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3,732,151

COPPER PLATING

Charles N. Abbott, Dayton, Ohio, assignor to Dayton
Bright Copper Company, Dayton, Ohio

No Drawing. Continuation-in-part of application Ser. No.
679,971, Nov. 2, 1967. This application Apr. 27, 1970,
Ser. No. 32,409

The portion of the term of the patent subsequent to
Mar. 12, 1985, has been disclaimed

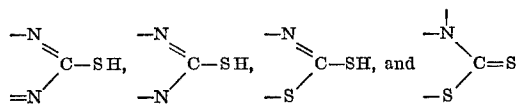
Int. Cl. C23b 5/20, 5/46

U.S. Cl. 204—52 R

6 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to improved extender compositions used in copper electroplating comprising a mixture of a sulfurized sulfonated aromatic or hydroaromatic hydrocarbon, or substitution product thereof; an amino derivative of a triarylmethane; and as a leveling agent a compound containing a radical selected from the group consisting of

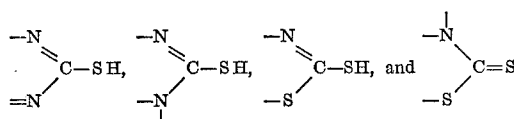


The combination of the three types of ingredients gives an additive composition of a synergistic character when used in copper plating in the form of improved brightness and leveling over a wider range of current density than previous additive compositions, and are particularly improved with respect to leveling.

FIELD OF THE INVENTION

The present application is a continuation-in-part of my Ser. No. 679,971, filed Nov. 2, 1967, now abandoned.

My invention relates to the electroplating of copper on metal bases from acidic electrolyte solutions, and to compositions for use therein. More particularly, it relates to the production of copper plated objects of improved physical characteristics by the incorporation in the plating composition of addition agents containing a grouping selected from the following:



Especially advantageous results are obtained by the use of leveling agents of the above character with other materials including a sulfurized sulfonated aromatic or hydroaromatic hydrocarbon, or substitution products thereof, and an amino derivative of a triarylmethane.

PRIOR ART

The plating of base metals with copper prior to plating with other metals has frequently been found advisable or necessary in order to obtain metal finishes having particular characteristics. In order, however, to obtain satisfactory coatings of the final metal it is essential to have on the base metal an initial plate or coating of copper of suitable characteristics. It is, for example, highly important that the copper plate adhere well to the base metal, and that a smooth, bright uniform surface be obtained, and also that the copper plate possess suitable ductility. A rough surface, or one produced under plating conditions which produce burning or treeing will not usually give a satisfactory secondary plate.

It has been found that when copper plating from an acidic electrolyte the incorporation in the electrolyte bath

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of certain addition agents greatly improves the characteristics of the copper plate and makes the latter more suitable for secondary plating with other metals. Various types of such addition agents have been used for the purpose of giving smooth, bright or semi-bright deposits of copper. Examples of such addition agents previously used include urea, thiourea and derivatives thereof, casein, sugar, glue and other materials of similar character. While these and many of the other additives previously tried have been found to give some of the desired characteristics to the copper plate, such as, for example, brightness or semi-brightness, the resulting deposits have generally been found to be subject to various defects such as brittleness, lack of uniformity, etc. Also, the plating operations using such addition agents have been difficult to carry out without incurring detrimental effects such as burning or treeing, and closer regulation of the plating temperature and other operating conditions such as current density have been necessary in order to obtain satisfactory results. In addition, the percentage of rejects is frequently high, thus increasing the cost of operation.

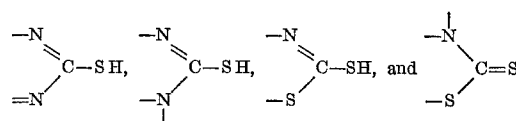
Attempts have also been made in the past to use mixtures of additives in order to neutralize or overcome the defects resulting from the use of single additives. Such attempts, however, have not been very successful since the use of such mixtures has usually magnified instead of reducing both operating problems and the defects in the resulting copper plates.

SUMMARY AND OBJECTS

Applicant has discovered a new type of additive composition for copper plating operations consisting of a mixture of agents which gives copper deposits of improved properties and which at the same time permits the plating operation to be carried out without experiencing many of the difficulties experienced with previously known types of additives. The incorporation in this additive composition of thiol or thion compounds of the type designated above has given especially good leveling characteristics, with the result that much less buffing of the copper deposit is required than has been necessary with previously known types of additives. This is of particular importance in reducing that cost of preparing plates for secondary plating. The copper plates obtained with my new additive compositions have excellent brightness, and ductility, thus improving their suitability for secondary plating. Of equal, if not greater importance, is the fact that the use of my new additive compositions permits the plating operation to be satisfactorily carried out over a wider operating range than is possible with previous types of additives, thus reducing the percentage of rejects as well as overall operating costs.

