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ACID COPPER PLATING

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The present invention relates generally to the electroplating art and is more particularly concerned with novel compositions for use in aqueous acid copper electroplating baths, with novel baths of this type having unique and valuable properties and with a new process for electrodepositing copper involving the use of said compositions and baths and affording special new advantages and results.

Copper, plated from the usual acid bath compositions, is dull and crystalline in appearance, and exhibits poor throwing power of the bath, in that recessed areas of an irregularly shaped surface are not uniformly covered by the copper deposit. The principal functional difference between acid copper baths and copper cyanide plating formulations, is that the former have very poor throwing or covering power, while the latter are excellent in both of these properties. My invention provides an additive combination to acid copper plating baths that permits them to compete commercially with copper cyanide baths with respect to throwing and covering powers, while retaining the well recognized operating advantages of the acid baths. Thus, my invention provides an acid copper plating bath that is commercially competitive with the cyanide bath with respect to uniform covering power, and that produces a deposit having superior physical properties such as luster, uniformity and smoothness of surface, ease of buffing to a bright finish and homogeneity of structure. The deposits from my new and novel bath composition are particularly suitable for use as bases for subsequent nickel plating, especially for use prior to plating from the modern bright nickel processes.

Modern chromium plated finishes are underlaid with electroplates of copper and nickel, respectively, on the base metal such as steel, for example. In this sequence it is important to provide a copper plate of superior physical properties such as uniform coverage, a very fine crystal structure, smooth, lustrous surface, dense homogeneous structure, ductility and ease of buffing. Even with all their well-known deficiencies, cyanide plating baths have generally been used for this purpose because acid baths could not produce the quality of deposit required. Cyanide copper plating baths usually operate at high temperatures, are extremely toxic and unpleasant to operate, require addition agents that produce rinsing problems and interfere with adhesion of the subsequent nickel deposit, produce copper deposits that are difficult to buff to a satisfactory finish and, like all cyanide plating baths, require expensive waste disposal systems for the destruction of cyanide in rinses and tank wastes to avoid stream pollution and sewage contamination, which is becoming an increasingly pressing industrial problem. Because of these difficulties, many attempts have been made to develop an acid copper plating bath to produce copper deposits of superior physical properties for use under nickel plating.

None of these attempts have been entirely successful. All depend on bath addition agents of various types, some

of which produce brittle deposits, some are not stable in the bath, requiring excessive additions and breaking down into deleterious decomposition products that must be removed from the plating bath frequently by carbon treatment, and some are not stable at temperatures much over 90° F., requiring bath cooling and thereby restricting the operating current densities and hence the productive capacity of the bath.

I have now found a combination of addition agents, which, when present in commercial acid copper plating baths, produce baths of superior covering power, are stable at high operating temperatures, form no deleterious decomposition products, and produce copper deposits of superior physical properties, as defined above, that are eminently suited for use under subsequent nickel deposits from either conventional or proprietary bright nickel plating baths. For convenience and to avoid repetition, the copper plates produced by the baths and processes of this invention will hereinafter be referred to as copper deposits having superior physical properties.

These valuable results are obtainable now for the first time because of my surprising and unpredictable discoveries upon which this invention in all its various aspects is predicated. One of the more basic of these discoveries is that certain organic compounds act synergistically in combination with chloride ion in aqueous acid copper plating baths to produce electrolytes having unique characteristics and copper deposits having superior physical properties, as described above. I have also found that this synergistic effect is not limited to a particular plating bath composition but is obtainable in all commercial acid copper plating baths. However, the concentration of the chloride ion must be controlled within a narrow range and there is a critical minimum amount of or concentration of the organic compound in these baths. Still further, I have found that except for the bromide ion in certain bath additives and bath compositions of this invention, the chloride ion has no equivalent in its present synergistic effect. There are, however, a number of satisfactory sources of chloride ion for this purpose although all chlorides are not suitable and some may be quite harmful to copper plating operations. Similarly, I have found that the organic compounds contemplated by this invention can be classified and that there are a relatively large number of these compounds which may be used successfully in these new baths and copper plating operations. In fact, I have found that special advantages are to be obtained by using mixtures of these compounds in the bath additives and plating bath compositions of this invention.

