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2,700,020

PLATING COPPER

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7 Claims. (Cl. 204—52)

This invention relates to copper plating, and more particularly, to decorative or ornamental bright copper plating from an acid bath.

Such copper plating involves the electro-deposition of copper from acid baths in the plating of, for example, automobile bumpers and bumper guards. The electro-deposition of copper upon such articles should effect formation of deposits which have smoothness or brilliance as well as good "bufferability," such that the deposits are capable of being buffed or "colored" by the usual buffing instrumentalities, when desired.

Such copper deposits must have suitable ductility, and sufficient smoothness and uniformity of color to be covered by bright or semi-bright (Perflow) nickel deposits. Also, the copper plating solution employed must have good stability and high impurity tolerance, and it must be capable of operating effectively at low as well as high current densities, since a wide range of current densities are often used in the plating of bumpers and bumper guards.

The copper plating baths currently employed are the usual sulphuric acid type, wherein copper is present in the form of copper sulphate ($CuSO_4.5H_2O$), and there is an excess of sulphuric acid present in an amount at least sufficient to prevent polarization. Up to 50% of the sulphuric acid may be replaced by phosphoric acid. A standard acid copper bath may contain, for example, 27 oz. of copper sulphate and 7.5 oz. more or less of sulphuric acid per gallon. In addition, certain of the workers in the art have suggested that various combinations of additives might be used in certain predetermined proportions in order to improve the brightness and structure of the resulting copper deposit.

In United States Patents Nos. 2,489,538 and 2,563,360, issued to William M. Philips and Frank L. Clifton, it is suggested that improvements in brightness and structure may be obtained by the use in combination of certain "primary" additive agents and certain "control" agents. The control agents may be inorganic compounds such as salts of cadmium, zinc, cobalt or nickel; or organic compounds such as certain of the well known aromatic sulfonate "wetting" agents. The primary addition agents or "brighteners" include such compounds as cyanamide, dicyandiamide, thioureas, isothiocyanates, thioacetamide, tetra methyl thiuram monosulfide, beta-dithioglycol, thiosalicylic acid, thiosinamine, and thiosemicarbazide. Thiourea is said to be preferred.

In the United States Patent No. 2,391,289, issued to John F. Beaver, Jr., it is suggested that improvements in brightness and structure may be obtained by the use of combinations of certain substituted thioureas, a wetting agent and a substance of the group consisting of dextrin, sugar and sulfonated creosote. The substituted thioureas include some aryl and alkyl substitution products as well as acetyl, hydrochloride, nitrate and metal salt derivatives of thiourea. Beaver acknowledges that most of such compounds have "certain faults," but alleges that acetyl thiourea is the preferred brightener for use with the wetting agent and the dextrin compound, in accordance with Beaver's teachings.

It has been found that each of the foregoing combinations of materials suggested by Philips et al. and Beaver leaves something to be desired from a commercial point of view. In particular, accurate temperature control is required for satisfactory operation in these processes. The stability and tolerance toward impurities of the bath solutions so obtained have not been satisfactory in many

cases. Also, other agents must be used in conjunction with the brighteners. The necessity of employing a plurality of ingredients is always more burdensome and time consuming than would be the use of one single ingredient. The concentrations of each of the various ingredients in the bath require accurate and constant control. Also, the resulting baths fail to perform suitably at very low current densities, and this is particularly so in the case of thiourea. Moreover, the ductility of the copper deposit is reduced appreciably, presumably because of the relatively high amount of total "organics" in the bath and/or the wetting agent in the bath.

It is, therefore, an important object of the instant invention to provide an improved method of and composition for plating copper.

It is a further object of the instant invention to provide an improved method of and composition for plating copper from an acid bath wherein only one organic addition agent is employed, the agent or brightener being adapted to operate suitably in the absence or presence of the various control agents, wetting agents and dextrin compounds suggested by the prior workers in the art.

It is another object of the instant invention to provide an improved method of and composition for plating copper in an acid bath wherein an additional organic brightener may be used over a wide range of concentrations and in absence of accurate temperature control.

It is yet a further object of the instant invention to provide an improved method of and composition for plating copper in an acid bath whereby the production of superior deposits of copper is effected in low current density areas as well as in high current density areas.

It is yet another object of the instant invention to provide an improved method of and composition for plating copper in an acid bath whereby there is obtained a copper deposit of superior ductility.

It is still a further object of the instant invention to provide an improved method of and composition for plating copper in an acid bath whereby copper deposits of suitable brightness are obtained over a wide range of bath compositions, such that these deposits are capable of accepting either bright nickel or Perflow nickel.

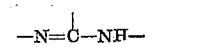
It is still another object of the instant invention to provide an improved composition for plating of copper in an acid bath, wherein the bath has superior stability and tolerance toward impurities.

Other objects, features and advantages of this invention will become apparent to one skilled in the art from the following description and examples relating to preferred embodiments of the instant invention.

