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 electrodeposition of copper from acid baths in the plating of, for example, automobile bumpers and bumper guards. The electrodeposition of copper upon such articles should effect formation of deposits which have smoothness or brilliance as well as good "buffer-ability," 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 (Perlow) 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 (CuSO₄·5H₂O), 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. 2,485,538 and 2,552,390, 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, thiourea, isothiocyanates, thiocyanamide, 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, 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 cresote. The substituted thioureas include some aryl and alkyl substitution products as well as acetyl, hydrochloride, nitrate and metal salt derivatives of thiouracil. 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 Phillips 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 thioureas. 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 for 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 inven-
tion 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 hereinafter 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 include members of a class characterized by molecules, each of which contains a heterocyclic ring and has the following "active" atomic arrangement:

(1) \[ N = O - S - \]

wherein C is a heterocyclic ring member and so is N. In the foregoing arrangement (1), the C and N are, respectively, quaternary and tertiary atoms (in which they have no direct linkages with a hydrogen atom). Also, S may be a ring member, or S may be an exocyclic atom and, if so, it is preferably contained in an \(-\text{SH}\) group. Expressed in other terms, the N free valence and one of the other two free valences must be connected to other heterocyclic ring members.

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) \[ -N = O - S - \] (preferably \(-N = O - \text{SH}\))

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) \[ C - O - N = C - S - \]

In such arrangement, the nucleus of the heterocyclic ring may contain the three Cs and the N, and preferably an S, in a thiazole nucleus:

(4) \[ O \]

However, the cyclic S may be replaced by oxygen (O) so as to obtain the following generic structure:

(6) \[ X - C - S - C - \]

wherein X is O or S.

Referring, therefore, to the active atomic arrangement (1), it will be seen that using the preferred additional nuclear atom X (i. e., O or S), the arrangement becomes:

(6) \[ \text{X} - C - S - C - \]

As will be demonstrated hereinafter, the best results have been obtained using a heterocyclic compound wherein X is S, such compound being 6-amino-2-mercaptobenzothiazole:

(7) \[ \text{X} - C - S - C - \]

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

(6) \[ \text{X} - C - S - C - \]

wherein Y is H or a lower alkyl radical, having one to four Cs, preferably the methyl radical, and 2-methylmercaptobenzothiazole:

(8) \[ \text{X} - C - S - C - \]

As hereinafter mentioned, the basic active atomic arrangement

(1) \[ C - O - X - \]

calls for the presence of S or O, as a heterocyclic atom; and if X, herein designated as the heterocyclic atom attached to the principal C is preferably S, the resulting structure being:

(10) \[ \text{O} - C - S - Y - \]

which structure is characteristic of 2-mercapto benzoazazole:
It has also been found that no S atom need be present in compounds as, for example, 2-amino benzoxazole (which imparts unusual smoothness and ductility) having the following formula: 

(11a)

On the other hand, it has been found that, in compounds wherein X is S, the principal C may be attached to exocyclic atoms other than another S, the resulting structural arrangement being:

(12)

wherein R may be $-S-Y$, as has been described, and R may also be another low molecular weight radical, such as $-NH_2$, $-NH$-alkyl, a lower alkyl radical (i.e., having one to four carbon atoms) preferably the methyl radical, or a phenyl radical. Examples of such compounds are 2-amino benzothiazole:

(15)

methyl benzothiozoyl amine:

(15a)

2-methyl benzothiazole:

(14)

and 2-phenyl benzothiazole:

(14a)

In general, it has been found preferable to employ in the instant invention having the condensed benzothiazole ring structure:

(15)

The benzothiazole structure is present in those compounds found to give superior results. Such benzothiazole compounds preferably have the $-SH$ grouping attached to the 2-carbon, and may have other substituents attached to benzene nuclear C's, such substitutes include lower alkyl radicals, halogen, $-SO_2OH$, $-OH$, $-SH$, $-NH_2$ and $-NO_2$ groups, as for example in 6-nitro-2-mercaptobenzothiazole:

(16)

6-hydroxy-2-mercaptobenzothiazole:

(16a)

5-sulfonic acid-2-mercaptobenzothiazole:

(16b)

2,5-dimercaptobenzothiazole:

(16c)

5-chloro-2-mercaptobenzothiazole:

(16d)

However, the basic azole structure of the invention may be employed with or without the condensed benzene ring structure. In other words, the structure:

(17)

may be employed wherein preferably either X or R (or both) contains an S; and wherein the $C-C$ grouping is part of another ring structure, such as the benzene ring, or is part of an aliphatic structure, such as:

(18)

wherein B and B' are each H or a lower alkyl radical, preferably the total number of C's in each such radical (B or B') does not exceed four. Examples of such compounds include 2-aminothiazole:

