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[54] **THIOSULFATE COPPER PLATING**
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ABSTRACT: A novel electroplating bath suitable for electrodepositing copper on steel which comprises an aqueous solution of soluble copper, an alkali metal thiosulfate, an alkali metal sulfite or bisulfite, and a heterocyclic nitrogen compound such as nicotine, 3-amino-1,2,4-triazole, etc. During the electroplating process, the bath is subjected to aeration. The steel is cleaned and cathodically activated prior to plating.

THIOSULFATE COPPER PLATING

This invention relates to a process for electroplating copper on steel and to a novel electroplating bath. More particularly, this invention relates to a thiosulfate-containing electroplating bath containing therein a heterocyclic nitrogen compound and to an electrolytic process for plating copper on steel-employing aeration.

A number of processes are known in the art for the plating of copper on steel. The cyanide copper process is almost universally used for electroplating copper for this purpose. Although heretofore the cyanide process has been the only copper-plating system producing a copper system coating or deposit which adhered directly to steel, it suffers from a number of distinct disadvantages, namely (1) the cyanide solution being toxic presents extreme waste disposal problems, (2) the specific resistivity of cyanide solutions is high, (3) during the electroplating process the cyanide is oxidized to carbonate at the anodes and the accumulation of carbonate in the solution limits its life and, additionally, requires periodic treatment for removal, (4) the cyanide solution is easily contaminated by chromium and as little as 0.001 molar concentration of chromate ion in the solution causes misplates and irregular deposits, (5) the plated specimens exhibit low specular brightness, and (6) nodular deposits built up during the plating process prevent the formation of heavy thicknesses such as required for electroforming operations. The acid copper sulfate bath has been widely used for the deposition of copper since plated specimens produced by this method have high specular brightness (i.e., mirror-type reflectivity). It, likewise, suffers from several disadvantages in that (1) it is not possible to plate directly on steel utilizing this method since immersion deposition occurs and (2) the process requires expensive, acid-proof equipment. In through-hole printed circuit technology the use of the pyrophosphate copper-plating process is favored since the specular brightness approaches that of copper plated from acid copper sulfate baths. However, this process also suffers from certain disadvantages. It is not possible to plate copper on steel from a pyrophosphate bath since the steel exhibits no adhesion to such copper plating, there is a strong ammonia odor present during the plating operations and the pyrophosphate hydrolyzes to orthophosphate proportionately with time, high temperature and high pH which limits the solution life and, although this may be controlled by dilution, the result is a substantial waste in plating materials.

The objects of this invention are: (1) to eliminate the use of cyanide solutions in copper plating on steel with its toxicity and disposal problems, (2) to provide a method of forming an adherent coating of copper directly to steel in the plating process, (3) to provide a copper coating with an improved specular brightness, (4) to provide a chemically and electrolytically stable copper-plating solution, and (5) to eliminate the problem of chromium contamination.

Thompson, in U.S. Pat. No. 58,037 (1866), discloses a process for plating copper on steel in which the steel specimen is first coated with pure iron and then a coating of copper is deposited from a solution of hyposulfite of soda saturated with hydrated oxide of copper. The result was a copper-plated steel article of very poor copper appearance, the deposition rate was low, the solutions employed were unstable and there was no adhesion directly to steel. Gernes in *Trans. Electrochem. Soc.*, 77, 177 (1940) investigated the plating of copper on steel from a thiosulfate bath. Gernes, who employed a highly purified grade of cuprous chloride, was not able to prepare bright copper deposits on steel even though he used low current densities and, in addition, considerable decomposition occurred in all his baths.

Plating processes set forth in the art employing sodium thiosulfate and cuprous chloride or other copper salts have yielded copper-plated, steel specimens in which the copper coating was a grayish to brown color, and the copper was laid down as rough, powdery, noncoherent, nonadherent deposits. Likewise, the thiosulfate solutions set forth in the prior art in the plating operation suffered from instability, and the

processes employing such solutions could only be operated at low current densities and within low-temperature limits.

