

Jan. 23, 1962

R. W. BISHOFF ET AL

3,018,232

ADDITION AGENT FOR CYANIDE PLATING BATHS

Filed June 5, 1958

Fig. 1.

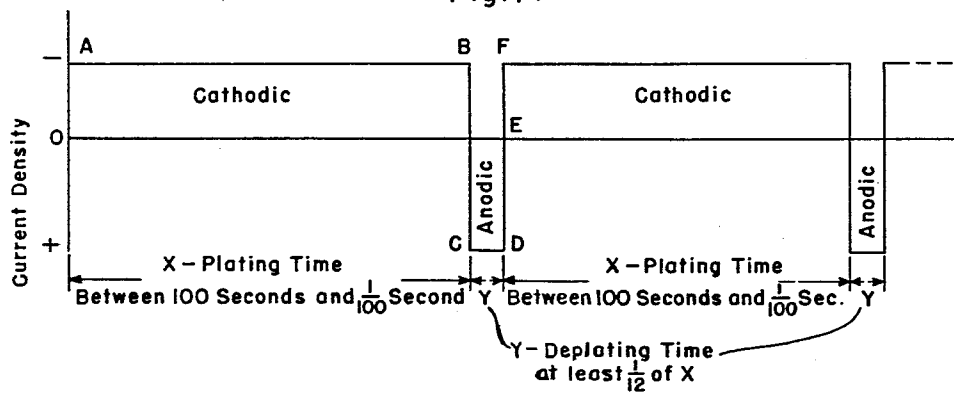
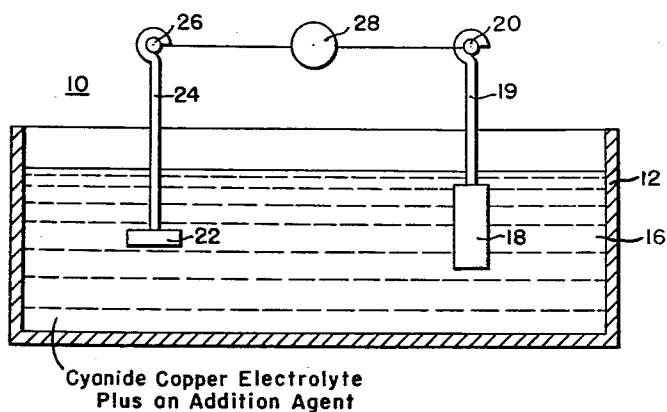


Fig. 2.



1

3,018,232 ADDITION AGENT FOR CYANIDE PLATING BATHS

Robert W. Bishoff, Pittsburgh, and Richard P. Cope, Jr.,
Wilksburg, Pa., assignors to Westinghouse Electric
Corporation, East Pittsburgh, Pa., a corporation of
Pennsylvania

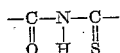
Filed June 5, 1958, Ser. No. 740,040
2 Claims. (Cl. 204-44)

The present invention relates to the deposition of metal from cyanide metal plating baths and has particular reference to novel products adapted for addition to cyanide metal plating baths whereby brighter and smoother metal electrodeposits are obtainable.

Generally, in the electroplating industry, it is desired to produce plated articles in which the surface is highly polished or bright. This may be obtained by a mechanical operation such as by buffing with a conventional buffing wheel. Although this method produces satisfactory results, it requires extra operations and increases the cost of the final product.

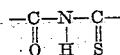
In an effort to obtain highly polished bright appearing metal deposits without the need for utilizing mechanical hand buffing techniques, efforts have been made in the art to find certain additives which may be added to conventional cyanide metal plating baths to provide finished plated members with the desired smooth and bright finish. The addition agents employed heretofore in cyanide plating baths have not proven satisfactory over a wide range of current densities.

The object of the present invention is to provide compounds comprising the reaction product of ammonia or certain derivatives thereof or certain monocyclic unsubstituted aromatic compounds and a compound having the nucleus



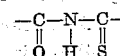
which compounds are suitable for addition to cyanide plating baths to promote brighter and smoother electrodeposition.

