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# ELECTRODEPOSITING COPPER

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This invention relates to a process for electrodepositing copper, and more particularly to making improved deposits from copper cyanide solutions.

Heretofore, various materials have been added to copper cyanide solutions such as, for example, lead, selenium, zinc and antimony, the materials being added in various proportions and amounts to improve electrodeposited copper. Such metals, however, have certain disadvantages. The quantities of each required are small and have to be controlled within relatively narrow limits to provide fair operating conditions. Because all are codeposited, they are depleted rapidly and frequent replacement is required to maintain their optimum concentrations. When used in combination, such as lead and selenium are, this problem arises: Each metal is codeposited with the copper in a preferential current density range. The amount of each removed from the bath depends upon the relationship of the current densities in the low and high current densities present on the parts being electroplated. It is easy to see that the amount of each removed by electrolysis can be variable and not in proportion to the original concentration. This complicates the selection of the replacement addition agents because they must be correct in both proportion and concentration for fair results.

An object of the present invention is to provide a novel process of producing an improved copper deposit. Another object is to provide addition agents of a metallic character which are not depleted by the electrode deposition process. A further object is to provide for an improved plating range of wider current densities. A still further object is to provide a copper deposit of excellent buffability. Yet another object is to provide a copper electroplating solution having a wide range of operating conditions which requires less care and exactness in obtaining optimum results. A still further object of the invention is to provide a copper electroplating solution having a smooth, lustrous deposit. Other specific objects and advantages will appear as the specification proceeds.

I have discovered that the electrodeposition of copper from cyanide solutions can be greatly improved by the addition of cobalt, which results in a deposit which is smooth, lustrous, and very easily buffed to a high luster. Nickel can also be employed, and to the cobalt or nickel can be added organic and other compounds for improving the quality of the deposit.

The lustrous, smooth, and fine-grained deposit obtained by the addition of nickel or cobalt to the copper cyanide solution is obtained even though the quantities of the added metal may be widely varied, and need not be confined within narrow or critical limits to produce good results. Further, the nickel or cobalt is not removed in any measurable amount by a codeposition; they are lost primarily by dragout. The concentrations for operation may be varied over wide ranges, and further they are effective over a wide range of solution-operating conditions. For example, cobalt used in quantities as small as .001 g./l. produces a favorable change in the electrodeposit, while quantities as large as .25 g./l. are useful and do not produce unfavorable results.

The nickel or cobalt may be added in any form which permits their introduction into the solution. They may be added in either organic or inorganic complexes or by electrolysis of the metal or copper alloy. I have found that cobalt or nickel may be combined with organic or other metal-organic compounds for special effects within the range of electroplating. They may be used in combination with other substances but the basic effect of cathode depolarization, luster, smoothness of the deposit and buffability is primarily determined by their presence in the electroplating solution. In addition, I have found that certain organic addition agents are helpful in promoting the buffability and extending the current density range. I have found that while piperidine produces some beneficial effect, other piperidine complexes are to be preferred. Substances such as: 2,4 lutidine, 2,6 lutidine are preferable. These were found to be beneficial in quantities as small as .05 g./l. The amount I prefer to use is .25 g./l. More may be used without bad effect.

I have found also that the addition of amino acids, or the secondary protein derivatives, such as peptones and peptides, have favorable effects on the deposit when used singly or in combination. I have found also that the addition of the hydrolysis products of hide proteins results in favorable effects. Because hydrolysis is not a perfectly controllable process, and it is difficult, if not impossible, to stop the reaction at a particular stage, the hydrolytic products of protein may be thought to be a mixture of the following:

Protein
↓
Metaprotein
↓
Proteoses
↓
Peptones
↓
Simple polypeptides
↓
Amino acids.

Although many proteins may be used for the hydrolysis, I prefer to use collagen or jelly-forming albuminoids, fibroids and keratins. I have found that, because of the variable amounts of the degradation products present, the required amounts of the mixture of hydrolysis products of protein can vary over a wide range. In general, an amount in the neighborhood of .25 to .5 g./l. is sufficient to produce satisfactory results, but a range of .05–.25 g./l. may be used.

I have found also that the addition of selenium to a cyanide copper solution containing cobalt or nickel is beneficial in producing a high luster in the deposit. I prefer to add selenium in the form of nickel or cobalt selenite. The amount of .001 g./l. is enough to produce an improvement in the luster, however I prefer to use .005 g./l. Greater or lesser amounts may be used, if desired. Copper selenite may be substituted for either, if desired.

I have found that the addition of the SCN (thiocyanate) radical to a copper solution containing either nickel or cobalt in the amount of at least .001 g./l. is beneficial. The thiocyanate may be added as sodium, potassium or ammonium salts. It is usually added in the amounts of between two and twenty grams/liter, a preferred range being 2.0–15.0 g./l.

