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BRIGHT PLATING SOLUTION AND METHOD

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The present invention relates to methods and baths for the treatment of metal surfaces to improve the appearance thereof, and in particular to improved plating solutions and methods for electrolytically depositing a zinc-tin alloy having bright surfaces.

Most metals and alloys deposited from aqueous electrolytic solutions have surfaces which are in a dull condition, frequently referred to as "matte finish." There are a number of suggested approaches by which brightness may be imparted to such electrolytically deposited surfaces, including mechanical buffing and polishing, use of chemical bright dips and electropolishing. Still another approach which has recently come into prominence is the use of addition agents directly in the plating solution. Advantageously, such addition agents are designed to brighten the electrodeposited surface in the "as-plated" condition thereby avoiding the necessity of submitting the metal surfaces to additional processing, with attendant increase in cost and production time. Broadly, addition agents for "as plated" brightening of the electrolytically deposited surfaces may be characterized as metal ions which are used in small amounts with the plating solution to codeposit with the principal elements being plated out whereby the structure of the plating is altered to render the plated surfaces bright; and inorganic and organic materials which usually do not codeposit, but influence the grain structure of the metal or metals being plated out of the solution.

Broadly, it is an object of the present invention to provide an improved method and baths for achieving bright surface deposition of metals which ordinarily are deposited in a dull or matte condition. Specifically, it is within the contemplation of the present invention to provide treatment methods bringing about brightening of electrodeposited metal surfaces in the "as-plated" condition.

With the recent advent of a solderable zinc-tin alloy, as described in application Serial No. 526,860, filed August 8, 1955, in the name of the inventor herein and assigned to the assignee of the present invention, there has developed a need for a commercially practical approach to brightening the normally dull surfaces of this alloy. The plating methods and baths described in said copending application are suitable for obtaining a solderable zinc-tin alloy containing between 75 and 95% zinc and between 25 and 5% tin, which alloy is inexpensive, solderable, and rust-resistant. However, the electrodeposited alloy as plated has a white matte finish, which apart from being relatively prone to finger staining, does not have bright enough surface properties for widespread commercial acceptance.

It is a further object of the present invention to provide an improved method and plating baths for electrodepositing a solderable zinc-tin alloy with bright surfaces in the "as-plated" condition. Advantageously, the improvement in the surface qualities of the alloy does not interfere with or alter the solderable characteristics

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which make the alloy exceptionally attractive for use in the electronic industry.

Attempts to brighten solderable zinc-tin alloy in accordance with conventional practices by the use of chemical bright dips known for zinc plating have not given satisfactory results. Likewise, proprietary materials known for producing bright zinc platings in the "as-plated" condition will not produce desired surface properties under the conditions of plating a zinc-tin alloy established in accordance with the teachings of said copending application.

In view of the somewhat specialized requirements for deposition of the high-zinc, low-tin solderable alloy in accordance with said copending application, a suitable brightener should improve the deposit appearance without reacting with the plating bath; attain brightness at current densities of the order of at least 50 amperes per square foot to permit rapid plating as is required for a commercial process; exhibit reasonable stability in the plating bath to minimize the need for replenishment of the brightener and/or build up of undesired impurities; and function to brighten the electrodeposited alloy during operation of the bath over a fairly wide range of current densities as is required for plating irregularly shaped objects. Although the several requirements are not all essential for brightener, their realization permits operation of the zinc-tin plating baths in a manner which is completely compatible with attaining bright "as-plated" surfaces.

I have found that bright zinc-tin "as-plated" deposits may be attained by electrodeposition from a zinc-tin plating bath which includes gelatin and at least one further additive selected from the group consisting of thio-urea and ammonium molybdate. With such brighteners, it is possible to obtain electrodeposits of solderable zinc-tin alloys having the requisite bright appearance at current densities of the order of 50 to 80 amps./sq. ft., and at current efficiencies of the order of 75 to 85%, higher values of efficiency being obtained at lower values of current density.

