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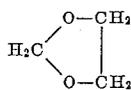
3,267,010
ELECTRODEPOSITION OF COPPER
FROM ACIDIC BATHS

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This invention relates to the electrodeposition of copper from aqueous acidic baths, especially from acidic copper sulfate and fluoborate baths. More particularly it relates to the use of certain organic compounds in the baths in new relationships which make possible bright, highly ductible, low stress, good leveling copper deposits.

While a rather large number of organic compounds have been proposed and used to decrease the grain size and increase the luster of the copper deposits from acidic baths, nevertheless, much remains to be desired from the standpoint of obtaining lustrous leveling copper plate without striations and ribbing and without substantially decreasing the very high ductibility of the copper plate from the acidic baths.

It has now been found that bath-soluble polymers of 1,3-dioxolane,



which have molecular weights greater than 296 and at least up to about 30,000, make possible smooth, low stress, ductile semi-bright copper plate that is free from striations, from acidic copper sulfate or acidic copper fluoborate baths. For example, if about 0.1 gram/liter of a poly-1,3-dioxolane of average molecular weight of about 5,000 is added to an acid copper bath made up of 150 to 275 grams/liter of blue vitriol and containing about 3 to 70 grams/liter of sulfuric acid, a very smooth semi-bright copper plate is obtained within a current density range from the very lowest to the burning point or limiting current density, which with ordinary agitation is around 100 to 150 amps./sq. ft., but is higher with very rapid solution agitation. In the acidic fluoborate bath containing about 150 to at least 450 grams/liter of copper fluoborate and about 0.5 to at least 30 grams/liter of fluoboric acid, even higher current densities can be used at the same bath temperatures and the same excellent copper plate can be obtained with the addition of about 0.1 gram/liter of the poly-dioxolane of average molecular weight of about 5,000. With lower molecular weight polymers, for example about 400 to 1,000, larger concentrations up to at least 5 grams/liter should be used. With the higher molecular weight polymers, i.e., about 5,000 and higher, concentrations as low as about 0.01 gram/liter can be used with good results, especially when used in conjunction with other organic additives.

In contrast with other high molecular weight polymers, no striations or ribbing of the plate occurs from the use of these poly-dioxolanes, and it is not essential to have present in the bath concentrations of chloride or bromide ion of at least about 0.02 to 0.1 gram/liter.

It was further found that the 1,3-dioxolane polymers when used together in the acidic copper baths with very low concentrations of certain organic sulfide (thiols, thioethers, etc.) compounds carrying sulfonic groups such as those of Table I, enable the electrodeposition of smooth bright copper plate without decreasing appreciably the ductility of the copper deposits. The organic sulfide compounds carrying sulfonic groups illustrated in Table I when used alone in the baths in the low concentrations

of 0.0005 to 0.04 gram/liter or even up to 0.1 gram/liter do not produce any noticeable or significant brightness and require a concentration of at least 1 gram/liter to produce brightness when used alone, though even then they do not produce the highest brightness. For example, the sulfonated organic sulfides first described for use in acidic copper baths by Henricks U.S. Patent 2,424,887, July 29, 1947, such as thianthrene sulfonic acids, Example 4, Table I, and the phenyl disulfide sulfonic acids, Example 5, Table I, used in as low concentrations as 0.0005 to 0.01 gram/liter with about 0.05 to 0.2 gram/liter of the high molecular weight 1,3-dioxolane polymers cooperate to give bright ductile copper deposits. However, when sulfonated thianthrene, for example, is used alone, or with a similar sulfonated organic sulfide, in an acidic copper bath as shown in Example 8 of U.S. 2,424,887, it is necessary to use 1 to 2 grams/liter for brightness. In other words, when used in conjunction with the high molecular weight polymers of 1,3-dioxolane less than one hundredth of the concentration of thianthrene sulfonic acid is required than when it is used alone, and besides much better brightness is obtained. The same relationship of concentration holds true for the sulfonated phenyl di-sulfides, and other sulfonated organic sulfides illustrated in Table I.

The effectiveness of the extremely small quantity of the organic sulfide compounds of this invention when used in conjunction with the high molecular weight polymers of 1,3-dioxolane, or other polyether polymers described in greater detail hereinafter, has the unexpected important advantage that no harmful breakdown products are formed which tend to reduce the brightness, especially in the low current density area, even from extensive use of the baths. When, however, the concentration of the organic sulfide sulfonic acid compound is greater than about 0.04 gram/liter, then harmful breakdown products do form on extended electrolysis.

