and fluoborate baths. Anode sludge is decreased by using oxygen-free, high-conductivity copper [124]. 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 baths is decreased by adding 0.02 to 0.04% phosphorus to cast copper [123, 125]. The films on phosphorized copper anodes are responsible for the slight polarization of about 0.5 V [124]. 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 phosphorized copper are frequently used in titanium anode baskets.

To avoid excessive polarization at any anode in the copper sulfate bath, the anode current density should not be more than about 5 A/dm² in unagitated baths. With vigorous air agitation, the limiting anode current density is more than 17 A/dm². The anode current density in an unagitated fluoborate bath can be as high as 40 A/dm², and with air agitation, it can be increased to 55 A/dm².

Small amounts of silver, sulfur, lead, tin, nickel, and other elements are common impurities in rolled, cast, and electrolytic copper [124]. Silver as an impurity in the anodes employed in sulfate and fluoborate baths is of much

less consequence than it is in cyanide baths. OFHC* and electrolytic copper were found to have a lower impurity content than rolled or ordinary cast anodes. The metallic impurities in OFHC and electrolytic copper totaled about 0.006%.

Grain size is considered inconsequential [124, 125]. Two batches of high-purity anodes with average grain sizes of 10 and 0.01 mm performed similarly [124]. On the other hand, high density is a desirable characteristic, because it promotes uniform anode dissolution.

An instance is reported of a preference for continuously using insoluble, conforming anodes in order to improve deposit thickness distribution [126]. Copper was replenished by circulating the solution through an auxiliary electrolytic tank connected in series with the electroforming tanks. The electrolytic corrosion tank was equipped with soluble copper anodes and scrap. On each side of a rotating disk cathode were microporous rubber diaphragms, which inhibited the diffusion of copper ions into the catholyte and kept the cathode efficiency low. The insoluble anodes in the electroforming tanks were made with silver-lead alloy (1% silver).

Lead containing 3% tin and 3% antimony has been proposed as an insoluble anode for facilitating the plating of printing rolls [127].

An insoluble anode that has been used in copper electrowinning was made of an alloy of copper, silicon, iron, and lead [44]. Graphite is the only electrically conductive material known to be insoluble as an anode in the fluoborate bath. When used as an anode, graphite produces a sludge of finely divided carbon particles.

EQUIPMENT

Steel tanks lined with rubber or plastic are preferred for large acid copper baths, 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 bath 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 bath 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 heat exchangers for copper fluoborate solutions [128]. For further details, see reference 129.

*Trademark, American Metal Climax Inc.

PREPARATION OF BASIS METALS

Because loose, nonadherent displacement films of copper are formed on steel and zinc when these basis metals are immersed in acid copper baths, a cyanide copper or nickel strike plate is required before plating in acid baths. If the basis metal is completely covered, the strike plate can be as thin as 1.3 μm , but 2.5 μm is sometimes preferred for parts of complex shape. After plating in the cyanide bath, the work should be thoroughly rinsed, dipped in a dilute solution of hydrochloric or sulfuric acid to neutralize any undissolved alkaline material, and rinsed again before plating in the acid bath.

Nickel or nickel alloys, when appropriately surface-activated by cathodic treatment, reverse current etching in sulfuric acid, or other method, can be plated directly in an acid copper bath. Contact should be made to the work before immersion. Stainless and chromium steels are plated in acid baths with adherent copper deposits by first striking in a solution concentrated in sulfuric acid but dilute in copper sulfate: 240 g/l sulfuric acid and 112 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [130].

The usual procedures for plating on aluminum are described in Chapter 3. An acid pyrophosphate bath for plating copper adherently on aluminum was described in 1958 [131].

MOLDS AND MANDRELS FOR ELECTROFORMING

Metallic and nonmetallic materials are used as molds or mandrels for electroforming. Surface passivity characteristics make chromium alloy steel, aluminum, magnesium, tantalum, and chromium-plated metals useful as metallic mandrels that require neither a surface treatment for providing conductivity nor a separating film for providing ready removal of the electroform. Surface-passive metallic mandrels can be used repeatedly without intermediate surface treatments, although a thin film of graphite is sometimes applied before each use to facilitate the final separation of the deposit. A mixture of graphite and wax has been utilized as a parting medium in the electroforming of tubing that was subsequently drawn into trombone slides [126]. A thin suspension of graphite in kerosene is sometimes used.

