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ELECTROPLATING PROCESS AND BATH

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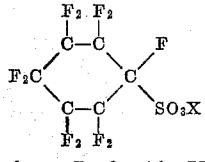
The present invention is directed to an improved bath and process for electroplating tin-nickel alloys.

Tin-nickel alloy electrodeposits have extremely good corrosion and tarnish resistance. The plating baths have excellent throwing power. Unfortunately, the electrodeposits from the presently known baths are often pitted. These pitted deposits are unsightly and permit basis metal corrosion. To avoid or reduce pitting, it is common practice to frequently carbon-treat and filter baths. The problems associated with pitting are accentuated when deposits greater in thickness than 13 microns are deposited. I have now discovered an improved bath for electroplating sound tin-nickel deposits from which the porosity associated with pitting is substantially reduced and often completely eliminated.

It is an object of this invention to provide an improved process for tin-nickel electrodeposition.

It is also an object of this invention to provide an improved bath for use in the electrodeposition of tin-nickel.

I have now discovered that sound tin-nickel may be electrodeposited from acidic baths which contain a small effective amount of a sulfonated cyclic fluorocarbon. These sulfonated cyclic fluorocarbons are characterized by the following general formula:



wherein X is a cation. Preferably X is hydrogen, ammonium, sodium, or potassium. It may also be such equivalent cations as the other alkali metal or alkaline earth metals, tin, nickel, magnesium, and other metals not deleterious in the bath. These cycle fluorocarbon compounds contain from 6 to 9 carbon atoms. When the compound contains more than 6 carbon atoms, one or more of the cyclic carbons is substituted by a fluorinated alkyl radical. Examples of such compounds include perfluoro-cyclohexyl sulfonic acid, perfluoro-4-methyl cyclohexyl sulfonic acid, perfluoro-2-methyl cyclohexyl sulfonic acid, perfluoro-1-methyl cyclohexyl sulfonic acid, perfluoro-2,5-dimethyl cyclohexyl sulfonic acid, perfluoro-4-ethyl cyclohexyl sulfonic acid, perfluoro-4-isopropyl cyclohexyl sulfonic acid, and the salts of these acids.

The amount of the sulfonated cyclic fluorocarbon in the bath which will be effective in substantially reducing the pitting or eliminating pitting is dependent upon the service conditions. When baths are badly contaminated and particularly when such baths are used to electrodeposit to thicknesses greater than about 13 microns, relatively large amounts of additive are necessary. Generally between about 0.05 g./l. and 3 g./l. are used. For most commercial operations between about 0.25 g./l. and 1 g./l. is preferred.

Tin-nickel is deposited from acid baths. The preferred baths contain both chloride and fluoride anions; stannous tin in the amounts of 26 to 37.5 g./l.; and nickel in amounts between 60 and 82.5 g./l. The total fluorine is between 34 and 45 g./l. in the mixed baths. The chloride content is not critical. The pH is maintained between 2 and 2.5, generally by the addition of ammonium hydroxide. The bath is operated at high temperatures, preferably between 65° and 71° C. Typical bath formulations follow:

TABLE I

Bath 1

Stannous chloride, anhyd., $SnCl_2$ (tin metal), grams per liter	42 – 26
Nickel chloride, $NiCl_2 \cdot 6H_2O$ (nickel metal), grams per liter	300 – 75
Sodium fluoride, Naf (fluorine), grams per liter	28 – 15
Ammonium bifluoride, NH_4HF_2 (fluorine), grams per liter	35 – 24
Total fluorine in bath, grams per liter	39
pH (colorimetric)	2.5
Temperature ° C	65
Cathode current density amp./sq.dm.	3

Bath 2

Stannous chloride grams per liter	49
Nickel chloride, $NiCl_2 \cdot 6H_2O$ do	300
Ammonium bifluoride, NH_4HF_2 do	56
Ammonium hydroxide, as needed to adjust pH.	

The baths are initially made up by adding the noted chemicals to water. However, equivalent chemicals may be added, e.g., stannous tin may be in the form of the oxide or the fluoride, as well as the chloride. During operation the metals may be replaced either chemically or by anodic corrosion of metallic anodes or a combination of both.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given.