The 1,3-dioxolane though a 5-membered ring, can be converted into high molecular weight polymers in accordance with well-known polymerization procedures, namely by heating the dioxolane in the presence of an acidic catalyst until a polymer of the desired molecular weight has been obtained, which for this application is about 5,000. The best acidic catalyst for the polymerization of the dioxolane is the boron tri-fluoride type. The polymers of 1,3-dioxolane are polyethers consisting of alternating methylene and ethylene groups interrupted by oxygen atoms. The polymers of 1,3-dioxolane can be further reacted with many organic compounds having a reactive hydrogen atom, such as alcohols, glycols, sugars, aryl amines, chlorohydrins, amides, thiol compounds, alkanol sulfonic acids, nitriles, thio-aryl, and thio- and thiol-alkane sulfonic acids, alkanolamines, etc., and such bath soluble polymers which can be formed in which the portion of poly-1,3-dioxolane predominates, that is, constitutes over 50% of the molecular weight of the polymer, usually produce beneficial effects on the copper plate, and often improved results are obtained.

It was also found that the sulfonated organic sulfide compounds, that is the compounds of Table I, in the very low concentrations of 0.0005 to 0.01 gram/liter, below the concentration where brightness is discernible from these compounds, prevent the harmful striations and ribbing effects that polyethers such as the high molecular weight polyethylene ethanols and glycols (average molecular weight of 220 to at least 30,000) cause in the absence of at least 0.02 to 0.1 gram/liter of chloride or bromide ion. Not only are the striations and ribbing effects eliminated without the need of chloride or bromide ions, but just as had occurred with the poly-dioxolanes, a very bright deposit was also obtained. This was an unexpected

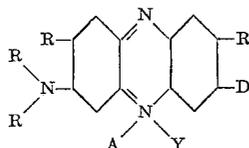
result, because with either material used alone in the bath, there is no indication of the remarkable enhancement of brightness which occurs when the two materials are used together. It will be appreciated that the elimination of the ribbing or striations effect is, in itself, an unexpected and important result, and this result is obtained with all of the compounds of Table I, though in the matter of obtaining the highest brightness, not all of the compounds of Table I are equally effective. Furthermore, polyethers such as polypropylene propanols and especially glycols of average molecular weight of about 290 to 1,000 which cause very severe striations especially with the higher molecular weight species, when used in concentrations of about 0.1 to 0.5 gram/liter were found to give no striations and even brighter plate than the high molecular weight polyethylene ethanols and glycols, when used similarly with the very low concentrations of the compounds of Table I. In general, with the low concentrations of the compounds of Table I, a large class of bath-soluble derivatives of polyethylene oxide or polypropylene oxide, or mixtures, can be used. Terminal groups other than the hydroxy group may be present on the polyether polymers of this invention, such as amino, chloride, bromide, sulfonic, mercapto, methoxy to heptoxy, naphthoxy, phenoxy, and chloro, bromo, nitro, methoxy and ethoxy substituted phenoxy groups, as well as small chain alkyl phenoxy groups where the alkyl group is less than 6 carbon atoms.

Otherwise stated, the class of polymers which are useful for the purposes of this invention, includes the polyether compounds containing at least six ether oxygen atoms and which are free from alkyl chains having more than 6 carbon atoms. It has been found that compounds containing alkyl chains of more than 6 carbon atoms tend to overfoam with air agitation but more importantly decrease the luster of the deposit, especially in the low current density areas.

In Table II are listed representative examples of the bath soluble polyether derivatives which can be used with the low concentrations of the compounds of Table I to give bright, ductile copper plate. The preferred compounds of Table II, besides the poly-dioxolane, from the standpoint of best cooperation with the compounds of Table I, to give smooth, striation-free, bright, ductile copper are the polypropylene propanols and glycols of average molecular weight of about 360 to about 1,000.

It was further found that if low concentrations (0.001 to 0.05 gram/liter) of the dye Janus Green B (see U.S. Patent 2,707,166, April 26, 1955) are used in conjunction with both of the above described additives of Tables I and II, the brightness and leveling is further improved and a very brilliant, high leveling, ductile copper plate is obtained over a much wider plating range, including the very low current density areas. This type of brilliance and extremely wide bright plate range is not obtained when the Janus Green B is used just with the organic sulfide compounds carrying sulfonic groups (the compounds of Table I), or when used just with the compounds of Table II. Also, the brilliance and ductility far exceed that obtained with Janus Green B type dyes used together with thiourea or such thiourea derivatives as acetyl or propionyl thioureas. (U.S. Patent 2,738,318, March 13, 1956.)

