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BRIGHT COPPER PLATING

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This invention relates to bright copper plating, and particularly to ornamental or decorative bright copper plating from an acid bath.

I have discovered that in contradiction of accepted practice, I am able to electrodeposit an ornamental bright copper plate on metal articles in an acid bath and obtain a plate of high covering or smoothing power and high throwing power with high cathode efficiency using a plating solution characterized by its long life and high tolerance of impurities.

Hitherto acid copper plating baths have been used chiefly in electrotyping, electroforming and for immersion copper coating using current densities of from 15 to 40 amperes per square foot, a voltage of from 0.75 to 2.0, and a temperature of from 75 to 120° F. It is known that more rapid deposition is possible if air agitation is used, and in such cases, the bath concentration is usually increased, the bath is warmed, and current densities of from 75 to 150 amperes per square foot are employed.

Acid copper plating baths, however, have not been considered suitable and have not been used commercially for bright copper plating. Cyanide copper solutions have been almost universally used for thin deposits for ornamental finishes, flashing of iron or steel prior to heavy copper deposits in the acid copper bath, and for plating an undercoat for other metals. In all these applications the current densities were not over 10 amperes per square foot, usually less, and while a cathode efficiency of 60% or better was a possibility, actual plant values were quite variable and astonishingly low.

Recognition of the value of heavy copper deposits under nickel and chromium on zinc base die casting and elsewhere emphasized the limitation of the conventional cyanide bath and stimulated the development of the relatively new Rochelle salt type bath. With its development the demand for high speed was satisfied and attention was directed then toward improving the brightness of the deposited copper in order to eliminate buffing prior to bright nickel and chromium plating. It will be understood that where buffing is required a greater thickness of copper is necessary in order to avoid the danger of cutting through the plate while buffing.

In spite of the decided advantages of the Rochelle salt type bath over the conventional copper cyanide bath, the bright copper plating bath and method of my invention offer decided advantages as compared with the hitherto known baths and methods. For instance, proper oper-

ation of the conventional copper cyanide bath requires a temperature of 75 to 100° F., a current density of 2.5 to 15 amperes per square foot, and a voltage of from 1.5 to 2 with a maximum cathode efficiency of about 60%. Likewise, operating conditions of the Rochelle salt type bath require a temperature of 140 to 160° F., a current density of 20 to 60 amperes per square foot, and a voltage of from 2 to 3 with a cathode efficiency of 40 to 70%.

The bright copper bath of my invention operates satisfactorily at a temperature ranging from below 90 to more than 120° F. The average current density is 100 amperes per square foot with a minimum of from 75 to 80 and a maximum in excess of 200 and a voltage of 2 to 3 with a cathode efficiency of 98 to 100%. Of course, the minimum and maximum practical current density will depend on the composition of the bath.

Furthermore, the plating bath and method of my invention are characterized by extremely high throwing power and the ability to plate over surface defects whereby a smoothening action is obtained which results in a higher grade of plated article particularly well adapted to receive a secondary coating of some other metal as, for instance, bright nickel or chromium.

By way of example and without thereby limiting my invention to the particular details set forth, I shall now give a typical outline of the method followed and plating bath used in a particular case for plating a bare steel article.

Preliminary treatment

1. The article is cleaned with an alkaline cleaner such as Oakite.
2. The article is acid dipped for removing rust and neutralizing the alkali.
3. The article is rinsed with water to remove the acid.
4. The article is plated for three to four minutes in a conventional cyanide copper bath. Such a conventional bath might contain, for example, 3 to 5 ounces of copper metal per gallon, 1½ to 3 ounces of free sodium cyanide, and 2 to 3 ounces of sodium carbonate.
5. The cyanide plated article is rinsed with water to remove cyanide.

Bright plating

The bright plating solution may comprise, for example, 26 ounces per gallon of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and 6.5 ounces per gallon of sul-

phuric acid. Such a solution will have a pH value of approximately 1.

In addition, the solution will contain a brightener. Thiourea has been used as a brightener in the course of my investigation, but it has the disadvantage of not holding up in the plating bath. Aryl and alkyl substitution products of thiourea such as thiourethane, phenyl thiourea, diphenyl thiourea, benzyl thiourea and benzo-thiourea have also been used with satisfactory results, although all of them have certain faults. Propyl, acetyl, hydrochloride, nitrate and metal salt derivatives of thiourea have also been used satisfactorily.