These new acid copper electroplating baths, briefly and generally described, contain a bath-soluble polyalkylene oxide having a molecular weight greater than 300, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, the polyalkylene oxide being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

In general, the organic portion of the combined additives contemplated by this invention can be classified as polyalkylene oxides with or without terminally substituted radicals. Compounds of this general type are widely used in industry and their methods of preparation are matters of record, being disclosed in several U.S. patents, among which may be cited 1,970,578; 1,922,459; 2,059,273; and 2,213,477. They are discussed by Staudinger in Die Hochmolekularen Organischen Verbindungen, 1932, page 287 et seq.

More specifically, the organic additives contemplated

by this invention may be represented by the general formula

$$R—(CH_2CH_2O—)_n—H$$

in which R is the hydroxyl radical (OH) in the case of unsubstituted compounds or in the case of substituted compounds, R is a radical derived from the group comprising phenols, alcohols, ethers, acids and amines, and n is a numerical value greater than 5.

In order to simplify the nomenclature of this document and avoid needless repetition, the compounds represented by the above general formula that are contemplated by this invention will be referred to as polyoxyethanols, and will include the unsubstituted polyethylene oxides as well as those having a terminal substituent, as set forth in detail subsequently. Since the molecular weight of the ethylene oxide group (C_2H_4O) is 44, it follows that the polyoxyethanols of this invention will have calculated molecular weights over 300, the actual figures depending on the values of n and the molecular weights of the substituent radicals.

Polyoxyethanols are stable in acid copper plating baths and form no deleterious decomposition products, thus eliminating this cause for frequent purification of the bath by carbon treatment. Similar compounds have been proposed for use in electro-plating baths, notably by Hoffman for tin plating baths in U.S. Patent 2,457,152 and by Rochl for lead-tin alloy baths in U.S. Patent 2,734,025.

Surprisingly enough, the presence of polyoxyethanols in conventional commercial acid copper plating baths produces highly undesirable results unless to these baths is also added bath-compatible compounds that produce in solution the chloride ion within specifically controlled limits of concentration. By the term "bath-compatible" is meant bath soluble compounds containing chlorine combined with anions that are either inert or harmless in the acid copper plating bath, such as, for example, hydrogen chloride, sodium chloride, cupric chloride, ammonium chloride, lithium chloride, potassium chloride, and in fact the chloride of any anion that will not co-deposit with copper from an acid bath nor adversely affect the deposition of copper from such a bath.

It may be noted here that the chloride ion is not a conventional constituent of commercial acid copper plating baths, nor is copper ever plated commercially from a chloride bath. In fact the chloride ion is generally considered undesirable as a constituent of commercial acid copper plating baths because it lowers the burning range, that is, it accentuates the tendency to form burned or dark, coarsely crystalline deposits at the higher current densities, thus lowering the operating current density range with consequent loss in the production capacity of the bath. For this reason, every effort is made to keep chlorides out of commercial baths. Also the chloride ion is known to act as a poison for most of the additive agents used in acid copper plating, as it partially or completely nullifies their effects, and therefore it is generally avoided in bath using additive agents.

Thus it will be seen that the essence of my invention resides in obtaining new, useful and unexpected results by combining in acid copper electroplating baths, two specific types of materials, either of which when present in the bath without the other, produces distinctly inferior and undesirable copper deposits. It appears that the function of the chloride ion in the baths of this invention is to enable the polyoxyethanol to exert its beneficial effect upon the plating reactions and the plate formation, while the polyoxyethanol ameliorates practically completely the deleterious effects of the chloride ion on the copper deposit. The novel bath addition agents or additive compositions constituting another aspect of my invention, succinctly stated, consist essentially of between about 10 and about 90 proportional parts of polyoxyethanol, which is soluble in such baths to the extent of at least 0.05 gram per liter, and between about 90 and about 10 parts, respectively, of a bath-compatible chloride which is similarly soluble and capable of providing a chloride ion concentration in such baths of at least 0.02 gram per liter. Thus the additives of this invention can be specially designed to be used as make-up additions to baths partially depleted during plating operations, and will consist of these same essential substances but contain them in different ratios, depending on the identity of the polyoxyethanols used and the requirements, as explained later.