The dyes of the phenazine class (the Safranin type) and more especially the phenazine azo dyes (the Janus Green B type) which make possible the greatly improved leveling and extended bright plating range can be represented by the following formula.



where R is H, CH₃, or C₂H₅; A is H, CH₃, C₃H₇, C₃H₅, C₃H₃, C₄H₉, C₆H₅CH₂, C₆H₅C₂H₄, HOC₂H₄, HSC₂H₄, C₆H₅, CH₃C₆H₄, (CH₃)₂C₆H₃; Y is an anion from the group consisting of Cl⁻, Br⁻, SO₄⁻, HSO₄⁻, CH₃SO₄⁻, C₂H₅SO₄⁻, C₂H₅SO₃⁻, C₃H₇SO₃⁻, -O₃SCH₂SO₃⁻,



HOC₂H₄SO₃⁻, HSC₂H₄SO₃⁻; and D is H, CH₃, C₂H₅, OH, NH₂, N(CH₃)₂, N(C₂H₅)₂,



SH, and N=N-Z where Z=a coupling group, such as dimethyl aniline, aniline, phenylene diamine, and substituted anilines and phenylene diamines, naphthols and substituted naphthols, phenols and substituted phenols, thiazoles, benzothiazoles and aminobenzothiazoles, coupled to the azo linkage N=N.

The preferred phenazine dyes are the Janus Green B type (Diethyl Safranin Azo Dimethyl Aniline or Dimethyl Safranin Azo Dimethyl Aniline, C. I. Nos. 11045, 11050), or the Janus Black R type, also C. I. 11975 (Colour Index, Second Edition, vol. 3, 1956-57), as these compounds make possible the highest leveling and the widest bright plate range. The anions of these cationic dyes are in general not important for its maximum activity, though there is evidence for ion pairing and small anions that are not surface-active in wetting are desirable, but surface-active anions such as dodecyl sulfonic are not desirable and tend to precipitate the phenazine dyes.

When acid copper baths are used for plating steel or ferrous articles, such as automobile bumper bars, hub caps, printing rollers, etc., a preliminary copper or brass strike from a cyanide bath or a nickel strike from an acidic, pH of about 0.5 to 5, nickel plating bath, is first used to avoid poorly adherent immersion deposits. The acidic nickel strike (low chloride, high sulfate type to minimize drag-in of chloride ions into the copper bath) is often preferred because it is easier to control and easier to rinse and easier for waste disposal. The inorganic composition of the acid copper plating baths such as the acidic sulfate or acidic fluoborate may vary over rather wide limits, an actually much lower acid content may be used with the unique combination of additives of this invention than is present in the usual standard compositions. However, when very low acid contents are used, higher tank voltages are needed. In the examples listed below as illustrations of lustrous copper plating baths, the standard types of acidic copper sulfate and fluoborate baths are used for the inorganic compositions. However, other acidic copper plating baths such as copper methane sulfonates, copper methane disulfonates, copper ethane sulfonates, copper ethane disulfonates, copper propane sulfonates with excess acidity supplied by the free sulfonic acids, can be used with the combinations of additives of this invention to give highly lustrous plate.

With high, unlike with low concentrations of these sulfonate anions, the solubility of the phenazine dyes is greatly decreased, due to ion pairing.

Many inorganic cations which do not plate out from the normal acidic copper plating baths, may be present in concentrations as high as at least 25 grams/liter without detrimental effects, for example, ferrous, nickel, cobalt, zinc and cadmium cations. Chloride and/or bromide anions should in general be kept below about 0.1 gram/liter, and preferably below about 0.02 gram/liter. Air agitation or cathode-rod agitation, or solution agitation and cathode-rod agitation is desirable for highest speed plating and optimum results. The best bath temperatures are 25-30° C., though lower or higher (even up to 50° C. in some cases) temperatures can be used.

In Table I, the various organic sulfide sulfonic compounds may have various substituting groups such as methyl, chloro, bromo, methoxy, ethoxy, carboxy and hydroxy on the molecules especially on the aromatic and

heterocyclic sulfide sulfonic acids without fundamental changes in brightness. The organic sulfide sulfonic acids of Table I can be added to the baths as the free acids, or the alkali metal salts, or the organic amine salts such as the triethanolamine, guanidine, aminoguanidine, phenyl-guanidine, ethylene diamine and pyridine salts. In most cases it is preferred to use the free acids.