Specific examples of copper solutions or baths prepared in accordance with the invention are as follows:

| | Range | Optimum |
|---|---|---|
| Copper cyanide..........grams.. | 50-120 | 85 |
| (Copper as metal)..........do.... | 40-95 | 60 |
| Potassium cyanide..........do.... | 70-140 | 100 |
| (free cyanide)..........do.... | .6-30 | 11.5 |
| Potassium carbonate..........do.... | 15-60 | 30 |
| Potassium hydroxide..........do.... | 15-45 | 30 |
| Rochelle salts [1]..........do.... | 30-75 | 45 |

Temperature 50°-80° C.

Current density to 100 amperes/ft.$^2$, dependent upon metal concentration and operating temperature.

[1] Other salts of organic acids may be substituted for Rochelle salts within the art of electroplating. Salts as sodium or potassium tartrate, oxalate, formate, etc.

The potassium formulation is preferred to the sodium formulation. However, either may be used and modified in composition within the art of electroplating to produce the desired results. All the above proportions are with respect to one liter of solution and the pH of the solution should be above 12.5.

Specific examples of the process may be set out as follows:

### *Example I*

To a standard type copper cyanide plating solution maintained at a temperature of about 60° C. and with a current density of 100 amperes/ft.$^2$, was added cobalt in the amount of .025 g./l., and the resulting copper deposit produced was smooth, lustrous, and had excellent buffability.

### *Example II*

To the process as described in Example I with the temperature maintained at about 70° C., nickel was added in the amount of .025 g./l., and a copper deposit of smooth and lustrous quality having excellent buffability was produced.

### *Example III*

In the process as described in Example I, .025 g./l. cobalt and .25 g./l. 2,4-lutidine was added, giving a copper deposit of wide range and excellent buffability. The substitution of a like amount of 2,6-lutidine for 2,4-lutidine was found also to give a smooth, lustrous copper deposit of wide range and excellent buffability.

### *Example IV*

In the process as described in Example I, .025 g./l. nickel and .25 g./l. 2,4-lutidine was added, to produce a smooth copper deposit of excellent buffability. The same result was obtained when 2,6-lutidine was added.

### *Example V*

To a copper cyanide plating solution was added cobalt in the amount of .025 g./l. and approximately .25 g./l. of the degradation products of the hydrolysis of proteins, producing a smooth, lustrous copper deposit of wide range and brilliance. The same result was obtained when nickel was substituted for cobalt in like amount.

### *Example VI*

To a copper cyanide plating solution maintained within the range of 50-80° C. was added cobalt in the amount of .025 g./l. and cobalt selenite in the amount of at least .001 g./l., producing a smooth, lustrous copper deposit of wide range and brilliance. The same result was obtained when nickel was substituted for cobalt and nickel selenite substituted for cobalt selenite.

### *Example VII*

Cobalt in the amount of .025 g./l. was added to a copper cyanide plating solution, together with at least .001 g./l. copper selenite, and there was produced a smooth, lustrous copper deposit of wide range and brilliance. The same result was obtained when nickel was substituted for cobalt in like amount.

### *Example VIII*

Nickel in the amount of at least .001 g./l. and KCNS in the amount of at least 2 g./l. were added to a copper cyanide plating solution, producing a smooth, lustrous deposit having good range and buffability. The same result was obtained when cobalt was substituted for the nickel in like amount and when NaCNS or $NH_4CNS$ was substituted for KCNS.

The copper deposit produced by the above described processes is changed in visible and physical ways. This deposit is formed with a decided bluish cast, in contrast to the red-orange deposit conventionally formed. The metallurgical hardness is affected to such a degree that formerly where a part was plated and required hard buffing and coloring to produce an acceptable finish, now only coloring with a soft buff and very light pressures are required. The deposit has the ability to "flow" readily under light pressure to cover imperfections in the basis metal, thus reducing the finishing cost drastically.

While, in the foregoing specification, I have set forth process steps in considerable detail, it will be understood that such details of proportion or procedure steps may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. In a process for electrodepositing coper from a copper cyanide solution, the step of adding at least .001 g./l. of a metal selected from the group consisting of cobalt and nickel, and at least .05 g./l. of a compound selected from the group consisting of 2,4-lutidine and 2,6-lutidine.

2. The process of claim 1, in which the metal is nickel.

3. In a process for electrodepositing copper from a copper cyanide solution, the steps of supplementing the solution with at least .001 g./l. of a metal selected from the group consisting of cobalt and nickel and with at least .05 g./l. of a compound selected from the group consisting of 2,4-lutidine and 2,6-lutidine, thereafter maintaining the said solution at a temperature in the range 50-80° C. and at a pH in excess of 12.5 while subjecting an object in said solution to a current having a density up to 100 amperes/foot$^2$ to provide the object with a copper deposit having a bluish cast and which deposit requires only soft buffing for finishing.

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