My new and novel combination of additives functions equally well in the cheaper and more common acid sulfate baths as well as in the newer and more expensive acid fluoborate baths. The general formulae for these baths are shown in Table I.

TABLE I

Compositions of commercial acid copper baths

(A) Sulfate Bath	Concentrations in grams per liter	
	Approx. Range	Preferred
$CuSO_4.5H_2O$	150–250	200
H_2SO_4	45–110	75
(B) Fluoborate Bath	**Low**	**High**
$Cu(BF_4)_2$	225	450
HBF_4	15	30
H_3BO_3 (optional)	15	30

As a general disclosure of my invention, I cite the addition to any acid copper plating bath of the combination of additive agents shown in Table II following:

TABLE II

Additive combination ranges and operating conditions

	Concentration in grams per liter		
	Operating Range	Preferred Range	Preferred
Polyoxyethanols	0.05–30.0	0.1–0.5	0.3
Chloride ion	0.02–1.0	0.05–0.3	0.1
Temp., ° F	80–160	120–140	130
Average Cathode: Current Density (amp. per sq. ft.)	10–400	30–250	125

Since the operating conditions depend on the degree and nature of the agitation employed, both mechanical and air systems being used, the above figures for temperature and cathode current density will of necessity vary considerably therewith relative to each other, all of which is conventional and well known to those skilled in the art.

Considering again the general formula for the polyoxyethanols of this invention:

$$R—(C_2H_2O—)_n—H$$

in which R is a radical derived from the group comprising phenols, alcohols, ethers, acids and amines, the general relationship between the nature of R and the value for n requires further discussion. In these polyoxyethanols, the values for n must be increased as the bath solubility of the compound from which R is derived decreases. This is necessary in order to provide adequate

bath solubility, since while it need not be great in each case, it must be sufficient to dissolve enough polyoxyethanol to produce copper deposits of superior physical properties.

For example, if R is derived from methyl alcohol or hydrochloric acid, both of which are highly bath soluble, a very low value for *n*, such as 6–8 is satisfactory, and is required for additive action only and not for bath solubility. On the other hand, if R is derived from beta-naphthol, which has a definite though low bath solubility, *n* need be only around 11–15 to produce a satisfactory bath soluble and effective polyoxyethanol, while if R is derived from octylphenol, which is much less bath soluble, *n* should be above about 15, preferably around 20 to 30 to produce a polyoxyethanol of adequate bath solubility and effectiveness. And if R is derived from a highly bath insoluble amine, such as for example, dehydroabietylamine, *n* should be over about 40 to obtain a satisfactory polyoxyethanol. It should be understood of course that this discussion applies to polyoxyethanols that are capable of producing optimum results in combination with the chloride ion. Less complete but still useful results can be obtained by using corresponding polyoxyethanols of lower *n* value, in which case they may have lower bath solubility and hence less activity in the bath. It is also sometimes desirable, as explained later, to use mixtures of polyoxyethanols in which *n* is lower than optimum for a single compound, hence the difficulty of specifying a particular value or limiting range of values for *n* for any given substance is apparent.