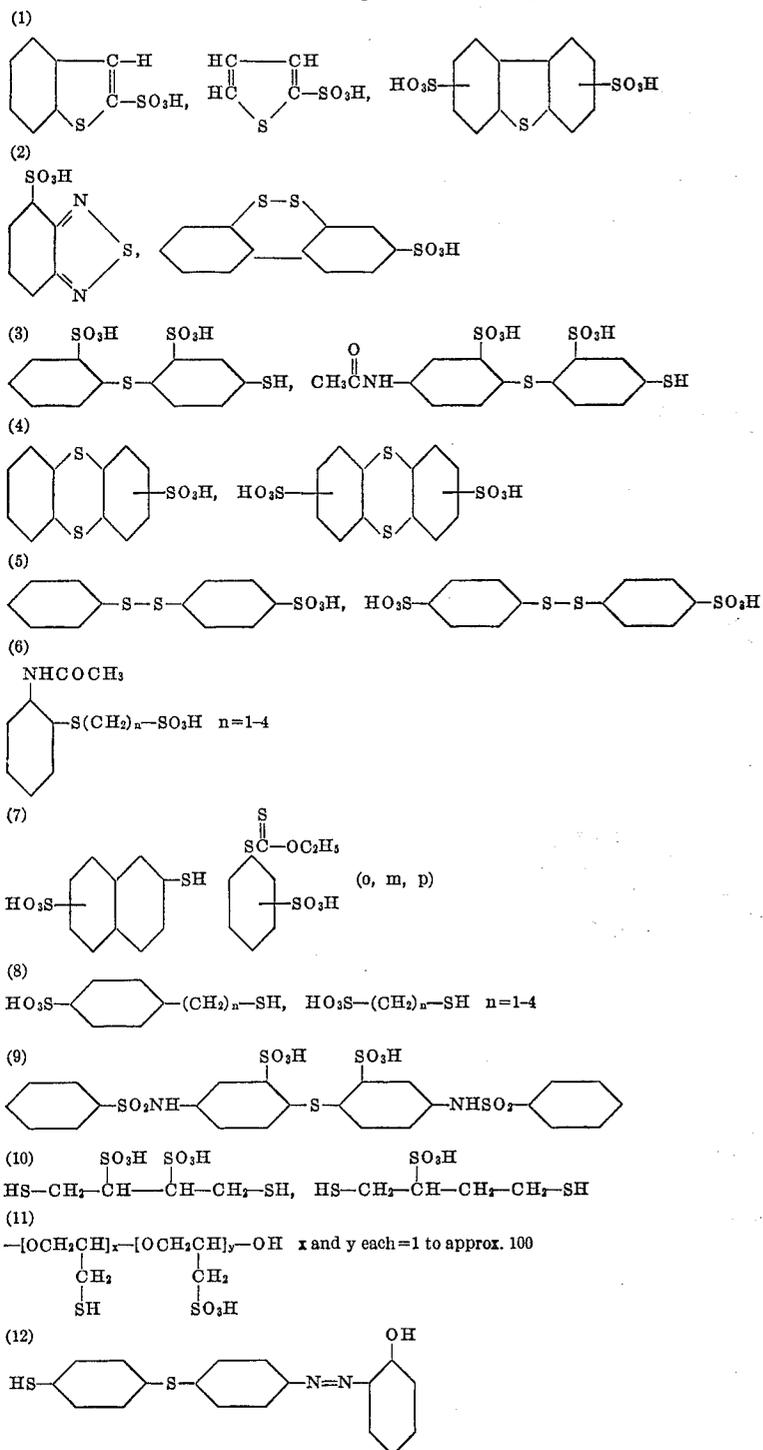
With the use of the combination of additives from Tables I and II and the combinations with the phenazine dyes, especially the Janus Green B types, it is preferred not to use surface-active agents, even though such anionic types as sodium octyl sulfate, sulfonated non-ionic types

such as Triton 720 (U.S. Patent 2,489,538, November 29, 1949), and similar materials, or polyoxy non-ionic wetting agents, have often been previously used in acidic copper plating baths with good results, they are not needed in the present type baths.

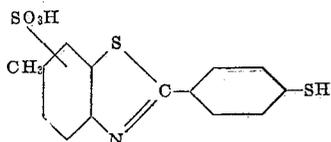
Below is a list of a number of acid copper plating baths for producing highly ductile, lustrous copper deposits. Baths A and B do not give as bright plate as the rest of the baths which employ combinations of addition agents. The highest brilliance, widest bright plate range, and best leveling is obtained with the baths using Janus Green as one of the brighteners.

