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ELECTROPLATING OF COPPER ALLOYS

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8 Claims. (Cl. 204—44)

This invention relates to improved methods of electroplating copper alloys. Specifically, it relates to an improved bath and process for electrodepositing bright and leveling copper-tin, copper-zinc, and copper-cadmium alloys.

Alkaline copper-tin plating baths which contain free cyanide are well known. Electroplates obtained from such baths are commercially dull and lusterless. Also the baths do not provide good leveling, and thus require a high degree of costly mechanical polishing and buffing before plating, as well as after plating. A bright and smooth plate is required for subsequent plating of nickel or chromium. Numerous attempts to obtain bright and level plates of this nature have been made. Prior art methods of obtaining a bright copper-tin electroplate include the addition of such materials in the plating bath as potassium pyrophosphate, glue and monobasic potassium orthophosphate, as in U.S. Patent 2,658,032.

Although the addition of these prior art brightening agents has made it possible to obtain a degree of brightness in electroplating of chromium-tin alloys, the leveling action has not been substantially improved. Also, in employing these methods it is necessary to adjust the plating baths to obtain electroplates containing greater than 15 percent, by weight, tin. If the tin content of the electroplate is permitted to drop below 15 percent, by weight, or above 50 percent, by weight, dull and lusterless electroplates are obtained. It has now been found that superior electroplates can be obtained from alkali copper-tin, free cyanide baths by employing as brightening and leveling agents certain combinations of known additions not heretofore revealed by the prior art.

Examples of copper-tin alloy baths, such as is the subject of the present invention, are illustrated in Patent 2,658,032, Faust et al. These baths contain ingredients considered unessential in the present application, such as glue, gelatin and hydrolysis products thereof, and orthophosphate, and omit essential brighteners and levelers of the present invention. Otherwise, the broad and preferred composition ranges as disclosed in the Faust et al. patent, illustrate the ranges of the various constitutents of the present baths. The baths of Faust et al. are as follows:

	Grams per liter	
	Broad	Preferred
Pyrophosphate (sodium, potassium, or ammonium)	8–300	40–90
Cuprous cyanide or halide	2–230	15–80
Cyanide (sodium, potassium, or ammonium)	2–350	22–120
Stannous compound (chloride, pyrophosphate, or sulfate)	2–50	5–15
Orthophosphate (ammonium, potassium, or sodium mono-, di-, and triorthophosphates)	5–120	10–30
Glue, gelatin, and hydrolysis products thereof	0.01–50	0.5–2

Other bath compositions applicable to the present invention, with some modification, are disclosed in copending patent application Serial No. 494,257, Safranek et al. These baths are as follows:

	Grams per liter	
	Broad	Preferred
Pyrophosphate (sodium, potassium, or ammonium)	8–300	40–90
Cuprous cynade	2–230	15–80
Cyanide (sodium, potassium or ammonium)	2–350	22–120
Stannous compound [1] (sulfate, chloride, or pyrophosphate)	0–50	0–15
Stannate [1] (sodium, potassium, or ammonium)	0–250	0–75
Orthophosphate (ammonium, potassium or sodium mono-, di- and triorthophosphates)	5–120	10–30
Glue, gelatin, and hydrolysis products thereof	0.01–5.0	0.5–2

[1] The total amount of tin must be 2 to 50 grams per liter of stannous salt or the equivalent as stannate, or mixtures of stannous salt and stannate. Five grams of stannate are equivalent to one gram of stannous salt. Thus, when no stannous salt is present, the permissible range of stannate is 10 to 250 grams per liter, and the preferred range 25 to 75 grams per liter.

Brightening and leveling additions of the present invention have been found to be similarly beneficial to the plating of copper-base alloys containing cadmium and zinc, as well as the copper-tin alloys.

It is therefore an object of the present invention to provide a method whereby superior bright and leveling copper-base alloys containing at least one of the alloying constituents, tin, cadmium, and zinc, may be obtained.

