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METHOD OF ELECTRODEPOSITING COPPER
AND BATHS AND COMPOSITIONS THERE-
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1

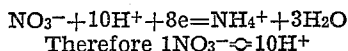
This invention relates to the electrodeposition of copper, and to baths and compositions therefor, and provides improvements therein.

In U. S. Patent 2,250,556, granted July 29, 1941, to Jesse E. Stareck, there is disclosed a process for the electrodeposition of copper, and also a pyrophosphate-copper plating bath, having a number of important advantages, among which may be mentioned brightness and smoothness of the copper deposit, speed of deposition, and insensitivity to impurities.

By the present invention, the advantages obtained by the aforesaid patented invention are retained, together with additional advantages of great importance; a higher speed of deposition is obtained (the speed is something like doubled), a more ductile deposit is obtained, a better covering power is obtained than with any other known copper plating process, better adherence of the deposited copper on aluminum and stainless steel is obtained, and a better process and bath for barrel plating than any other is obtained. The invention can also be used to good advantage for obtaining "strike" deposits of copper. The low operating pH makes the process particularly favorable for plating over the more difficult metals, such as, magnesium, aluminum, zinc, lead, stainless steel and certain alloy steels and castings.

The bath is like that of Patent #2,250,566, in that it contains the complex copper pyrophosphate ion, $\text{Cu}(\text{P}_2\text{O}_7)_2$; according to the present invention the bath contains the nitrate ion, NO_3 , and has a pH between 6.5 and 7.5, with the optimum at about 7.2 (measured by a glass electrode pH meter).

The use of the NO_3 radical inhibits the formation of hydrogen at the cathode, thereby enabling higher operating current densities and voltages to be used.



The higher current densities give a faster plating speed, while the higher voltages decrease the tendency of Cu_2O formation at the cathode, thus producing a better bond between the deposit and the base metal. With baths having compositions given in the examples which follow, the quantity of NO_3 which is used is from 5 to 20 g./l.

The concentrations of the bath constituents may be varied widely to give satisfactory plating baths. An example of a bath according to the present invention is one containing in solution from 7.5 to 45 g./l. of metallic copper, with a

2

pyrophosphate content from that necessary to convert the copper to the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ to an excess limited by saturation. The copper may be conveniently added in the form of copper pyrophosphate, copper sulphate (blue vitriol), or other common cupric compounds of copper. The pyrophosphate radical may be added in the form of an alkali metal pyrophosphate salt either in the hydrated or anhydrous state. From the standpoint of economy of solution cost, the sodium pyrophosphate may be used. However, certain of the other alkali metal pyrophosphates, notably the potassium salt, are more soluble than the sodium salt, and when used can produce baths which are more concentrated, and which, in turn, permit a corresponding increase in plating current densities at the cathode to be attained.

The bath is advantageously made by dissolving a prepared solid composition in warm water, all as more fully hereinafter set forth.

The pyrophosphate radical may be said to combine with the copper in the molecular weight ratio of 2 to 1 to form a pyrophosphate copper complex radical having the formula $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ (see Jour. American Chemical Society 1936, pp. 1412-1429).

In baths used for the electrodeposition of copper on the more noble metals, the proportion of the pyrophosphate radical to copper may vary considerably, but it is advantageous when electrodepositing copper on iron, steel, and other less noble metals, to have an excess of pyrophosphate dissolved in the bath beyond that necessary to give the molecular weight ratio of 2 to 1 between P_2O_7 and Cu. The baths given in the specific examples contain such an excess of pyrophosphate radicals. The free pyrophosphate content of the bath decreases the tendency for the deposition of copper by immersion on the less noble metals. It also tends to prevent the formation of traces of insoluble salts in the bath and promotes anode corrosion.