TABLE I.—SULFONATED ORGANIC SULFIDES

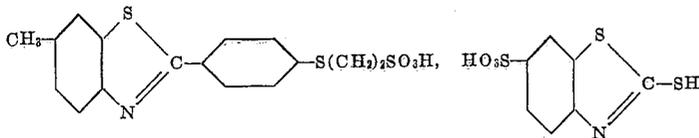
[Concentration range 0.0005 to 0.04 grams/liter when used with the compounds of Table II]



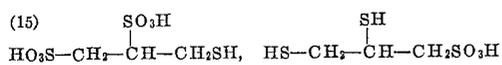
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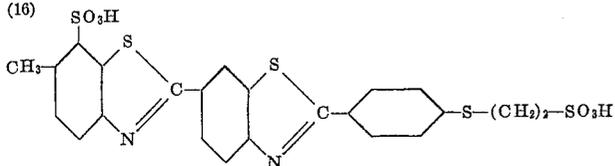
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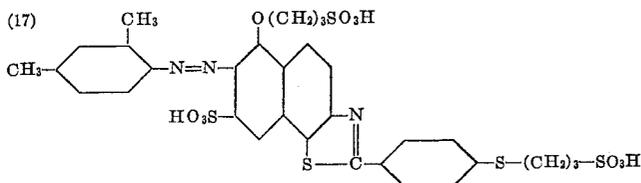
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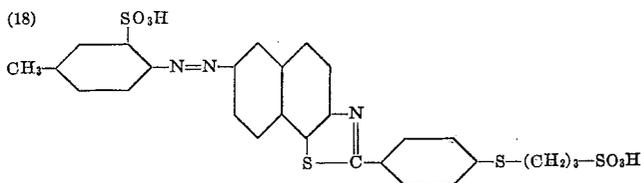
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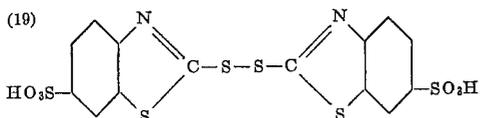
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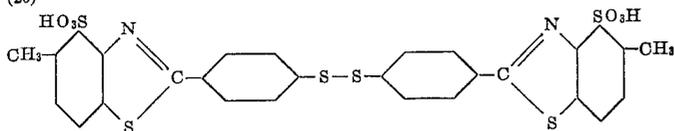
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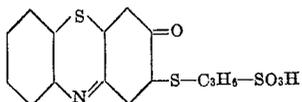
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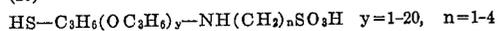
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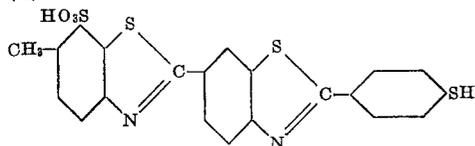
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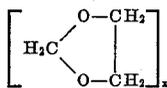
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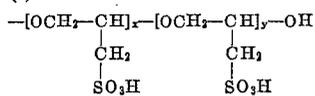


(1)



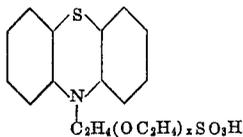
polymers av. mol. wt. 388-30,000

(2)



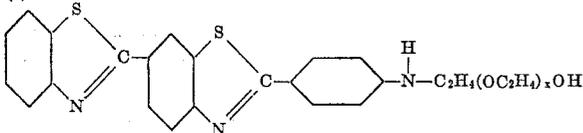
x and y each=5 to approx. 100

(3)



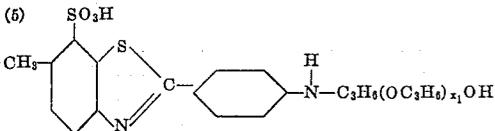
x=20-100

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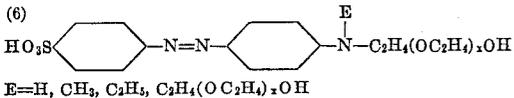


x=5-100

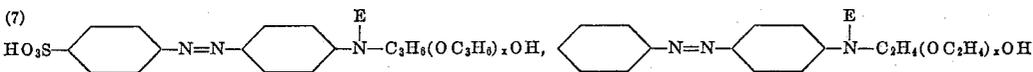
(5)

x₁=4-10

(6)

E=H, CH₃, C₂H₅, C₂H₄(OC₂H₄)_xOH

(7)



(8)

HO-C₂H₄(OC₂H₄)_{9-1,000}OH
 av. mol. wt.=400-50,000(-C₂H₄OC₂H₄O-)_x
 x=10-1,000

(9)