DESCRIPTION

My new additive compositions for use in copper electroplating electrolytes essentially comprise a mixture of sulfurized sulfonated aromatic or hydroaromatic hydrocarbons, or substitution products thereof; amino derivatives of a triarylmethane; and a thiol or thion containing a grouping selected from the following:



The sulfurized sulfonated aromatic or hydroaromatic hydrocarbon, or substitution products thereof, have been previously described and used as brightening agents in copper electroplating compositions in U.S. Pat. No. 2,424,887, granted July 29, 1947. However, as previously noted, the use of such material alone appears to affect only the

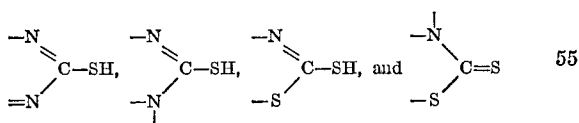
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brightness of the deposits of copper and, in addition, its use is accompanied by certain operating difficulties. Applicant has discovered that when used in his claimed composition, these compositions serve their function as brighteners in an effective manner without the attendant difficulties incurred when the materials are used alone. Of importance also is the fact that much less of the material is required when used in my claimed composition.

A wide range of sulfurized sulfonated aromatic or hydroaromatic hydrocarbons, or substitution products thereof, can be satisfactorily used in my new additive compositions, when soluble to the specified degree in the plating solution. Examples of suitable compounds of this type include sulfurized sulfonated benzene, sulfurized sulfonated toluene, sulfurized sulfonated xylenes, sulfurized sulfonated naphthalene, sulfurized sulfonated anthracene, sulfurized sulfonated phenanthrene, sulfurized sulfonated diphenyl, and substitution derivatives of the same. These materials comprise the colloidal sulfonated reaction products of an aromatic or hydroaromatic hydrocarbons, or substitution products thereof, with a sulfurizing agent such as, for example, sulfur chloride, sulfur chloride or thionyl chloride. The sulfurized sulfonated aromatic or hydroaromatic hydrocarbons, or substitution derivatives thereof, may be sulfonated by conventional means, as by fuming sulfuric acid. Or, the sulfonation may first be effected and followed by sulfurization. The product in either case is water soluble or water dispersible. Sulfurized sulfonated benzene suitable for use in the present invention may, for example, be produced by sulfonating 112 g. of benzene with 350 g. of oleum by conventional means and then sulfurizing the resulting mixture with 3 g. of sulfur monochloride by conventional means.

The amino derivatives of triarylmethane are dyestuffs soluble in the plating solutions to the specified amounts. Suitable amino derivatives of this type include dyestuffs commonly known as Guinea Green B, Brilliant Milling Green B, Patent Blue V, Light Green SFA, Neptune Blue, Erioglycine or Alphazurine F.G., Chromoxane Brilliant Violet 5R, Soluble Blue, Methyl Blue or Helvetia Blue, Brilliant Indocyanine 6B, Acid Violet 6B, and Wool Fast Blue FBL. The structural formulae and properties of these dyestuffs are shown in "The Chemistry of Synthetic Dyes and Pigments" by Herbert A. Lubs, published in 1955 in New York by Rheinhold Publishing Company, and in other reference books.

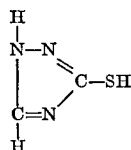
The addition agents, serving primarily as leveling agents, used in my additive compositions are thiol and thion compounds containing a grouping selected from the following:



These compounds and methods of producing same are well known in the art.

