United States Patent [19]

Kowalski

[11] **3,879,270**

[45] **Apr. 22, 1975**

[54] **COMPOSITIONS AND PROCESS FOR THE ELECTRODEPOSITION OF METALS**

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[73] Assignee: **Monsanto Company**, St. Louis, Mo.

[22] Filed: **Jan. 10, 1974**

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[52] **U.S. Cl.**..... **204/52 R;** 204/DIG. 2; 204/43 R; 204/44; 204/45 R; 204/46 R; 204/46 G; 204/48; 204/49; 204/50 R; 204/51; 204/54 L; 204/55 R

[51] **Int. Cl.**..... **C23b 5/02;** C23b 5/18; C23b 5/46

[58] **Field of Search**..... 260/248 A, 248 R; 204/52 R, 52 Y, 45 R, 45 M, 45.5, 46 R, 46 G, 47, 48, 49, 50 R, 50 Y, 51, 53, 54 R, 54 L, 55 R, 55 Y, 43, 44, 1.5

[56] **References Cited**

UNITED STATES PATENTS

2,849,352	8/1958	Kirstahler et al.	204/44
2,862,861	12/1958	Moy	204/52 Y
3,296,101	1/1967	Crain	204/44
3,528,894	9/1970	Stoddard et al.	204/49 X

FOREIGN PATENTS OR APPLICATIONS

1,131,217	6/1962	Germany	260/248 A
882,626	11/1961	United Kingdom	204/49

OTHER PUBLICATIONS

B. Egeberg et al., Trans. Electrochem. Soc., vol. 66, pp. 211–227, (1938).

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—W. R. Eberhardt; T. B. Leslie

[57] **ABSTRACT**

A cyanide free electrolyte for the electrodeposition of metals comprises an aqueous solution of (a) a metal ion, (b) a cyanidine compound and optionally, (c) a phosphonic acid compound.

16 Claims, No Drawings

COMPOSITIONS AND PROCESS FOR THE ELECTRODEPOSITION OF METALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the electrodeposition or electroplating of metals, and to the composition of the electroplating bath from which the metal is deposited. More particularly, the present invention relates to electrolyte compositions useful as a strike bath for copper and other metals.

2. Description of the Prior Art

The electrodeposition of metals from aqueous solutions of metal ions is an old art. The typical electroplating system consists of an electroplating bath and two or more electrodes. The cathode of the electrode system is the object to be plated. The anode may be carbon or a solid piece of the metal to be plated upon the cathode. A solid metal anode is consumed in the electroplating process and provides a constant source of metal ions to the plating bath.

In electroplating metals such as copper or tin onto active metals such as iron or zinc, it is necessary to make the initial deposit from a "strike bath" in order to avoid immersion plating or chemical deposition of metal as would occur in a regular plating bath. The strike bath is specially formulated with a low metal ion concentration to avoid such immersion plating. One typical cyanide copper strike bath has the following composition and operational parameters:

Copper (as metal)	1.8 –3.5	oz./gal.
Free cyanide	.75–1.5	do.
Rochelle salt	2 –5	do.
Soda ash	2 –8	do.
pH	11.5 –12.5	do.
C.D.	15–75 amp./ft.^{2}	
Temperature	120–140°F.	
Time	¼–3 minutes, depending on C.D. used	

In making the copper strike, the current must be on when the parts are immersed in the solution. Following the copper strike, the parts are transferred to the regular copper plating bath for the balance of the copper deposit.

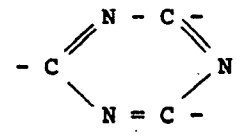
Electroplating baths and strike baths comprising aqueous alkaline solutions of metal cyanides have several disadvantages associated with the toxic nature of cyanide. The use of metal cyanide solutions can be hazardous if the pH of the electroplating medium should drop to neutral or below since there is a danger of poisonous hydrogen cyanide gas being produced. Also, the Toxic metal cyanides present a disposal problem, and removing cyanides from used baths prior to disposal requires special equipment and adds to the cost of the electroplating operation.