Another object of this invention is to provide a process for preparing a reaction product of ammonia or certain derivatives thereof or certain monocyclic unsubstituted aromatic compounds and a compound having the nucleus



which compounds are suitable for addition to cyanide electrolyte plating baths to promote brighter and smoother electrodeposition.

Still another object of the present invention is to provide cyanide electrolyte plating baths comprising metal, free cyanide, and containing a novel addition agent comprising the reaction of ammonia or certain derivatives thereof or certain monocyclic unsubstituted aromatic compounds and a compound having the nucleus



said addition agent being present in an amount sufficient to promote brighter and smoother copper electrodeposition.

Other and further objects of the present invention will, in part, be obvious and will, in part, appear hereinafter.

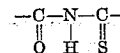
For a more complete understanding of the present invention, reference is made to the following description taken in conjunction with the accompanying drawing, in which:

FIGURE 1 is a graph illustrating one type of periodic reverse current electroplating; and

2

FIG. 2 is a sectional view in elevation of apparatus suitable for use in electroplating.

In the attainment of the foregoing objects and in accordance with the present invention, there are provided novel reaction products suitable for addition to cyanide plating baths in specified amounts to promote brighter and smoother copper electrodeposition. These novel reaction products are obtained by reacting substantially equimolar quantities of at least one compound having the nucleus

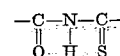


with ammonia or certain derivatives thereof or certain monocyclic unsubstituted aromatic compounds.

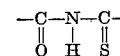
The inclusion of these reaction products in the electrolyte provides a bath with relatively high throwing power. Furthermore, the bright range at both the high and low current density ends is extended beyond the limits normally attained with presently available addition agents. The relatively high throwing power and the extension of the bright range make it possible to plate all surfaces of members having recesses, which are low current density areas, with uniformly bright and smooth deposits. The high current density extensions of the bright range also permits higher than normal current densities to be used, thus affording a savings in deposition time for any given thickness of plate.

Usually the metal, for example, copper deposited from plating baths containing the addition agents of this invention is so bright that it requires no buffing at all. However, should a full bright plate not be obtained for one reason or another, the metal deposit is of such high quality and fine grain that only a very light buffing operation is necessary to prepare it for subsequent bright deposits of nickel, chromium or the like.

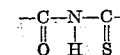
In preparing the novel reaction products of this invention, any of the several compounds having the nucleus



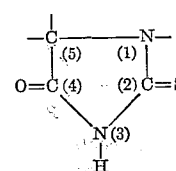
may be reacted with ammonia or certain derivatives thereof as will be described more fully hereinbelow. An example of a particularly suitable aliphatic compound having the nucleus



is acetylthiourea. Examples of other compounds having the nucleus



are 2-thiohydantoin and substitution derivatives of 2-thiohydantoin having at least one organic substituent in the 1,5 positions. The nucleus of these 2-thiohydantoin substitution derivatives has the following structure:



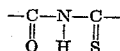
Various organic radicals may be substituted at one or both of the 1 or 5 positions, providing the resultant compound obtained upon reaction with ammonia or deriva-

3

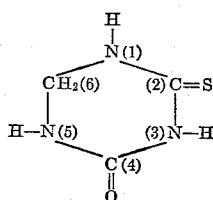
tives thereof is soluble in the cyanide metal electrolyte. Examples of suitable compounds are:

2-thiohydantoin
1-acetyl-2-thiohydantoin
5(2-hydroxybenzal)-2-thiohydantoin
5-furfural-2-thiohydantoin
5-benzal-2-thiohydantoin
1-methyl-2-thiohydantoin

Other examples of compounds having the nucleus



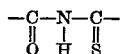
which are suitable for reaction with ammonia or derivatives thereof to produce novel compounds of this invention include 2-thiobarbituric acid and substitution derivatives of 2-thiobarbituric acid. The nucleus of these 2-thiobarbituric acid derivatives has the following structure:



Various organic radicals may be substituted for hydrogen at any one or more of the 1,5 or 6 positions, providing the resultant compound obtained upon reaction with the ammonia or derivatives thereof is soluble in the cyanide metal electroplating bath. Examples of suitable compounds of this nature include:

