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ELECTRODEPOSITION OF COPPER AND
BATH THEREFOR

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This invention relates to the electrodeposition of copper, and to electrolytic solutions or baths for use therein; and provides improvements therein.

In order to obtain dense and adherent coatings of copper on a wide variety of metals and alloys, including iron, steel, nickel, zinc, zinc alloys, lead, lead alloys, aluminum, etc. it is necessary to have the copper ion higher (more electro-negative) in the electromotive series* than said metals or constituent metals, or at least behave as though it (copper ion) had a higher place in the electromotive series.

It is for this reason that copper cyanide baths are used initially when copper is to be plated on most other metals.

The use of cyanide copper baths, when certain other coatings are deposited on the copper coating, has been found to give rise to stains and streaks in the coating deposited on the copper.

The present invention provides a copper plating process and baths therefor, which not only produce dense and adherent coatings of copper on a wide variety of metals, including iron, steel, nickel, zinc, zinc alloys, lead, lead alloys, aluminum, etc., but also bright copper deposits. On aluminum however the adherence of the copper deposit is not as good as on the other metals. This bright plating characteristic enables bright composite coatings to be obtained on a polished base without subsequent polishing or buffing of the electro-deposited coating or coatings, as for example, a nickel coating on a copper coating on polished steel, or a chromium coating on a nickel coating on a copper coating, on polished steel, by the use of a bright nickel plating process and of a bright chromium plating process in conjunction with the present bright copper plating process.

I have discovered that dense, adherent and bright copper deposits can be obtained from pyrophosphate copper baths containing in solution sufficient pyrophosphate radical to convert the copper therein to the complex copper pyrophosphate ion $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$, and having a pH between about 7.5 and 9.5 (as measured by the glass electrode pH meter). The upper pH is limited by reference to the condition where copper salts precipitate in the bath, some latitude being allowed between the pH of the baths as used and the pH of the baths at which copper salts pre-

cipitate. The optimum pH as regards the quality of the copper deposited lies about midway between the pH limits. The optimum pH will vary somewhat with the concentrations of the bath make-up ingredients. Copper deposits which are dense, adherent and bright can be regularly and uniformly obtained by regulating the pH at a chosen pH within said limits, and by maintaining the composition of the bath substantially constant, all as will be hereinafter more fully set forth. When the pH is excessively high, a rough or streaky deposit is obtained; when too low, a loosely adherent or dull copper deposit is obtained.

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 3.7 to 22.5 g./l. ($\frac{1}{2}$ to 3 oz./gal.) of metallic copper, with a pyrophosphate content from that necessary to convert the copper to the complex $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ to an excess limited by saturation, where the pyrophosphate radical is provided by the sodium salt. The copper may be conveniently added in the form of copper pyrophosphate, copper sulfate (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 is generally 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 the alkali-metal pyrophosphate salt in warm water adding the copper salt and stirring to dissolve the latter. 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 $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ (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

*See Blum & Hogaboom, "Principles of Electroplating and Electroforming," second edition, McGraw Hill Book Co., Inc., New York, Table 10.

weight ratio of 2 to 1 between P_2O_7 and Cu. The bath given in the specific example is one containing such an excess of pyrophosphate radical. The free pyrophosphate content of the bath decreases the tendency for 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.

Citric acid, oxalic acid, tartaric acid, or a salt thereof, especially an alkali-metal or ammonium salt thereof, or a carbonate, is 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. The addition of an alkali-metal chloride also gives effects similar to the citrates, etc.

The pH of the bath is adjusted by adding a suitable acid such as sulphuric acid for a sodium bath, or pyrophosphoric acid, when a test with the glass electrode pH meter 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 or ammonium hydroxide, 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 80° F. to 130° F. are usually preferred. 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 50 amperes per square foot or more may be obtained, but for bright lustrous deposits on polished surfaces values of about two to ten amperes per square foot are generally more satisfactory for a sodium bath, and ten to thirty amperes per square foot for a potassium bath. Copper anodes are ordinarily used. The operating voltage between anode (soluble) and cathode is usually in the neighborhood of 1 volt when bright plating current densities are used. The voltage is adjusted to and maintained at a value sufficient to deposit metallic copper, but not sufficient to liberate hydrogen gas. Liberation of hydrogen gas causes the deposit to become dark and striated and the current efficiency to fall considerably below 100%, a result not desired.