It is also an object to provide an electroplating bath capable of providing a superior bright and leveling copper-base alloy containing at least one alloying constitutent from the group consisting of tin, cadmium, and zinc, when subjected to electrolysis.

It is a particular objective of the present invention to provide a plating bath and method whereby bright and leveling copper-tin electroplates may be obtained.

It is a further object of the present invention to provide a plating bath and method of producing a mirrorlike and leveling copper alloy containing from about 5 to 15 percent tin.

Other objects and advantageous features are apparent from the following specification.

In general, the present invention relates to the electrolysis of aqueous alkali copper plating baths which contain, in addition to dissolved copper compounds, dissolved compounds which supply at least one alloy metal selected from the group consisting of tin, zinc, and cadmium, and, additionally, as brightening and leveling agents, dissolved lead, pyrophosphate, and a salt of an aliphatic carboxylic acid. The invention particularly relates to improvements in the brightening and leveling action of copper-tin, copper-zinc, or copper-cadmium cyanide plating baths by the addition of a combination of leveling and brightening agents consisting of a lead salt, and alkali metal pyrophosphate, and a water-soluble salt of an aliphatic carboxylic acid containing from 1 to 6 carbon atoms.

The baths of the present invention conform with the desired broad and preferred ranges disclosed in the above-identified Faust patent and Safranek et al. application except they preferably do not contain the materials considered essential and novel in those disclosures, such as glue, gelatin, and the hydrolysis products thereof or a halide salt. The latter additions have an adverse effect on the leveling properties of the electroplates of the present invention. The composition ranges of the present baths are as follows:

	Grams per liter	
	Broad	Preferred
Pyrophosphate (sodium, potassium, or ammonium)	8–300	40–90
Cuprous cyanide	2–230	15–80
Cyanide (sodium, potassium, or ammonium)	2–350	22–120
Stannous compound [1] (sulfate, chloride, or pyrophosphate)	0–50	0–15
Stannate [1] (sodium, potassium, or ammonium)	0–250	0–75
Lead acetate or equivalent amount of soluble lead compounds	0.05–0.6	0.2–0.4
Rochelle salt or equivalent amount of a lower aliphatic acid salt	15–200	50–70

[1] The total amount of tin must be 2 to 50 g./l. of stannous salt or the equivalent as stannate or mixtures of stannous salt and stannate. Five grams of stannate are equivalent to one gram of stannous salt. Thus when no stannous salt is present, the permissible range of stannate is 10 to 250 g./l. and the preferred range 25 to 75 g./l.

Zinc and cadmium compounds may be substituted for the stannate or stannous compounds, or two or more soluble tin, zinc, and cadmium salts may be employed simultaneously. The preferred broad and narrow ranges of the total amount of stannous, stannate, zinc and cadmium salts employed should be equivalent to 2–50 g./l. of the stannous salt, broad range, and 2–15 g./l. of the stannous salt, preferred range.

Electroplating baths of the present invention provide brighter plates, more consistently than heretofore known, and also provide greater leveling than prior art baths. By greater leveling is meant the ability of the electroplate to fill in scratches and defects present on the surface of the base metal and thereby diminishing or eliminating evidence of such defects on the surface of the resulting electroplate. The necessity of good leveling properties is extremely important in that when the bath is not capable of providing level plates, leveling must be accomplished by extensive and expensive surface preparation of the base metal prior to electroplating, or by wasteful and expensive buffing after plating. In the prior art methods of electroplating such copper-alloying plates as copper-tin, it has been necessary to polish and buff the base metal to a far greater extent than is necessary when employing the baths of the present invention. This has been the case even where brighteners are employed and bright electroplates have been obtained. By using the plating baths of the present invention bright and level copper alloy electroplates containing from 5 to 15 percent tin may be obtained. Copper alloy plates produced by prior known methods and plating baths were dull and required buffing to obtain brightness.

The smoothness of surfaces is conventionally measured in terms of root-mean-square microinches. The surfaces of many common base materials must obviously be buffed and polished to obtain a smoothness approximately equivalent to that which one desires to obtain on the plated article, usually no rougher than about 5 or 7 R.M.S. microinches.

