This invention relates to improvements in or relating to copper pyrophosphate electroplating baths and is a modification of the invention of our copending U.S. application No. 125,363.

According to conventional methods, copper is electrodeposited from an acid bath such as a copper sulphate/sulphuric acid bath or from a cyanide/sodium or potassium cyanide bath. In the latter bath the sodium or potassium cyanide is present in excess so that all the copper is Complexed to form the double cyanide. This excess is known as "free cyanide." The cyanide type of bath gives rise to health hazards and there is also an elfluent disposal problem. Both types of bath have the further disadvantage that smooth thick deposits are difficult to obtain. As electrolysis proceeds and the copper deposit thickens, the surface of the deposit becomes dull and noduled. Indeed with such baths the deposit may be dull and noduled at a thickness of only 0.001--0.002 inch.

It is also known that copper may be electrodeposited from a pyrophosphate bath. In this instance much thicker deposits, usually five to ten times as thick as deposits obtained from the acid or cyanide baths, can be obtained before dulling and noduling of the surface start. For example, when using the following electrolyte, noduling does not occur until a deposit, about 0.01 inch thick, is obtained:

Copper pyrophosphate (hydrated) 85--105
Tetra potassium pyrophosphate (anhydrous) 300--375
Potassium citrate 25

In use the preferred pH for such a bath is 8.0--8.5, though electrodeposition can occur from such a bath at pH values from 3 to 11, the current density is up to 80 amps/sq. ft. the temperature is 55--60° C. and the bath is vigorously air-agitated. However, such a bath produces only semi-bright deposits.

In our copending U.S. application No. 125,363 we describe how bright, smooth, thick deposits can be produced from copper pyrophosphate electroplating baths if there is present in the bath a small amount of a compound containing a 2-mercapto-1:3:4-thiadiaz-2-yl radical as brightness additive.

We have now found that 2-mercaptothiazole and hydrocarbon derivatives thereof may replace the thiadiazyl compounds used in earlier invention as brightness additives in copper pyrophosphate electroplating baths for the production of bright, smooth, thick deposits.

The present invention therefore provides an aqueous solution for electroplating metal substrates with copper which contains dissolved therein a copper salt, an alkali metal pyrophosphate in an amount at least sufficient to form the complex X(P_2O_7)_2, where X represents an alkali metal, characterised in that the solution also contains from 0.5 part per million to saturation of a brightness additive which is 2-mercaptothiazole in the free or combined state or a hydrocarbon derivative thereof, preferably the molecular ratio of pyrophosphate to copper in the solution is more than 2.0:1 but not more than 2.5:1.

The invention also comprises solid compositions for solution in water to provide a solution according to the invention. The invention further comprises a method of electroplating metal substrates with copper which comprises immersing the article in a solution of the invention and passing an electric current therethrough with the article as cathode; and also comprises the copper-plated substrates so produced.

In general, the electrolyte solution is prepared by dissolving anhydrous tetra sodium or teta potassium pyrophosphate in water and then adding the calculated amount of copper pyrophosphate so that the concentration of alkali metal pyrophosphate is from 250 to 300 g./l. of teta sodium pyrophosphate or from 300 to 400 g./l. of teta potassium pyrophosphate and the concentration of copper pyrophosphate is from 85 to 100 g./l.

Copper may be electroplated from such a bath onto all the usual basis metals and furthermore, because of its low alkalinity, the electrolyte does not readily attack light metals such as aluminium and zinc. It is possible, therefore, to obtain smooth bright deposits of copper on these light metals. In addition dense adherent deposits of copper may be produced on heavier metals, for example iron, steel, copper and copper alloys, nickel and lead. This type of bath also has the advantage that fume extraction is not necessary as with the cyanide bath.

The mercaptothiazole brightness additive may be incorporated in the present solution in the free or combined state, that is as such or as a salt thereof, particularly in the form of a copper or alkali metal salt, or in the form of a precursor, such as a bis-thiazyl sulphide or disulphide, which can break down to form the mercaptothiazole or a salt thereof under the alkaline conditions obtaining in the solution. Particularly suitable hydrocarbon derivatives of 2-mercaptothiazole are 2-mercaptophenazol and alkyl-substituted derivatives thereof, especially 6-alkyl-2-mercaptobenzthiazole in which the alkyl group contains from 1 to 4 carbon atoms.

The most effective concentration of the brightness additive in the solution for use in electroplating is from 5 to 10 parts per million, though improved copper deposits are obtained at concentrations as low as 0.5 part per million and the additives may also be used in excess up to the saturation level of concentration.