2-thiobarbituric acid
1-acetyl-2-thiobarbituric acid
1-benzoyl-2-thiobarbituric acid
1,5-diacetyl-2-thiobarbituric acid
2-thiopyrrolidinone-4
4-thiohydantoin
5-thiol-1,2,4-triazolidinone-3
4-thioxazolidinone-4
4-thiothiazolidinone-4
3-thio-1,2,4-oxadiazolidinone-5
3-thio-1,2,4-thiadiazolidinone-5
2-thioazolidinone-6
2-thio-1,3-diazolidinone-4
2-thio-1,4-diazolidinone-6
3-thio-1,2,4-triazolidinone-5
2-thio-1,3,5-triazolidinone-4
5-thio-1,2,4-triazolidinone-3
1-thio-2-benzazolone-3
3-thio-2-benzazolone-1

Compounds which may be reacted with compounds having the nucleus



to form the addition agents of this invention comprise compounds selected from the group consisting of (A) monocyclic unsubstituted aromatic compounds containing in the ring structure from 4 to 6 carbon atoms and from 1 to 2 nitrogen atoms per molecule and (B) compounds having the formula



wherein R is a radical selected from the group consisting of hydrogen; monovalent and divalent saturated aliphatic hydrocarbon radicals having from 1 to 4 carbon atoms and in which the substituents are selected from the group consisting of —NH₂ and —OH radicals; monovalent and divalent alicyclic radicals containing from 5 to 6 carbon

4

atoms in the ring in which the substituents are selected from the group consisting of —CH₃, —NH₂, and —OH radicals; monovalent and divalent heterocyclic radicals having from 5 to 6 carbon atoms in the ring and in which hetero atoms occur only in the ring structure and the substituents occur only on the carbon atoms and are selected from the group consisting of —NH₂ and —OH radicals; phenyl radicals; and aminophenyl radicals.

Specific examples of compounds included within the scope of the terms identified as (A) and (B) above include:

Ammonia, isopropylamine, monoethanolamine, ethylenediamine, dibutylamine, methylethanolamine, diisopropanolamine, methylpropylenediamine, diethylenediamine, propylolmethylenediamine, cyclopentylamine, dicyclohexylamine, cyclopentylmethylamine, cyclohexylisopropylamine, cyclopentylethylenediamine, 3-methylcyclohexylamine, 1,2-diaminocyclopentane, 4-hydroxycyclohexylamine, 2-aminothiazol, 3,5-diamino-1,2,4-triazole, 4-amino-2-pyridol, aniline, p-aminoaniline, methylaniline, methyl-2-amino-thiazole, 2-ethylolaminoimidazoline, 3-methylamino-5-amino-1,2,4-triazole, 2-methylamino-4-hydroxyimidazolidine, 2-cyclohexylaminothiazole, 3-methylolamino-5-amino-1,2,4-triazole, ethyl-4-methylcyclohexylamine, 4-cyclohexylamino-5-amino-2-pyridine, 4-methylaminocyclohexylamine, 1-methylamino-2-hydroxycyclopentane, p-aminomethylaniline, 3,3'-diisothiazolylamine, cyclohexylaniline, 2-methylcyclohexylthiazol-2, diphenylamine, 2-methylhexylethylamine, 3-amino-5-phenylamino-1,2,4-triazole thiazolyl-2-phenylamine, 4-hydroxy-6-cyclopentylaminopyrimidine N-ethylolamine, pyridine, pyrimidine, pyrazine, s-triazine, phenyl-4-aminocyclohexylamine, N-ethylol-p-aminoaniline, 4-methylcyclohexylpropylenediamine, N-(2-thiozyl)-p-aminoaniline, 2-methylolamine-4-hydroxyimidazolidine, dimethylcyclohexylamine, 4,4'-di-2-pyridolylamine, phenylethylenediamine, di-4-aminocyclohexylamine, N-cyclopentylaminobenzylamine, 3-isopropylaminocyclohexanol, 3-(2'-thiazolylamino)-5-amino-1,2,4-triazole, ethylol-1,4-diaminocyclohexane, phenylcyclohexanolamine, phenyl-p-aminoaniline, 2-thiazolylethylenediamine, 2-imidazolylcyclopentanamine, 3-p-aminophenyl-5-amino-1,2,4-triazole, N-(2'-aminoethylene)-1,4-diaminocyclohexane, N-(2'-aminoisopropylene)-4-aminocyclohexanol, N-(2-hydroxypyrimidyl-4)-aniline, N-cyclopentyl-1,4-diaminocyclohexane, cyclohexylmethylcyclohexylamine, N-(2'-thiazolyl)-1,2-diaminocyclopentane, 2-thiazolyl-4-pyrimidol-2-ylamine, dip-aminophenylamine, p-aminophenyl-4-methylcyclohexylamine, 4-methylcyclohexylphenylamine, p-amino-phenylethylenediamine, p-aminophenyl-3-aminocyclopentylamine, N-(2-hydroxy-1,4-pyranil)-p-aminoaniline, N-(3'-hydroxycyclohexyl)-p-aminoaniline, N-(2'-aminoethylene)-3,5-diaminopyridine, N-(3'-aminoisobutyl)-3-aminopyridol-5, 4-cyclohexylaminocyclopentanol-3, 4-hydroxyisothiazolyl-4'-methylcyclohexylamine, N-(3-amino-1,4-thiapyranil-5)-4'-methylcyclohexylamine, N-(3'-methylcyclopentyl)-1,4-diaminocyclohexane, N-(3'-cyclohexanol)-3,5-diamino-1,2,4-triazole, 4,4'-dicyclohexanolyamine, N-(3'-methylcyclohexyl)-4-aminocyclohexane, 4-cyclopentanoly-3-pyridolylamine, N-(2'-hydroxycyclohexyl)-1,4-diaminocyclohexane, 3'-aminocyclohexyl-3-aminopyridyl-5-amine, 3'-aminocyclohexylpyridol-3-yl-5-amine, di-2-amino-1,4-pyranil-4-amine, and N-(3'-hydroxy-1,4'-thiapyranil-5')-3,5-diamino-1,2,4-triazole.