By employing the baths of the present invention, base materials exhibiting an 18 R.M.S. microinch finish have been given a copper-tin electroplate approximately .00075 inch thick, producing a finish measuring 7 R.M.S. microinches. In a similar manner surfaces exhibiting 8.5 R.M.S. microinches have been given a .0075-inch plate to obtain an R.M.S.-microinch value as low as 4. Thus it can be seen that the baths of the present invention exhibit a far greater leveling action than has heretofore been known.

The addition of aliphatic carboxylic acid salts, in combination with small additions of lead and pyrophosphate to the alkali alloy copper-plating baths, have been found to be essential in providing superior brightness and leveling not heretofore known. The function of such compounds may be that of a complexing agent for either lead or one of the other metallic components in the bath; however, this is speculative in nature and in no way restricts the baths or process of the present invention. Particularly satisfactory results have been obtained by supplying the salts of hydroxy-substituted aliphatic carboxylic acid salts. Best results are obtained by using Rochelle salt, thus providing tartrates to the plating bath. However, other additions that may be employed are acetates, gluconates, citrates, or glycolates. The preferred compounds are the alkali metal salts of compounds, such as sodium and potassium. However, other metal salts may be used. Lead salts may be conveniently employed, thus supplying some or all of the necessary lead at the same time as when introducing lower aliphatic acid salts to the baths. The compounds should be capable of easily dissolving in the plating baths; thus it is desirable to employ the lower aliphatic compounds, particularly those containing 6 carbon atoms or less. Such compounds in amounts of from a trace to the saturation of the bath have a brightening effect on the copper-tin, copper-zinc, or copper-cadmium plates in combination with pyrophosphate and lead. However, best results have been obtained by employing from about 50 to 70 grams per liter of Rochelle salt or the molecular equivalent of the other compounds. The broad and preferred concentrations of Rochelle salt in moles are 0.05 to 0.75 mole, broad range, and 0.18 to 0.25 mole, preferred range. Optimum results have been obtained by employing about 70 grams per liter of tartrates (Rochelle salt). From a trace to saturation of the other salts of hydroxy-substituted carboxylic acids will effect improved brightness and leveling. Additions of such compounds which will provide aliphatic carboxylic acid salts containing from 1 to 6 carbon atoms in mole equivalents of 50 grams per liter to 70 grams per liter of Rochelle salt will produce bright and level plates.

Lead may be provided to the bath by the addition of any soluble lead compound, such as lead acetate. Best results have been obtained by providing from about 0.15 to 0.25 gram per liter of lead in the plating bath. However, concentrations up to 0.4 gram per liter may be effective. Concentrations above about 0.4 gram per liter result in a highly stressed electroplate. An optimum concentration is about 0.24 gram per liter. In terms of lead acetate, the broad and preferred ranges in grams per liter are 0.05 to 0.6, broad range, and 0.2 to 0.4, preferred range. In terms of moles, these ranges are about 0.00015 to 0.0018 broad range, and 0.0006 to 0.0012, preferred range. Additional acetate may be provided to the bath in the form of acetate salts, such as sodium or potassium acetate, in order to provide the required amount of carboxylic acid salt. For example, to provide 0.20 mole of acetate 0.0018 mole may be supplied as lead acetate and 0.198 mole or 19.4 grams per liter may be supplied as potassium acetate.

The effect of the pyrophosphate addition to the bath is believed to be that of a complexing agent. The addition is preferably in the form of the sodium, potassium, or ammonium salt; however, other pyrophosphate compounds, such as lead pyrophosphate, may be employed.

It may be desirable also to add an alkali metal dihydrogen orthophosphate for the purpose of buffing against changes in pH. In any event, orthophosphate will be present in the bath after a short period of electroplating in that some of the pyrophosphate compounds will break down into the orthophosphate. The ranges of orthophosphate employed in Patent 2,658,032 have been found to be satisfactory for the present electroplating baths.