The electrolyte solution of the invention desirably also contains small quantities of other additives which provide an improved electrolyte process. Thus ammonia may be added to provide a concentration of from 1 to 3 g./l. in order to promote anode dissolution; likewise aliphatic carboxylic acids such as citric acid, tartaric acid or oxalic acid. Also, the addition of amino-acids acids may be made. These carboxylic acids have the effect of increasing the current density range from which electrodeposits of good appearance and mechanical properties may be obtained. The useful current density range may be further extended by additions of nitrite ion, nitrate ion or nitrito ions. The nitrite or nitrate ions are usually added in the form of potassium or sodium salts. Such additions are normally added to the bath after dissolution of the copper salt and pyrophosphate. The thiazole additive is often added as a solution in an alkali metal hydroxide.

In use the electrolyte may be suitably contained in a rubber-lined mild steel tank fitted with a stainless steel steam-heating coil and a plastic air-agitation coil. The concentrations of the bath constituents may vary over a wide range: the higher the concentration of the bath, the higher the maximum current density. As stated above, however, it is preferred to employ a molecular ratio of P_2O_7:Cu of 2.0--2.5:1. The copper content of the solution may be less than 1 g./l. up to saturation but we have found 30 g./l. a good practical value. The anodes may be prepared from electrolytic copper. The pH of the
bath is desirably between 7 and 11, normally between 7.5 and 9.5 and preferably from 8.6 to 8.9. The pH may be adjusted by adding pyrophosphate acid, nitric acid, sodium hydroxide, potassium hydroxide or ammonia solution. In use the temperature range of the bath is 35-60°C and a suitable current density is up to 80 amps/sq. ft., though with irregularly shaped articles as cathode it is difficult to attain a density of greater than 60 amps per square foot.

After the necessary preliminary cleaning, the articles to be plated are immersed in the bath and made cathodic. The electrolyte solutions of the invention may be used for the production of bright smooth deposits of up to 0.002 inch of copper on metals for decorative purposes and bright, smooth and very thick deposits 0.002-1 inch or more on electrically conducting surfaces for electroforming purposes. With the latter little or no mechanical aftertreatment is required.

The following examples illustrate the invention:

**Example 1**

In this example copper was plated onto a stainless steel cylinder and the bath composition is as follows:

- Copper pyrophosphate (hydrated) -------g./l.---- 100
- Tetra potassium pyrophosphate (anhydrates) g./l. ---- 389
- Ammonia ---------------------------g./l.---- 2.0
- 2-mercaptobenzthiazole -------------------------p.p.m.----- 5

The pH of the bath was 8.7, the current density employed was 35 amps/sq. ft., the temperature was 60°C, and the bath was agitated by means of air and a rotating cathode.

Under the above conditions a deposit approximately 0.5 inch thick was obtained after 100 hours of plating. This deposit was bright, level and smooth and was an excellent example of electroforming.

**Example 2**

The electroplating process of Example 1 was repeated, but with the plating time reduced to 15 minutes. The electrodeposit of copper having a thickness slightly greater than 0.0005 inch was formed. This electrodeposit was an excellent undercoat for subsequent electrodeposition of nickel or chromium in the formation of decorative articles.

**Example 3**

In this example a small brass cylinder was made cathodic in a bath containing copper at a concentration of 30 g./l., pyrophosphate at a concentration of 200 g./l., ammonia at a concentration of 1 g./l., and 5 p.p.m. of 6-methyl-2-mercaptobenzthiazole. The pH of the bath was 8.8 and it was operated at 55°C.

The brass cylinder was then electroplated at a current density of 30 amps per square foot for 2 hours. There was obtained a bright smooth copper electrodeposited on the cylinder of thickness 0.003 inch which was an entirely satisfactory example of electroforming.

What we claim is:

1. An aqueous solution for electroplating metal substrates with copper which contains dissolved therein: a copper salt; an alkali metal pyrophosphate in an amount at least sufficient to form the complex X₅Cu₅(P₂O₁₀)ₙ, wherein X represents an alkali metal; and from 0.5 part per million to saturation of a brightness additive which is selected from the group consisting of 2-mercaptotiazole and 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms.

2. The solution of claim 1 wherein said brightness additive is in an amount between 5 and 10 parts per million.

3. The solution of claim 1 wherein said brightness additive is 6-alkyl-2-mercaptobenzthiazole in which the alkyl group contains from 1 to 4 carbon atoms.