HO C₃H₆(OC₃H₆)₅₋₂₀OH
 av. mol. wt.=350-1,000(-C₃H₆OC₃H₆O-)_y
 y=4-20

(10)

HS-C₂H₄(OC₂H₄)₉₋₁₀₀OH

(11)

H₂N-C₂H₄(OC₂H₄)₉₋₅₀₀OH, H₂N-C₂H₄(OC₂H₄)₅₋₅₀₀NH₂, HO₃S-C₂H₄NHC₂H₄(OC₂H₄)_{5-1,000}OH

(12)

H₂N-C₃H₆(OC₃H₆)₅₋₂₀OH, H₂N-C₃H₆(OC₃H₆)₅₋₂₀NH₂, HO₃S-C₃H₆NHC₃H₆(OC₃H₆)₅₋₃₀OH

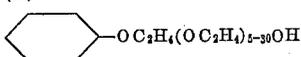
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HO₃S-C₃H₆(OC₃H₆)₅₋₅₀OH

(14)

CH₃C₇H₁₄(OC₂H₄)₅₋₁₅OH

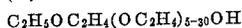
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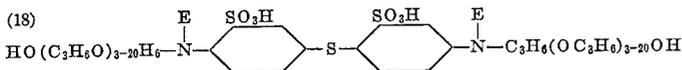
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CH₃OC₂H₄(OC₂H₄)₅₋₃₀OH

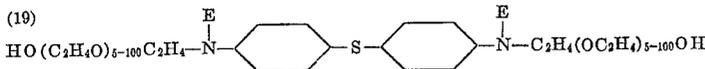
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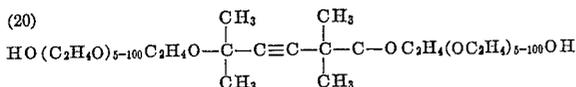
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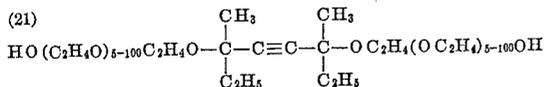
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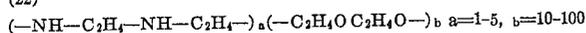
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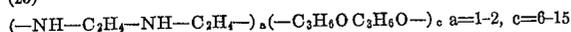
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(22)



(23)



Example A

	Concentration,	
	grams/liter	
CuSO ₄ ·5H ₂ O	150-225	
H ₂ SO ₄	30-75	
1,3-dioxolane polymer, av. mol. wt. 5,000	0.03-0.15	
Temp. 20-35° C.		
Average cathode current density, 5 amps/sq. dm.		

Example B

	Concentration,
	grams/liter
Cu(BF ₄) ₂	150-425
HF ₄	10-30
H ₃ BO ₃	0-30
1,3-dioxolane polymer av. mol. wt. 1,000 to 10,000	0.01-1

Temp. 20-35° C.
Av. cathode current density, 8 amps/sq. dm.

Example C

	Concentration,
	grams/liter
CuSO ₄ ·5H ₂ O	150-250
H ₂ SO ₄	30-75
1,3-dioxolane polymer av. mol. wt. 5,000	0.1-0.2
Diethyl safranine azo dimethyl aniline (Janus Green B)	0.001-0.01
Thiophene-2-sulfonic acid (Example I, Table I)	0.001-0.01

Temp. 20-35° C.
Av. cathode current density, 5 amps/sq. dm.

Example D

	Concentration,
	grams/liter
CuSO ₄ ·5H ₂ O	150-250
H ₂ SO ₄	30-75
1,3-dioxolane polymer, av. mol. wt. 5,000	0.05-0.15
Thianthrene sulfonic acid (Example 4, Table I)	0.001-0.01

Temp. 20-35° C.
Av. cathode current density, 5 amps/sq. dm.

Example E

	Concentration,
	grams/liter
CuBF ₄	150-425
HF ₄	10-30
H ₃ BO ₃	0-30
1,3-dioxolane polymer, av. mol. wt. 5,000	0.1-0.3

25	Example 7, Table I	0.001-0.02
	Janus Green B	0.001-0.02
	Temp. 20-35° C.	
	Av. cathode current density, 5-10 amps/sq. dm.	

Example F

	Concentration,	
	grams/liter	
30	CuSO ₄ ·5H ₂ O	150-250
	H ₂ SO ₄	30-75
	Polypropylene glycol, av. mol. wt. 350-750	0.05-0.2
	Thianthrene sulfonic acid	0.001-0.02
	Dimethyl safranine azo dimethyl aniline	0.001-0.01
	Temp. 20-35° C.	
	Av. cathode current density, 5 amps/sq. dm.	