(19)

2-mercapto-4,5-dimethylthiazole:

(20)

and 2-mercapto-4-ethylthiazole:

(21)

Although the fundamental chemical characteristics of the brighteners of the invention are now understood to be based upon the particular reactivity of the basic active atomic arrangement:

$\text{N}=\text{O}-\text{X}$ (preferably $\text{N}=\text{O}-\text{S}$)

present in the heterocyclic ring, as described, those compounds which have been found to be
highly suitable for use in the invention and are, therefore, preferred may be classified according to the following general formula:

\[
\begin{align*}
\text{X} & \quad \text{R} \\
\text{A} & \quad \text{N} \\
\end{align*}
\]

wherein \(X\) and \(R\) have the meanings hereinbefore designated (and there is preferably at least one \(S\) in the molecule, in \(X\) and/or \(R\)); and \(A\) is a divalent organic radical wherein the two valences are connected to adjacent carbon atoms which atoms are, in turn, connected by a double bond, and any groups in such radical other than hydrocarbon groups being halogen, \(-\text{SO}_2\text{OH}\), \(-\text{OH}\), \(-\text{SH}\), \(-\text{NH}_2\) or \(-\text{NO}_2\) groups, or expressed in other terms, any atoms other than \(C\) and \(\text{H}\) in \(A\) being halogen, \(S\), \(O\) or \(N\) contained in the aforementioned groups.

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-aminobenzothiazole to the maximum which may be utilized 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 15.

One of the most important features of the invention resides in the fact that the instant brighteners are uniquely capable of producing stable solutions for effecting plating deposits of unique uniformity and suitable brightness and smoothness to permit subsequent nickel deposit coverage having superior properties. The emphasis herein is not only on suitable brightness (for nickel coverage) but also on the various other extremely important properties such as deposit ductility and pressure variations in bath concentrations, current densities and impurities present.

The superiority of performance of a brightener of the instant invention with respect to certain of the foregoing properties may be demonstrated as follows:

A plating bath was charged with a solution containing 28 ounces per gallon of copper sulphate and 8 ounces per gallon of sulphuric acid. The brightener (6-amine-2-mercapto benzothiazole) was added as a solid to the plating solution. Steel cathodes previously cleaned and plated in a conventional cyanide copper solution, were plated in this solution.

To demonstrate the wide range of brightness concentration permitted in this process, cathodes were plated while the brightener concentration was varied from 1 to 60 parts per million.

A distinct improvement in cathode appearance was noticed when the brightener concentration was one part per million.

Deposit brightness increased with increased brightener concentration until a concentration of 6 parts per million was reached. With the brightener concentration between 6 and 60 parts per million, there was no noticeable difference in deposit brightness, smoothness or ductility; all cathodes having at least a satisfactory semi-bright deposit.

Cathodes were also plated in this solution at current densities ranging from 10 amperes per square foot, and acceptable deposits were obtained in every case. The addition of 6 grams per liter of iron to the solution had no adverse effect on the deposits obtained. The addition of 0.1 gram per liter of nickel had no effect on the copper deposit.

In a second demonstration, a plating bath was made up using the same proportions as those employed in the previous demonstration. An initial brightener addition of 0.024 gram per liter of 6-amine 2-mercapto benzothiazole was made. Cathodes were then plated at 15 and 60 amperes per square foot and the deposit found to be semi-bright, smooth and ductile. This solution was subjected to both intermittent and sustained periods of electrolysis, and it was found that the desired degree of brightness could be easily maintained by infrequent small additions of the brightener. The remarkable stability of this solution was shown by discontinuing the electrolysis and allowing it to remain idle for periods up to eight days.

On resumption of plating, good semi-bright deposits were obtained which were equal in every way to the deposit secured before the shut down period. Plating in this solution was continued for a period of seven months at which time the solution was still producing excellent deposits.

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 10-50 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. For example, all of the deposits obtained by carrying out the foregoing procedures in the demonstration were tested for ductility and evidence no cracking upon being bent 180°. Deposits obtained employing commercially available solutions under substantially the same conditions have been found to fail when bent 45-50°.

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.

The brighteners which may be used in the instant invention include such compounds, some of which have been mentioned hereinbefore, as 6-amino 2-mercaptobenzothiazole, 2-methyl mercapto benzothiazole, 3-mercaptobenzoxazole, 2-amino benzothiazole, 2-methyl benzothiazole, 6-nitro-2-mercapto benzothiazole, 2-mercapto benzothiazole, 2-mercapto benzothiazole, 4-ethylthiazole, 2-aminobenzoxazole, 2-phenyl benzothiazole, 6-hydroxy-2-mercaptobenzothiazole, 5-sulfonic acid-2-mercaptobenzothiazole, 2,5-dimercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole, and methyl, benz-
thiazoyl amines. Each of the foregoing compounds may be used in substantially the manner hereinafter described to obtain superior results characteristic of the instant invention, and each indicates clearly the ability to effect suitable plating operation over a wide range of current densities.