The instant invention consists in an improved method of and composition for copper plating in an acid bath wherein improvements according to the foregoing objects may be obtained by the use of a single heterocyclic organic agent. Such an agent will be referred to hereinafter as a "brightener," for the sake of simplicity, although it will be understood that the instant brightener carries out additional functions, including those apparently necessary for successful plating which were heretofore carried out by wetting agents, dextrin compounds and the like. The instant brighteners distinguish chemically as well as functionally from any of the various agents heretofore used for related purposes, first of all, in that they are heterocyclic compounds. Secondly, they possess a unique heterocyclic molecular arrangement wherein certain critically important atoms are arranged in a particular manner so as to be suitably active, to impart the desired properties to the heterocyclic molecule.

The brighteners of the present invention are members of a class characterized by molecules, each of which contains a heterocyclic ring and has the following "active" atomic arrangement:

(1)



wherein

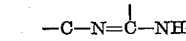


is a heterocyclic ring member and so is —N=. In the foregoing arrangement (1), the

and —N= are, respectively, quaternary and tertiary atoms (in that they have no direct linkages with a hydrogen atom). Brighteners wherein the —NH— of arrangement (1) is replaced by —S— or —O— are described and claimed in my copending application Serial 291,344, now Patent 2,663,684.

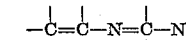
It has been found that the ring member to which the —N= free valence is preferably connected is another C, thereby resulting in the arrangement:

(2)



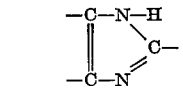
Also, it has been found most preferable that the additional C be connected to still a third C by a double bond, whether aromatic or aliphatic in character; thereby giving the resulting arrangement:

(3)



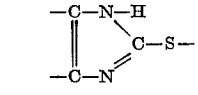
In such arrangement, the nucleus of the heterocyclic ring may contain the three C's and the —N=, and preferably the —NH—, in a diazole nucleus:

(4)



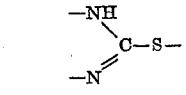
It has also been found preferable to include in the structure an —S— atom that is exocyclic so as to obtain the following structure:

(5)



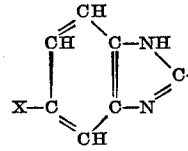
Referring, therefore, to the active atomic arrangement (1), it will be seen that using the preferred additional exocyclic —S— atom, the arrangement becomes:

(6)



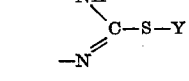
As will be demonstrated hereinafter, the best results have been obtained using a heterocyclic compound wherein S is contained in the —SH group, and X is a monovalent radical such as hydrogen or amino radical, such compounds being 2-benzimidazolethiol and 5-amino-2-benzimidazolethiol:

(7)



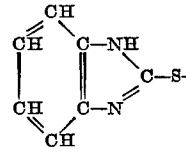
It has also been found that good results may be obtained by the use of compounds having the structure:

(8)



wherein Y is H or a lower alkyl radical, having one to four C's, preferably the methyl radical as in 2-methyl mercapto benzodiazole:

(9)



The total number of C's in the compound, being an indication of its solubility, is within the range from the minimum of 3 as exemplified by 2-aminodiazole to the maximum which may be used without so reducing the solubility of the compound that an appreciable amount thereof (i. e., at least about 1, and preferably about 5 parts per million) may not be dissolved in the bath so as to give noticeable results in the practice of the invention, the number of carbon atoms corresponding thereto being about 18.

The use of the preferred brightener of the instant invention may be demonstrated as follows:

A plating cell is charged with a solution containing 140 g./l. of $CuSo_4.5H_2O$, 50 g./l. of H_2SO_4 and 0.02 g./l. of 5-amino-2-benzimidazolethiol. The cell is equipped with electrolytic sheet copper anodes, in accordance with commercial practice. Polished steel cathodes previously cleaned and plated in a conventional copper cyanide plating solution were plated at 110° F. and 45 amperes per square foot for 15 minutes. The deposits secured were smooth, ductile and semi-bright. Substantially the same results are obtained by carrying out the same plating procedure using other of the brighteners hereinbefore mentioned. It was found that the necessary degree of brightness could be easily maintained by small additions of brightener as needed.

It will be appreciated, of course, that the amount which should be used is approximately that relatively small amount which has been used for other brighteners heretofore known to the workers in the art. The amount is essentially a matter of experiment and can be determined readily by those skilled in the art in the light of the instant teachings.

It has been found that brightness may be maintained at the necessary standard by the addition of such a brightener at a rate of about 0.5 gram per one thousand ampere hours. The rate at which the brightener may be added depends to a certain extent upon the rate at which it may be put into solution, which in turn may depend upon pretreatment of the brightener, for example, by intimately admixing the same with a copper bath solution in a colloid mill. The rate at which brightener must be added may range from about 0.25 to about 2 grams per thousand ampere hours, being preferably about 0.5–1 grams.