Example G

	Concentration,	
	grams/liter	
40	CuSO ₄ ·5H ₂ O	150-250
	H ₂ SO ₄	30-60
	Example 12, Table II	0.05-0.5
	Phenyl disulfide sulfonic acid (Example 5, Table I)	0.001-0.02
	Janus Green B	0.001-0.01
50	Temp. 25-30° C.	
	Av. cathode current density, 5 amps/sq. dm.	

Example H

	Concentration,	
	grams/liter	
55	CuSO ₄ ·5H ₂ O	150-250
	H ₂ SO ₄	30-60
	Polypropylene glycol, av. mol. wt. 350-750	0.02-0.4
	Example 3, Table I	0.001-0.02
	Temp. 25-30° C.	
	Av. cathode current density, 5 amps/sq. dm.	

Example I

	Concentration,	
	grams/liter	
60	CuBF ₄	150-425
	HF ₄	10-30
	H ₃ BO ₃	0-30
65	Example 12, Table II	0.02-0.3
	Example 2, Table I	0.001-0.01
	Janus Black R	0.001-0.01
	Temp. 25-30° C.	
	Av. cathode current density, 5-10 amps/sq. dm.	

	Concentration, grams/liter
CuSO ₄ ·5H ₂ O -----	150-250
H ₂ SO ₄ -----	30-60
Polypropylene glycol, av. mol. wt. 300-750 --	0.01-0.2
Janus Green B -----	0.001-0.02
Example 13, Table I -----	.001-0.02

Temp. 25-30° C.

Av. cathode current density, 5 amps/sq. dm.

The addition agents of Tables I and II can be combined in the same molecule or combined with one of the phenazine dyes, or they may be used as individual molecules as listed in Tables I and II mixed together in the same solution with or without the phenazine dyes because they all deplete from the solution at very nearly the same rate. The compounds of Table I used in the very low concentrations of 0.0005 to about 0.025 gram/liter deplete practically exactly at the same rate as the phenazine dyes used in the concentration range of 0.001 to 0.05 gram/liter.

The rate of depletion of the unique combination of additives of this invention is very closely the same in the acidic copper sulfate, copper fluoborate and copper methane sulfonate baths which are the preferred baths. In the case of the baths containing the small alkyl chain disulfonates the solubility of the copper salts of these compounds are much smaller than, for example, the copper methane, ethane or propane monosulfonates, and it is therefore necessary to use the disulfonates in much lower concentrations than the monosulfonates.

It is generally preferred to use phosphorized copper anodes, especially when the additives in the acidic baths consist of combination of compounds selected from Tables I and II. In fact, if pure copper anodes are used, such as electrolytic copper or oxygen-free copper anodes, the anode corrosion is less smooth and also the brightness of the plate is less. Just why the plate is less bright is not clear. The phosphorized anodes contain from about 0.02 to about 0.2% phosphorous and the cathode copper plate obtained with the use of these phosphorized anodes also contains a very similar percent phosphorous, and it is the inclusion of this phosphorous in the plate that may aid in the brightening. The phosphorized copper anodes usually contain about 0.01 to 0.05% silver and smaller traces of nickel, iron, sulfur, arsenic, antimony, and bismuth. The cathode plate contains even less of these impurities. The silver seems to be precipitated out as the chloride, which probably explains its very much smaller concentration in the cathode plate.

However, when a phenazine dye such as Janus Green is also present in the acidic baths besides one or more of the compounds of Tables I and II, then the copper plate is about equally brilliant, independent of the type of the above-mentioned copper anodes used in the plating.

When the bright copper plates of this invention are heated to high temperatures in a hydrogen atmosphere, the plate from the fluoborate bath seems to be stronger than that from the sulfate bath.

What is claimed is:

1. A bath for electrodepositing ductile, lustrous copper comprising an aqueous acidic copper plating bath containing dissolved therein about 0.0005 to about 0.04 gram per liter of an organic sulfide compound carrying at least one sulfonic group, together with 0.01 to 5 grams/liter of a bath-soluble polyether compound containing at least 6 ether oxygen atoms and being free from alkyl chains having more than 6 carbon atoms.

2. A bath as claimed in claim 1 wherein said polyether is a polymer of 1,3-dioxolane having a molecular weight in the range of 296 to at least 30,000.