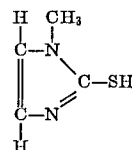
The following are examples of typical compounds of the above types which have given excellent results as leveling agents in my new additive compositions for copper plating:

(1) s-Triazole-3-thiol

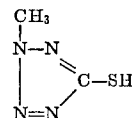


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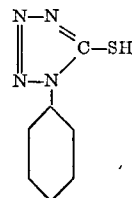
(2) 1-methylimidazole-2-thiol



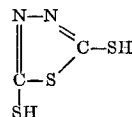
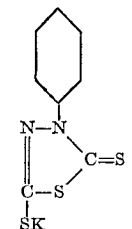
(3) 2-methyl-2H-tetrazole-5-thiol



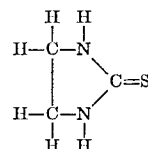
(4) 1-phenyl-1H-tetrazole-5-thiol



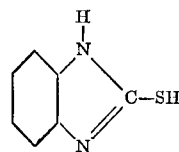
(5) 1,3,4-thiadiazole-2,5-dithiol

(6) Δ^2 -1,3,4-thiadiazoline-5-thion, potassium derivative

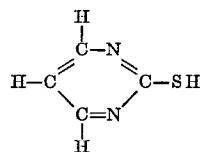
(7) 2-imidazolidinethione



(8) Benzimidazolethiol



(9) 2-pyrimidinethiol



Examples of methods of producing the compounds of the above type may include the following:

- (1) 2-benzimidazolethiol.—A mixture of 32.4 gms. of o-phenylenediamine, 52.8 gms. of potassium ethyl xanthate, 300 ml. of 95% ethanol and 45 ml. of water is heated under reflux for 3 hours. The resulting product is cooled to 60–70° C., and 300 ml. of warm water added, and then 25 ml. of acetic acid in 50 ml. of water is added and the resulting product filtered and dried.

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(2) 2-imidazolidinethione.—A mixture of 120 gms. of 92% ethylenediamine, 300 ml. of 95% ethanol and 300 ml. of water is placed in a flask provided with a reflux condenser. Carbon disulfide (121 ml.) is then slowly added while maintaining the temperature at 60° C. After all of the carbon disulfide has been added, the temperature is raised to 100° C. and the mixture is refluxed for one hour. Then 15 ml. of concentrated hydrochloric acid is added and the mixture is refluxed under good hood (bath at 100° C.) for 9–10 hours. The mixture is then cooled in an ice bath and the product filtered off and washed with 200–300 ml. of cold acetone.

My new leveling agents of the above types can be used in plating compositions with satisfactory results in concentrations ranging from 0.00005 to 0.1 g./l., although I prefer to use concentrations ranging from 0.0001 to 0.04 g./l. When used in combination with the other additives described herein, the sulfurized sulfonated aromatic or hydroaromatic hydrocarbons, or substitution products thereof, are used in amounts ranging from 0.0015 to 0.5 g./l., and preferably within the range of 0.01 to 0.04 g./l. The concentration of the amino derivative of triarylmethane used can vary between 0.001 and 2.0 g./l., with a preferred range of 0.015 to 0.5 g./l.

I have found that when using combination additives of the above type, smaller quantities of additives are required to give copper plates having physical properties of materially improved physical characteristics over those obtainable with previously known additives or combinations of additives for copper plating. I have found that not only can copper plates of greatly improved physical characteristics be obtained by the use of my new additive compositions but that improved results can be obtained over a wider range of operating conditions, as well as with smaller amounts of additives than previously possible. I obtain improved results by adding to a copper electrolyte of the conventional type from 0.00005 to 0.1 g./l. of the above leveling agent and the specified amounts of one of each of the other types of addition agents described above. Using such additive compositions and a current density ranging from 5 to 300, and even higher, amperes per square foot, and with the temperature of the electrolyte at 20 to 40° C., but preferably within the range of 24 to 30° C., I have produced semi-bright to bright deposits of copper on base metals which were suitable for nickel plating without the necessity of buffing or polishing or otherwise pre-treating the copper plate prior to nickel plating. The use of the above-designated addition agents in the plating composition is particularly effective in producing copper plates of improved leveling characteristics, with the result that the subsequently plated deposits were more nearly perfect. The copper deposits were quite resistant to corrosion, yet ductile and easily buffed in the relatively few instances where this was necessary or desirable. The fine grain deposits of copper were normally obtained over a wide range of current density without the hazard of burning or tree formation. An additional advantage in the use of my new additive compositions is that the improved results described above are obtainable at substantially reduced costs, as well as with fewer breakdown products in the bath, resulting in fewer purifications being required.

Electroplating tests were carried out with my new additive compositions in a 300 ml. Hull cell with air agitation at temperatures ranging from 20 to 40° C., using amounts of the additives specified above, and for comparison purposes, equivalent amounts of additives customarily used in the industry. It was uniformly found that my new additive compositions not only permitted the use of smaller amounts of additives but in addition, these reduced amounts gave copper plates of smaller grain structure, of increased resistance to corrosion, and increased ductility. The plates were also more uniform in appearance, more level, of improved brightness and substantially free from burning and tree formation and other irregular-

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ities, even when plated with high current densities ranging from 5 to 300 amperes/sq. ft., and even higher.