It is particularly significant that, once a solution has produced plates of optimum brightness, it will continue to do so even under long periods of sustained electrolysis. In other words, after a solution has been properly started with the necessary amount of brightener in solution, it has been found that brightener additions may be made effectively so that the necessary amount of brightener in solution will not be depleted. In fact, whenever the deposits tend to dull somewhat, this may be remedied by additions of the brightener directly to the solution. The presence of undissolved particles of the brightener floating around in the solution cause no trouble in the operation of the process. Moreover, the response to such additions is rapid.

The process of the instant invention may be carried out at temperatures ranging from a minimum of about 70° F., below which there is a tendency toward obtaining a grainy deposit, to temperatures as high as 140° F. Preferably, about 95–100° F. is the preferred temperature.

It has been found that the amount of the brighteners which may be used in the practice of the instant invention may range from as little as 2–3 parts per million to 100% saturation of the brightener in the solution (and, in fact, substantially in excess thereof in the case of those brighteners which dissolve relatively slowly).

In the practice of the instant invention, current densities ranging from about 5 amperes per square foot to about 200 amperes per square foot, and preferably 10–80 amperes per square foot, may be used in order to obtain superior deposits that are ductile, free from striations and are unusually smooth and uniform.

One of the most important advantages of the instant invention resides in the superior ductility of the deposit obtained thereby.

In addition, it is found that under optimum operating conditions deposits of remarkable smoothness and brightness may be obtained and under all of the ordinary operating conditions the resulting deposits may be covered suitably with 0.0003" of (Perflow) nickel so as to obtain a superior product.

As hereinbefore mentioned, the amount of brightener used is that amount necessary to carry out its "brightening" function. In general, the amount of brightener may range from 0.002 gram per liter to about 5 grams per liter and, preferably, ranges from about 0.005 to about 0.1 gram per liter.

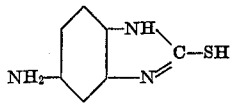
One particular advantage of the instant invention is based upon the fact that only one agent (brightener) need be used and that may be used over a substantial concentration range, to obtain superior results. Another advantage resides in the fact that other agents or ingredients, which may or may not have been used with brightener heretofore, may be present. Such compounds include various salts such as the nickel salts, dextrin, molasses,

sugar, sulfonated creosote, glycine and di-p-tolyl disulfide.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the instant invention.

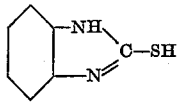
I claim as my invention:

1. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous sulfuric acid-copper sulfate bath, having dissolved therein, as a brightener, a compounds having the following heterocyclic ring structure



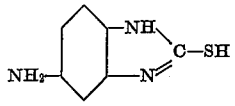
that compound having a concentration in the solution within the range of 0.005–1 gram per liter.

2. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous sulfuric acid-copper sulfate bath, having dissolved therein, as a brightener, a compound having the following structure



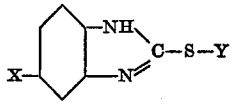
that compound having a concentration in the solution within the range of 0.005–1 gram per liter.

3. In the process of depositing copper on metallic surfaces by electro-deposition from a sulfuric acid-copper sulfate aqueous bath, the step of carrying out said process in the presence of a dissolved brightener having the following formula



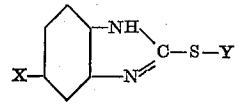
the brightener having a concentration in the solution within the range of 0.005–1 gram per liter.

4. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous sulfuric acid-copper sulfate bath, having dissolved therein, as a brightener, a compound having the following structure



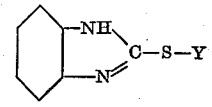
wherein X is a monovalent radical selected from the group consisting of hydrogen and amino radicals and Y is selected from the group consisting of H and alkyl radicals having one to four C's, that compound having a concentration in the solution within the range of 0.005–1 gram per liter.

5. In the process of depositing copper on metallic surfaces by electro-deposition from a sulfuric acid-copper sulfate aqueous bath, the step of carrying out said process in the presence of a dissolved brightener having the following formula



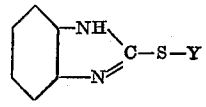
wherein X is a monovalent radical selected from the group consisting of hydrogen and amino radicals and Y is selected from the group consisting of H and alkyl radicals having one to four C's, the brightener having a concentration in the solution within the range of 0.005–1 gram per liter.

6. An electrolyte for the electro-deposition of copper consisting essentially of an aqueous sulfuric acid-copper sulfate bath, having dissolved therein, as a brightener, a compound having the following heterocyclic ring structure



wherein Y is from the group consisting of H and alkyl radicals having 1 to 4 C's, that compound having a concentration in the solution within the range of 0.005–1 gram per liter.

7. In the process of depositing copper on metallic surfaces by electro-deposition from a sulfuric acid-copper sulfate aqueous bath, the step of carrying out said process in the presence of a dissolved brightener having the following heterocyclic ring structure



wherein Y is selected from the group consisting of H and alkyl radicals having one to four C's, the brightener having a concentration in the solution within the range of 0.005–1 gram per liter.

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