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2,739,933

ELECTRODEPOSITION OF TERNARY ALLOYS

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This invention relates to the electrodeposition of copper, tin and zinc from alkaline electrolytes embodying certain addition agents to promote brighter and smoother plating.

In using plating solutions for electrodepositing a ternary alloy comprising copper, tin and zinc on a metallic base member, it has been usually necessary to add a betaine composition to the solution in order to produce a bright and smooth deposit. A difficulty with the use of the betaine additive was the problem of obtaining the betaine of the optimum composition necessary for the bright deposition of the ternary alloy from the plating solution. The betaine compositions as obtained commercially apparently do not have a constant composition or purity thus causing considerable difficulty in the satisfactory operation of a copper, tin and zinc bath commercially.

An object of this invention is to provide an improved plating solution for electrodepositing a ternary alloy by incorporating a brightener of 2-thiohydantoin or certain substitution derivatives of 2-thiohydantoin in the solution.

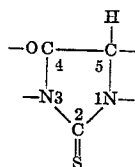
A further object of this invention is to provide a method of electrodepositing a continuous, corrosion resistant, pit-free ternary alloy by incorporating a brightener of 2-thiohydantoin or certain substitution derivatives of 2-thiohydantoin, or mixtures of two or more, and molybdc acid in the plating bath.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description.

I have discovered that the addition of either 2-thiohydantoin or substitution derivatives of 2-thiohydantoin or two or more of such compounds, to alkali cyanide electrolytes having present therein copper, tin, zinc and carbonate ions will enable electrodeposits with highly refined grain size and having smooth, bright surfaces to be plated therefrom which are fully equivalent to those obtained with betaine compounds under optimum conditions. Also, it has been discovered that the further addition of molybdc acid to the 2-thiohydantoin compound additions will result in still better ternary alloy deposits.

More particularly, the present invention is based on the addition of predetermined amounts of at least one 2-thiohydantoin compound having at least one organic substituent in any one of the 1, 3 and 5 positions. The base of these compounds is the following thiohydantoin nucleus:



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Various organic radicals may be substituted at any one or more of the 1, 3 or 5 positions, so long as the compound is not rendered so insoluble that it will not dissolve in the alkali cyanide electrolyte in an amount sufficient to produce an appreciable result. Examples of suitable compounds are:

2-thiohydantoin
1-acetyl-2-thiohydantoin
5(2-hydroxybenzal)-2-thiohydantoin
5-furfural-2-thiohydantoin
1-benzoyl-2-thiohydantoin
5-benzal-2-thiohydantoin
1-benzal-2-thiohydantoin
1-methyl-2-thiohydantoin
3-acetyl-2-thiohydantoin

The best results have been secured with 2-thiohydantoin derivatives having a carbonyl group



attached at any one or all of the 1, 3 and 5 positions, and with an organic radical being attached to the carbonyl group.

It has been found that as little as 0.0005 ounce per gallon of one or more of these 2-thiohydantoin derivatives will produce an improvement in the ternary alloy alkali cyanide electrolyte. In some cases as much as 0.5 ounce per gallon of the compound may be added. It will be appreciated that the relative solubility of the compounds will determine the maximum amount that may be applied. Extremely good results have been secured with 1-acetyl-2-thiohydantoin and specific reference will be made hereinafter to this compound, though, it will be understood that others may be substituted in whole or in part therefor.

The ternary alloy which is electroplated in practicing this invention may consist of from 50% to 75% copper, 15% to 35% tin, and 5% to 20% zinc. In some cases, these proportions may be departed from to a slight extent. The presence of minor amounts of other metals or impurities is believed not to affect the nature of the electroplated product. Particularly good results are obtained if the copper content of the electroplate is from 55% to 65%, the tin from 20% to 30% and the zinc from 8% to 20%.

Alkali cyanide electrolytes suitable for plating copper, tin and zinc are well known. Such electrolytes are disclosed in Patents 2,468,825 and 2,435,967. As an example one can employ an aqueous solution having dissolved therein approximately 4.4 ounces per gallon sodium cyanide, 0.2 ounce per gallon zinc oxide, 0.22 ounce per gallon sodium stannate, 4.0 ounces per gallon sodium carbonate, and 0.35 ounce per gallon copper cyanide. Into the alkali cyanide bath, there may be added 1-acetyl-2-thiohydantoin in an amount from 0.0005 to 0.5 ounce per gallon. The optimum proportions appear to be from 0.005 to 0.05 ounce per gallon. It will be appreciated that if the electrolyte is used in plating, the addition agent will require replenishing from time to time. When the electrolyte incorporates these proportions of 1-acetyl-2-thiohydantoin, an excellent ternary alloy of copper, tin and zinc is plated therefrom at any temperature from room temperature up to 150° F. Fine, smooth tin, zinc and copper alloy deposits have been produced from baths operating at temperatures of 125° F., which appears to be the optimum temperature.