As to the details of the plating bath, in accordance with the criteria established in said copending application and the earlier filed applications mentioned therein, sodium or potassium formulation baths may be prepared which will deposit a solderable alloy containing between 75 and 95% zinc balance tin, at cathode efficiencies of 60 to 100% and at current densities of up to 25 amperes per square foot for sodium baths and 50 amperes per square foot for potassium baths, with the zinc concentration varying between the limits of 5 and 50 grams per liter, and the tin concentration varying between the limits of 15 to 75 grams per liter. For all formulations the total amount of hydroxide and cyanide content present in the baths should be sufficient to complex all of the zinc as the complex zinc radical. Optimum temperatures for the respective baths is 65° C. with a range of between 45° C. to 85° C. Typical formulations for plating at cathode current efficiencies of the order of 85% and zinc alloy content in excess of 87% based upon the use of sodium are as follows:

Example 1

Zn(CN) ₂ -----	22.5 g./l.
Na ₂ SnO ₃ ·3H ₂ O-----	67 g./l.
NaCN-----	12 g./l.
NaOH-----	32 g./l.
Temperature-----	65°.
Cathode current density---	20 amp./sq. ft. (optimum), 50-40 amp./sq. ft. (useful range).

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Example 2

ZnO.....	15.5 g./l.
Na ₂ SnO ₃ ·H ₂ O.....	67 g./l.
NaCN.....	30 g./l.
NaOH.....	20 g./l.
Temperature.....	65° C.
Cathode current density....	20 amp./sq. ft. (optimum), 50-40 amp./sq. ft. (useful range).

The above baths based upon sodium formulation produce alloy platings whose composition does not change over extensive use of the bath and which compositions are deposited at high current efficiencies.

Examples of baths based upon potassium formulations are as follows:

Example 3

(Using zinc cyanide)

Zn(CN) ₂	27 g./l.
K ₂ SnO ₃ ·3H ₂ O.....	100 g./l.
KOH.....	60 g./l.
KCN.....	17.5 g./l.
Temperature.....	65°.
Cathode current density....	50 amp./sq. ft. (optimum), 20-100 amp./sq. ft. (useful range).

Example 4

(Using zinc oxide)

ZnO.....	18.7 g./l.
K ₂ SnO ₃ ·3H ₂ O.....	100 g./l.
KOH.....	34 g./l.
KCN.....	47 g./l.
Temperature.....	65°.
Cathode current density....	50 amp./sq. ft. (optimum), 20-100 amp./sq. ft. (useful range).

In accordance with the present invention a preferred addition agent for the above baths is the combination of gelatin and ammonium molybdate. However it must be emphasized that good results are obtained with gelatin and thiourea, and mixtures of gelatin, ammonium molybdate and thiourea.

The addition agents are added into the zinc-tin plating baths in a concentration of between 1/8 to 2 ounces per gallon for each of the addition agents. A preferred concentration for the preferred formulation consisting of gelatin and ammonium molybdate is between 1/4 to 1/2 ounce per gallon of gelatin, and between 1 to 2 ounces per gallon of ammonium molybdate. If thiourea is to be substituted for the ammonium molybdate, the preferred concentration with gelatin is between 1 to 2 ounces per gallon of thiourea and between 1/4 to 1/2 ounce per gallon of gelatin.

Although the several constituents of the brightening agent may be added directly to the zinc-tin plating bath in the above concentrations, the brightening agent may take the form of a mixture of the several constituents which mixture may be added directly to the plating solution. In a preferred mixture the gelatin will be present in a concentration of 1 part by weight and the further additive, either ammonium molybdate or thiourea, will be present in a concentration of 4 parts by weight.

Brighteners prepared in accordance with the present invention will improve deposit appearance, are capable of operating at comparatively high current densities, are reasonably stable in the zinc-tin plating bath and achieve the requisite brightness property in the ultimate deposit over a fairly wide range of operating current densities for the plating bath, without in any way impairing the solderability of the plated surface.

A latitude of modification and substitution is intended in the foregoing disclosure and in certain instances some features of the invention will be used without a corre-

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sponding use of other features. Accordingly it is appropriate that the appended claims be construed in a manner consistent with the spirit and scope of the disclosure.

What I claim is:

5 1. A process for producing a solderable, bright zinc-tin deposit by electrodeposition from a zinc-tin plating bath containing cyanides and hydroxides which consists in adding to said bath only the following: gelatin and ammonium molybdate, each of said additives being present in a concentration of between one-eighth to two ounces per gallon.