The prior art has suggested certain techniques for electroplating without the use of cyanides. U.S. Pat. No. 3,475,293, for example, suggests the use of certain diphosphonates or monoamino lower alkylene phosphonates in electroplating divalent metal ions. U.S. Pat. Nos. 3,706,634 and 3,706,635 suggest combinations of ethylene diamine tetra(methylene phosphonic acid), 1-hydroxy ethylidene-1,1-diphosphonic acid, and amino tri(methylene phosphonic acid) as particularly useful complexing compositions. U.S. Pat. No. 3,617,343 is similarly directed toward a nickel plating system employing certain phosphonic acid compounds.

While the cyanide-free electroplating systems of the prior art are suitable for some plating operations, there is a tendency for immersion plating to occur on iron or zinc base stocks unless a metal strike is first applied. Metal deposited by immersion is spongy and adheres poorly so that subsequent metal deposited electrically has a tendency to crack and peel. It is accordingly an object of the present invention to provide a cyanide-free electrolyte composition suitable for use as a strike bath for depositing copper and other metals directly onto iron or zinc. It is a further object of the present invention to provide a method and cyanide-free electrolyte composition for electrically depositing metallic copper from a solution containing monovalent copper Cu(I).

SUMMARY

In accordance with the present invention there is employed as the electroplating bath an aqueous solution comprising (a) from 0.01 to about 5 percent by weight of a monovalent, divalent or polyvalent metal ion; (b) from about 0.01 percent to the solubility limit of a cyanidine compound containing the ring radical



and optionally (c) an organodiphosphonic acid compound having the structure

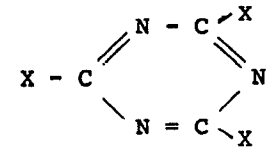
$$M_2O_3P - R - PO_3M_2$$

wherein M is hydrogen, alkali metal or ammonium, and R is an alkyl, alkylene or alkylidene radical having from 1 to 11 and preferably from 1 to 5 carbon atoms optionally substituted with —OH or halide. Such electroplating bath compositions are useful in plating metals at a pH of from about 7 to 12 and at a temperature of from about 30° to 90°C.

DESCRIPTION OF PREFERRED EMBODIMENTS

In a preferred embodiment of the present invention, a thin deposit of copper is electrically plated upon active base metals from a cyanide-free strike bath comprising monovalent copper Cu(I). While the ensuing description is directed primarily toward the plating of copper on zinc, it is contemplated that metals other than copper, particularly silver, tin, nickel, chromium and gold are also deposited in a like manner on zinc and other active base metals such as aluminum, magnesium and iron in accordance with the method and teaching of the instant invention.

Cyanidine compounds useful in the practice of the present invention are those compounds containing the trivalent ring radical



where X is any cation which will render the compound at least slightly soluble in the electroplating bath com-

position. Preferably, X is selected from the group consisting of —OM, halogen, —NH_2, and mixtures thereof, where M is hydrogen, alkali metal or ammonium. Most preferably, X is —OM and the cyanidine compound is cyanuric acid or an alkali metal salt thereof.

Organodiphosphonic acid compounds useful in the practice of the instant invention are those compounds having the general structure

$$M_2O_3P - R - PO_3M_2$$

where R is an alkyl, alkylene or alkylidene radical of from 1 to about 11 and preferably from 1 to about 5 carbon atoms, or a said radical substituted with hydroxy or halide, and each M is individually hydrogen, alkali metal, or ammonium ions. Examples of preferred compounds include, but are not limited to, methylene diphosphonate, 1,1-ethylene diphosphonate, 1-hydroxy ethylidene-1,1-diphosphonate, and 1-chloroethylidene-1,1-diphosphonate.

The electroplating bath or electrolyte of the present invention comprises an aqueous solution of the metal to be plated, the cyanidine compound, pH adjusters and optionally one or more additives including brighteners, buffering agents, levelers, and organodiphosphonic acid compounds which are intended to improve the performance or life of the bath or the quality of the metal deposit, or to impart other beneficial effect. It is common in the electroplating art to utilize many and varied additives which are selected by the skilled electroplater according to the particular system being used. The use of such additives in the electroplating bath compositions of the present invention in order to adapt these compositions to individual circumstances are included within the scope of the present invention.