Citric acid, or a salt thereof, especially an alkali-metal salt, is often advantageously added to increase the permissible cathode current density range, to increase the conductivity of the bath, and to increase the brightness of the cathode deposit. It also increases the tolerance of the bath to impurities and aids in anode corrosion. In place of citric acid, other organic hydroxy acids which are capable of forming alkali-heavy-metal complexes, such as lactic acid, tartaric acid, glycollic acid, malic acid, or soluble salts thereof, may be used.

The pH of the bath is adjusted by adding a suit-

able acid such as pyrophosphoric acid, or citric acid, or nitric acid, when a test shows that the pH of the bath is higher than the pH desired, or by adding a suitable alkali such as sodium hydroxide for a sodium bath, or potassium hydroxide for a potassium bath, when the test shows that the pH of the bath is lower than the pH desired.

The baths herein described are stable at temperatures up to the boiling point of the solution. No poisonous fumes are evolved. The operating current efficiency is nearly 100%. The throwing power of the baths is excellent. Under ordinary operating conditions, temperatures from 120° to 150° F. are usually preferred. For a "strike" solution, temperatures of about 70° to 80° F. are preferred.

Agitation of the solution is desirable. Air agitation is generally used because it is simple, convenient, and causes no buildup of carbonates in this bath. Mechanical agitation or combinations thereof are also satisfactory. Agitation of the solution increases the operable current density range. The operable current density range also increases with rising temperature and decreases with increasing free pyrophosphate content of the bath.

Operating current densities of 100 amperes per square foot or more may be obtained. Electrolytic or rolled copper anodes are ordinarily used. The operating voltage between anode (soluble) and cathode is usually between 2 and 5 volts when bright plating current densities are used.

Examples of baths and of operating conditions for using the invention to the base advantage are given below.

Composition for ordinary tank plating

	Optimum range	
Cu, 30 g./l.-----	24	to 36
P ₂ O ₇ , 200 g./l.-----	150	to 250
Citrate, 15 g./l.-----	5	to 25
NO ₃ , 10 g./l.-----	5	to 20
pH, 7.2-----	6.8	to 7.5
Temperature, 135° F.-----	120° F.	to 150° F.

Composition for maximum plating speeds

	Range	
Cu, 35 g./l.-----	33	to 38
P ₂ O ₇ , 230 g./l.-----	190	to 250
Citrate, 15 g./l.-----	5	to 25
NO ₃ , 10 g./l.-----	5	to 20
pH, 7-----	6.8	to 7.5
Temperature, 150° F.-----	140° F.	to 160° F.

Composition for barrel plating

	Optimum range	
Cu, 25 g./l.-----	15	to 30
P ₂ O ₇ , 225 g./l.-----	180	to 250
Citrate, 10 g./l.-----	5	to 20
NO ₃ , 10 g./l.-----	5	to 20
pH, 7.5-----	7	to 8
Temperature, 120° F.-----	100° F.	to 130° F.

Composition for "strike plating"

Cu, 15 g./l.-----	7.5	to 22.5
P ₂ O ₇ , 150 g./l.-----	100	to 225
Citrate, 7.5 g./l.-----	5	to 10
NO ₃ , 7.5 g./l.-----	5	to 10
pH, 7.5-----	7.0	to 8.0
Temperature, 70° F.-----	60° F.	to 80° F.

As hereinbefore stated, current densities of 100 amperes per square foot and more may be used; with rotating cathodes the current density per square foot may be 300 amperes per square foot,

thus making the process ideally suitable for building up heavy coatings on rolls, electroforms, electrotypes, etc.

The above described process gives deposits which are smooth, fine grained, dense, ductile and relatively bright. Being fine grained and dense, the deposit is particularly good as a stopoff for carburizing, often requiring less thickness than usual to prevent carbon penetration.

For making up the baths, a composition of matter is used consisting of soluble bivalent copper, pyrophosphate (P₂O₇), citrate (C₆H₅O₇), and nitrate (NO₃) compounds, and for maintaining the baths, a similar composition usually omitting the bivalent copper compound is used. For rotating cathodes it is sometimes advantageous to omit the citrate radical from the composition and thus also from the plating bath made therefrom.