To obtain even better results, molybdc acid may be added with the 1-acetyl-2-thiohydantoin, the amount of acid being from 0.03 to 3.0 ounces with the optimum concentration being at approximately 0.15 ounce per gallon of the electrolyte.

As a result of numerous tests run under comparable conditions, both in the laboratories and in the shop, we have found that 1-acetyl-2-thiohydantoin, for instance, enables the brightest copper, tin and zinc alloy to be deposited that we have secured with any single known addition agent, and furthermore the electrodeposited ternary alloy is relatively non-brittle and free from pitting.

Alkali cyanide copper, tin and zinc aqueous electroplating electrolytes with 1-acetyl-2-thiohydantoin added thereto may be employed for plating metal by passing either continuous direct current, superimposed alternating current and direct current, or periodically reversed electrical current or other suitable electrical current therethrough. Excellent results have been obtained with direct-current plating from such electrolytes. It will be understood that other addition agents may be present in the electrolyte.

The following examples are exemplary of the preparation of an alkali cyanide electrolyte for depositing copper, tin and zinc on a metallic base member in accordance with this invention.

Example I

An alkali cyanide electrolyte suitable for plating copper, tin and zinc was prepared by dissolving in an aqueous solution 4.4 ounces per gallon sodium cyanide, 0.2 ounce per gallon zinc oxide, 0.22 ounce per gallon sodium stannate, 4.0 ounces per gallon sodium carbonate, and 0.35 ounce per gallon copper cyanide. Into this solution, there was admixed 0.005 ounce per gallon of 1-acetyl-2-thiohydantoin. The solution thus prepared was used as a plating bath, operating at various temperatures from room temperature up to 150° F., with excellent results. A temperature of 125° F. appeared to give optimum plating results.

Copper, tin and zinc was deposited on a member by passing an electric current from an anode to a cathode member to be plated immersed in the bath of this Example I by direct-current using current densities of up to 200 amperes per square foot. The results obtained from these tests, both in the laboratory and in the shop, were comparable with those using a conventional betaine compound for a brightening agent under ideal conditions.

Example II

An alkali cyanide electrolyte was prepared and tested in the same manner as Example I except that 0.15 ounce per gallon of molybdic acid was also admixed with the solution. The results obtained in each test produced excellent smooth deposits of the ternary alloy better than anything obtained under the same conditions using many other addition agents previously known in the art.

Example III

An alkali cyanide electrolyte was prepared in the same manner as Example I except that 0.005 ounce per gallon of 3-acetyl-2-thiohydantoin was used in place

of the 1-acetyl-2-thiohydantoin. Substantially the same results were obtained.

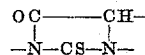
Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope hereof, it is intended that all matter contained in the disclosure shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. In an aqueous alkali cyanide plating solution for electro-depositing a ternary alloy composed of from 50% to 75% copper, 15% to 35% tin, and 5% to 20% zinc on a metallic base member, an organic brightener comprising 1-acetyl-2-thiohydantoin admixed with the solution in an amount of from 0.0005 oz. to 0.5 oz. per gallon of solution.

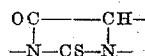
2. The plating solution of claim 1 in which there is present from 0.03 to 3.0 oz. of molybdic acid per gallon of solution.

3. An alkali cyanide electrolyte for depositing a ternary alloy composed of from 50% to 75% copper, 15% to 35% tin, and 5% to 20% zinc, having present therein from 0.0005 oz. to 0.5 oz. per gallon of at least one 2-thiohydantoin compound selected from the group consisting of 2-thiohydantoin and its derivatives having the nucleus



4. The electrolyte of claim 3 in which there is present from 0.03 to 3.0 oz. of molybdic acid per gallon of electrolyte.

5. In the method of depositing a ternary alloy composed of from 50% to 75% copper, 15% to 35% tin, and 5% to 20% zinc, the steps comprising passing electric current from an anode to a cathode-member to be plated immersed in an aqueous plating bath comprising an alkali cyanide, zinc oxide, alkali stannate, alkali carbonate and copper cyanide, there being present in the bath an organic brightener comprising from 0.0005 oz. to 0.5 oz. per gallon of bath of at least one 2-thiohydantoin compound having the nucleus



6. The process of claim 5 wherein the compound is 1-acetyl-2-thiohydantoin.

7. The method of claim 5 in which there is present in the plating bath from 0.03 to 3.0 oz. per gallon of molybdic acid.

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