4. The solution of claim 1 wherein said brightness additive is 2-mercaptobenzthiazole.

5. The solution of claim 1 wherein said brightness additive is 6-mercaptobenzthiazole.

6. The solution of claim 1 wherein said brightness additive is 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms.

7. An aqueous solution for electroplating metal substrates with copper which has a pH of from 7 to 13 and contains dissolved therein: a copper salt; an alkali metal pyrophosphate; the group consisting of sodium and potassium pyrophosphates in an amount sufficient to provide a molar ratio of pyrophosphate to copper of more than 2.0:1 but not more than 2.25:1 and a concentration of copper pyrophosphate of from 85 to 100 grams per litre; and from 0.5 part per million to saturation of a brightness additive which is selected from the group consisting of 2-mercaptotiazole and 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms.

8. An aqueous solution as claimed in claim 7, which also contains at least one further additive selected from the group consisting of ammonia in a concentration of from 1 to 3 grams per litre, an aliphatic carboxylic acid, an alpha-amino acid, nitrite ions and nitrate ions.

9. An aqueous solution for electroplating metal substrates with copper which contains dissolved therein: a copper salt; an alkali metal pyrophosphate in an amount at least sufficient to form the complex X₅Cu₅(P₂O₁₀)ₙ, wherein X represents an alkali metal; and from 0.5 part per million to saturation of a brightness additive which is selected from the group consisting of 2-mercaptobenzthiazole and 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms.

10. An aqueous solution as claimed in claim 9, wherein said brightness additive is a 6-alkyl-2-mercaptobenzthiazole in which the alkyl group contains from 1 to 4 carbon atoms.

11. An aqueous solution as claimed in claim 7, which contains dissolved therein: a copper salt; an alkali metal pyrophosphate selected from the group consisting of sodium and potassium pyrophosphates in an amount sufficient to provide a molar ratio of pyrophosphate to copper of more than 2.0:1 but not more than 2.25:1 and a concentration of from 85 to 100 parts per million to saturation of a brightness additive which is selected from the group consisting of 2-mercaptobenzthiazole and 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms.

12. An aqueous solution as claimed in claim 11, which contains at least one further additive selected from the group consisting of ammonia in a concentration of from 1 to 3 grams per litre, an aliphatic carboxylic acid, an alpha-amino acid, nitrite ions and nitrate ions.

13. An aqueous solution as claimed in claim 11, which also contains at least one further additive selected from the group consisting of ammonia in a concentration of from 1 to 3 grams per litre, an aliphatic carboxylic acid, an alpha-amino acid, nitrite ions and nitrate ions.

14. The solution of claim 13 wherein said brightness additive is 6-alkyl-2-mercaptobenzthiazole in which the alkyl group contains from 1 to 4 carbon atoms.

15. The solution of claim 13 wherein said brightness additive is 2-mercaptobenzthiazole.

16. The solution of claim 13 wherein said brightness additive is 6-mercaptobenzthiazole.

17. A solid composition consisting essentially of water-soluble copper salt; an alkali metal pyrophosphate in an amount at least sufficient to form the complex X₅Cu₅(P₂O₁₀)ₙ, wherein X represents an alkali metal; and a brightness additive which is selected from the group consisting of 2-mercaptobenzthiazole in the free state, 2-mercaptothiazole-
zole and 2-mercaptobenzthiazole in which the benzene moiety may be substituted with at least one alkyl group having 1 to 4 carbon atoms, the said composition being water soluble to provide an aqueous solution suitable for use in electroplating metal substrates with copper, and containing from 0.5 part per million to saturation of said brightness additive.

18. A solid composition as claimed in claim 17, wherein the said alkali metal pyrophosphate is selected from the group consisting of sodium and potassium pyrophosphates and is present in an amount sufficient to provide a molar ratio of pyrophosphate to copper of more than 2.0:1 but not more than 2.5:1.

19. The composition of claim 17 wherein the brightness additive is a 6-alkyl-2-mercaptobenzthiazole in which the alkyl group contains from 1 to 4 carbon atoms.

20. The composition of claim 17 wherein said brightness additive is 2-mercaptobenzthiazole.

21. The composition of claim 17 wherein said brightness additive is 6-methyl-2-mercaptobenzthiazole.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,157,586

November 17, 1964

Frederick Herbert Wells et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 48, for "8.5 part per million" read -- 0.5 part per million --; column 4, line 75 and column 5, line 1, strike out "2-mercaptotiazole in the free state, 2-mercaptopthiazole and 2-mercaptopbenzthiazole in which the benzene" and insert instead -- 2-mercaptotiazole and 2-mercaptopbenzthiazole in which the benzene --.

Signed and sealed this 13th day of April 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
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