Temporary mandrels are used only once and are then deformed or destroyed when deposition is completed. Low-melting alloys containing lead, tin, bismuth, cadmium, or mercury, or combinations of these, are melted out and recast. In electroforming Pitot-static tubes, low-melting mandrels were employed [132]. Aluminum and zinc can be cast or machined into mandrels and subsequently chemically dissolved.

Nonmetallic materials used for mandrels are asbestos, asphalt, cloth,

gelatin, glass, paper pulp, plastics, plaster, pottery and other ceramics, rubber, wax, and wood. Each of these must be made surface conductive by one of the procedures discussed in Chapter 28 after molding is completed. Plaster, wood, and ceramics require sealing to fill pores near the surface before the application of the conductive film.

Thermoplastic sheet, such as vinyl acetate and vinyl chloride copolymer, has found wide acceptance in the electrotyping industry as a molding medium. Impressions of printing surfaces are made in the heated plastic sheet, which is then cleaned, sensitized with a stannous chloride solution, and silvered by simultaneously spraying an ammoniacal silver nitrate solution and a solution of a reducing agent such as hydrazine sulfate, formaldehyde, or hydroxylamine hydrochloride [133]. Such molds largely replace the graphitized wax and lead molds used formerly. Copper is deposited on the silver (using a low current density for a few minutes) until the metal film is thick enough to carry a higher current. Then the current density is raised to about 22 A/dm² or more for another 40 to 70 min until a shell 180 to 380 μm thick is deposited. Flexing the plastic mold releases the shell. Edges of the electrodeposited shell are trimmed, and the back is tinned in preparation for backing up with electrotype metal, a lead alloy containing 3% Sn and 3% Sb. Fidelity of reproduction of the final electrotype is good enough to duplicate photoengravings containing more than 264 dots/mm² in 133-screen halftone subjects.

Original, master phonograph records are cut in wax or lacquered aluminum disks and then metalized by cathode sputtering gold or copper, or by silvering; chemical reduction methods like that used in the electrotyping industry [134] are employed. After electroforming and separating the mother negative from the original master recording, a metal master is electroformed on the negative and subsequently used as a mold for electroforming the number of record stampers needed for production of the record. To facilitate the separation of record stampers from the metal master, the master is dipped in a solution of potassium dichromate (15 g/l) before electroforming is started.

Gravure cylinder shells are examples of electroformed articles that are detached from their mandrels after their service life is completed. An immersion nickel or silver deposit, or other separating film, is applied to copper-plated steel cylinders. A 150- to 200- μm thick copper layer is deposited on the cylinder and etched through a resist of carbon tissue or pigment paper to produce the printing surface [135]. After the shell is no longer serviceable because of excessive wear, it is removed mechanically and replaced with a new shell. The shells are deposited from both sulfate and fluoborate [136] baths.

In addition to those mentioned, many other kinds of molds, parting

media, and methods for making surfaces conductive have been used [137]. Electroless copper or nickel has become popular for metalizing plastic or other nonconducting mandrels used for electroforming.

TESTS OF DEPOSITS

The thickness of copper on zinc die castings is measured on magnified microsections, or by anodic dissolution in accordance with coulometric principles [138]. Magnetic instruments can be used for measuring the thickness of copper deposits on steel. See Chapter 30.

Copper-plated steel wire for electrical cable is tested for thickness and thickness uniformity, electrical conductivity, and tensile strength. Electroformed shapes are frequently given physical tests, in order to control strength and ductility, by determining such properties as hardness, tensile strength, elongation, and resistance to impact or denting.

PHYSICAL PROPERTIES AND STRUCTURE

Data on the physical, mechanical, and electrical properties of electrodeposited copper were comprehensively reviewed [139]. Table 2 summarizes the ranges for high-strength, hard, lowly stressed, good leveling, or thermally stable electrodeposited copper. The high-strength copper was deposited from copper sulfate baths containing triisopropanolamine [140] or molasses and thiourea [68] and in copper cyanide baths containing potassium thiocyanate, operated with periodically reversed current [141]. Hard deposits also were produced in the copper cyanide-potassium thiocyanate solution with PR current and in the copper sulfate bath containing naphthalene disulfonic acid and thiourea [142] or several other addition agents.

The deposits with a low electrical resistivity were obtained in copper fluoborate and sulfate baths at 30°C, which contained no addition agents [68, 141]. These deposits also were thermally stable to 400°C, changed very little in density, and exhibited low stress, less than 3.0 kg/cm². The properties for the good-leveling copper were measured for specimens deposited [68] in a copper sulfate bath containing a sulfonated compound and an azo dye [143]. The influence of modifying the bath formulations and the operating conditions on the properties and structure of copper electrodeposits is described in references 68, 139, and 141.