The main shortcoming of the prior art plating solutions employing thiosulfate has been the instability of the electroplating solution. Gernes indicated in *Trans. Electrochem. Soc.* 77, 177 (1940) that spontaneous decomposition of the bath takes place at temperatures above about 50° C. Furthermore, Gernes disclosed that the limiting current density was that at which a loose, black precipitate "probably Cu_2S " was formed at the cathode which caused a turbid solution. The current density employed by Gernes was not more than about 10 amperes per square foot.

The novel electroplating bath of this invention comprises an aqueous solution containing (1) soluble copper in the equivalent of about 0.2 to 0.5 molar concentration, (2) at least one alkali metal thiosulfate selected from the group consisting of sodium, potassium, and lithium thiosulfate in about 0.4 to about 1.50 molar concentration, (3) at least one alkali metal compound selected from the group consisting of sodium, potassium, and lithium sulfite and sodium, potassium and lithium bisulfite, in about 0.1 to about 0.5 molar concentration, and (4) at least one organic brightener in an amount of from about 0.005 to about 0.25 molar concentration; the pH of the bath being maintained at about 6.2 to about 7.5. Preferably, the soluble copper is derived from cuprous oxide, the alkali metal thiosulfate is sodium thiosulfate and the alkali metal compound is sodium sulfite.

Surprisingly, it has been found that the solution instability experienced by others when utilizing thiosulfate copper-plating bath can be overcome and even reversed through the aeration of the novel plating bath of this invention during the plating operation. It is believed that the Cu_2S formed is oxidized and converted to $\text{S}_2\text{O}_3^{2-}$ by combining with the sulfite present in the bath. Strong aeration such as used in air-agitated plating baths, is not necessary. A small amount of air introduced through a sparger, an open tube or by other suitable means at a location substantially below the surface of the solution in the plating tank is satisfactory. The exact amount of air introduced is not critical but should be several times that required to theoretically effect the oxidation reaction. Air agitation as used in the best of modern plating practice does have the advantage of increasing the current density range and such agitation may be employed, if desired. It has been found that the solution stability of the novel electroplating bath of this invention is maintained even on prolonged boiling and with current densities above 80 amperes per square foot cathodic.

Although good color and brightness were claimed by prior workers in the art such coatings would be unacceptable by today's standards for bright copper plating. Attempts to produce a true copper color using the solutions of the prior art workers yielded only grayish-brown deposits with no specular reflectivity. It has been found that the addition of a small amount of certain cationic heterocyclic nitrogen compounds to the electroplating bath yields a copper coating having specular brightness. Heterocyclic nitrogen compounds useful as brighteners in the novel electroplating bath of this invention include compounds having from one to two inclusive heterocyclic rings in which each of the said rings has between five and six members inclusive including at least one N atom and wherein the substituents on the carbon atoms of the said heterocyclic rings are selected from the group consisting of H, $-\text{NH}_2$ and alkyl of from one to 10 carbon atoms as exemplified by methyl, ethyl, propyl, isopropyl, butyl, isoamyl, hexyl, isohexyl, octyl, nonyl, decyl, etc.

An especially useful group of heterocyclic nitrogen containing compounds employed in the electroplating bath compositions of this invention includes pyridine, picoline, bipyridine, quinoline, 2,7-dimethylquinoline, imidazole, 2-methylimidazole, benzimidazole, 3-amino-1,2,4-triazole, 5-aminotetrazole, 3,5-dimethylpyrazole, 2,5-dimethylpiperazine, indole and nicotine.

Not all heterocyclic nitrogen compounds are suitable for use as brighteners in this invention. For example, no brightening effect was achieved with heterocyclic nitrogen compounds having carboxyl groups, such as 3-carboxypyridine, or with compounds having sulfonate, hydroxy, or keto substituent groups.

It has been found that the efficiency of the heterocyclic nitrogen compounds (brighteners) varies somewhat with the temperature of the plating bath employed. For example, pyridine exhibits a maximum brightening effect at about 80° F. while with nicotine this is achieved at about 135° F. It is to be understood that compounds such as nicotine can be added as the acid salt. For example, nicotine can be introduced as nicotine sulfate ((C₁₀H₁₄N₂)₂·H₂SO₄) or as the hydrochloride ((C₁₀H₁₄NBH₂)₂·2HCl). The compound 3-amino-1,2,4-triazole, in addition to being an excellent brightener, possesses the unique property of preventing anodic polarization when utilized in the novel electroplating bath of this invention. It has been found that at a concentration of 5 grams per liter (0.06M), the anode can be operated at from 10 to about 120 amperes per square foot at 100 percent efficiency.