A specific mode of procedure (with a specific example of bath) embodying the present process, is as follows:

A uniform and lustrous copper deposit was desired on a set of intricately assembled locks and catches of cabinet hardware. The locks were constructed of iron frames, steel springs, brass cases and zinc-base die-cast key-slots. The assembled articles were placed on a rack, cleaned, and connected to the cathode bus bar of an alkaline pyrophosphate copper bath of the make-up composition.

	G./l.
$CuSO_4 \cdot 5H_2O$ -----	200
$Na_4P_2O_7 \cdot 10H_2O$ -----	200
$NaCl$ -----	30

and the pH was adjusted to 8.3, using an electrometric glass electrode pH meter. The voltage was adjusted to 0.8 volt, and a current den-

sity of about 10 amperes per square foot was used. The bath was operated at a temperature of 95° F. Copper anodes were used. At the end of five minutes the pieces were removed from the plating bath and thoroughly rinsed. A bright, adherent deposit of copper completely covered the assemblies.

An example of a makeup composition of a bath made up with potassium pyrophosphate and copper pyrophosphate, is as follows:

	G./l.
$Cu_2P_2O_7 \cdot 3H_2O$ -----	110
$K_4P_2O_7$ -----	404

About 3 g./l. of ammonia is added to aid anode corrosion and 10 g./l. of citric acid is added to improve the brightness of the deposit.

The pH of the solution was adjusted by the addition of pyrophosphoric acid to 8.5 as shown by a glass electrode. Good deposits of copper on steel have been obtained at voltages .8 to 1.5 volts, with current densities from 5 to 50 amperes per square foot, at 120° F.

The above described process gives mirror bright deposits in limited thicknesses. It has been found that additions of organic substances such as citric acid, phenol and naphthalene disulfonic acid or small amounts of metallic compounds such as those of arsenic, bismuth, iron, chromium, tin, zinc, lead and cadmium produce deposits which are mirror bright in greater thicknesses than without them.

Smooth, dense, bright deposits are obtained even in relatively thick plates.

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

The present application is a continuation in part of my application Serial No. 153,363, filed July 13, 1937, allowed October 23, 1940.

What is claimed is:

1. An aqueous bath for the electrodeposition of copper containing a copper pyrophosphate complex in which complex the pyrophosphate and copper are in the molecular weight ratio of 2 to 1, and having a pH between 7.5 and 9.5.

2. An aqueous bath for the electrodeposition of copper containing a copper pyrophosphate complex associated with alkali-metal radicals in which complex the pyrophosphate and copper are in the molecular weight ratio of 2 to 1, and having a pH between 7.5 and 9.5.

3. An aqueous bath for the electrodeposition of copper containing a copper pyrophosphate complex in which complex the pyrophosphate and copper are in the molecular weight ratio of 2 to 1, and having a pH between 7.5 and 9.5 and containing pyrophosphate radical in excess of that required to form the copper pyrophosphate complex.

4. A method of depositing dense and adherent copper, comprising passing an electric current to the article to be copper plated as a cathode through a bath containing a copper pyrophosphate complex in which complex the pyrophosphate and copper are in the molecular weight ratio of 2 to 1 and the pH of which is between 7.5 and 9.5.

5. A method of depositing dense and adherent copper, according to claim 4, further comprising regulating the voltage drop between anode and cathode to approximately one volt and below that at which hydrogen gas is liberated.

6. An aqueous bath according to claim 2, wherein the alkali-metal radicals are mainly potassium radicals.

7. An aqueous bath according to claim 2, wherein the alkali-metal radicals are mainly potassium radicals, and wherein the bath also contains ammonia.

8. An aqueous bath according to claim 2,

wherein the alkali-metal radicals are mainly potassium radicals, and wherein the bath also contains ammonia, and citrate radicals.

9. An aqueous bath according to claim 1, wherein the bath also contains a radical selected from the group consisting of citrate, carbonate, tartrate and oxalate.

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