3. A bath as claimed in claim 1 wherein said poly-

ether contains the group $(-C_2H_4OC_2H_4O-)_x$ where x is an integer of magnitude of at least 3.

4. A bath as claimed in claim 1 wherein said polyether contains the group $(-C_3H_6OC_3H_6O-)_y$ where y is an integer of magnitude of 3 to 10.

5. A bath as claimed in claim 1 wherein there is also present a bath-soluble phenazine dye in a concentration of 0.001 to 0.05 grams per liter.

6. A bath as claimed in claim 5 wherein said phenazine dye is diethyl safranin azo dimethyl aniline.

7. A bath as claimed in claim 5 wherein said phenazine dye is dimethyl safranin azo dimethyl aniline.

8. A bath as claimed in claim 5 wherein said phenazine dye is Janus Black.

9. A bath as claimed in claim 1 wherein said acid copper plating bath contains at least one copper salt selected from the group consisting of copper sulfate, copper fluoborate, copper methane sulfonates, copper methane disulfonates, copper ethane sulfonates, copper ethane disulfonates, copper propane sulfonates and copper propane disulfonates.

10. A method for electrodepositing ductile lustrous copper comprising the step of electrodepositing copper from an aqueous acidic copper plating bath containing dissolved therein about 0.0005 to about 0.04 gram/liter of an organic sulfide compound carrying at least one sulfonic group, together with 0.01 to 5 grams per liter of a bath-soluble polyether compound containing at least 6 ether oxygen atoms and being free from alkyl chains having more than 6 carbon atoms.

11. A method as claimed in claim 10 wherein said polyether in the said acidic copper baths is a polymer of 1,3-dioxolane having a molecular weight in the range of 296 to at least 30,000.

12. A method as claimed in claim 10 wherein said polyether in the said acidic copper baths contains the group $(-C_2H_4OC_2H_4O-)_x$ where x is an integer of magnitude of at least 3.

13. A method as claimed in claim 10 wherein said polyether in the said acidic copper baths contains the group $(-C_3H_6OC_3H_6O-)_y$ where y is an integer of magnitude 3 to 10.

14. A method as claimed in claim 10 wherein said acid copper plating bath contains a bath-soluble phenazine dye in a concentration of 0.001 to 0.05 gram per liter.

15. A method as claimed in claim 14 wherein said phenazine dye is diethyl safranin azo dimethyl aniline.

16. A method as claimed in claim 14 wherein said phenazine dye is dimethyl safranin azo dimethyl aniline.

17. A method as claimed in claim 14 wherein said phenazine dye is Janus Black.

18. A method as claimed in claim 10 wherein said acid copper plating bath contains at least one copper salt selected from the class consisting of copper sulfate, copper fluoborate, copper methane sulfonates, copper methane disulfonates, copper ethane sulfonates, copper ethane disulfonates, copper propane sulfonates and copper propane disulfonates.

19. A bath as claimed in claim 1, wherein said organic sulfide compound is a thianthrene sulfonic acid and wherein said polyether contains the group $(C_2H_4O)_x$ where x is an integer of magnitude of at least 6.

20. A bath as claimed in claim 1, wherein said organic sulfide compound is a disulfide sulfonic acid and wherein said polyether contains the group $(C_2H_4O)_x$ wherein x is an integer of magnitude of at least 6.

21. A bath as claimed in claim 1, wherein said organic sulfide compound is a thianthrene sulfonic acid and wherein said polyether contains the group $(C_3H_6O)_y$ where y is an integer of magnitude of about 6-20.

22. A bath as claimed in claim 1, wherein said organic sulfide compound is a disulfide sulfonic acid and wherein said polyether contains the group $(C_3H_6O)_y$ where y is an integer of magnitude of about 6-20.

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23. A method as claimed in claim 10, wherein said organic sulfide is a thianthrene sulfonic acid and wherein said polyether contains the group $(C_2H_4O)_x$ wherein x is an integer of magnitude of at least 6.

24. A method as claimed in claim 10, wherein said organic sulfide is a disulfide sulfonic acid and wherein said polyether contains the group $(C_2H_4O)_x$ wherein x is an integer of magnitude of at least 6.

25. A method as claimed in claim 10, wherein said organic sulfide is a disulfide sulfonic acid and wherein said polyether contains the group $(C_3H_6O)_y$ wherein y is an integer of magnitude of about 6-20.

26. A method as claimed in claim 10, wherein said organic sulfide is a thianthrene sulfonic acid and wherein said polyether contains the group $(C_3H_6O)_y$ where y is an integer of magnitude of about 6-20.

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