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ELECTRODEPOSITION OF COPPER-TIN ALLOYS

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ABSTRACT OF THE DISCLOSURE

In the plating of copper-tin alloys from alkaline baths containing free cyanide, the tendency of tin to sludge out is suppressed by the addition of alkali aminoacetate chelating agents, such as EDTA, in amounts of over 25 g./l., i.e., in excess of the amounts added to function as a brightener.

This invention relates to an improved process of electroplating copper-tin alloys, i.e. bronzes and to electrolytic compositions for plating such alloys.

One of the problems in prior art plating of copper-tin alloys and, indeed, of tin plating itself has been the tendency of the tin to sludge out, making it difficult in the case of the alloy bath to maintain the proper Cu:Sn ratio even though anodes of the alloy were soluble in the bath.

Among the objects of this invention is to provide an aqueous electrolytic bath composition containing tin and copper in which the tendency for tin to sludge out is nullified.

This invention is based on the discovery that the tendency of tin to sludge out of a copper-tin bath can be prevented by incorporating considerable quantities of the salts of acetic acid substituted aliphatic amines, such as the salts of ethylenediaminetetracetic acid (EDTA) and diethylenetriaminepentaacetate, into the plating bath. The addition of small quantities of EDTA and similar compounds in acid-tin baths has been described to function as a brightener, and such addition has also been disclosed for extending the bright range of brass solutions but the discovery of the effectiveness of relatively large quantities of this material as a sludge inhibitor was totally unexpected. We have consistently found that the addition of a large amount of such a chelating or complexing agent does in fact provide a plating bath much more stable than the same formulation, absent the EDTA or similar salt.

Among other objects of the invention is to provide an aqueous electrolytic bath composition for plating bright bronze in which the tendency for tin to sludge out is nullified.

Aside from the requirement that relatively large quantities of the EDTA type of complexing agents be added to the bath, the range of other components is not extremely critical. The relative proportions of tin and copper in the bath of course will be governed by the proportion of such metals desired in the plating layer. Alkali is present in sufficient amount to provide a pH of at least

12.5. A certain amount of free potassium cyanide is desirable in the bath.

Various other ingredients such as brighteners, etc., can be added to the bath without undesirability affecting its operation. Soluble lead salts are particularly effective as brighteners.

Thus the bath of the invention comprises the following ingredients:

	Preferred	Range
Copper cyanide (g./l.)	40	10–70
Alkali Stannate (g./l.)	50	15–90
Alkali cyanide (g./l.)	85	60–120
Alkali hydroxide (g./l.)	45	10–80
Alkali aminoacetates (g./l.)	100	25–200
pH	≥12.5	12.5–13.8

The foregoing composition will be understood not to be limiting as to the way in which the various ingredients are added. The copper cyanide is at least partially present in said bath as the double cyanide of copper and alkali and the copper may be added in the form of said double cyanide. Potassium and sodium are the usual alkalis referred in the table but ammonium and lithium compounds can also be employed. The term "alkali" amino acetates will be understood to include the ammonium compounds, and to include such amines carrying acetate groups having a pK value between about 12 and 22. The acid amino acetates (instead of salts) can be added and the tin can be added as the stannic oxide provided the additional alkali hydroxide necessary to form the corresponding salts is taken into account to provide the required pH.

The deposits obtained from this bath are smooth, but not fully bright. The addition of brighteners described as effective in bronze solutions, particularly about 0.05–0.07 g./l. of lead, as a salt soluble in the bath, makes it possible to obtain fully bright and highly levelled deposits from this bath.

The bath is operated above room temperature (approx. 110–160° F.) preferably at a current density of 1 to 10 amp/dm.^{2}. The pH is higher than 12.5 as stated above.

Bronze anodes will dissolve but can lead to sludge formation so we generally prefer to operate with insoluble anodes, stainless steel is satisfactory, and to feed the metals into the bath in the form of compounds as the alloy is plated out.

The invention will be exemplified in the following specific examples with the understanding that these examples are preferential and illustrative and not to be considered as limiting the invention to the data given.

Example 1

A bath is made of the following components:

Copper cyanide	g./l.	40
Potassium stannate, K_2SnO_3	g./l.	50
KCN	g./l.	85
KOH	g./l.	45
Na_2EDTA	g./l.	100
pH		13.5

With brass or steel panels as the cathode, at a current

density of 4 amp/dm.^{2} and at a temperature of 140° F., smooth deposits are obtained. The deposit is approximately 80% Cu. This bath was stable for 120 days, showing no sludge formation and at the end of this time, plated panels equivalent to those obtained from the freshly made bath were obtained.

Example 2

The process was conducted as in Example 1 except that 0.1 g./l. of lead as lead acetate was added to the bath. The panels obtained were fully bright. The bath has the same stability as that of Example 1.

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

We claim:

1. The process for co-electrodepositing copper and tin which comprises electrolyzing an aqueous solution containing the following ingredients:

	G./l.
Copper cyanide	40
Potassium stannate	50
KCN	85
KOH	45
Na_2EDTA	100

2. The process of co-electrodepositing copper and tin which comprises electrolyzing an aqueous solution containing the following ingredients:

	G./l.
Copper cyanide	10–70
Alkali metal stannate	15–90
Alkali cyanide	60–120
Alkali hydroxide (to pH=12.5)	10–80
Alkali metal alkylene aminoacetates selected from the group consisting of alkali metal alkylene diamino tetra acetate and alkali metal alkylene triamino penta acetate	25–200

3. A process as claimed in claim 2, comprising in addition 0.05 to 0.75 g./l. of lead, added as a soluble lead salt.

4. An aqueous electrolytic bath for co-electrodepositing copper and tin containing the following ingredients:

	G./l.
Copper cyanide	10–70
Alkali metal stannate	15–90
Alkali cyanide	60–120
Alkali hydroxide (to pH=12.5).	
Alkali metal alkylene aminoacetates selected from the group consisting of alkali metal alkylene diamino tetra acetate and alkali metal alkylene triamino penta acetate	25–200

5. An aqueous electrolytic bath as claimed in claim 4 wherein the alkali of said alkali metal stannate, alkali cyanide and alkali hydroxide is potassium.

6. An aqueous electrolytic bath according to claim 4 containing in addition a lead compound in the amount of about 0.05 to 0.75 g./l. calculated as lead.

7. An aqueous electrolytic bath as claimed in claim 4 wherein the alkali aminoacetate is alkali metal alkylene EDTA.

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