The bath is prepared according to conventional techniques by simply dissolving the desired ingredients into a quantity of water. The water is preferably low in mineral content and may be deionized. The metal to be plated is often added in the form of a water soluble salt such as a metal sulfate, chloride, phosphate, citrate, carbonate or acetate. Carbonate and acetate salts are often preferred because the anions of these salts may be thermally decomposed and thereby removed from the bath when the metal ion is released. In preparing a bath for copper striking, monovalent copper is most conveniently added as cuprous chloride.

The optimum concentration of metal salt and cyanidine compound in the electroplating bath will be largely determined by the identity of the metal and by the characteristics of the individual electroplating system. As a rule, the concentrations are limited primarily by the solubilities of the compounds. As an example, in a copper strike bath based upon Cu(I) there is usually employed from about 0.01 percent to about 0.5 percent by weight of metal in solution and from about 0.01 to about 0.25 percent by cyanuric acid, the maximums being the respective solubility limits. When plating Cu(II) or other more soluble metals, the metal ion concentration may be increased to 5% or higher.

The copper strike bath is generally operated within a pH range of from about 10 to 12. The optimum pH will depend to some extent upon the composition of the particular bath. Since pH is easily adjusted by the addition of alkaline materials such as alkali metal hydroxides, or acid materials such as mineral acids, it is a relatively simple matter to adjust the pH in either direction until optimum plating characteristics are achieved. As a general rule it is often found that higher pH values, that is within the range of from about 11 to 12, give better results when striking copper from Cu(I) than lower pH levels although exceptions to this rule may be found.

The use of the organodiphosphonic acid compound as defined above is found to enhance the performance of the electroplating bath, particularly with respect to depositing copper. A combination of cyanuric acid and 1,1-ethylene diphosphonic acid (EDP) is particularly effective to produce bright, uniform, and tightly adhering deposits of copper on brass, zinc and steel by striking at a pH of about 11.5. The concentration of EDP used in the composition of this invention is sufficient to provide a mole ratio of EDP to copper of from about 0.5:1, although from about 1:1 to about 2:1 is preferred.

While the aforegoing description is directed primarily to the composition of the electroplating or strike bath, the present invention further provides a process for the electrodeposition of monovalent, divalent or trivalent metals which comprises the steps of electrolyzing an aqueous solution of any of the metal ions hereinbefore described, a cyanidine compound, and any of the optional additives hereinbefore described. By the process of this invention, metal such as copper, iron, nickel, zinc and cadmium may be electrically deposited upon a cathode such as steel, aluminum, brass, zinc and the like with little or no chemical deposition.

During the electrodeposition process, the electroplating bath is maintained at a temperature within the range of the freezing point to boiling point of the bath, generally within a range of from about 30°C. to about 90°C. For reasons of current efficiencies it has been found preferable to maintain the temperature of the electroplating bath within the range from about 40°C. to about 70°C.

The amount of current employed in the electrodeposition may vary widely, depending upon the particular metal being plated, the temperature of the bath and whether or not the bath is agitated during the electroplating process. In general, the amount of current employed will be sufficient to provide a current density of from about 1 to 300 amperes per square foot of electrode surface. Ordinarily when the electroplating bath is quiescent or unagitated, the current density will be in the range of from about 15 to 75 amperes per square foot, while when the electroplating bath is agitated current densities up to about 150 amperes per square foot may be utilized. The optimum or preferred current density for any particular electroplating situation will depend upon the individual characteristics of the operation and is readily determined by employing conventional electroplating techniques.

The time required to electroplate or to electrically deposit the metal will vary with the kind of metal, the current density, and bath composition and concentration, as well as upon the thickness of the plate or deposit desired. Generally, the greater the current density, the shorter will be the time required to produce a metal strike or a plate of a given thickness.

In accordance with a preferred embodiment of the present invention, a copper strike is electrically deposited upon a wide variety of base metals or substrates such as zinc, iron, brass, steel, aluminum and the like. This preferred process comprises passing an electric current, at a density in the range of from about 15 to

about 75 amperes per square foot of cathode surface, through an aqueous solution containing monovalent copper ions and cyanuric acid or a mixture of cyanuric acid and EDP and having a pH in the range of from about 10.0 to about 12.0 and preferably about 11.5. The concentration of copper in the electroplating bath composition is preferably from about 0.01 to about 0.5 percent by weight, based on the weight of the solution. The temperature of the solution is preferably maintained within the range of from about 40°C. to about 70°C. during the electroplating operation.

