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METHOD OF MAKING DUCTILE COPPER PLATINGS

Eugene N. Castellano, Seymour, Conn., assignor to The Seymour Manufacturing Company, Seymour, Conn., a corporation of Connecticut

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This invention relates as indicated to electrodeposition of metals and, more specifically, to a process of and materials for use in the process of electrodepositing copper characterized in that the resulting copper plate as deposited, displays exceptional ductility, smoothness and throwing power. More particularly, the present invention has to do with new addition agents for producing the above-named desirable characteristics in the copper plate and which may be used with acid copper baths of usual composition operating under usual conditions.

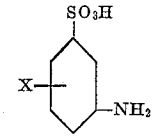
Heretofore, various additives have been proposed for electrolytic copper plating baths to improve the ultimate quality of the copper plate. Some of the proposed addition agents are colloidal aliphatic and aromatic sulphides which are intended to produce smooth and ductible deposits of copper from the electrolyte. Electrolytic copper plating baths including such proposed additives do not have the required degree of throwing power which is demanded for many specialized applications. By throwing power is meant the ability of the copper plate to form smooth and adherent coatings of copper on base metals having apertures, pits and other surface irregularities.

Various aliphatic and aromatic sulfonated additives have been proposed for producing bright copper platings. However, the main object of the present invention is not to produce bright copper deposits, but rather to substantially increase the stability of the resulting copper plate and to provide an essentially permanent copper plate which has the qualities of ductility, smoothness and throwing power to an exceptional degree of thickness. The only known additives for this purpose have been dextrin, glue, molasses and the like which are subject to the objection that over a period of time as the bath is aging, they will break down and contaminate the solution. The result of this break down is that the copper deposit is extremely brittle. Moreover, this break down necessitates the periodic purification of the electrolyte for the removal and elimination of these break down impurities.

It is, accordingly, a primary object of the present invention to produce electrodepositable solutions of copper which are characterized by an exceptionally high degree of smoothness, ductility and throwing power wherein the additives are stable and free of break down products. The electrolytic solutions of the present invention, accordingly, form copper plate which is free of brittleness and retains the desirable characteristics enumerated above indefinitely. The additives which are discovered to substantially enhance these qualities of electrolytic copper solutions possess a high degree of solubility in the plating baths as distinguished particularly from the colloidal additives heretofore suggested in the prior art. The base metals to which the copper plating baths of the present invention are applicable include the various types of steel, zinc, nickel, tin, alloys of these metals as well as other metals and their alloys.

According to the present invention, it has been found that the preferred additives for producing the indicated

characteristics in copper plating baths are selected from the class consisting of those having the formula



and their soluble salts, wherein X is selected from the class consisting of hydrogen, lower alkoxy and halogen, and is located in a position relative to the SO_3H group selected from the class consisting of the ortho and para positions. Preferred derivatives falling within this general formula for the practice of the invention are as follows:

m-Aminobenzenesulfonic acid, sodium salt, also called sodium metanilate
m-Aminobenzenesulfonic acid
3-amino-4-methoxybenzenesulfonic acid
3-amino-4-chlorobenzenesulfonic acid
3-amino-6-chlorobenzenesulfonic acid

These compounds are preferably used in the form of their soluble salts. The first compound of the above list is preferred because of its exceptionally high solubility as compared with the second and third compounds of the list. Compounds 4 and 5 of the above list are characterized by high solubility similar to the first compound but the chloride substituent reduces the solubility of the resulting compound to a certain degree.

The composition of the bath exclusive of the novel addition agents is of standard character. For example, aqueous solutions containing from 187.5 to 262.5 of copper sulfate ($CuSO_4.5H_2O$) 60 to 90 grams per liter of sulfuric acid (7½) and the remainder water are conventional and appropriate for the practice of the invention. Other well-known copper salts and corresponding acids such as aqueous solutions of copper fluoborate and fluoboric acid may be used with equal facility with the addition agents of the present invention to produce ductile platings of high throw power. A typically optimum plating bath for purposes of the present invention contains approximately 240 grams per liter copper sulfate, 75 grams per liter sulfuric acid operated at a temperature of aproximately 100° F. and at a current density of from 10 to 100 amperes per square foot.

In connection with conventional plating solutions of the indicated character, current densities of from 0 to 300 amperes per square foot and temperatures within the range of from room temperatures to 130° F. may be employed depending upon the thickness and quality of the coating desired.

