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COPPER CYANIDE PLATING PROCESS AND SOLUTION THEREFOR

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11 Claims. (Cl. 204—52)

This invention relates to a copper plating process and to a novel copper plating solution. More particularly, the invention relates to the electroplating of copper from copper cyanide plating solutions wherein thio substituted 6-member heterocyclic nitrogen containing ring compounds having an in-ring azomethine group are employed for imparting increased luster and brightness to copper deposits obtained therefrom. This application is a continuation-in-part of my prior application bearing Serial Numbers 560,076 and 624,729, filed January 19, 1956, and November 28, 1956, respectively, both now abandoned.

I have found that certain of the brightening agents set forth in my prior applications are quickly consumed during plating operations, and, accordingly, require frequent replenishment, thereby making them impractical for commercial plating operations. It has been found that the true aromatic thioalcohols described in my prior applications suffer from this disadvantage, whereas, the in-ring nitrogen containing compounds described therein are more stable in copper plating solutions. This invention is directed to the use of thio substituted compounds having at least one azomethine group in a 6-member heterocyclic ring since compounds of this type have been found especially stable in copper cyanide type plating solutions and production of copper deposits having increased luster.

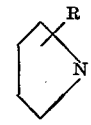
One object of the invention is to provide for novel plating solutions containing brightening agents which impart increased luster to copper deposits obtained therefrom. Another object of the invention is to provide novel plating solutions containing as addition agents thereto certain thio substituted compounds which impart brightness and luster to copper deposits obtained from copper cyanide type solution. Another object is to provide a process for plating copper from cyanide solutions. Other and further objects will be apparent from the following description and disclosure.

Copper is frequently employed as a base plate in nickel-chromium plating operations, the copper taking the place of some of the nickel in obtaining a corrosion resistant object. In plating zinc die-castings, for example, a substantial thickness of copper (.2 to .8 mil) is almost universally used prior to the nickel deposit. One of the benefits derived from the discovery set forth herein is the fact that the copper deposits obtained are exceptionally ductile and form an excellent coating for the adherence of the nickel thereto. Still another advantage resides in obtaining a bright, lustrous copper deposit. As is well known, buffing costs are decreased when bright deposits are obtained directly from the plating solution.

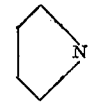
Table I sets forth typical brightening agents according to the invention which may be broadly described as thio substituted 6-member heterocyclic nitrogen containing ring compounds having at least one in-ring azomethine group (=C=N—). The triazine type thio substituted 6-member heterocyclic nitrogen containing ring compounds wherein there are three azomethine groups are preferred because of their relative cheapness and generally good brightening qualities. Although there may be only one

thio substituent on a 6-member heterocyclic nitrogen containing ring compound having more than one in-ring azomethine group, nevertheless, where there is more than one thio substituent, the thio substituents should be attached to carbon atoms of separate in-ring azomethine groups, i. e., where there is more than one thio substituent, each substituent should be attached to a carbon atom of a different azomethine group. Thiol groups and alkylthiol groups have been found to be satisfactory thio substituents, and it is apparent that a mercaptide group may also be employed such as —SNa, —SK or other metal thio salts since equivalent compounds are formed upon dissolution in the plating solutions.

Structurally, the thio substituted 6-member heterocyclic nitrogen containing ring compounds may be considered as having the basic formula

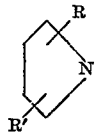


wherein

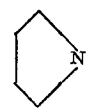


represents a 6-member heterocyclic ring nucleus wherein the members of the ring are selected from the group consisting of carbon and nitrogen atoms and the nucleus has at least one in-ring azomethine group, and wherein R represents one or more thio substituents individually attached to a carbon atom of a separate in-ring azomethine group. R is preferably selected from the group consisting of a thiol group, a mercaptide group and an alkylthiol group having from one to three carbon atoms. The 6-member heterocyclic nitrogen containing nucleus may have substituents thereon which do not adversely interfere with the brightening capacity of the compounds such as by rendering them insoluble, and no particular type of substituents have been found to date which appreciably interfere with this brightening capacity. Such substituents as hydrogen, an amino group, a hydroxyl group, and an alkyl group having from one to three carbon atoms may be found to be suitable as exemplified in Table I.