2. A brightening agent for addition to a zinc-tin plating bath including cyanides and hydroxides which brightening agent consists of gelatin and ammonium molybdate, said gelatin being present in a concentration of 1 part by weight, and said ammonium molybdate being present in a concentration of 4 parts by weight.

3. A brightening solution to be added to an alkaline cyanide plating bath for the deposition of a zinc-tin alloy containing between 75 and 95 percent zinc and between 25 and 5 percent tin, said brightening solution consisting of gelatin, thiourea and ammonium molybdate, said gelatin being present in a concentration of between one-quarter to one-half ounce per gallon, said thiourea and ammonium molybdate being each present in a concentration of between one and two ounces per gallon.

4. A brightening solution to be added to a plating bath containing hydroxides and cyanides for the deposition of a zinc-tin alloy containing between 75 and 95 percent zinc and between 25 and 5 percent tin, said brightening solution consisting of gelatin and ammonium molybdate, each of said additives being present in a concentration of between one-eighth to two ounces per gallon of said plating bath.

5. In the electrodeposition of a zinc-tin alloy containing between 75% and 95% zinc and between 25% and 5% tin from an alkaline plating bath including zinc, tin, and cyanide ion and hydroxide ion in quantities sufficient to complex all of the zinc in said bath, the method which consists in adding to said bath an addition agent containing gelatin, thiourea, and ammonium molybdate and electrodepositing said alloy on a workpiece, the gelatin of said addition agent being present in a concentration of 1/4 to 1/2 ounces per gallon, the thiourea of said addition agent being present in concentration of one to two ounces per gallon and the molybdate of said addition agent being present in a concentration of one to two ounces per gallon, said addition agent acting to produce a bright alloy without affecting the solderability of said alloy.

6. In the electrodeposition of a zinc-tin alloy containing between 75% and 95% zinc and between 25% and 5% tin from an alkaline plating bath including zinc, tin, and cyanide ion and hydroxide ion in quantities sufficient to complex all of the zinc in said bath, the method of which consists in adding to said bath an addition agent containing gelatin in the amount 1/4 to 1/2 ounce per gallon and ammonium molybdate in the amount of one to two ounces per gallon and electrodepositing said alloy from said bath containing said addition agent on a workpiece.

7. A process for producing a bright zinc-tin deposit containing between 75% and 95% zinc and between 25% and 5% tin by electrodeposition from an alkaline-cyanide zinc-tin alloy plating bath which process consists in adding to said bath a brightening solution containing gelatin in a concentration of 1/4 to 1/2 ounce per gallon of said bath and ammonium molybdate in a concentration of between 1 and 2 ounces per gallon whereby the solderability of said zinc-tin deposit is not adversely affected.

8. A process for producing a bright zinc-tin deposit by electrodeposition from an alkaline-cyanide zinc-tin alloy plating bath which process consists in adding to said bath

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a brightening solution containing gelatin in a concentration of $\frac{1}{4}$ to $\frac{1}{2}$ ounce per gallon of said bath and thiourea and ammonium molybdate, each of the latter present in a concentration of between 1 and 2 ounces per gallon whereby the solderability of said zinc-tin deposit is not adversely affected.

9. A zinc-tin alloy plating bath made up of zinc, tin, a source of hydroxide ions and a cyanide, and a brightening agent consisting of gelatin and ammonium molybdate, the gelatin being present in a concentration of $\frac{1}{4}$ to $\frac{1}{2}$ ounce per gallon, the ammonium molybdate being present in a concentration of one to two ounces per gallon, said brightening agent acting to produce a bright alloy plating on a workpiece, without adversely affecting the solderability of the deposited alloy.

10. A zinc-tin alloy plating bath made up of zinc, tin,

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a source of hydroxide ions and a cyanide, and a brightening agent consisting of gelatin in a concentration of $\frac{1}{4}$ to $\frac{1}{2}$ ounce per gallon of bath, ammonium molybdate and thiourea, the latter two ingredients being present in a concentration of between 1 and 2 ounces per gallon of bath, whereby a bright alloy plating is produced on a workpiece without adversely affecting the solderability of the deposited alloy.

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