The additives may be employed in the proportion range and concentration of from one-tenth gram per liter to 100 grams per liter and above. The optimum concentration, however, is approximately 5 to 20 grams per liter with excellent results being accomplished at approximately 10 grams per liter.

The following are specific examples of the operation of the invention. The baths listed below are generally operated under condition normally used in industry as above indicated. The proportions given in the examples are in grams per liter and during the plating process the work is made the cathode.

Example I

There is provided a copper sulfate plating bath containing sodium m-aminobenzenesulfonate and having the following compositions:

Copper sulfate	240
Sulfuric acid	75
Sodium m-aminobenzenesulfonate	10

Nickel flashed steel plate was made the cathode in an electrolytic bath having the above composition and a current density of 100 amperes per square foot, direct current was applied to the solution. The plating proceeded for approximately two hours whereupon a smooth ductile copper plate of 0.012 had occurred. This ductile copper plate was, nevertheless, hard with a dense grain structure. The general appearance of the plate showed an exceptional smooth ductile copper deposit.

Example II

A cooper plating bath is prepared having the following composition:

Copper fluoborate	200
Fluoboric acid to within the range of 0 to 2.0 pH.	
Sodium m-amino-benzenesulfonate	15

The temperature of the bath was maintained at 100° F. and a current density of 75 amperes per square foot applied to the solution for approximately one and one-half hours. A superior copper plate of 0.007 thickness was found to have occurred having the characteristics indicated in the preceding example.

Example III

A copper plating bath was prepared according to the specifications indicated in Example I but using 3-amino-4-methoxybenzenesulfonic acid instead of sodium metanilate. While a current density of 100 amperes per square foot was applied to the solution a smooth ductile copper plate of superior characteristics and having a thickness of about 0.012 was obtained in approximately two hours.

Example IV

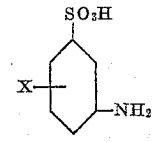
An aqueous copper fluoborate plating bath was prepared having the same composition as the plating bath of Example II but employing 3-amino-6-chlorobenzenesulfonic acid as the addition agent instead of sodium metanilate. An exceptionally smooth ductile plating of copper having a thickness of approximately 0.018 inch was obtained in a period of three hours at a current density of 100 amperes per square foot.

Other examples illustrate the general applicability of the novel addition agents involving the plating of other base metals such as zinc, nickel and tin with correspondingly superior results over methods heretofore employed.

While preferred embodiments of the invention have been specifically described herein for illustrative purposes, it will be understood that changes in modification may be made without departing from the spirit and scope of the invention as defined by the accompanying claims.

What I claim is:

1. An electrolytic bath comprising an aqueous acid solution of a copper salt and from one-tenth to 100 grams per liter of a compound selected from the class consisting of compounds having the formula



and their soluble salts, wherein X is selected from the class consisting of hydrogen, lower alkoxy and halogen, and is located in a position relative to the SO_3H group selected from the class consisting of the ortho and para positions.

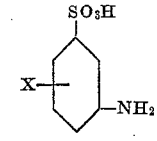
2. An electrolytic bath comprising an aqueous acid solution of a copper salt and from one-tenth to 100 grams per liter of sodium metanilate.

3. An electrolytic bath comprising an aqueous acid solution of a copper salt and from one-tenth to 100 grams per liter of metanilic acid.

4. An electrolytic bath comprising an aqueous acid solution of a copper salt and from one-tenth to 100 grams per liter of 3-amino-4-chlorobenzenesulfonic acid.

5. An electrolytic bath comprising an aqueous acid solution of a copper salt and from one-tenth to 100 grams per liter of 3-amino-6-chlorobenzenesulfonic acid.

6. An electrolytic bath comprising from 187.5 to 262.5 grams per liter of copper sulfate, 60 to 90 grams per liter of sulfuric acid, 5 to 20 grams per liter of a compound selected from the class consisting of compounds having the formula



and their soluble salts, wherein X is selected from the class consisting of hydrogen, lower alkoxy and halogen, and is located in a position relative to the SO_3H group selected from the class consisting of the ortho and para positions, the remainder being water.

7. An electrolytic bath comprising from 187.5 to 262.5 grams per liter of copper sulfate, 60 to 90 grams per liter of sulfuric acid, 5 to 20 grams per liter of a soluble salt of metanilic acid.

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