The following specific examples are set forth to illustrate the preparation of the novel addition components suitable for addition to cyanide plating baths in accordance with the present invention.

EXAMPLE A

About 1 mol of 1-acetyl-2-thiohydantoin and one mol of ammonia (28% aqueous solution) are dissolved in three liters of ethanol and placed within a suitable reaction vessel. The resultant solution then is heated to boiling and refluxed for about 30 minutes. The solution then

5

is evaporated to about one liter in volume. The resultant product is a viscous slurry. It is cooled, filtered, and the separated crystals are air dried. The reaction product is a light brown, crystalline solid which darkens to a reddish brown on exposure to air. This reaction product, when added to cyanide copper plating baths, brings about an improved brightness in copper electrodeposited therefrom.

EXAMPLE B

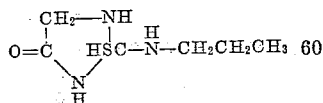
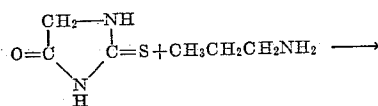
One mol of acetylthiourea is dissolved in 1.1 mols of n-propyl amine by heating the components in a suitable reaction vessel. Upon cooling, a solid reaction product crystallizes from the solution. The product obtained upon air drying is a white crystalline mass suitable for addition to a cyanide metal electrolyte for the purpose of bringing about improved brightness of metal electrodeposited therefrom. The product has a melting point of 170°–173° C. The melting point of this product when admixed with acetylthiourea, is 126° C.

EXAMPLE C

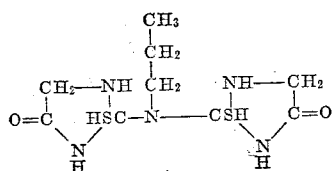
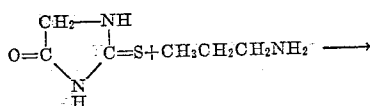
One mol of 1-acetyl-2-thiohydantoin and 1.1 mols of diethylamine are dissolved in 2 liters of ethanol, and the mixture is heated to reduce it in volume to about 500 ml. Upon cooling, a reddish-brown, tar-like product crystallizes out of the solution. The crystals are washed with alcohol to remove viscous material leaving a yellow crystalline product suitable for addition to a cyanide metal plating bath. This product melts at 229°–235° C.