In the following examples tin-nickel (approximately 65% tin and 35% nickel) was electrodeposited from the following bath under the conditions noted. In each case, a standard was run with the bath before any addition of the fluorocarbon additive.

Stannous chloride, $SnCl_2$ g./l.	49
Nickel chloride, $NiCl_2 \cdot 6H_2O$ g./l.	300
Ammonium bifluoride, NH_4HF_2 g./l.	54
Ammonium hydroxide, added to bring pH to 2.0–2.5.	
Temperature ° C	68
Time of test minutes	60
Current density, 3.7 amp./sq.dm. average current density (approximately 8.1 amp./sq.dm. on edge of panel).	

EXAMPLE I

A steel panel was electrolyzed in the above bath for an hour. Approximately 165 pits were counted in a distance of about 5.1 cm. along the high current density edge of the panel. Then 0.75 g./l. of perfluoro-4-methyl cyclohexyl sulfonic acid (sodium salt) was added to the bath. With the same test described above, only 14 pits were counted along the high current density edge. This was a reduction of 91% in number of pits at the high current density edge of the panel where the thickness of deposit was estimated to be 125 microns.

EXAMPLE II

To a bath similar to the one in Example I was added 0.5 g./l. of perfluoro-4-methyl cyclohexyl sulfonic acid (sodium salt). This bath was electrolyzed at 1, 1.6 and 2.1 amp./sq. dm. to give deposit thicknesses of 75, 125 and 120 microns respectively with no pitting on the panels. The panels plated from baths with no anti-pitting agent showed some pitting at 1 amp./sq. dm. and more at 1.6 and 2.1 amp./sq. dm.

The baths and compounds used for the examples are

illustrative. The equivalent potassium, ammonium, or acid salts, or the acid itself are the equivalent of the sodium salt illustrated. Similarly, the equivalent sulfonated cyclic fluorocarbons specified hereinbefore may be used in place of the illustrated compound.

Utilizing the present process and bath, it is possible to electrodeposit sound tin-nickel directly on most basis metals including steel, copper and copper alloys, tin, nickel and nickel alloys, etc. Conventional cleaning of the basis metal prior to electrodeposition should be practiced. The use of a bronze or copper undercoat on some basis metals, particularly those electrochemically active in acid baths, may be used to obtain maximum corrosion resistance.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. An improved acidic tin-nickel bath for electroplating in which the improvement comprises incorporating in said bath a small amount of a sulfonated perfluoro cyclohexyl hydrocarbon effective to eliminate pitting.

2. An acidic bath for tin-nickel electroplating containing Sn^{++} ions, Ni^{++} ions, Cl^- ions, F^- ions, and as an anti-pitting agent a small effective amount of a sulfonated cyclic fluorocarbon having the general formula

$$R_FSO_3X$$

wherein R_F is a fluorinated cyclohexyl hydrocarbon radical selected from the class consisting of the perfluorocyclohexyl radical, and mono- and di-substituted perfluoro-cyclohexyl radicals containing 7 to 9 carbon atoms in the substituted cyclohexyl radical, and wherein X is a cation.

3. The bath of claim 2 in which the sulfonated cyclic fluorocarbon is present in an amount between 0.05 g./l. and 3 g./l.

4. The bath of claim 2 in which the sulfonated cyclic fluorocarbon is present in an amount between 0.25 g./l. and 1 g./l., and in which X is a cation selected from the class consisting of hydrogen, ammonium, sodium, and potassium.

5. A chlorine and fluorine containing acidic bath for tin-nickel electroplating having a pH between about 2 and 2.5, and containing between 26 g./l., and 37.5 g./l. of Sn^{++} ions, between 60 g./l. and 82.5 g./l. of Ni^{++} ions, between 34 g./l. and 45 g./l. of F^- ions, and between 0.05 g./l. and 3 g./l. of a sulfonated cyclic fluorocarbon having the general formula

$$R_FSO_3X$$

wherein R_F is a fluorinated cyclohexyl hydrocarbon radical selected from the class consisting of the perfluoro-cyclohexyl radical and mono- and di-substituted perfluorocyclohexyl radicals containing 7 to 9 carbon atoms in the substituted cyclohexyl radical and wherein X is a cation selected from the class consisting of hydrogen, ammonium, sodium, and potassium.