PLATING BATH COMPOSITION

For maximum cathodic efficiency it is desirable to keep the copper content of the solution as high as possible. In the novel plating bath of this invention the copper content of the solution is present as a complex with the thiosulfate radical. When employing cuprous oxide as a source of copper, the complexing ratio is 2 moles of sodium thiosulfate for each mole of cuprous oxide added as a minimum and, desirably, the plating bath will contain about 2.5 moles of sodium thiosulfate for each mole of cuprous oxide present. The concentration of copper in the electroplating bath solution will be limited by the solubility of alkali metal thiosulfate used which with the other ingredients will be somewhat more than about 1.5 molar concentration. The alkali metal sulfite is used to prevent atmospheric oxidation of the thiosulfate present in the bath composition. A minimum concentration of about 0.04 molar is desirable although concentrations of from about 0.01 to about 0.5 molar can be employed satisfactorily.

The copper present in the plating bath is most economically added as cuprous oxide although cuprous sulfite or cuprous chloride can be utilized. Likewise, it is also possible to employ a divalent copper compound, such as cupric sulfate, cupric chloride, etc., as a source of copper in the plating bath. In such instances, the copper will be reduced to the monovalent form by the action of the alkali metal sulfite and the quantity of the sulfite should be increased to allow for this reduction if divalent copper compounds are employed.

The organic brighteners are all effective over a wide range of about 0.001 to about 0.25 molar concentration. A preferred range of the heterocyclic nitrogen brighteners is from about 0.005 to about 0.20 molar. The compound 3-amino-1,2,4-triazole which functions not only as a brightener but as an anode depolarizer as well is most effectively employed at concentrations ranging from about 0.03 to about 0.15 molar when anode depolarization is required. During the plating operation it is important to maintain the pH of the plating bath composition at about 6.2 to about 7.5 and, preferably, from about 6.5 to about 7.1 with the addition of sodium hydroxide or sulfuric acid as required.

PREPARATION OF THE PLATING BATH SOLUTION

The aqueous plating bath itself can be prepared by a variety of ways. Preferably, the alkali metal thiosulfate is added to the aqueous copper solution. In the next step, the alkali metal sulfite, and the heterocyclic nitrogen compound are introduced. The pH is then adjusted to about 6.2 to about 7.5 on addition of potassium hydroxide, sodium hydroxide, or sulfuric acid and the resulting solution is filtered to remove any insoluble residue which may be present.

Although satisfactory plating of copper of steel is achieved under ordinary conditions, the best adhesion of the copper plate to steel is obtained by cathodic activation of the steel in about 1 N sulfuric acid or sodium bisulfate for about 1 to 10 minutes or more at 50 to 100 amperes per square foot and at a temperature of about 70° to about 100° F.

The electrolytic plating baths exemplifying the compositions of this invention are generally operated under conditions normally used in the industry, the temperature of the baths ranging from about 120° to about 150° F. Current densities of 5 to about 50 amperes per square foot are used and the bath is air agitated.

The following examples illustrate various embodiments of this invention are to be considered not limitative:

EXAMPLE I

The following aqueous plating bath composition was prepared:

Copper, added as cuprous oxide	0.5 molar
Sodium thiosulfate	1.25 molar
Sodium sulfite	0.04 molar
Nicotine	0.1 molar
Water	As required
pH adjusted to 6.8 with sulfuric acid.	

In the above-described plating bath, a steel cathode was plated at 120° C. at 2 amperes for 5 minutes while the bath was agitated with air. The plated cathode exhibited a good copper color with specular brightness utilizing current densities up to about 50 amperes per square foot.

EXAMPLE II

In this example, 3-amino-1,2,4-triazole was added to the plating bath solution of example I in 2 concentration of 0.1 molar and a steel cathode was plated under the same conditions as in example I. At the end of the 5-minute plating period, the plated cathode exhibited a good copper color with high specular brightness at current densities up to about 50 amperes per square foot and, in addition, the anode was clean whereas in the previous example a dark brown to black coated anode resulted.