EXAMPLE D

0.2 mol of 2-thiohydantoin was slurried in 500 ml. of ethanol and 0.22 mol of n-propylamine were added thereto in a suitable reaction vessel. The mixture was refluxed for one hour at which time all of the solids were in solution. The reaction mixture was cooled in an ice bath and filtered. 8.9 gms of a white, plate-like crystalline product was recovered. The filtrate was evaporated to 100 ml. and allowed to cool at which time brown plates of the reaction product crystallized. Upon filtration, 18.9 gms were recovered. The second crystalline material was dissolved in boiling ethanol, 5 grams of carbon were added thereto, and the mixture maintained at a temperature just under its boiling point for about 5 minutes. The hot mixture was filtered and cooled in an ice bath whereupon a light pink colored product crystallized from the solution. The crystals were filtered and air dried. When heated, a portion of the light pink crystals melted at 119°–120° C., and the remainder did not melt until a temperature of 139°–140° C. was reached. It is believed that the crystalline product is a mixture of two reaction products comprising the mono- and di-hydan-



and



6

EXAMPLE E

One mol of 2-thiobarbituric acid, three mols of dimethylamine and three mols of diethylamine are heated in a suitable flask to the boiling point and refluxed for one hour. The resultant mixture is cooled in an ice bath, filtered, and air dried. The crystalline product obtained is suitable for addition to a cyanide metal plating bath.

EXAMPLE F

Equimolar quantities of 2-thiohydantoin and 2-aminothiazol were slurried in ethanol and heated to boiling. The reaction mixture was refluxed for one-half hour, cooled, and filtered. The red crystalline, needle, reaction product melted at 235°–237° C. This reaction product when added to cyanide copper plating baths, brings about an improved brightness in copper electrodeposited therefrom.

EXAMPLE G

Two mols of 2-thiohydantoin and one mol of methanediamine were heated to boiling in ethanol. The reaction mixture was boiled down to 40% of its original volume, cooled, and filtered. A brown-colored crystalline reaction product was recovered which melted at 227°–229° C.

EXAMPLE H

An equimolar mixture of pyridine and 2-thiohydantoin was refluxed in ethanol for one-half hour. The reaction mixture was boiled until its volume had been reduced 50%. It then was cooled, filtered, and air dried. A yellow-brown crystalline reaction product was recovered which melted at 231°–232° C.

Electrodeposits of improved brightness are obtained when the novel addition agents of this invention are employed in cyanide metal plating baths in concentrations within the range of from about 0.005 to 0.50 ounces per gallon. Particularly satisfactory results are obtained when the addition components are incorporated in amounts within the range of from about 0.02 to about 0.08 ounce per gallon.

A metal such as copper may be plated from a cyanide electrolyte containing the addition agent of this invention by means of a periodically reversed electrical current. The current flow through the member being plated is composed of cycles, each of which first passes the electrical current through the member for a period of time of from about 0.01 second to 100 seconds to plate copper on the base member and then reverses the direction of flow of the current to deplate a portion of the previously plated copper. The time and the magnitude of the deplating current is such that it applies from about 8% to 90% of the coulombs applied during the previous plating period. Assuming 100% efficiency during the deplating period, this means that from 8% to 90% of the copper deposited during the previous plating period in each cycle is deplated. The increment of copper remaining on the base after the cycle consists of smooth, sound copper upon which a second layer of copper is plated by the plating portion of the next cycle of periodic reversed current. A portion of this second increment then is deplated by the passage of deplating current leaving a second increment of still smoother copper than the first increment, and so on with additional cycles.

Referring to FIG. 1 of the drawing, a graph is shown illustrating one type of periodic reverse current as it is applied to the plating of a given base member. Such periodic cycles may be produced by periodically reversing the flow of uniform direct current. It is assumed that the base member when first immersed in the electrolyte is at a zero potential so that no current flows. When the first cycle of periodically reversed current is applied, a cathodic or plating current of a density of the value A is applied and metal is plated for a period of time X to a point B. Then the direction of flow of the current is re-

versed so that the current density in the member drops from the value B to zero and then becomes anodic and will deplate copper, reaching a deplating current density of C. Metal is deplated for a period of time Y, which is about at least $\frac{1}{12}$ of the length of period X, at the current density of C to D until sufficient coulombs of deplating current have been applied to equal from about 8% to 90% of the coulombs applied during the plating period X. The cycle A—B—C—D deposits an increment of sound, smooth copper on the base. The direction of current flow is again reversed from D through zero and then plating current of a density value of F is applied to begin another cycle which will plate a second increment of copper.