In general, the copper sulphate employed in the instant plating solutions may range from 100 g. to 270 g. per liter, but in the interests of economy and maximum uniformity of deposits about 100-150 g./l., in the lower portion of the range, is preferred.

Example 1

A plating cell was charged with 0.5 liters of plating solution containing 140 g./l. of CuSO₄·5H₂O, 50 g./l. of H₂SO₄ and 0.03 g./l. of 2-methyl mercapto benzothiazole (brightener).

The cell was equipped with electrolytic sheet copper anodes, in accordance with commercial practice. Polished steel cathodes previously cleaned and plated in a conventional cyanide copper solution were plated in this bath. Plating was carried out for 15 minutes at 110° F. and 45 amperes per square foot. The resulting plate was bright, and repeated tests consistently yielded suitable deposits ranging from "semi-bright" to "bright.

Example 2

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 125
H₂SO₄ ------------ gm./l. 75
2-methyl mercapto benzothiazole ------------ gm./l. 0.04
Temperature ------------ ° F. 100
Cathode current density ------------ ASF. 50

and the results obtained were substantially the same as those described in Example 1.

Example 3

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 200
H₂SO₄ ------------ gm./l. 125
2-amino benzoxazole ------------ gm./l. 0.08
Temperature ------------ ° F. 100
Cathode current density ------------ ASF. 50

and the results obtained were substantially the same as those described in Example 1.

Example 4

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 150
H₂SO₄ ------------ gm./l. 50
2-mercapto benzoxazole ------------ gm./l. 0.02
Temperature ------------ ° F. 120
Cathode current density ------------ ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 5

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 175
H₂SO₄ ------------ gm./l. 65
2-amino benzothiazole ------------ gm./l. 0.04
Temperature ------------ ° F. 110
Cathode current density ------------ ASF. 50

and the results obtained were substantially the same as those described in Example 1.

Example 6

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 125
H₂SO₄ ------------ gm./l. 50
2-methyl benzothiazole ------------ gm./l. 0.5
Temperature ------------ ° F. 110
Cathode current density ------------ ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 7

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 130
H₂SO₄ ------------ gm./l. 50
2-phenyl benzothiazole ------------ gm./l. 0.3
Temperature ------------ ° F. 120
Cathode current density ------------ ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 8

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 150
H₂SO₄ ------------ gm./l. 50
6-hydroxy-2-mercapto benzothiazole ------------ gm./l. 0.4
Temperature ------------ ° F. 100
Cathode current density ------------ ASF. 40

and the results obtained were substantially the same as those described in Example 1.

If a procedure such as the foregoing is carried out using a compound wherein the 6-hydroxy group is replaced by a 6-nitro group (i.e., 6-nitro-2-mercapto benzothiazole), substantially the same results are obtained.

Example 9

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

CuSO₄·5H₂O ------------ gm./l. 130
H₂SO₄ ------------ gm./l. 50
2-mercapto benzothiazole-5-sulfonic acid ------------ gm./l. 0.3
Temperature ------------ ° F. 100
Cathode current density ------------ ASF. 50

and the results obtained were substantially the same as those described in Example 1.

Example 10

A procedure was carried out that is the same
as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

- CuSO₄·5H₂O .......................... gm./l. 150
- H₂SO₄ .................................. gm./l. 50
- 2,5-dimercapto benzothiazole ...... gm./l. 0.02
- Temperature ........................... °F. 110
- Cathode current density ............... ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 11

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

- CuSO₄·5H₂O .......................... gm./l. 250
- H₂SO₄ .................................. gm./l. 50
- 5-chloro-2-mercapto benzothiazole ... gm./l. 0.03
- Temperature ........................... °F. 120
- Cathode current density ............... ASF. 50

and the results obtained were substantially the same as those described in Example 1.

Example 12

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

- CuSO₄·5H₂O .......................... gm./l. 130
- H₂SO₄ .................................. gm./l. 50
- 2-amino thiazole ...................... gm./l. 0.5
- Temperature ........................... °F. 100
- Cathode current density ............... ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 13

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

- CuSO₄·5H₂O .......................... gm./l. 130
- H₂SO₄ .................................. gm./l. 50
- 2-mercapto-4,5 dimethyl thiazole ... gm./l. 0.1
- Temperature ........................... °F. 110
- Cathode current density ............... ASF. 40

and the results obtained were substantially the same as those described in Example 1.