EXAMPLE III-XV

A number of additional examples were performed in the same manner as example I utilizing a plating bath of the same composition with the exception that the nicotine brightener was replaced with another brightener in each instance. The pertinent data relating to these examples is shown below:

Example No.	Compound	Brightener	Concentration
III	Pyridine		0.1 Molar
IV	Picoline		" "
V	Bipyridine		" "
VI	Quinoline		" "
VII	2,7-Dimethylquinoline		" "
VIII	Imidazole		" "
IX	2-Methylimidazole		" "
X	Benzimidazole		" "
XI	Amino-1,2,4-triazole		" "
XII	5-Aminotetrazole		" "
XIII	3,5-Dimethylpyrazole		" "
XIV	2,5-Dimethylpiperzine		" "
XV	Indole		" "

In each of the above-mentioned examples the cathode showed a good copper color with high-specular brightness at current densities of up to about 50 amperes per square foot.

EXAMPLE XVI

The steel cathode employed in this example was cleaned first in a conventional alkaline cleaner following which it was cathodically activated in 5 percent sulfuric acid for 3 minutes at 7.5 amperes per square foot at 75° F. After plating 0.001 inch of copper on the cathode utilizing the bath set forth in example II the steel panel was bent repeatedly until it broke but the copper plating on the steel remained unimpaired condition indicating excellent adhesion.

EXAMPLE XVII

The following is an example of a dry plating bath composition of this invention which has been found to give good results:

DRY BATH COMPOSITION

Component	Percent by Weight
Cuprous oxide	12
Sodium thiosulfate (anhydrous)	67.5
Sodium bisulfite (anhydrous)	19
3-Amino-1,2,4-triazole	1.0
Nicotine Sulfate	0.5

To prepare an electroplating solution from the above dry composition the ingredients are dissolved in water to a concentration of about 2.5 pounds per gallon. The pH is adjusted to 6.6-7.0 with sodium hydroxide and the resulting solution is filtered to remove any insoluble material which may be present. If desired, the dry mix can be made up with only the three major ingredients and the additives introduced separately.

To illustrate the importance of air agitation and the use of heterocyclic nitrogen compounds as brighteners in the process of this invention three comparative experiments were conducted. With a plating bath of the same composition as that employed in example I with the exception that it contained no nicotine, a brass cathode was plated in a standard cell (i.e., a Hull cell) at 120° F. at 2 amperes for 5 minutes with no agitation and with no aeration. The cathode turned black within a few seconds and the solution became very turbid indicating decomposition of the plating bath. In a second experiment, a plating solution of the same type as employed in example I with the exception that nicotine was not present was utilized in plating a brass cathode at 120° F. at 2 amperes for 5 minutes with air agitation of the bath (i.e., aeration). The result was a dull, copper-plated brass cathode of poor color but no solution decomposition was experienced thus indicating the effectiveness of aeration in the plating bath. In a third experiment, carried out in the same manner as the second experiment above, air agitation was replaced with nitrogen agitation and in this instance the brass cathode exhibited a copper coating of poor color similar in appearance to that when air agitation was employed and the solution again became turbid.

The last experiment shows that nitrogen agitation does not prevent sulfide formation and solution decomposition. Replacing the nitrogen with air cleared the turbidity and restored normal plating conditions within a half hour.

What is I. is:

1. An electroplating bath comprising an aqueous solution of: (1) soluble copper in the equivalent of about 0.2 to about 0.5 molar concentration, (2) at least one alkali metal thiosulfate selected from the group consisting of sodium, potassium and lithium thiosulfate in about 0.4 to about 1.5 molar concentration, (3) at least one alkali metal compound selected from the group consisting of sodium, potassium, and lithium sulfite, and sodium, potassium and lithium bisulfite, in about 0.01 to about 0.01 molar concentration, and (4) at least one heterocyclic nitrogen compound in an amount of from about 0.005 to about 0.25 molar concentration; the said heterocyclic nitrogen compound having from one to two in-

clusive heterocyclic rings in which each of the said rings has between 5 and 6 member inclusive including at least one N atom; wherein the substituents on the carbon atoms of the said heterocyclic rings are selected from the group consisting of H,—NH₂ and alkyl of from one to 10 carbon atoms; and wherein the pH of the bath is about 6.2 to about 7.5.