I prefer to use the acetyl derivative in proportions of from 0.005 to 0.1 ounce per gallon.

Furthermore, a small quantity of wetting agent should be added to the bright plating solution. I have used a wide variety of commercial wetting agents, including, for example, Duponol-80, Duponol-WA, Duponol Special-WA paste, Alkanol-SA, Triton and sodium lauryl sulfate in proportions of approximately 0.3 ounces per gallon. It is generally understood in the art Duponol-80 and Duponol-WA are sodium salts of sulfated alcohols, that Duponol Special-WA paste is a sodium salt of sulfated alcohols containing cetyl compounds, that Alkanol-SA is isopropyl naphthalene sulfate, and that Triton is a high molecular alcohol.

In addition, the bright copper solution may contain small quantities of agents adapted to permit higher current densities. For instance, dextrin, sugar and sulfonated creosote are typical examples.

The article to be bright plated after receiving the preliminary treatment above described is immersed in the bright copper solution for the time required for the desired degree of brightness. For instance, two minutes immersion suffices for a plate of from 1.5 to $\frac{1}{10,000}$ inch (depending on the current density). In a present practice of my invention, a commercially acceptable bright surface is obtained using a solution including 0.02 ounce of acetyl thiourea, 0.30 ounce Duponol Special-WA paste, and 0.25 ounce of dextrin at a temperature of 110° F. with a plating time of five minutes with cathode agitation. When a new solution is being started, it is advantageous to add to it approximately 0.03 ounce per gallon of 100 volume hydrogen peroxide.

It will be understood that I do not limit myself to the particular formulation above indicated. The following are further typical examples of formulations I have successfully used in commercial practice according to my invention:

Example I

	Ounces per gallon
Copper sulfate.....	26.00
Sulphuric acid.....	6.50
Acetyl thiourea.....	0.02
Duponol Special-WA paste.....	0.30
Dextrin	0.25
Hydrogen peroxide (100 vol.).....	0.03

Example II

	Ounces per gallon
Copper sulfate.....	26.00
Sulphuric acid.....	6.50
Acetyl thiourea.....	0.01
Sodium lauryl sulfate.....	0.30
Sulfonated creosote.....	0.25

Example III

	Ounces per gallon
Copper sulfate.....	26.00
5 Sulphuric acid.....	6.50
Acetyl thiourea.....	0.02
Duponol-80	0.30

Example IV

	Ounces per gallon
Copper sulfate.....	15.00
10 Sulphuric acid.....	4.50
Acetyl thiourea.....	0.01
15 Sodium lauryl sulfate.....	0.30
Dextrin	0.25

Example V

	Ounces per gallon
Copper sulfate.....	30.00
20 Sulphuric acid.....	7.50
Acetyl thiourea.....	0.02
Duponol-WA	0.30
25 Dextrin	0.30
Hydrogen peroxide (100 vol.).....	0.03

Example VI

	Ounces per gallon
Copper sulfate.....	26.00
30 Sulphuric acid.....	7.00
Acetyl thiourea.....	0.01
Alkanol-SA	0.30
35 Dextrin	0.30
Hydrogen peroxide (100 vol.).....	0.03

Example VII

	Ounces per gallon
Copper sulfate.....	30.00
40 Sulphuric acid.....	8.00
Acetyl thiourea.....	0.02
Triton	0.30
45 Sodium lauryl sulfate.....	0.30
Dextrin	0.30

Example VIII

	Ounces per gallon
Copper sulfate.....	30.00
50 Sulphuric acid.....	6.00
Acetyl thiourea.....	0.02
Phosphoric acid.....	1.50
Duponol Special-WA paste.....	0.30
55 Dextrin	0.30
Hydrogen peroxide (100 vol.).....	0.03

Example IX

	Ounces per gallon
Copper sulfate.....	26.00
60 Sulphuric acid.....	5.50
Phosphoric acid.....	1.00
Acetyl thiourea.....	0.02
65 Duponol-WA	0.30
Sulfonated creosote.....	0.25

Example X

	Ounces per gallon
Copper sulfate.....	30.00
70 Phosphoric acid.....	7.50
Acetyl thiourea.....	0.02
Duponol Special-WA paste.....	0.30
Dextrin	0.30
75 Hydrogen peroxide (100 vol.).....	0.03

Example XI

	Ounces per gallon
Copper sulfate.....	30.00
Phosphoric acid.....	8.00
Acetyl thiourea.....	0.02
Triton	0.30
Sodium lauryl sulfate.....	0.30
Dextrin	0.30

Example XII

	Ounces per gallon
Copper sulfate.....	15.00
Phosphoric acid.....	4.50
Acetyl thiourea.....	0.01
Sodium lauryl sulfate.....	0.30
Dextrin	0.25

It is well to point out that as the temperature of the bath increases the permissible current density also increases and faster plating results. However, the throwing power of the plating solution is reduced.