More particularly, the thio substituted compounds having substituents on the 6-member ring nucleus may be described by the following formula:



wherein



represents a 6-member heterocyclic ring nucleus wherein the members of the ring are selected from the group consisting of carbon and nitrogen atoms and the nucleus has at least one in-ring azomethine group, and R represents one or more thio substituents individually attached to a carbon atom of an in-ring azomethine group and being selected from a group consisting of a thiol group, a mercaptide group and an alkylthiol group having from one to three carbon atoms. R' in this case may be one or more substituents on the ring and selected from hydrogen, an amino group, a hydroxyl group, and an alkyl group having from one to three carbon atoms.

TABLE I

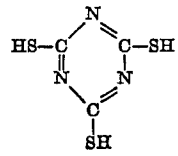
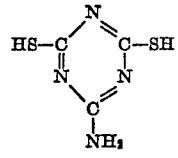
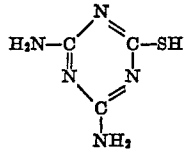
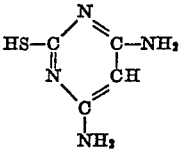
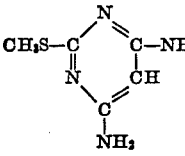
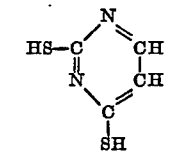
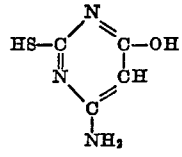
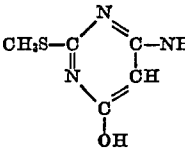
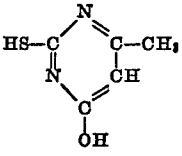
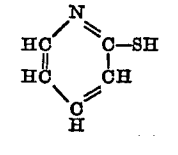
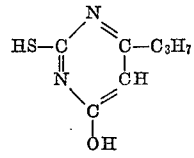
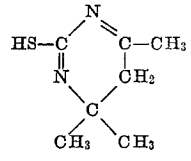
Typical Brighteners	Structural Formulae	Practical Commercial Limits (g./l.)	Optimum Concentration Without Agitation (g./l.)	Optimum Concentration With Agitation (g./l.)	Resulting Plate
2,4,6-trimercapto triazine		.05-10	2-6	.05-3.5	Bright.
dithioammelide		.05-10	2.5-6	.2-.75	Very Bright.
thioammeline		.05-10	2.5-6	.3-3.5	Do.
4,6-diamino-2-mercapto pyrimidine.		.05-8	1.3-4.5	.05-2	Do.
4,6-diamino-2-methylmercapto pyrimidine.		.05-10	2.5-6	.2-.75	Do.
2,4-dimercapto pyrimidine		.05-8	1.3-4.5	.05-2	Do.
4, amino-6-hydroxy-2-mercapto pyrimidine.		.05-8	1.3-4.5	.05-2	Do.
6, amino-4-hydroxy-2-methyl mercapto pyrimidine.		.5-10	2-6	.75-2.5	Do.
4, hydroxy-2-mercapto-6-methyl pyrimidine.		.05-8	1.3-4.5	0.1-2	Do.
2, mercapto pyridine		.05-8	1.3-4.5	0.1-2	Do.

TABLE I.—Continued

Typical Brighteners	Structural Formulae	Practical Commercial Limits (g./l.)	Optimum Concentration Without Agitation (g./l.)	Optimum Concentration With Agitation (g./l.)	Resulting Plate
4, hydroxy-2-mercapto-6-propyl pyrimidine.		----------	----------	.15-3.5	Semi-bright.
2, mercapto-4, 4, 6-trimethyl-4, 5-dihydro pyrimidine.		----------	.75-4.5	.15-3.5	Do.

The brightening agents of the invention are most specifically limited in their use to copper cyanide type plating operations since attempts to evaluate the brightening power of these compounds in other copper solutions have met with relatively little success. Preferably the cyanide solution is of the potassium cyanide type although the brightening power of the thio substituted compounds is also evident in cyanide solutions of the sodium cyanide type under similar operating conditions and with similar concentrations of the basic ingredients of the plating solutions.