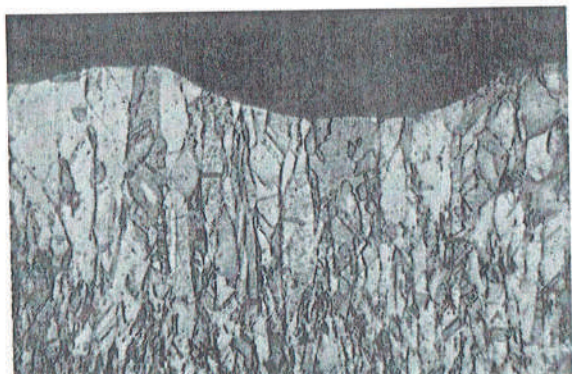
The grain structures of copper deposits usually correspond to one of four types, shown in Figure 1. Deposits from the sulfate baths containing no addition agents are columnar (Figure 1a). Additions of gelatin, phenolsulfonic acid, and many other agents cause the fibrous structure shown in Figure

Table 2. PROPERTIES OF COPPER ELECTRODEPOSITS USEFUL FOR DIVERSE APPLICATIONS

Outstanding Characteristic	Tensile Strength, kg/mm ²	Elongation, % (5cm)	Internal Stress, ^a kg/mm ²	Hardness (VHN200), kg/mm ²	Electrical Resistivity, microhm-cm
High strength	45-63.5	4-18	-4.2 or 3.6 to 5.5	131-159	1.75-2.02
Hardness	3.5-55.5	0-10	-4.2 or 3.0	193-350	1.96-4.60
Low electrical resistivity	18.5-27	15-41	-0.5 to -1.6	48-64	1.70-1.73
Near zero stress	14-16	8-24	-0.08-0.06	56-57	1.71-1.72
Good leveling	36-36.5	14-19	2.0	128-137	1.82
Thermal stability ^b	22.5-30	26-39	0.5-2.9	55-106	1.73-1.76

^aNegative values indicate a compressive stress.

^bDeposits that changed less than 0.02% in length after heating to 400°C.



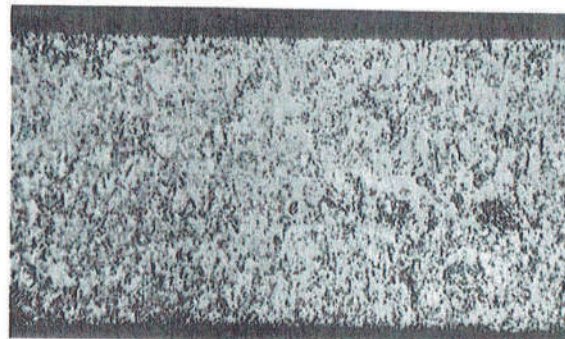
(a)



(b)

Fig. 1 Structure of copper deposits—cross-sectional views (about 500 $\times$) after etching with ferric chloride reagent. (a) Columnar; (b) fibrous; (c) fine-grained, equiaxed; and (d) banded.

1b. Such copper usually is 15 to 20% harder than columnar copper. The fine-grained deposit in Figure 1c is characteristic of copper deposited in copper cyanide solutions at high temperatures (70–80°C), copper pyrophosphate baths, copper sulfate solutions containing triisopropanolamine or other amines, and copper sulfate solutions containing popularly used



(c)



(d)

Fig. 1 (Continued)

brighteners. The banded copper in Figure 1d is characteristic of copper deposited with periodic current reversal from cyanide baths containing brighteners.

Copper is deposited from the sulfate bath as fcc crystals that are randomly oriented [144], unless deposited at less than 1.5 A/dm², when the basis metal can exert an influence on the structure so that crystals in the basis metal and plate are oriented similarly [145]. Hardness has generally been associated with fine grains [102, 105], yet it can be increased by introducing crystal orientation in the absence of grain refinement.

Grain continuity from the basis metal into sulfate-copper deposits has

been detected by many investigators [104, 146, 147]. 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 [148, 149], but was not reproduced when the basis metal was cleaned but not dipped in acid solution before plating [149]. The grain size of the substrate appeared to influence the reproduction of the basis metal structure in the copper deposit [149]. 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 [150]. Oxide and sulfide particles in the surface layer of the substrate behaved as nucleation sites.

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