It will be noted that the structure of the general formula is similar to that of commercial surfactants of the nonionic type, in which the value for *n* is generally in the low range specified for the polyoxyethanols of this invention. It is also well known that as the value for *n* increases in such products, their surface activity diminishes. I have found that as *n* increases, the bath solubility of the polyoxyethanol increases, and this is generally desirable for my purpose. Also, I have found that a slight amount of surface activity is usually desirable to eliminate any tendency toward pitting of the deposit, while on the other hand, any great amount of surface activity must be avoided for practical operating reasons, otherwise the air agitation generally used in commercial baths would cause a prohibitive amount of foaming on the bath. For these reasons it is sometimes advantageous in compounding additive mixtures for commercial applications to use selected mixtures of the polyoxyethanols contemplated by this invention. Thus the difficulty of specifying an exact value or a limiting range of value for *n* in the case of polyoxyethanols containing substituent radicals is apparent. In such cases however, because of the bath solubility factor, I generally prefer to use a relatively high value for *n*, of the order of 20–60, although for reasons that are readily apparent, I do not desire to be so limited.

The amount of polyoxyethanols required in solution in the plating bath may vary somewhat with the nature of the substituent radical. In general it is desirable to use the minimum concentration consistent with satisfactory results or to produce the effects desired and maintain consistent operating conditions. In the case of polyoxyethanols containing substituent radicals this concentration has been found to be around 0.1 to 0.5 gram per liter, preferred being 0.2–0.3 gram per liter. In the case of the unsubtituted polyoxyethanols somewhat higher concentrations may be found desirable. In both cases, substituted and unsubstituted, a reasonable excess of polyoxyethanols in the bath does no harm. Baths containing various concentrations of various polyoxyethanols up to as high as 30 grams per liter have been operated successfully. However such high concentrations are unnecessary, and might be considered undesirable in some cases on the general principle that the less organic matter present in a plating bath the better. One of the desirable features of this invention, from a functional standpoint, is the low concentration of organic additive constituent required to produce satisfactory results.

Table III following illustrates some of the organic compounds from which R of the general formula has been derived to make polyoxyethanols containing substituent radicals and which have been found satisfactory for the purposes of this invention.

TABLE III

	Approximate optimum range for *n*
Phenols:	
Phenol	10–30
Octyl phenol	20–40
Nonyl phenol	25–50
Beta-naphthol	12–30
Ethers:	
Biphenyl ether	15–40
Disecondary butyl phenyl ether	20–40
Alcohols:	
Methyl alcohol	6–25
Sorbitol	20–40
Lauryl alcohol	20–40
Acids:	
Hydrochloric acid	6–20
Caproic acid	20–60
Oleic acid	20–60
Stearic acid	20–60
Rosin acids	20–60
Abietic acid	20–60
Amines:	
Ethylene diamine	30–60
Rosin amines	40–60
Dehydroabietylamine	40–60
Tertiary-alkyl primary amines ($C_{18-24}H_{37-49}NH_2$)	30–60

The foregoing Table III is illustrative only and by no means complete as will be evident from a perusal of the references hereinbefore cited covering the preparation of this type of compounds. It should also be noted that the values given for *n* are approximate optimum values only. They are shown for purposes of illustration only, and are in no way limiting for reasons already cited.

The unsubstituted type of polyoxyethanols that have been found most satisfactory for the purposes of this invention are those in which *n* of the general formula is about 10 or greater and R is the hydroxyl radical. These materials have calculated molecular weights in excess of 600, and may go as high as 20,000. One that I have found to be particularly satisfactory has a calculated molecular weight around 6000 and *n* approximates 135. As illustrative of this type of polyoxyethanols those shown in Table IV compare average molecular weight with calculated approximate values for *n*.

TABLE IV

Unsubstituted polyoxyethanols

Average calculated molecular weight:	Approximate value for *n*
1000	20
2000	45
4000	90
6000	135
9000	200
20,000	450

It should be realized that in the case of these unsubstituted polyoxyethanols as well as in the case of the polyoxyethanols with a substituent radical, the commercial products are mixtures of compounds the molecular

weights of which vary within commercial limits of manufacture and purification, hence the figures given in this document for molecular weights are average values only and therefore the values for *n* can only be approximate and also representing average values.

