

UNITED STATES PATENT OFFICE

2,493,092

METHOD OF ELECTRODEPOSITING COPPER
AND BATHS THEREFORJesse E. Stareck, Birmingham, Mich., assignor to
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Serial No. 640,680

2 Claims. (Cl. 204-52)

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

In U. S. Patent 2,250,556, granted July 9, 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 superior process and bath for barrel plating 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 #2,250,556, 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 ammonia (NH_3), and has a pH between 7.5 and 9.5 (measured by a glass electrode pH meter).

With baths having composition given in the examples which follow, the quantity of NO_3 ion which is present 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 pyrophosphate content from that necessary to convert the copper to the complex radical $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ 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

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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 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 $(\text{CuP}_2\text{O}_7)_2^{6-}$ (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.

About 3 g./l. of ammonia are added to aid anode corrosion with an optimum range from 1 to 3 g./l.

The pH of the bath ranges from 7.5 to 9.5 and is adjusted by adding a suitable 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 hereinafter described are stable at higher 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, although 70 to 160° F. may be used. 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 a combination thereof with air agitation is also satisfactory. Agitation of the solution increases the operable current density range. The operable current density range also increases with rising tempera-

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tures 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 best advantage are given below.

Bath 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 radical, 15 g./l.	5 to 25
NO ₃ , 10 g./l.	5 to 20
NH ₃ , 1.5 g./l.	1 to 3
pH, 8.5	8.0 to 9.5
Temperature, 135° F.°F.	120 to 150

Bath composition for maximum plating speeds

Cu, 35 g./l.	33 to 38
P ₂ O ₇ , 230 g./l.	190 to 250
Citrate radical, 15 g./l.	5 to 25
NO ₃ , 10 g./l.	5 to 20
NH ₃ , 1½ g./l.	1 to 2
pH, 8.5	8.0 to 9.5
Temperature, 140° F.°F.	130 to 150

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

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dense, the deposit is particularly good as a stop-off for carburizing or for nitriding, often requiring less thickness than usual to prevent carbon penetration.

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

A related bath is described in my co-pending application Serial No. 503,846, filed September 25, 1943, which has become Patent 2,437,865, granted March 16, 1948.

What is claimed is:

1. A method of depositing dense and adherent copper, consisting in passing electric current from an anode to a cathode-object immersed in an aqueous bath having a pH between 7.5 and 9.5, and a temperature between 70° F. and 160° F., and in which the bath consists essentially of 7.5 to 45 g./l. bivalent copper, 100 to 250 g./l. pyrophosphate (P₂O₇), 5 to 20 g./l. nitrate (NO₃) and 1 to 3 g./l. ammonia (NH₃).

2. An aqueous bath for copper deposition consisting essentially of 7.5 to 45 g./l. bivalent copper, 100 to 250 g./l. pyrophosphate (P₂O₇), 5 to 20 g./l. nitrate (NO₃) and 1 to 3 g./l. ammonia (NH₃) and having a pH between 7.5 and 9.5.

JESSE E. STARECK.

REFERENCES CITED

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

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Number	Name	Date
2,250,556	Stareck	July 29, 1941
2,437,865	Stareck	Mar. 16, 1948

OTHER REFERENCES

Circular No. 52, Bureau of Standards, second edition, June 28, 1916, page 19.