Example 14

A procedure was carried out that is the same as that described in Example 1 except that the following concentrations, ingredients and conditions were used:

- CuSO₄·5H₂O .......................... gm./l. 130
- H₂SO₄ .................................. gm./l. 50
- 2-mercapto-4-ethyl thiazole .......... gm./l. 0.2
- Temperature ........................... °F. 100
- Cathode current density ............... ASF. 40

Example 15

If a procedure is carried out that is the same as that described in Example 1 except that the "brightener" used consists of 0.1 g./l. of 2-amino benzothiazole plus 0.1 g./l. of 2-mercapto benzo- thiazole, the results obtained are substantially the same, the deposit having unusually good reflectance.

A very bright deposit may also be obtained by carrying out the procedure using a "brightener" combination of 0.4 g./l. of 2-amino thiazole and 1.0 g./l. of glycine. In particular, it has been found that unusually good results may be obtained using glycine, in amounts of about 0.5-5 g./l. and preferably about 1-2 g./l., in combination with one of the brighteners of the instant invention. Di-p-tolyl disulfide, likewise, may be used in place of glycine for this purpose.

One of the particular advantages 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, sometimes used with other brighteners, may be present, without poisoning or otherwise impairing the effectiveness of the brighteners of the invention. In fact, as has been pointed out, certain agents such as glycine and di-p-tolyl disulfide may be added to obtain improved results. On the other hand, those ingredients which formerly were thought to be necessary, namely, dextrin, molasses, sugar, sulfonated creosote and the like, may be present or absent.

As herebefore 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.

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 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

\[ \text{C-S} \]

wherein X is an atom of group six of the periodic system selected from the group consisting of oxygen and sulphur, that compound having a concentration in said solution within the range of 0.005-1 gram per liter.

2. An electrolyte for the electrodiposition 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

\[ \text{C-S} \]

that compound having 0.005-1 gram per liter.

3. An electrolyte for the electrodiposition 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

\[ \text{C-S} \]

that compound having 0.005-1 gram per liter.

4. 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 thiazole nucleus:

the brightener having a concentration in said 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 thiazole nucleus:

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

6. 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 thiazole nucleus:

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

7. An electrolyte for electro-depositing copper consisting essentially of an aqueous acid solution of copper sulfate and free sulfuric acid and having dissolved therein, as a brightener for the electro-deposited copper, a heterocyclic compound having the following heterocyclic ring structural arrangement

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

8. An electrolyte for electro-depositing copper consisting essentially of an aqueous acid solution of copper sulfate and free sulfuric acid and having dissolved therein, as a brightener for the electro-deposited copper, a heterocyclic compound having the following heterocyclic ring structural arrangement

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

9. An electrolyte for electro-depositing copper consisting essentially of an aqueous acid solution of copper sulfate and free sulfuric acid and having dissolved therein, as a brightener for the electro-deposited copper, a heterocyclic compound having the following heterocyclic ring structural arrangement

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

10. An electrolyte for electro-depositing copper consisting essentially of an aqueous acid solution of copper sulfate and free sulfuric acid and having dissolved therein, as a brightener for the electro-deposited copper, a heterocyclic compound having the following heterocyclic ring structural arrangement

said compound having a concentration in said solution within the range of 0.005–1 gram per liter.
15 furic acid-copper sulfate aqueous bath, the step of carrying out said process in the presence of a dissolved brightener having the following heterocyclic ring structural arrangement.

![Chemical Structure]

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

16. In the process of depositing copper on metallic surfaces by electro-deposition from 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 structural arrangement.

![Chemical Structure]

wherein X is an atom of group VI of the periodic system selected from the group consisting of oxygen and sulfur, said brightener having a concentration in said solution within the range of 0.005-1 gram per liter.

17. In the process of depositing copper on metallic surfaces by electro-deposition from 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 structural arrangement.

![Chemical Structure]

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

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

![Chemical Structure]

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

19. An electrolyte for electrodepositing copper consisting essentially of an aqueous acid solution of copper sulfate and free sulfuric acid and having dissolved therein, as a brightener for the electro-deposited copper, a heterocyclic compound having the formula.

![Chemical Structure]

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

WILLIAM J. PIERCE.

References Cited in the file of this patent

<table>
<thead>
<tr>
<th>UNITED STATES PATENTS</th>
<th>FOREIGN PATENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Country</td>
</tr>
<tr>
<td>2,609,339</td>
<td>Canada</td>
</tr>
<tr>
<td>461,186</td>
<td>Passal</td>
</tr>
</tbody>
</table>