The particular advantage of the unsubstituted type of polyoxyethanols is that they offer all the advantages of synergistic additive action with the chloride ion without lowering the surface tension of the bath, therefore can be used either alone or in mixtures with the substituted type of polyoxyethanols, some of which do lower the surface tension of the bath, so as to regulate the surface tension effect as desired without adversely affecting additive action, as previously mentioned. This permits control of pitting on the deposit when encountered, without producing excessive foaming from air agitation.

In general, a little more of the unsubstituted polyoxyethanols can be used to advantage, and I prefer around 0.5 gram per liter of bath, although I have used as high as 30 grams per liter with excellent results and no ill effect.

One commercial line of the unsubstituted type of polyoxyethanols now available is offered by the Carbide and Carbon Chemicals Company under the designations polyethylene glycols and "carbowaxes." Of these, I prefer to use "Carbowax" 6000 at a bath concentration around 0.5 gram per liter.

As for the other essential ingredient in my new and novel combination of additives for acid copper plating baths, the chloride ion and the bromide ion are practically equivalent and are unique among cations as being the only ones that work synergistically with my organic polyoxyethanols to produce the copper deposits having superior physical properties resulting from this invention. Further, the critical amounts of chloride ion and bromide ion are the same on a chemical equivalent or molal basis. Thus the values given for the chloride ion can be converted to values for the bromide ion by multiplying by the ratio of the chemical equivalent or molecular weights: 79.9/35.5 or approximately 2.25. The chemical equivalent on a molal basis in each case corresponds to a range of 0.00055 to about 0.028 mol of either chloride ion or bromide ion. The bromine salts that are bath-compatible and effective in the baths of this invention correspond to the chlorine salts stated above to be suitable or preferred for use herein, on a chemical equivalent or molal basis.

Contrary to what might be expected, none of the acids or salts of the other two halogens have the synergistic effect of this invention. However, this effect can be obtained by using mixtures of chlorides and bromides as long as the aggregate of chloride and bromide ions in the plating bath is within the aforesaid critical range for chloride alone on a molal equivalent basis and as long as there is no interaction between the chloride and bromide compounds or with other bath constituents resulting in the formation of substances having detrimental effect upon the copper plating operations or the resulting products.

In its method aspect this invention in general comprises the step of adding to an acid copper electroplating bath prior to its use a bath-compatible chloride and thereby establishing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, and also adding to the bath a polyoxyethanol of molecular weight greater than 300 and thereby establishing in solution in the bath an amount of said polyoxyethanol effective to act synergistically with the chloride ion to produce uniform copper deposits of superior physical properties.

It is also a process of this invention to maintain in the plating bath synergistic quantities or concentrations of chloride or bromide ion and polyoxyethanol. This involves the step of periodically adding to the bath a make-up quantity of one or both the synergistic constituents or compounds which function as sources of said chloride ion or polyoxyethanol in solution. In preferred practice the additions will be in the form of mixtures specially prepared for restoring depleted baths and containing therefore between about 10 and about 90 proportional parts of polyoxyethanol and between about 90 parts and about 10 proportional parts of bath-compatible chloride.

The novel combination process or method of my invention comprises in general the preparation of the plating bath containing the synergistic quantities of organic compound and chloride ion, electro-depositing copper from the bath, and as the bath becomes depleted of synergistic amounts of said organic compound and chloride periodically adding a make-up amount of the depleted bath substituents.

The chloride ion can be added to the bath in the form of any bath-compatible compound as hereinbefore explained. For convenience I prefer to use hydrochloric acid, sodium chloride or cupric chloride. The chloride concentration that I prefer to maintain is around 0.1 gram of Cl per liter. This can be done by frequent bath analysis, the procedures for determining chloride being simple and well known to those skilled in the art, and a bath-compatible chloride added as required. The preferred concentration is not critical, but should not be allowed to drop below 0.02 gram of Cl per liter which I consider to be the extreme lower limit. For safe, flexible operation I prefer to keep the chloride concentration above 0.05 gram of Cl per liter, usually around 0.1 gram of Cl per liter. There is no operational advantage to be gained in maintaining the chloride concentration over 0.1 gram of Cl per liter except possibly to minimize the analytical control operations, however it does no harm to the cathode deposit to have the chloride as high as 1.0 gram of Cl per liter. However, as the chloride content of the bath exceeds (about) 0.5 gram of Cl per liter, there is a growing tendency for the anodes to polarize, especially at high current densities, and this anode effect is the limiting factor in setting and maintaining the maximum practical operating chloride concentration.