It has been found that the use of my new additive compositions in an acid electrolyte of the type customarily used in the industry permitted a 10% increase in current density without encountering the usual burning or treeing effect at the edges of the workpiece. At the same time, the overall bright plating range was increased and the deposits of the copper were of a more even, uniform lustre than when using conventional copper electrolytes containing conventional additives. It was further observed that finished chrome plated products, e.g., plated 20 minutes in an acid copper electrolyte bath, followed by 12 minutes in a nickel sulfate bath and then chrome plated, were far superior in color and appearance and more level than a similar plate obtained using the same process cycle and a conventional type additive.

The following specific examples are illustrative but not limitative of my invention, it being understood that similar improved results are obtainable with other combinations of the different ingredients of my new additive compositions specified above.

EXAMPLE 1

A steel panel was plated for one-half hour at 80° F. at a current density of 60 amperes/sq. ft. in an aqueous electroplating electrolyte of the following composition:

	G./l.
Copper sulfate	225
Sulfuric acid	60
Sulfurized sulfonated benzene	0.05
Light Green SFA dye	0.03
s-Thiazole-3-thiol	0.0003

The resulting copper plated panel was of excellent brightness, possessed excellent ductility and leveling, and was free from surface defects.

EXAMPLE 2

In this experiment, carried out as described in Example 1, the electrolyte had the following composition:

	G./l.
Copper sulfate	225
Sulfuric acid	60
Sulfurized sulfonated toluene	0.05
Acid fast Violet dye	0.03
1-methylimidazole-2-thiol	0.0001

The plating results were similar to those of Example 1.

EXAMPLE 3

In this experiment, carried out as described in Example 1, the electrolyte had the following composition:

	G./l.
Copper sulfate	225
Sulfuric acid	60
Sulfurized sulfonated xylene	0.05
Patent Blue V dye	0.03
2-methyl-2H-tetrazole-5-thiol	0.00025

The plating results were similar to those obtained in Example 1.

EXAMPLE 4

In this experiment, carried out as described in Example 1, the electrolyte had the following composition:

	G./l.
Copper sulfate	225
Sulfuric acid	60
Sulfurized sulfonated naphthalene	0.05
Neptune Blue dye	0.02
1,3,4-thiadiazole-2,5-dithiol	0.0003

The plating results were similar to those obtained in Example 1.

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EXAMPLE 5

In this experiment, carried out as described in Example 1, the electrolyte had the following composition:

	G./l.	
Copper sulfate -----	225	5
Sulfuric acid -----	60	
Sulfurized sulfonated diphenyl -----	0.05	
Methyl Blue -----	0.05	
Benzimidazolethiol -----	0.0003	10

The plating results were similar to those obtained in Example 1.

EXAMPLE 6

In this experiment, carried out as described in Example 1, the electrolyte had the following composition:

	G./l.	
Copper sulfate -----	225	15
Sulfuric acid -----	60	
Sulfurized sulfonated benzene -----	0.05	
Methyl Blue -----	0.03	20
2-pyrimidinethiol -----	0.0003	

The plating results were similar to those obtained in Example 1.

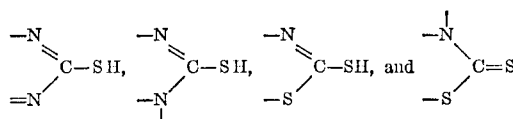
In order to obtain satisfactory plating results, it has been found to be necessary to use all three of the constituents of my new additive composition set forth above. When using only the sulfurized sulfonated aromatic or hydroaromatic hydrocarbon and a dye of the specified type, a low level of brightness and a narrow brightness range in relation to current density, with very poor leveling, is obtained. When using only a dye of the specified type and the new leveling agent of the present application, only semibright deposits with very little leveling and only in low current areas were obtained. When using only a sulfurized sulfonated aromatic or hydroaromatic hydrocarbon and the above described leveling agent, substantially the same results were obtained as when using only a sulfurized sulfonated aromatic hydrocarbon and a dye of the specified type, that is, only semi-bright deposits with little or no leveling were obtained. While it may be found desirable to vary the amounts of the three constituents within the ranges specified above in order to obtain particular desired results, it is only when all three constituents are used, and within the ranges specified above, that the most desirable results are obtained. From this it will be seen that the results obtained from the use of the three constituents of my new additive composition are in no sense merely additive but, in fact, are of a synergistic character and are not predictable from any knowledge of the results obtained from the use of the individual constituents alone or in any combination thereof other than the claimed combination.