The alloying constituents of tin, zinc, and cadmium may be added to the bath by means of convenient soluble salts. Particularly useful and desirable compounds are commercial grades of the alkali metal stannates, such as potassium or sodium stannate, and stannous sulfate. Electroplates showing some superior brightness and leveling qualities are obtained by employing both stannate

and stannous compounds in the bath. The preferable operating conditions of the present electroplating baths are similar to those described in Patent 2,658,032, Faust et al. The pH is preferably adjusted to be from 8½ to 13. An electric current is passed from the anodes through the bath to the cathode to create a current density at the cathode preferably not in excess of 90 amps. per square foot. The temperature of the bath should not be in excess of 190° F.

Example I

A copper-tin bath was prepared having the following composition:

	Grams per liter
Potassium pyrophosphate (anhydrous $K_4P_2O_7$)	73
Potassium cyanide (KCN)	50
Copper cyanide (CuCN)	27
Stannous sulfate, commercial	0.4
Potassium stannate, commercial	9
Potassium phosphate (monobasic (KH_2PO_4)	12
Rochelle salt	75
Lead acetate	0.2
Water	Balance

pH, 12.5.

Plating was conducted on polished steel panels having profilometer readings of 18 and 8 R.M.S. microinches. The temperature was maintained at about 145° F. and the current density was 30 amps. per square foot. Bright copper-tin plates containing approximately 10 percent tin .0007 to .0009 inch thick were obtained. Leveling was between 50 and 60 percent. The plates on the steel panels which originally had an R.M.S. microinch reading of 18 proved to have R.M.S. microinch readings of from 9 to 6. The plates on the steel panels which originally had an R.M.S. microinch reading of 8 exhibited an R.M.S. microinch reading of about 4.

Example II

A copper-tin-zinc bath was prepared having the following composition:

	Grams per liter
Potassium pyrophosphate (anhydrous $K_4P_2O_7$)	85
Potassium cyanide (KCN)	50.0
Copper cyanide (CuCN)	26
Stannous sulfate, commercial	0.6
Potassium stannate, commercial	9.0
Potassium phosphate (monobasic), or potassium dihydrogen orthophosphate (KH_2PO_4)	14.5
Rochelle salt	75
Lead acetate	0.4
Zinc acetate	18
Water	Balance

pH, 11.5–12.

The temperature was maintained at about 140° F. and the cathode current density was 25 amps. per square foot.

Golden yellow bright and level plates were obtained which, on analysis, consisted of about 10 percent tin, 15 percent zinc, balance copper.

Example III

	Grams per liter
Potassium pyrophosphate (anhydrous $K_4P_2O_7$)	85
Potassium cyanide (KCN)	50
Copper cyanide (CuCN)	26
Potassium phosphate (monobasic) (KH_2PO_4)	14.5
Rochelle salt	70
Lead acetate	0.4
Zinc acetate	35

pH, 7.8.

The temperature was maintained at about 130° F. and the cathode current density was 30 amps. per square foot.

Yellow semibright and level plates were obtained which, consisted of 20 to 30 percent zinc, balance copper.

What is claimed is:

1. A process for electrodepositing a copper-tin alloy comprising: passing an electric current through a bath which consists essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium	8 to 300
Cuprous cyanide	2 to 230
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	2 to 350
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 50
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 250
A lead compound in an amount equivalent to lead acetate	0.05 to 0.6

A lower aliphatic carboxylic acid salt, 0.05 to 0.75 mole.

said total amount of tin compounds being within the equivalent range of from 2 to 50 grams per liter of the stannous salt.

2. A process for electrodepositing a copper-tin alloy comprising: passing an electric current through a bath which consists essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium	8 to 300
Cuprous cyanide	2 to 230
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	2 to 350
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 50
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 250
A lead compound in an amount equivalent to lead acetate	0.05 to 0.6

A lower hydroxy-substituted aliphatic carboxylic acid salt, 0.05 to 0.75 mole.

said total amount of tin compounds being within the equivalent range of from 2 to 50 grams per liter of the stannous salt.