It may be understood that the showing in FIG. 1 is merely schematic and that the current density is not necessarily uniform from A to B or C to D, as shown, but will usually vary and be relatively non-uniform. Also, in reversing from B to C and from D to F the time required is finite and these lines will not be vertical, as shown, but will take an appreciable period of time, depending upon the various factors involved in the plating installation. The deplating or anodic current density C—D may be equal to the plating current density A—B, or exceed it or may be as low as 8% of the plating current density. Reference should be had to Patents 2,451,341, 2,678,909 and 2,470,775 for additional information as to periodic reverse current cycles.

Referring to FIG. 1 of the drawing, there is illustrated an apparatus 10 suitable for practicing the present invention. This apparatus comprises a tank 12 carrying an electrolyte 16 composed of, for example, dissolved copper, free alkali cyanide, alkali and the addition agent as described herein. Disposed within the electrolyte is an anode 18 composed of copper. The anode 18 is suspended by a support 19 from a conductor bar 20. A base member 22 to be plated with copper is suspended by a support 24 from a second conductor bar 26. The conductor bars 20 and 26 are provided with electrical current from a suitable source 28 which may be a generator capable of delivering periodic reversed current, or a direct current supply source such as a rectifier, storage batteries or the like equipped with suitable current reversing devices. Periodically reversed electrical current passing from the source 28 to the conductor bars 20 and 26 passes through the anode 18, electrolyte 16 and the member 22 causes a net deposit of copper to be deposited from the electrolyte upon the base.

The addition agents of this invention will cause bright copper to be deposited over an extremely wide range of current densities. Unlike other organic brighteners, the use of the addition agents of the present invention does not result in the formation of pits or discolorations in the deposited copper.

In order to indicate even more fully the advantages and capabilities of the present invention, the following specific examples are set forth to illustrate the utilization of the novel addition agents of this invention in cyanide metal plating baths.

Example I

An aqueous electroplating electrolyte of the following composition was prepared:

	Oz./gal.
Copper	8.0
KOH	4.3
Free KCN	1.2
Reaction product of 1-acetyl-2-thiohydantoin and diethylamine (Example C)	0.05

This bath was operated at temperatures of from 175° F. to 185° F. with excellent results. Bath temperatures of about 180° F. appeared to give optimum plating results.

Copper was plated on rectangular steel panels from the

bath using a periodic reverse current having the following successive cycles:

	Plating time, seconds	Deplating time, seconds	Reverse amperes (percent of Plating amperes)
(a)	2	$\frac{1}{4}$	100
(b)	5	1	100
(c)	20	7	50
(d)	28	38	50
(e)	60	45	70
(f)	60	55	50
(g)	60	55	75

The current density during each plating portion of the cycles varied from 30 to 200 amperes per square foot. The periodic reverse current cycles in each case produced excellent smooth deposits of bright copper which were better than anything secured under the same conditions using certain of the best known addition agents in the art.

Example II

Example I was repeated using as the brightener 0.02 ounce per gallon of the reaction product of 1-acetyl-2-thiohydantoin and ammonia (Example A) instead of the reaction product of Example C. The plating solution produced copper deposits over a much wider bright range than is possible in the absence of the brightener. Equally satisfactory brass plating may be achieved using a brass plating bath and this particular brightener.

Example III

Example I was repeated using as the brightener 0.1 ounce per gallon of the reaction product of acetylthiourea and n-propylamine (Example B) instead of the reaction product of Example C. The plating solution produced extremely bright copper deposits on base members and required no additional color buff.

Equally satisfactory silver plating is obtainable using a silver plating bath and the brightener of this Example III.

Example IV

An aqueous bath of the following composition was operated at 180° C. to plate steel panels as described in Example I.