6. The bath of claim 2 in which R_F is the perfluorocyclohexyl radical.

7. The bath of claim 2 in which R_F is the perfluoro-4-methyl-cyclohexyl radical.

8. The bath of claim 2 in which R_F is the perfluoro-2-methyl cyclohexyl radical.

9. The bath of claim 2 in which R_F is the perfluoro-1-methyl cyclohexyl radical.

10. The bath of claim 2 in which R_F is the perfluoro-2,5-dimethyl cyclohexyl radical.

11. The bath of claim 2 in which R_F is the perfluoro-4-ethyl cyclohexyl radical.

12. The bath of claim 2 in which R_F is the perfluoro-4-isopropyl cyclohexyl radical.

13. An acidic bath for tin-nickel electroplating containing about 49 g./l. of stannous chloride, about 300 g./l. of hydrated nickel chloride, about 56 g./l. of ammonium bifluoride, and sufficient ammonium hydroxide to adjust the pH to between 2 and 2.5, and between 0.25 g./l. and 1 g./l. of a sulfonated cyclic fluorocarbon having the general formula

$$R_FSO_3X$$

wherein R_F is a fluorinated cyclohexyl hydrocarbon radical selected from the class consisting of the perfluorocyclohexyl radical and mono- and di-substituted perfluorocyclohexyl radicals containing 7 to 9 carbon atoms in the substituted cyclohexyl radical and wherein X is a cation selected from the class consisting of hydrogen, ammonium, sodium, and potassium.

14. In the process of electrodepositing tin-nickel from an acidic bath containing Sn^{++} ions, Ni^{++} ions, Cl^- ions, and F^- ions, the improvement which comprises incorporating in said bath as an anti-pitting agent a small effective amount of a sulfonated cyclic fluorocarbon having the general formula

$$R_FSO_3X$$

wherein R_F is a fluorinated cyclohexyl hydrocarbon radical selected from the class consisting of the perfluorocyclohexyl radical and mono- and di-substituted perfluoro-cyclohexyl radicals containing 7 to 9 carbon atoms in the substituted cyclohexyl radical and wherein X is a cation.

15. The process of claim 14 in which more than 0.25 g./l. of the sulfonated cyclic fluorocarbon is incorporated in the bath, and in which X is a cation selected from the class consisting of hydrogen, ammonium, sodium, and potassium.

16. A process for electroplating tin-nickel from a chlorine and fluorine containing acidic bath having a pH between about 2 and 2.5, and containing between 26 g./l. and 37.5 g./l. of Sn^{++} ions, between 60 g./l. and 82.5 g./l. of Ni^{++} ions, between 34 g./l. and 45 g./l. of F^- ions, and between 0.25 g./l. and 1 g./l. of a sulfonated cyclic fluorocarbon having the general formula

$$R_FSO_3X$$

wherein R_F is a fluorinated cyclohexyl hydrocarbon radical selected from the class consisting of the perfluorocyclohexyl radical and mono- and di-substituted perfluoro-cyclohexyl radicals containing 7 to 9 carbon atoms in the substituted cyclohexyl radical and wherein X is a cation selected from the class consisting of hydrogen, ammonium, sodium, and potassium, at a temperature between about 65° C. and 71° C.

17. The process of claim 16 in which R_F is the perfluoro-cyclohexyl radical.

18. The process of claim 16 in which R_F is the perfluoro-4-methyl cyclohexyl radical.

19. The process of claim 16 in which R_F is the perfluoro-2-methyl cyclohexyl radical.

20. The process of claim 16 in which R_F is the perfluoro-1-methyl cyclohexyl radical.

21. The process of claim 16 in which R_F is the perfluoro-2,5-dimethyl cyclohexyl radical.

22. The process of claim 16 in which R_F is the perfluoro-4-ethyl cyclohexyl radical.

23. The process of claim 16 in which R_F is the perfluoro-4-isopropyl cyclohexyl radical.

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