2. The electroplating bath of claim 1 wherein the soluble copper is derived from cuprous oxide.

3. The electroplating bath of claim 1 wherein the said alkali metal thiosulfate is sodium thiosulfate.

4. The electroplating bath of claim 1 wherein the said alkali compound is sodium sulfite.

5. The electroplating bath of claim 1 wherein the said heterocyclic nitrogen compound is selected from the group consisting of pyridine, picoline, bipyridine, quinoline, 2,7-dimethylquinoline, imidazole, 2-methylimidazole, benzimidazole, 3-amino-1,2,4-triazole, 5-aminotetrazole, 3,5-dimethylpyrazole, 2,5-dimethylpiperazine, indole and nicotine.

6. The electroplating bath of claim 1 wherein the said heterocyclic nitrogen compound is nicotine.

7. The electroplating bath of claim 1 wherein the said heterocyclic nitrogen compound is 3-amino-1,2,4-triazole.

8. The electroplating bath of claim 1 wherein the said soluble copper is derived from cuprous oxide, the said alkali metal thiosulfate is sodium thiosulfate, the said alkali metal compound is sodium sulfite and the said heterocyclic nitrogen compound is nicotine.

9. A dry composition suitable for use in preparing an aqueous solution from which copper may be electrodeposited on steel which comprises the following ingredients in the following approximate percentages by weight:

Cuprous oxide	12
Sodium thiosulfate, anhydrous	67.5
Sodium bisulfite, anhydrous	19.0
3-amino-1,2,4-triazole	1.0
Nicotine sulfate	0.5

10. A method of electrodepositing copper on a steel cathode in which copper is electrodeposited from an electroplating bath composition comprising an aqueous solution of (1) soluble copper in the equivalent of about 0.2 to about 0.5 molar concentration, (2) at least one alkali metal thiosulfate selected from the group consisting of sodium, potassium, and lithium thiosulfate in about 0.4 to about 1.50 molar concentration, (3) at least one alkali metal compound selected from the group consisting of sodium, potassium and lithium sulfite and sodium, potassium and lithium bisulfite in about 0.01 to about 0.5 molar concentration and (4) at least one heterocyclic nitrogen compound in an amount of from about 0.005 to about 0.25 molar concentration; the said heterocyclic nitrogen compound having from 1 to 2 inclusive heterocyclic rings in which each of the said rings has between 5 and 6 members inclusive including at least one N atom and wherein the substituents on the carbon atoms of the said heterocyclic rings are selected from the group consisting of H,—NH₂ and alkyl of from one to 10 carbon atoms, wherein the pH of said aqueous solution is maintained between 0.2 and about 7.5 and wherein the electroplating bath is aerated during the electroplating operation.

11. The process of claim 10 wherein the said alkali metal thiosulfate is sodium thiosulfate.

12. The process of claim 10 wherein the said alkali metal compound is sodium sulfite.

13. The process of claim 10 wherein the said heterocyclic nitrogen compound is selected from the group consisting of pyridine, picoline, bipyridine, quinoline, 2,7-dimethylquinoline, imidazole, 2-methylimidazole, benzimidazole, 3-amino-1,2,4-triazole, 5-aminotetrazole, 3,5-dimethylpyrazole, 2,5-dimethylpiperazine, indole and nicotine.

14. The process of claim 10 wherein the said heterocyclic nitrogen compound is nicotine

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15. The process of claim 10 wherein the said heterocyclic nitrogen compound is 3-amino-1,2,4-triazole.

16. The process of claim 10 wherein the said soluble copper is derived from cuprous oxide, the said alkali metal thiosulfate is sodium thiosulfate, the said alkali metal compound is sodium sulfite and the said heterocyclic nitrogen compound is nicotine.

17. The process of claim 10 wherein the said steel cathode prior to being plated is subjected to a metal cleaning cycle fol-

lowing which it is cathodically activated in a solution of a material selected from the group consisting of sulfuric acid and sodium bisulfate for a period of about 1 to about 10 minutes at 50 to 100 amperes per square foot at a temperature of about 70° to about 100° F.

18. The process of claim 17 wherein the said material is a 5 percent sulfuric acid solution.

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