Only small amounts of the brightening agents are necessary to impart increased brightness to the copper deposit obtained from the cyanide plating solutions. In general, quantities in excess of about .05 gram per liter up to the solubility of the particular compound in the plating solution are adequate. In this respect quantities ranging from about .05 gram per liter to about 10 grams per liter may be considered as the practical commercial limits which may be employed in the cyanide type plating solutions. It will be evident hereinafter that the optimum concentration of any one particular brightening agent for obtaining the maximum luster and brightness may vary and is dependent in many respects upon the concentration of the basic ingredients of the plating solution and also the operating conditions employed. In general, once the maximum luster and brightness is obtained, further quantities of the brightener do not increase the brightness. Whether or not the solution is agitated has been found to be especially influencing upon the optimum concentration of the brightening agent which is employed. Table I contains typical brightening agents according to the invention together with their structural formulae, and also indicates concentrations thereof which may be employed in nonagitated and agitated solutions together with the relative brightness usually obtained. It will be evident that lesser quantities of the brightening agents may be employed with agitated solutions.

The optimum concentrations of the typical brighteners set forth in Table I where agitation is employed may be considered as representative of situations where cyanide plating solutions are vigorously agitated. Vigorous agitation in this respect relates to that degree of agitation which would be encountered by placing a plurality of air nozzles below the surface of the plating solution and passing air therethrough to secure an effective agitation which may be related in type to that accomplished in boiling water. Mechanical means may be employed for agitating the solutions. It is further recognized that the degree of agitation my vary. Accordingly, the degree of change in the optimum range of concentrations of the brighteners is related thereto. As will be apparent hereinafter, the optimum operating conditions and concentrations of the other bath constituents are also related to the degree of agitation.

Table II sets forth typical copper cyanide plating conditions which may be employed according to the invention, and also sets forth typical operating conditions which may be employed for obtaining optimum results in the form of increased luster and brightness of copper deposit obtained therefrom through the use of the brighteners described herein.

A broad range of copper cyanide concentration may be employed with the brightening agents of the invention, and, in this respect, the copper cyanide concentra-

TABLE II

Typical copper cyanide plating solutions and operating conditions

Bath No.	1	2	3	4	5	6
Copper Cyanide (CuCN) g./l.	100-120	100-120	55-85	55-85	60	100
Free Cyanide:						
(KCN) g./l.	4-10	4-10	9-12	9-12	----------	----------
(NaCN) g./l.	----------	----------	----------	----------	10	10
Rochelle Salts	----------	----------	----------	----------	5-45	5-45
Potassium Citrate	45-65	45-65	45-65	45-65	----------	----------
Operating Conditions:						
pH	11.5-12.5	11.5-12.5	12-13.5	12-13.5	12.5	12.5
Temp., ° F.	140-160	140-160	150-160	150-160	160	160
Cathode Current Density (ASF)	10-35	10-40	10-20	10-60	10-35	10-35
Agitation	None	None	Vigorous	Vigorous	Vigorous	None
Type Current [1]	CC	IC	CC	IC	IC	IC
Cycle (Sec.) (on-off)	----------	8-2	----------	7-2	7-2	7-2

[1] IC=interrupted current. CC=continuous current.

tion may range from about 45 to about 225 grams per liter. When no agitation is employed, best results are obtained when the concentration is from about 100 grams per liter to about 120 grams per liter. When the concentration falls below about 100 grams per liter it has been found that the brightness is adversely affected, and that below a concentration of about 85 grams per liter only dull deposits result in the absence of agitation. In general, an increase in the copper cyanide concentration above about 120 grams per liter does not appreciably affect the brightness of the deposit obtained in non-agitated solutions, and concentrations as high as about 225 grams per liter may be employed. On the other hand, when the plating solution is agitated, it has been found that the preferred copper cyanide concentration should be materially reduced for the obtainment of optimum results. Thus, when vigorous agitation is employed, a copper cyanide concentration ranging generally from about 55 to about 85 grams per liter has been found best. With vigorous agitation as heretofore described it has been found, generally, that the brightness of the copper deposit is adversely affected when the concentration of copper cyanide falls outside a range which extends from about 45 to about 90 grams per liter. When the solution is agitated, therefore, it will be found that the brightness contributed by any one of the disclosed thio substituted compounds is seriously affected unless the copper cyanide concentration is adjusted to compensate for the degree of agitation, or vice versa.