Chloride is eliminated from the bath at the anode in the form of insoluble cuprous chloride (CuCl) which precipitates in the anode sludge. The rate of chloride elimination varies greatly with chloride concentration, anode current density and bath temperature, but once determined for a given installation, it can serve as a basis for chloride replacement, thus diminishing the number of analyses required. Under average commercial operating conditions I have found the rate of chloride precipitation to be of the order of 0.01 ounce of chloride per ampere hour per 1000 gallons of bath.

Since the polyoxyethanols of this invention are bath stable and only the chloride of my combination of additives is lost by anodic precipitation, it is possible to operate a bath containing adequate concentrations of polyoxyethanols for considerable periods of time by periodic additions of chloride to replace that which is lost. Such bath operation is considered to be within the scope of this invention.

Acid copper plating baths in which the chloride ion is maintained between 0.02 and 1.0 gram of chloride per liter in order to secure the synergistic effects of organic additive agents are new and novel and in themselves constitute one phase of this invention.

The following Examples 1–7 inclusive specifically illustrate some of the preferred formulations of my invention:

EXAMPLE 1

	Grams per liter
$CuSO_4.5H_2O$	200
H_2SO_4	75
$CuCl_2.2H_2O$	0.25
Polyoxyethanol in which R=beta-naphthyl and *n* approximates 15	0.3

EXAMPLE 2

	Grams per liter
$CuSO_4.5H_2O$	200
H_2SO_4	75
HCl (100%)	0.1
Polyoxyethanol in which R is the OH group and *n* approximates 135	0.5

EXAMPLE 3

$CuSO_4.5H_2O$	200
H_2SO_4	75
NaCl	0.17
Polyoxyethanol in which R=octylphenyl and *n* approximates 30	0.3

EXAMPLE 4

$CuSO_4.5H_2O$	200
H_2SO_4	75
$CuCl_2.2H_2O$	0.25
Polyoxyethanol in which R is derived from biphenyl ether and *n* approximates 25	0.3

EXAMPLE 5

$CuSO_4.5H_2O$	200
H_2SO_4	75
$CuCl_2.2H_2O$	0.25
Polyethyleneglycol chloride	0.3

EXAMPLE 6

$CuSO_4.5H_2O$	200
H_2SO_4	75
$CuCl_2 2H_2O$	0.25
Methoxypolyethylene glycol	0.3

EXAMPLE 7

Copper fluoborate	350
Fluoboric acid	30
Boric acid (optional)	30
Cupric chloride crystals	0.25
Polyoxyethanol in which R=nonylphenyl and *n* approximates 40	0.3

Average operating conditions for all of above examples:

Temperature, 0 ° F.	120–140
Average cathode current—density, amperes per sq. ft.	100–200

Agitation, optional.

Since commercial operators of acid copper plating baths make up their solutions from chemicals or concentrates, as for example, copper sulfate crystals and sulfuric acid to meet their needs and then put in additives, the most expedient manner in which this invention can be made available to commercial platers is to provide a composition of matter suitable for adding to acid copper plating baths which contains the combined additives of this invention in proper proportions so that when added to the plating bath in correct amounts it will produce a copper deposit having superior physical properties. I have made a convenient liquid additive for acid copper plating baths by dissolving in water:

	Percent
Polyoxyethanol in which R is derived from beta-naphthol and *n*=15	6
Cupric chloride ($CuCl_2.2H_2O$)	6

This mixture or liquid additive was added to commercial acid copper plating baths in the proportion of about 4 cc. per liter or about one-half fluid ounce per gallon. It is apparent that more dilute or more concentrated solutions of the combined additives could be made and used in less or greater amounts as convenient. Since some polyoxyethanols may be used at higher concentrations than others, while the chloride component of the bath is best held at around 0.1 gram chloride per liter, the ratio of polyoxyethanols to chloride will vary with the identities of the respective ingredients and the concentrations used.