While the invention has been described and specific examples of suitable electroplating baths and conditions for obtaining the improved plating results aforementioned set forth, it will be understood that changes and substitutions can be made by those skilled in the art without departing from the scope of the described invention. For example, acid copper compositions made from copper salts other than copper sulfate can be used. Likewise, different concentrations of copper salts and sulfuric acid may be used. Also, other additives may be incorporated in the composition. Any of the various ingredients shown in the specific examples can be substituted by the specified amounts of any of the other specified additives so long as they are soluble in the electrolyte to the specified extent.

What is claimed is:

1. A bath for the electrodeposition of copper comprising an aqueous acidic copper plating bath containing dissolved therein 0.0015–0.5 g./l. of a sulfurized sulfonated aromatic or hydroaromatic hydrocarbon, or substitution product thereof, 0.001–2.0 g./l. of an amino derivative of triarylmethane, and 0.0005–0.1 g./l. of a compound containing a 5- or 6-member heterocyclic ring containing a radical selected from the following:

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2. Bath for the electrodeposition of copper according to claim 1, wherein said bath contains 0.0005–0.1 g./l. of a compound containing a 5- or 6-member heterocyclic ring selected from the group consisting of s-triazole-3-thiol, 1-methyl-imidazole-2-thiol, 2-methyl-2H-tetrazole-5-thiol, 1,3,4-thiadiazole-2,5-thiol, benzimidazolethiol, 2-pyrimidinethiol, 1-phenyl-1H-tetrazole-5-thiol, and Δ^2 -1,3,4-thiazoline-5-thione.

3. Bath for the electrodeposition of copper according to claim 1, wherein the sulfurized sulfonated aromatic or hydroaromatic hydrocarbon, or substitution product thereof is selected from the group consisting of sulfurized sulfonated benzene, sulfurized sulfonated toluene, sulfurized sulfonated xylene, sulfurized sulfonated naphthalene, sulfurized sulfonated anthracene, sulfurized sulfonated phenanthrene, sulfurized sulfonated diphenyl, and substitution products thereof.

4. Bath for the electrodeposition of copper according to claim 1, wherein the amino derivative of triarylmethane is selected from the group consisting of Guinea Green B, Brilliant Milling Green B, Patent Blue V, Light Green SFA, Neptune Blue, Erioglycine or Alphazurine F.G., Chromoxane Brilliant Violet 5R, Soluble Blue, Methyl Blue or Helvetia Blue, Brilliant Indocyanine 6B, Acid Violet 6B and Wool Fast Blue FBL.

5. Method for the electrodeposition of copper which comprises subjecting an electrically conductive base to electrodeposition of copper thereon in the bath of claim 1 at a current density of 5–300 amperes per square foot and temperature of 20 to 40° C. until the desired thickness of metallic copper is obtained.

6. Method for the electrodeposition of copper according to claim 5, wherein the bath has dissolved therein 0.0015–0.5 g./l. of a sulfurizer sulfonated aromatic or hydroaromatic hydrocarbon or substitution product thereof, selected from the group consisting of sulfurized sulfonated benzene, sulfurized sulfonated toluene, sulfurized sulfonated xylene, sulfurized sulfonated naphthalene, sulfurized sulfonated anthracene, sulfurized sulfonated phenanthrene, sulfurized sulfonated diphenyl, and substitution products thereof, 0.001–2.0 g./l. of an amino derivative of triarylmethane selected from the group consisting of Guinea Green B, Brilliant Milling Green B, Patent Blue V, Light Green SFA, Neptune Blue, Erioglycine or Alphazurine F.G., Chromoxane Brilliant Violet 5R, Soluble Blue, Methyl Blue or Helvetia Blue, Brilliant Indocyanine 6B, Acid Violet 6B and Wool Fast Blue FBL, and 0.0005–0.1 g./l. of a compound containing a 5- or 6-member heterocyclic ring selected from the group consisting of s-thiazole-3-thiol, 1-methyl-imidazole-2-thiol, 2-methyl-2H-tetrazole-5-thiol, 1,3,4-thiadiazole-2,5-thiol, benzimidazolethiol, 2-pyrimidinethiol, 1-phenyl-1H-tetrazole-5-thiol, and Δ^2 -1,3,4-thiazoline-5-thione.

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GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.