In the make-up composition the parts by weight are as follows:

	Parts
Bivalent copper -----	24 to 36
Pyrophosphate (P ₂ O ₇) -----	150 to 250
Citrate (C ₆ H ₅ O ₇) -----	0 to 25
Nitrate (NO ₃) -----	5 to 20

In a specific example of the make-up composition, the parts by weight were:

	Per cent
Copper pyrophosphate -----	19.8
Potassium pyrophosphate -----	72.2
Citric acid -----	3.7
Potassium nitrate -----	4.3

The percentages may be varied about 25%, plus or minus.

In the maintenance composition, the parts by weight are as follows:

	Parts
Pyrophosphate (P ₂ O ₇) -----	150 to 250
Citrate (C ₆ H ₅ O ₇) -----	0 to 25
Nitrate (NO ₃) -----	5 to 20

In a specific example of maintenance composition, the parts by weight were:

	Per cent
Potassium pyrophosphate -----	92
Citric acid -----	3.7
Potassium nitrate -----	4.3

The percentages may be varied about 25%, plus or minus.

In preparing the compositions, the ingredients are pulverized and intimately mixed.

The mixing of the bath is troublesome when the ingredients are added separately. The copper pyrophosphate cakes on the bottom of the tank and requires undue stirring and hoeing to bring it into solution. In intimate admixture with the other ingredients, the copper pyrophosphate is readily soluble, requiring only a few minutes from the time the admixture is placed into water until copper plating operations can be started. Moreover, potassium nitrate being classified as an explosive, it must be shipped under an "explosive license" and requires special handling in packaging and shipping; in admixture with the other ingredients given above it is so dispersed and diluted that no special precautions are needed or required.

The baths and compositions may have other embodiments than those herein specifically described, and the process may be practiced in other modes than that specifically described.

What is claimed is:

1. A composition of matter for making up a copper plating bath consisting of a soluble bi-

5

valent copper compound, a soluble pyrophosphate compound, and a soluble nitrate compound, in intimate admixture, the composition consisting of, by weight, 7.5 to 45 parts bivalent copper, 100 to 250 parts pyrophosphate (P_2O_7), and 5 to 20 parts nitrate (NO_3).

2. A composition of matter for making up a copper plating bath according to claim 1, further containing radicals of organic hydroxy acids of the group consisting of citric acid, lactic acid, tartaric acid, glycollic acid, malic acid, capable of forming alkaline heavy metal complexes, equivalent to 5 to 25 parts citrate, ($C_6H_5O_7$).

3. A composition of matter for making up a copper plating bath according to claim 1, further containing 5 to 25 parts citrate ($C_6H_5O_7$).

4. A composition of matter for replenishing a pyrophosphate copper plating bath consisting of a soluble alkali metal pyrophosphate and a soluble nitrate compound in intimate admixture, in amounts by weight of 150 to 250 parts pyrophosphate (P_2O_7) and 5 to 20 parts nitrate (NO_3).

5. A composition of matter for replenishing a pyrophosphate copper plating bath according to

6

claim 4, further containing radicals of organic hydroxy acids of the group consisting of citric acid, lactic acid, tartaric acid, glycollic acid, malic acid capable of forming alkaline heavy metal complexes, equivalent to 5 to 25 parts citrate ($C_6H_5O_7$).

6. A composition of matter for replenishing a pyrophosphate copper plating bath according to claim 4, further containing 5 to 25 parts citrate ($C_6H_5O_7$) by weight.

7. A method of depositing dense and adherent copper characterized by the bath having a pH between 6.5 and 7.5, and in which the bath consists essentially of 7.5 to 45 g./l. bivalent copper, 100 to 250 g./l. pyrophosphate (P_2O_7), and 5 to 20 g./l. nitrate (NO_3).

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REFERENCES CITED

20 The following references are of record in the file of this patent:

Bureau of Standards, Circular No. 52, 2d edition, issued June 28, 1916, page 19.