As stated above, the electroplating and strike solutions of the present invention can contain known brighteners, buffers, and leveling agents and other additives commonly used in electroplating operations. Boric acid and its salts are compatible buffers for many formulas of the invention, and selenites and arsenites are useful brighteners for copper plating baths while aldehydes and ketones are useful for zinc plating. Other additives which may be employed in the electroplating solutions of the present invention include those disclosed in the 39*th Annual Edition of Metal Finishing Guidebook Directory*, 1973, published by Metals and Plastics Publications, Inc., 99 Kinderkamack Road, Westwood, N.J.

Certain preferred embodiments of the present invention concerning the electrodeposition of copper as illustrated by the following Examples which are not limiting of the invention. All parts and percentages are by weight unless otherwise specified. Plating tests were conducted according to conventional procedures in a "Hull Cell".

The Hull Cell is constructed substantially as the electrolysis cell described in U.S. Pat. No. 2,149,344. This type of Hull Cell is standard equipment for the evaluation of electroplating solutions by the subjective determination of "brightness rating" as based on the width of the brightness range, uniformity of brightness, and the presence or absence of smudges, stains and discoloration. In addition, the effectiveness of the bath is also evaluated on the basis of adhesion of plated metal to the cathode. The particular cathodes utilized in this test were brass or zinc as indicated and were each 5 × 3-½ inches in size. The anode utilized in these tests was made of copper and was 2-⅜ × 2-⅛ inches in size. The Hull Cell utilized in this test had a capacity of 1,000 milliliters.

EXAMPLE I

An electrolyte was made according to the following formulation:

0.99 g.	CuCl
12 g.	CYA (cyanuric acid)
300 ml.	D.I. Water

The pH was adjusted to 11.7 by the addition of NaOH, and the solution filtered to remove undissolved CYA. A brass panel was cleaned and plated in the Hull Cell at 2 amps for 2 minutes at 41°C. A bright, thin, uniform, very good deposit of copper was obtained. Similarly good results are obtained when depositing copper on zinc and iron panels.

EXAMPLE II

An electrolyte was made according to the following formulation:

1.5 g.	CuCl
20 g.	K_2HCYA (partial K salt of CYA)
5 g.	NaH_2CYA(partial Na salt of CYA)
5 g.	EDP.4 Na (Na salt of 1,1-ethylene diphosphonic acid)
300 ml.	D. I. Water

The pH was adjusted to 11.5 by the addition of NaOH and the solution filtered to remove undissolved solids. A brass panel was cleaned and plated in the Hull Cell at 1 amp. for 2 minutes at 45°C. A very good bright deposit of copper was obtained.

A zinc panel was cleaned and immersed in the solution for 30 seconds at 45°C. No evidence of immersion plating was observed. The zinc panel was electroplated in the Hull Cell at 1 amp. for 2 minutes at 45°C. A very good, thin deposit of copper was obtained.

EXAMPLE III

An electrolyte was made according to the following formulation:

1 g.	CuCl
12.6 g.	Melamine
12 g.	NaOH
10 g.	EDP.4 Na
200 ml.	D.I. Water

The pH was adjusted to 11.0 by the addition of orthophosphorus acid, and the solution filtered to remove undissolved solids. Brass and zinc panels were individually cleaned and plated in the Hull Cell at 1 amp. for 2 minutes at 35°C. The copper depositions were judged as fair to good in brightness and uniformity. No immersion plating was observed.

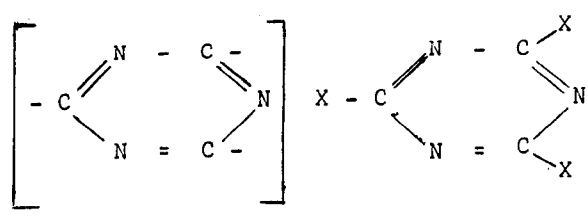
Although the invention has been illustrated by reference to the electrodeposition of copper and particularly copper striking utilizing the method and compositions of this invention, the present invention is not limited thereto but is also useful in electrodepositing other metals upon other cathode materials as hereinabove described. Accordingly, the present invention is not to be limited except as defined in the claims appended hereto.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A cyanide-free process for the electrodeposition of monovalent, divalent and polyvalent metal ions which comprises the steps of electrolyzing an aqueous solution comprising

a. a monovalent, divalent or polyvalent metal ion, and

b. a cyanidine compound having the general formula



wherein X is selected from the group consisting of —OM, $—NH_2$ and halogen ions, where M is hydrogen or alkali metal ion, the concentration of (a) in said aqueous solution being from about 0.01 percent to 5 percent; the concentration of (b) being from about

0.01 percent to the limit of solubility; the pH of said aqueous solution being from about 7 to 12, and the temperature of said aqueous solution being from about 30° to 90°C.