Likewise, the same results occur as the acid concentration in the bath increases.

Furthermore, as the concentration of brightener in the bath increases the hardness of the plate and its brightness also increase but the throwing power is reduced.

As the time of plating increases the thickness and smoothness of the plate will increase and as the surface tension of the solution is reduced the throwing power or bright range of the bath is increased.

As will be noted from some of the examples given hereinbefore, phosphoric acid may be substituted to good advantage for a portion of the sulphuric acid in the formula. For example, the amount of sulphuric acid may be 5.50 ounces per gallon together with phosphoric acid in the amount of 1.00 ounce per gallon. This addition of phosphoric acid or substitution of a portion of the sulphuric acid by phosphoric acid results in increasing the throwing power of the plating bath of my invention, and in the case of some specific articles, this is a very valuable attribute.

As has hereinbefore been mentioned, the plating bath of my invention is characterized by the fact that it permits a cathode efficiency of 98 to 100% together with extremely high current densities.

In the case of plating brass or copper the cyanide copper plating hereinbefore described in the case of a bare steel article is omitted.

In the commercial practice of my invention metal articles of various shapes intended for various purposes are handled. It is common practice to subject such articles to bright copper plating substantially as outlined in the typical procedure hereinbefore first described. An article subjected to such treatment for a period of substantially five minutes is characterized by a smooth, hard and extremely homogeneous bright surface free from burned edges, and particularly well adapted for receiving a secondary plate of other metal. For instance, some of the articles commercially

plated according to my invention are subjected to bright nickel plating for a period of only one minute and the resulting plate is characterized by a smoothness and brightness of surface far superior to that obtainable by straight bright nickel plating for six minutes under standard conditions.

Bright copper plated articles commercially plated according to my invention for a period of substantially five minutes are also regularly subjected to bright nickel plating for a period of one minute followed by chromium plating for a period of substantially ten to fifteen seconds. The resulting chromium plate is characterized by extreme brightness and homogeneous texture and is far superior in appearance to a chromium plate deposited on a similar article having had a previous plating treatment comprising six minutes of bright nickel plating.

As is well known to those skilled in the art, copper sulfate and sulphuric acid are preferred for use in the plating bath of my invention because of their low cost. However, other copper salts and other inorganic acids may be used in place of copper sulfate and sulphuric acid so far as the operative technique and results are concerned.

It will be understood that while I have herein set forth and described certain embodiments of my invention, it is not my intent to have my invention limited to or circumscribed by the specific details of proportions and procedure herein set forth, since my invention may be varied widely within the spirit of this disclosure without departing from the scope of the appended claims.

I claim:

1. A bright copper plating bath comprising copper sulfate, sulfuric acid, a brightener in proportion of from 0.005 to 0.1 ounce per gallon, said brightener being selected from the group consisting of aryl and alkyl substitution products of thiourea and acetyl, hydrochloride, nitrate and metal salt derivatives of thiourea, a wetting agent in proportion of approximately 0.3 ounce per gallon, said wetting agent being selected from the group consisting of sodium salts of sulfated alcohols, sodium salts of sulfated alcohols which contain cetyl compounds, isopropyl naphthalene sulfate, sodium lauryl sulfate and a substance adapted to permit high current densities in proportion of approximately 0.25 ounce per gallon, said substance being selected from the group consisting of dextrin, sugar and sulfonated creosote.

2. A bright copper plating bath comprising substantially from 15 to 30 ounces per gallon of copper sulfate, substantially 4.5 to 8 ounces per gallon of sulfuric acid, substantially 0.01 to 0.02 ounce per gallon of acetyl thiourea, substantially 0.3 ounce per gallon of sodium lauryl sulfate, substantially 0.25 ounce per gallon of dextrin, a maximum of substantially 0.03 ounce per gallon of 100 volume hydrogen peroxide and a maximum of substantially 1.5 ounces per gallon of phosphoric acid.

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