	Oz./gal.
Copper	6.7
NaOH	5.2
Free NaCN	1.48
Zinc oxide	0.4
Sodium cyanide	
Sodium thiocyanate	
Lithium hydroxide	
Reaction product of 2-thiohydantoin and n-propylamine (Example D)	0.05

This plating bath produced copper deposits as bright as Example I and the deposits were leveled.

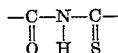
The addition agents of this invention are compatible with and suitable for use in conjunction with certain aryl sulfonates conventionally used in the plating industry. These agents may be used in alkali cyanide baths employed for plating gold, silver, copper, bronze, brass, zinc and cadmium. These baths will contain at least 0.5 ounce per gallon of alkali hydroxide and free cyanide.

While the present invention has been described with particular reference to preferred embodiments thereof, it will be understood, of course, that certain changes, substitutions, modifications and the like may be made therein without departing from its true scope.

We claim as our invention:

1. A process for preparing a metal electrodeposition solution which comprises mixing together in an aqueous medium a soluble compound of a metal selected from the group consisting of gold, silver, copper, bronze, brass, zinc and cadmium, an alkali cyanide in an amount suf-

ficient to provide at least about 0.5 ounce per gallon of alkali hydroxide and free cyanide, and from 0.005 to 0.5 ounce per gallon of the product obtained by reacting substantially equimolar quantities of at least one compound having the nucleus



with at least one compound selected from the group consisting of (A) monocyclic unsubstituted aromatic compounds containing in the ring structure from 4 to 6 carbon atoms and from 1 to 2 nitrogen atoms per molecule and (B) amines having the formula



wherein R is a radical selected from the group consisting of hydrogen, not more than one R being hydrogen; monovalent and divalent saturated aliphatic hydrocarbon radicals having from 1 to 4 carbon atoms and in which the substituents are selected from the group consisting of —NH₂ and —OH radicals; monovalent and divalent alicyclic radicals containing from 5 to 6 carbon atoms in the ring in which the substituents are selected from the group consisting of —CH₃, —NH₂ and —OH radicals; monovalent and divalent heterocyclic radicals having from 5 to 6 carbon atoms in the ring and in which hetero atoms occur only in the ring structure and the substituents occur only on the carbon atoms and are selected from the group consisting of —NH₂ and —OH radicals; phenyl radicals; and aminophenyl radicals.

2. A process for preparing a metal electrodeposition solution which comprises mixing together in an aqueous medium a soluble compound of a metal selected from the group consisting of gold, silver, copper, bronze, brass, zinc and cadmium, an alkali cyanide in an amount suf-

ficient to provide at least about 0.5 ounce per gallon of alkali hydroxide and free cyanide, and from 0.005 to 0.5 ounce per gallon of the product obtained by reacting substantially equimolar amounts of 1-acetyl-2-thiohydantoin in an alcoholic medium with at least one compound selected from the group consisting of (A) monocyclic unsubstituted aromatic compounds containing in the ring structure from 4 to 6 carbon atoms and from 1 to 2 nitrogen atoms per molecule and (B) amines having the formula



15 wherein R is a radical selected from the group consisting of hydrogen, not more than one R being hydrogen; monovalent and divalent saturated aliphatic hydrocarbon radicals having from 1 to 4 carbon atoms and in which the substituents are selected from the group consisting of —NH₂ and —OH radicals; monovalent and divalent alicyclic radicals containing from 5 to 6 carbon atoms in the ring in which the substituents are selected from the group consisting of —CH₃, —NH₂ and —OH radicals; monovalent and divalent heterocyclic radicals having from 5 to 6 carbon atoms in the ring and in which hetero atoms occur only in the ring structure and the substituents occur only on the carbon atoms and are selected from the group consisting of —NH₂ and —OH radicals; phenyl radicals; and aminophenyl radicals.

References Cited in the file of this patent

UNITED STATES PATENTS

2,451,341	Jernstedt	Oct. 12, 1948
2,739,933	Ceresa	Mar. 27, 1956
2,777,810	Ostrow	Jan. 15, 1957
2,853,443	Harrover	Sept. 23, 1958