As is well known to those skilled in the art of copper cyanide plating, a complex potassium cuprous cyanide compound is formed between the potassium cyanide and copper cyanide. The actual formula of the complex varies according to the temperature conditions of the solution among other things. In this regard, the potassium cyanide concentration excluding the free potassium cyanide generally amounts to about 1.46 times the amount of copper cyanide employed. Thus, for a bath containing copper cyanide in amounts between about 45 and 225 grams of copper cyanide per liter should contain potassium cyanide excluding the "free cyanide," of from about 65 to about 325 grams per liter to form the complex. Similarly, for a solution having amounts of copper cyanide ranging between about 100 and 120 grams of copper cyanide per liter the potassium cyanide concentration, excluding the "free cyanide," should be between about 145 and 175 grams of potassium cyanide per liter. The potassium cyanide concentration is thus based upon a potassium copper cyanide complex having the approximate formula $K_2Cu(CN)_3$. It is necessary in copper cyanide solutions to have sufficient cyanide present to form a complex, otherwise, unstable conditions result. In this regard, there must be an excess of free cyanide such as sodium or potassium cyanide to insure that the complex is formed.

It has been found that generally greater quantities of free cyanide must be present when the solution is agitated than when the solution is not agitated. For example, when the solution is not agitated, it has been found that when the concentration of the free cyanide falls below about 2.5 grams of free potassium cyanide per liter, a dull deposit results. A similar dullness is detected above a free cyanide concentration of about 25 grams per liter. The best results in nonagitated solutions are obtained when the free cyanide concentration ranges from about 4 grams per liter to about 10 grams per liter. On the other hand, when vigorous agitation is employed as described heretofore, it has been found that best results are obtained when the free cyanide concentration ranges generally from about 9 to about 12 grams per liter. With vigorous agitation excessive anode polarization occurs, and a thick black coating is formed on the anode surface when the free cyanide concentration falls below about 6 grams per liter. When the concentration of free cyanide exceeds about 13 grams per liter, the cathode efficiency is decreased appreciably. On the other hand, where no agitation is employed, it is found that the free cyanide concentration may fall as low as about 2.5 grams per liter, below which, however, excessive anode polarization occurs, and a thick black coating is formed on the anode surface. Usually the free cyanide concentration in excess of about 17 or 18 grams per liter is not recommended since the cathode efficiency decreases above this concentration due to excessive gassing, and only dull deposits are obtained above about 25 grams per liter of free cyanide. It will be apparent because of the necessity for "free cyanide" that the maximum limiting quantity of potassium cyanide is about 350 grams per liter when the copper cyanide concentration is about 225 grams per liter. The 350 grams per liter of potassium cyanide being the sum of the potassium cyanide associated with the copper cyanide and the free cyanide.

In preparing the basic solution, copper cyanide is preferably added to an aqueous solution of potassium or sodium cyanide in the desired amounts, and potassium or sodium hydroxide thereafter added to obtain the desired operating pH range. In general, a wide range of pH may be tolerated in the solution with optimum results being obtained in the pH range between about 11.5 and 12.5 in the case where there is no agitation, and in a pH range between about 12 and 13.5 in the case where there is vigorous agitation. Good results may be obtained in either case, however, at pH's ranging from about 9 to 14.

To buffer the solution against changes in pH, potassium citrate in amounts generally ranging from about 35 to about 75 grams per liter has been found suitable. Best results have been obtained when the potassium citrate is employed in amounts ranging from about 45 grams per liter to about 65 grams per liter. It will be apparent that it is not essential that potassium citrate be employed as a buffer or, in fact, that any buffer be utilized in the plating solution. Other buffers such as Rochelle salts may be employed also, and, in this regard, the Rochelle salts may be employed generally in amounts ranging from about 5 to about 55 grams per liter. Usually the Rochelle salts have been found to be more effective in the agitated solutions than in the nonagitated solution.