3. A process for electrodepositing a copper-tin alloy comprising: passing an electric current through a bath which consists essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium pyrophosphate	40 to 90
Cuprous cyanide	15 to 80
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	22 to 120
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 15
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 75
A lead compound in an amount equivalent to lead acetate	0.2 to 0.4

A lower aliphatic carboxylic acid salt, 0.18 to 0.25 mole.

said total amount of tin compounds being within the equivalent range of from 5 to 15 grams per liter of the stannous salt.

4. A process for electrodepositing a copper-tin alloy comprising: passing an electric current through a bath which consists essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium pyrophosphate	40 to 90
Cuprous cyanide	15 to 80
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	22 to 120
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 15
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 75
A lead compound in an amount equivalent to lead acetate	0.2 to 0.4
A lower hydroxy-substituted aliphatic carboxylic acid salt, 0.18 to 0.25 mole.	

said total amount of tin compounds being within the equivalent range of from 5 to 15 grams per liter of the stannous salt.

5. An aqueous bath for electrodepositing a copper-tin alloy consisting essentially of:

	Grams per liter
At least one pyrophosphate selected from the the group consisting of sodium, potassium, and ammonium	8 to 300
Cuprous cyanide	2 to 230
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	2 to 350
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 50
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 250
A lead compound in an amount equivalent to lead acetate	0.05 to 0.6
A lower aliphatic carboxylic acid salt, 0.05 to 0.75 mole.	

said total amount of tin compounds being within the equivalent range of from 2 to 50 grams per liter of the stannous salt.

6. An aqueous bath for electrodepositing a copper-tin alloy consisting essentially of:

	Grams per liter
At least one pyrophosphate selected from the the group consisting of sodium, potassium, and ammonium	8 to 300
Cuprous cyanide	2 to 230
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	2 to 350
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 50
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 250

	Grams per liter
A lead compound in an amount equivalent to lead acetate	0.05 to 0.6
A lower hydroxy-substituted aliphatic carboxylic acid salt, 0.05 to 0.75 mole.	

said total amount of tin compounds being within the equivalent range of from 2 to 50 grams per liter of the stannous salt.

7. An aqueous bath for electrodepositing a copper-tin alloy consisting essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium pyrophosphate	40 to 90
Cuprous cyanide	15 to 80
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	22 to 120
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 15
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 75
A lead compound in an amount equivalent to lead acetate	0.2 to 0.4
A lower aliphatic carboxylic acid salt, 0.18 to 0.75 mole.	

said total amount of tin compounds being within the equivalent range of from 5 to 15 grams per liter of the stannous salt.

8. An aqueous bath for electrodepositing a copper-tin alloy consisting essentially of:

	Grams per liter
At least one pyrophosphate selected from the group consisting of sodium, potassium, and ammonium pyrophosphate	40 to 90
Cuprous cyanide	15 to 80
At least one cyanide selected from the group consisting of sodium, potassium, and ammonium	22 to 120
At least one stannous compound selected from the group consisting of sulfate, chloride, and pyrophosphate	0 to 15
At least one stannate compound selected from the group consisting of sodium, potassium, and ammonium	0 to 75
A lead compound in an amount equivalent to lead acetate	0.2 to 0.4
A lower hydroxy-substituted aliphatic carboxylic acid salt, 0.18 to 0.75 mole.	

said total amount of tin compounds being within the equivalent range of from 5 to 15 grams per liter of the stannous salt.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,793,990	Heymann et al.	May 28, 1957

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,886,500 May 12, 1959

John E. Bride et al.

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

Column 3, line 40, for "alloying" read -- alloy --; column 5, line 20, Example 1, after "monobasic" insert a closing parenthesis; column 8, lines 28 and 53, for "0.75", each occurrence, read -- 0.25 --.

Signed and sealed this 1st day of September 1959.

(SEAL)

Attest:

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