While formulations of the various polyoxyethanols and bath-compatible chlorides similar to the above may be made and sold for initial installations, it will be observed that since the chloride is lost by anode precipitation and bath drag-out while the polyoxyethanol is lost by drag-out only, maintenance additions should be correspondingly higher in chloride content and lower in polyoxyethanol content. Such compositions can be worked out to fit any given installation, based on consumption data, and such formulations will necessarily vary considerably, but I have found that the following proportions will fit most cases, and can serve until accurate proportions are worked out.

Polyoxyethanols	grams per liter 15
HCl (conc.)	cc. per liter 50

This maintenance solution is suitable for adding to a chloride depleted bath, either as dictated by the chloride deficiency, or if chloride is very low, at the rate of about one-half fluid ounce per gallon of bath, in which case the addition would put about 0.1 gram of chloride per liter into the bath. Wide variations may be encountered in the relative rates at which polyoxyethanols and chloride are lost and must be replaced, hence the compositions of appropriate maintenance solutions will vary accordingly.

Because of the wide range of constituent concentrations encountered in compounding suitable additive mixtures for use with new baths and to maintain baths in optimum operating condition, due to variations in requirements, differences in molecular weight of the organics and the bath-compatible chlorides or bromides used, and differences in rate of bath depletion it is difficult to specify exact limits of composition for such additive mixtures. However it will generally be found that for all practical purposes they will fall within the following range of proportionate parts:

	Parts
Polyoxyethanols	90–10
Bath-compatible chlorides	10–90

It should be understood that these proportionate parts represent the numerical ratio of the constituents, and if present in solution, these figures do not include the solvent, since it is apparent that the ratio of constituents is the important factor, not the actual concentration in solution, as such mixtures may be dissolved in water to any convenient concentration and directions furnished the plater as to how to add the solution to the bath to best advantage.

If desired, combinations of additives for initial installation and for maintenance comprising selected polyoxyethanols and bath-compatible chlorides may be compounded in the above tabulated proportions and offered to the plater in concentrated or dry form so that he can make his own additive solutions by dissolving them in water, or he can add them directly to the bath.

The above illustrations will make clear to those skilled in the art all the principles involved in compounding additive mixtures contemplated by this invention.

To the extent that they are sufficiently soluble in aqueous acid copper plating baths other polyalkylene oxide compounds may be used instead of or together with polyoxyethanols. For example, bath-soluble polyoxypropanols are suitable for this purpose, producing the synergistic results described above.

Wherever in this specification or in the appended claims parts, proportions or percentages are recited, reference is to the weight basis rather than the volume basis unless the contrary is expressly stated.

Having thus described this invention in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains to make and use the same, and having set forth the best mode contemplated of carrying out this invention, I state that the subject matter which I regard as being my invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or modifications of,

or substitutions for, parts of the above specifically described embodiments of the invention may be made without departing from the scope of the invention as set forth in what is claimed:

What is claimed is:

1. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

2. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with beta-naphthol, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

3. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with a phenol, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

4. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with an ether, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

5. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with an alcohol, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

6. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with an acid, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

7. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having a molecular weight greater than 300 consisting of polyethylene oxide terminally substituted with an amine, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

8. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol consisting of on unsubstituted polyethylene oxide having a molecular weight greater than 600, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

9. An aqueous acid copper electroplating bath containing a mixture of bath-soluble polyoxyethanols having molecular weights greater than 300, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanols being in aggregate in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

10. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having molecular weight greater than 300, and a bath compatible compound providing concentration in the bath of between 0.00055 and about 0.028 gram mols per liter of an ion selected from the group consisting of chloride ion and bromide ion, said polyoxyethanol being in solution in the bath in amount effective to act synergistically with the said ion in the bath to produce uniform copper deposits of superior physical properties.

11. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol having molecular weight greater than 300, and a bath-compatible bromide providing a bromide ion concentration in the bath of between 0.045 and about 2.25 grams per liter, said polyoxyethanol being in solution in the bath in amount effective to act synergistically with the bromide ion in the bath to produce uniform copper deposits of superior physical properties.

12. An aqueous acid copper electroplating bath containing a mixture of bath-soluble unsubstituted polyethylene oxide having molecular weight greater than 600, and a bath-compatible bromide providing a bromide ion concentration in the bath of between 0.045 and about 2.25 grams per liter, said polyethylene oxide being in solution in the bath in amount effective to act synergistically with the bromide ion in the bath to produce uniform copper deposits of superior physical properties.

13. An addition agent composition for use in aqueous acid copper electroplating baths comprising as its essential ingredients between about 10 and about 90 parts of a polyoxyethanol which is soluble in such baths to the extent of at least 0.05 gram per liter and has a molecular weight in excess of 300, and between about 90 parts and about 10 parts, respectively, of a bath-compatible chloride which is sufficiently soluble in such baths to provide a chloride ion concentration in the baths of at least 0.02 gram per liter.

14. An addition agent composition for use in aqueous acid copper electroplating baths comprising as its essential ingredients between about 10 and about 90 parts of a polyoxyethanol which is soluble in such baths to the extent of at least 0.05 gram per liter and has a molecular weight in excess of 300, and between about 90 parts and about 10 parts, respectively, of a bath-compatible bromide which is sufficiently soluble in such baths to provide a bromide ion concentration in the baths of at least 0.045 gram per liter.

15. An addition agent composition for use in aqueous acid copper electroplating baths comprising as its essential ingredients between about 10 and about 90 parts of an unsubstituted polyethylene oxide which is soluble in such baths to the extent of at least 0.05 gram per liter and has a molecular weight greater than 600, and between about 90 parts and about 10 parts, respectively, of a bath-compatible chloride which is sufficiently soluble in

such baths to provide a chloride ion concentration in the baths of at least 0.02 gram per liter.

16. In a process for the electrodeposition of copper the step comprising effecting electrodeposition from an aqueous acid copper plating bath containing in solution 0.05 gram per liter of a polyoxyethanol and a bath-compatible chloride in sufficient amount to provide a bath concentration of from 0.02 to about 1.0 gram of chloride ion per liter.

17. In a process for the electrodeposition of copper from an aqueous acid copper plating bath containing a polyoxyethanol in an amount sufficient to produce in the presence of chloride ion a copper deposit having superior physical properties, the step of maintaining the chloride ion concentration within the range of from 0.02 to about 1.0 gram per liter by adding a bath-compatible chloride.

18. The method of electroplating copper from an aqueous acid copper plating bath which comprises the steps of adding to the bath prior to its use a bath-compatible chloride and thereby establishing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, adding to the bath a polyoxyethanol of molecular weight greater than 300 and thereby establishing in solution in the bath an amount of said polyoxyethanol effective to act synergistically with the chloride ion to produce uniform copper deposits of superior physical properties, electro-depositing copper from the bath, and as the bath becomes depleted of synergistic amounts of chloride ion and polyoxyethanol periodically adding to the bath a mixture containing between about 10 and about 90 parts of the said polyoxyethanol and between about 90 and about 10 parts, respectively, of the said bath-compatible chloride and thereby maintaining the concentration of chloride ion and polyoxyethanol in solution in the bath in the synergistic range.

19. An aqueous acid copper electroplating bath containing a bath-soluble polyoxyethanol chloride having a molecular weight greater than 300, and a bath-compatible chloride providing a chloride ion concentration in the bath of between 0.02 and about 1.0 gram per liter, said polyoxyethanol chloride being present in solution in the bath in amount effective to act synergistically with the chloride ion in the bath to produce uniform copper deposits of superior physical properties.

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