With respect to the temperature of the plating solution during the plating process optimum results in nonagitated solutions may be obtained over a somewhat wider temperature range than in the case where vigorous agitation is employed. For example, temperatures ranging from about 140° F. to about 160° F. may be employed without agitation of the solution, whereas, a temperature from about 150° F. to about 160° F. is preferably employed when there is vigorous agitation. Again, it will be apparent that the ranges set forth herein with respect to an agitated and nonagitated solution are principally illustrative of the invention, and that with varying degrees of the agitation the concentrations and operating conditions will vary so far as their optimum is concerned. Between the extreme case of agitation illustrated, and the other extreme where there is relatively no agitation, solution temperatures of from about 130° F. to about 180° F. may be employed. Although temperatures as low as 130° F. have been successfully employed, they are not strongly recommended since the brightness of the plate obtained tends to diminish if the temperature of the plating solution falls below about 140° F. in the case where agitation is not employed. On the other hand, when temperatures in excess of about 160° F. are employed without agitation slightly higher current densities should be utilized. The bright plating current density range tends to increase somewhat when higher temperatures are employed. In low current density areas the brightness usually diminishes when the temperature is increased much above 160° F. without a compensating increase in the average current density employed. It is

pointed out, however, that temperatures as high as about 180° F. have been employed with success utilizing the brightening agents described herein.

Broadly, current densities from about 5 to about 65 amps. per square foot of cathode surface area may be utilized according to the invention. Interrupted current appears to permit a wider and somewhat higher range of current densities and is usually preferred since it aids in eliminating polarization, and further minimizes film deposits on the anode. Suitable cycles for the use of interrupted current may have an "on time" of up to about 90 seconds and an "off time" of from about 5 to about 50% of the "on time." With a continuous current, optimum results in the form of maximum brightness have been obtained in nonagitated solutions when the current density ranges from about 10 to about 35 amps. per square foot of cathode surface area, whereas, with an interrupted current, one may use from about 10 to about 40 amps. per square foot without agitation. On the other hand, when vigorous agitation and a continuous current are employed, it has been found that a preferred range of current densities from about 10 to 20 amps. per square foot is best, whereas, with an interrupted current, the range is broadened out and may be raised to from about 10 to 60 amps. per square foot.

Because they produce a very bright copper deposit in the plating solutions and are economically available, dithioammelide and thioammeline are preferred brightening agents. Either compound may be employed in amounts ranging from about .05 to about 10 grams per liter although optimum results are usually obtained, for example, in nonagitated solutions when they are employed in amounts ranging from about 2.5 to about 6 grams per liter. In vigorously agitated solutions, on the other hand, it has been found that the concentration to obtain an equivalent brightness may be materially decreased, and in the case of dithioammelide it has been found that a concentration ranging from about .2 to about .75 will produce a relatively very bright plate. In the case of thioammeline, the concentration to produce a very bright plate in a vigorously agitated solution preferably ranges from about .3 to about 3.5 grams per liter. Excess quantities of dissolved brighteners are unnecessary and do not appear to increase the brightness once maximum brightness is obtained.

The process of the herein described invention may be carried out utilizing either soluble or insoluble anodes although soluble anodes are preferably employed. The bright deposits have been obtained on such metals as zinc and steel cathodes, and it is contemplated that the process may be employed with other metallic cathodes customarily employed with copper solutions such as copper and brass cathodes. Generally, the brightening capacity is not limited to the thickness of the deposit, the brightening having been successfully realized on objects where the thickness of the deposit ranges from about 0.1–3.0 mils and higher.

As another phase of the invention it has been found that small quantities of divalent tin, usually from about 0.5 to about 15 grams per liter of the metal, when dissolved in the solutions of the herein described invention, facilitate the obtainment of the uniformly bright bronze deposit. The tin may be added as stannous chloride or as any ionizable stannous salt such as sodium or potassium stannite. Preferred quantities generally range from about 0.75 to about 2 grams per liter as divalent tin. Divalent tin also has the useful function of offsetting the harmful effect of hexavalent chromium impurities. For example, 0.04 gram per liter of Cr^{+6} is very harmful to the brightness of the copper deposit, but the addition of 0.2 gram per liter of Sn^{+2} will restore the brightness.

The following are examples showing the use of different brightening agents falling within the general classification in copper cyanide plating solutions.

EXAMPLE 1

A copper cyanide plating solution consisting of the following constituents was prepared, 2,4,6-trimercaptotriazine being dissolved therein in the amount of from 2 to 4 grams per liter:

	Grams per liter
Copper cyanide (CuCN)	100–120
Potassium cyanide (KCN)	145–175
Free cyanide (KCN)	4–10
Potassium hydroxide to a pH of 11.5 to 12.5.	
Potassium citrate	45–65

A bright lustrous plate was obtained on a steel panel utilizing an interrupted current density (8–2) from about 25 to 35 amps. per square foot of cathode surface area while maintaining the temperature of the solution of from about 140° F. to about 160° F. The solution was not agitated.

EXAMPLE 2

Utilizing dithioammelide in amounts between 2.5 and 4 grams per liter in an identical basic solution as set forth in Example 1, gave a very bright deposit when operated at temperatures between 140° F. and 160° F. and at a continuous cathode current density between 20 and 35 amps, per square foot. The solution was not agitated.

EXAMPLE 3

Thioammeline utilized in an amount from about 2.5 to 4 grams per liter in a basic copper cyanide solution identical to that set forth in Example 1 and while operating under the same conditions therein stated permitted the obtainment of a very bright plate. The solution was not agitated in this case.

EXAMPLE 4

A copper cyanide plating solution having the following composition may be employed.

Copper cyanide (CuCN)	grams per liter	75
Free potassium cyanide (KCN)	do	10
Rochelle salts	do	50
Dithioammelide	do	0.5
pH		12.5

The solution is vigorously agitated with the addition of air through a plurality of inlets below the cathode and operated at a temperature of about 155° F. When employing a continuous current at a cathode current density of 15 amps. per square foot of cathode surface area a very bright deposit will be produced. Utilizing a current density of 30 amps. per square foot with an interrupted current cycle of 7 seconds on and 2 seconds off under the same conditions a very bright plate may be obtained.

EXAMPLE 5

Substituting 2,4,6-trimercaptotriazine in the amount of 0.5 gram per liter for the dithioammelide in Example 4 will produce substantially the same result.

EXAMPLE 6

Substituting thioammeline in the amount of 0.5 gram per liter for the dithioammelide in Example 4 will produce substantially the same result.

EXAMPLE 7

A copper cyanide plating solution having the following composition may be employed:

Copper cyanide (CuCN)	grams per liter	60
Free sodium cyanide (NaCN)	do	10
Rochelle salts	do	45
Dithioammelide	do	0.25

The solution is vigorously agitated with air. When operating the solution at a temperature of 160° F. and at a pH of 12.5 with a 7–2 second "on-off" cycle of interrupted current, the current density being from 10 to

35 amps. per square foot of cathode surface area, a very bright plate may be obtained on steel panels.

EXAMPLE 8

A copper cyanide plating solution having the following composition may be employed:

Copper cyanide (CuCN)	grams per liter	100
Free sodium cyanide (NaCN)	do	10
Rochelle salts	do	45
Dithioammelide	do	1

When operating the solution without agitation at a temperature of 160° F. at a pH of 12.5 with a 7–2 second "on-off" cycle of interrupted current the current density being from 10 to 35 amps. per square foot of cathode surface area, a very bright plate may be obtained on brass panels.

EXAMPLE 9

Any of the brighteners listed in Table I may be employed in an amount corresponding to that set forth under "Optimum Concentration Without Agitation" in bath numbers 1, 2 or 6 of Table II, and it will be found that a copper deposit will be obtained having increased luster and brightness when the bath is operated according to the conditions set forth under the bath employed.

EXAMPLE 10

Any of the brighteners set forth in Table I under "Optimum Concentration With Agitation" may be employed in amounts indicated therein with bath numbers 3, 4, and 5 of Table II under the operating conditions set forth therein, and it will be found that the copper deposit obtained therefrom has increased luster and brightness.

EXAMPLE 11

By adding 1.5 grams of divalent tin in the form of potassium stannite to any of the baths indicated in Examples 9 and 10, a bright bronze deposit will result when operated according to the conditions specified therein.

In the cases of some of the compounds set forth in Table I it has been discovered that they lose their specific identity when dissolved in the cyanide plating solution and yet the brightening qualities associated with the compounds remain. Accordingly, when reference is made herein to a plating solution containing a particular brightener, it will be understood that reference is made to the particular brightener as added to the solution.

I claim:

1. A copper plating solution comprising an aqueous solution of copper cyanide, free cyanide of the class consisting of potassium and sodium cyanides and an added thio-substituted six-member heterocyclic ring compound wherein the members of the ring comprise from one to three nitrogen atoms and the balance carbon atoms, each nitrogen atom forming a part of a separate azomethine group and being connected to two carbon atoms, at least one carbon atom of one azomethine group carrying a substituent of the class consisting of thiol, mercaptide and alkylthiol, said alkylthiol having from one to three carbon atoms, said thio-substituted compound being dissolved in said plating solution in an amount from about 0.05 gram per liter to about 10 grams per liter.

2. The solution defined in claim 1 wherein further in said thio-substituted compound one of the carbon atoms carries an amine group.

3. The solution defined in claim 1 wherein further said thio-substituted compound is dithioammelide.

4. The solution defined in claim 1 wherein further said thio-substituted compound is thioammeline.

5. The solution defined in claim 1 wherein further said thio-substituted compound is 4,6-diamino-2-mercapto pyrimidine.

6. The solution defined in claim 1 wherein further said thio-substituted compound is 4,6-diamino-2-methylmercapto pyrimidine.

7. The solution defined in claim 1 wherein further said thio-substituted compound is 2,4-dimercapto pyrimidine.

8. A copper plating process comprising electrolyzing between an anode and a cathode to be copper plated, an alkaline copper cyanide solution as defined in claim 1.

9. A copper plating solution as defined in claim 1 wherein said six-member heterocyclic ring compound is selected from the class consisting of 2,4,6-trimercapto triazine, dithioammelide, thioammeline, 4,6-diamino-2-mercapto pyrimidine,4,6-diamino-2-methylmercapto pyrimidine, 2,4-dimercapto pyrimidine, 4-amino-6-hydroxy-2-mercapto pyrimidine, 6,amino-4-hydroxy-2-methyl mercapto pyrimidine, 4,hydroxy-2-mercapto-6-methyl pyrimidine, 2,mercapto pyridine, 4-hydroxy-2-mercapto-6-propyl pyrimidine, and 2,mercapto-4,4,6-tri methyl-4,5-dihydro pyrimidine.

10. The solution defined in claim 9 wherein said solution additionally contains from 0.5 to 15 grams per liter of divalent tin.

11. A copper plating process comprising electrolyzing between an anode and a cathode to be copper plated, an alkaline copper cyanide solution as defined in claim 9.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

Certificate of Correction

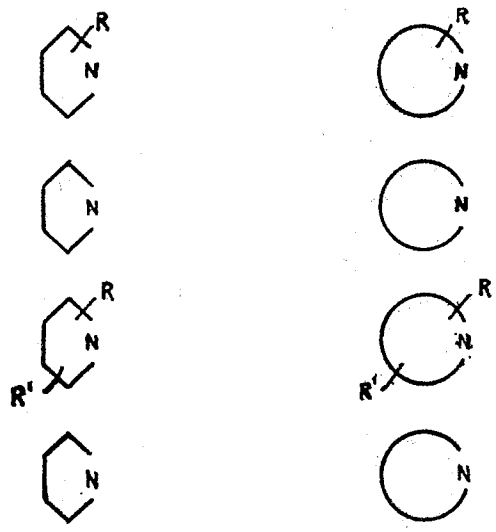
Patent No. 2,862,861 December 2, 1958

Paul W. Moy

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 23, for "application" read *applications*; column 2, all four diagrams shown therein, should be corrected as follows:

from to



column 6, line 41, for "my" read *may*; lines 47 and 48, for "conditions" read *solutions*; column 10, line 25, Example 2, for "35 amps, per square foot." read *35 amps. per square foot.*

Signed and sealed this 10th day of March 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.