2. A process of claim **1** wherein said aqueous solution comprises, in addition to (a) and (b), a compound (c) having the structure

$$M_2O_3P - R - PO_3M_2$$

wherein M is hydrogen, alkali metal or ammonium ion, and R is selected from the group consisting of alkylene or alkylidene radical having from 1 to about 11 carbon atoms and hydroxy and halogen substituted derivatives thereof, in a concentration sufficient to provide a mole ratio of at least about 0.5:1 of (c) to (a).

3. A process of claim **2** wherein said compound (c) is 1,1-ethylene diphosphonic acid.

4. A process of claim **3** wherein (b) is cyanuric acid or an alkali metal salt thereof.

5. A process of claim **4** wherein said metal ion (a) is monovalent Cu(I), the concentration of said metal ion is from about 0.01 to about 0.5 percent by weight, and the pH of said aqueous solution is from about 11 to 12.

6. A process of claim **1** wherein said metal ion (a) is monovalent Cu(I), the concentration of said metal ion is from about 0.01 to about 0.5 percent by weight and the pH of said aqueous solution is from about 11 to 12.

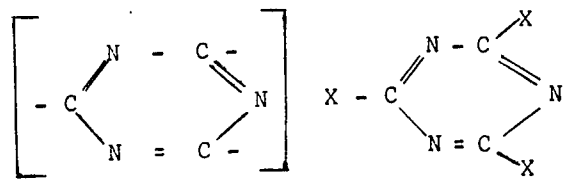
7. A process of claim **6** wherein (b) is cyanuric acid or alkali metal salts thereof.

8. A process of claim **1** wherein said metal ion (a) is selected from the group consisting of copper, iron, nickel, zinc, cadmium, tin, silver, chromium and gold.

9. A cyanide-free electroplating bath composition comprising an aqueous solution of

a. from about 0.01 to about 5 percent by weight of a monovalent, divalent or polyvalent metal ion, and

b. from about 0.01 percent to the solubility limit of a cyanidine compound having the general formula



wherein X is selected from the group consisting of —OH, —NH_2 and halogen ions, where M is hydrogen or alkali metal ion and the pH of said aqueous solution being from about 7 to 12.

10. A composition of claim **9** comprising in addition to (a) and (b), a compound (c) having the structure

$$M_2O_3P - R - PO_3M_2$$

wherein M is hydrogen, alkali metal or ammonium ion, and R is selected from the group consisting of alkylene or alkylidene radical having from 1 to about 11 carbon atoms, and hydroxy and halogen substituted derivatives thereof, in a concentration sufficient to provide a mole ratio of at least about 0.5:1 of (c) to (a).

11. A composition of claim **10** wherein (b) is cyanuric acid or an alkali metal salt thereof.

12. A composition of claim **11** wherein said metal ion (a) is monovalent Cu(I) and the concentration of said metal ion is from about 0.01 to about 0.5 percent by weight.

13. A composition of claim **10** wherein said compound (c) is 1,1-ethylene diphosphonic acid.

14. A composition of claim **9** wherein (b) is cyanuric acid or alkali metal salts thereof.

15. A composition of claim **14** wherein said metal ion is monovalent Cu(I) and the concentration of said metal ion is from about 0.01 to about 0.5 percent by weight.

16. A composition of claim **9** wherein said metal ion (a) is selected from the group consisting of copper, iron, nickel, zinc, cadmium, tin, silver, chromium and gold.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,879,270

DATED : April 22, 1975

INVENTOR(S) : Xavier Kowalski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 9, column 8, line 9, "-OH," should be -- -OM, --.

Signed and Sealed this

fifth Day of *August 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks