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NOVEL PLATING PROCESS AND COMPOSITION

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The present invention relates to a process for immersion plating of aluminum, including aluminum alloys, with tin and to compositions used in making up these baths.

Tin may be plated on aluminum by immersing aluminum in aqueous baths containing an alkali metal stannate. These baths may be operated over a wide temperature range from room temperature to about 90° C., at pH typically higher than 12.5, to produce a tin deposit which may vary in color from gray to white, and may have a matte appearance. Tin may deposit from the bath in accordance with Equation I.

$$3Na_2Sn(OH)_6+4Al\rightarrow 3Sn+4NaAlO_2+2NaOH+8H_2O \quad (I)$$

The deposition of tin releases free hydroxide, and the amount of free hydroxide formed per square foot of aluminum treated may depend on such factors as temperature, concentration of the various bath components, and immersion time. It has been found that the thickness of the tin layer deposited on aluminum by this process and the rate of deposition thereof increases at an undesirably high rate with increase of free alkali content. It is desirable to be able to control the thickness and rate of deposit and to operate the process so that the resulting plate meets a specified minimum thickness, but does not exceed a predetermined maximum thickness.

Prior art techniques have attempted to remedy the build-up of free hydroxide and control it within operative limits by the addition of acids such as acetic acid. Unfortunately it is not possible to readily control this reaction and over-neutralization (particularly at the point of introduction of the acid) occurs, even when using dilute acid. The local excess of acetic acid may react immediately with the alkali metal stannate to precipitate tin as the hydroxide in the form of a sludge, typically according to reaction II which illustrates a reaction which may occur when acetic acid is used to neutralize the caustic.

$$Na_2Sn(OH)_6+2CH_3COOH\rightarrow Sn(OH)_4+2CH_3COONa+2H_2O \quad (II)$$

The stannic hydroxide sludge, once formed, may be substantially impossible to redissolve during normal operation of the immersion tinning bath and represents lost tin. A loss of tin (of as much as 25% of the tin present) in the form of sludge is not uncommon and this depletion considerably decreases the life of the bath. Furthermore, sludge particles in the bath may adhere to the surface of the work resulting in an unsatisfactory surface finish. Often the baths are prematurely discarded since sludge may build-up to such an extent that making up a new solution may be more economical than trying to rectify the old one.

In attempts to minimize problems resulting from the use of acetic acid neutralization of excess free hydroxide, other compounds have been used in the bath to neutralize the caustic as it is formed; but the inclusion of such compounds has not produced completely satisfactory results.

Specifically, it has been suggested that condensed phosphates, such as pyrophosphates and polyphosphates, may be employed to reduce problems of sludging and free hydroxide build-up. However, these compounds must be present in the plating bath in relatively high concentrations. It may also be found that baths containing the condensed phosphates do not satisfactorily plate certain aluminum alloys, particularly those which contain a high percentage of copper.

It is an object of this invention to provide improved immersion tin plating baths containing polyphosphates. It is a further object to provide a novel process for immersion tin plating of aluminum. It is a further object to provide a novel technique for improving the performance of immersion tin plating baths containing phosphates. Other objects will become apparent to those skilled in the art upon reading the following disclosure.

In accordance with certain of its aspects, the process of this invention for treating aluminum to form a surface layer of tin thereon may comprise immersing said aluminum in an aqueous bath containing a stannate salt selected from the group consisting of sodium stannate and potassium stannate, an alkali metal polyphosphate, and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereof; and withdrawing said aluminum from said bath.

In accordance with certain of its other aspects, this invention provides novel alkaline aqueous immersion tinning baths comprising a stannate salt selected from the group consisting of sodium stannate and potassium stannate; an alkali metal polyphosphate; and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminocarboxylic acids and aminoalcohols.

The aluminum which may be treated by the practice of this invention may be commercially pure aluminum or an alloy of aluminum. Typical of such alloys may be those containing copper, magnesium, or both copper and magnesium. One of the more common aluminum alloys which may be treated by the process of this invention may contain 2%–4%, say 3% copper, 1%–1.5%, say 1.5% magnesium, 9%–13%, say 10% silicon, and quantities of other metals such as zinc, iron, and nickel. Such alloys are commonly used for the fabrication of aluminum pistons. A specific illustration of one of these alloys may be that identified as Permanent Mold Casting Alloy D–132 containing 3% copper, 1% magnesium, 10% silicon, 0.5% manganese, 0.5% zinc, and the remainder essentially aluminum. The technique of this invention may be particularly advantageous for plating on higher copper alloys, e.g. permanent mold casting alloys containing greater than about 3.5% copper.

The immersion baths which may be used in practice of this invention may typically be made up by dissolving potassium stannate and/or sodium stannate in water to form a bath containing from about 15 g./l. (grams per liter) to saturation, typically about 70 g./l. of the stannate salt, the resulting solution containing about 30 g./l. of tin. Sufficient potassium hydroxide and/or sodium hydroxide may be initially added to form a bath containing about 4 g./l. of the alkali metal hydroxide to prevent precipitation of tin due to low pH during makeup. During operation, the free alkali metal hydroxide may be maintained between about 0.5 g./l. to about 12 g./l., preferably between 1 g./l. and 8 g./l., say 4 g./l. Proper operation of the bath may normally be carried out at a pH sufficiently high to keep the stannate in solution. Since tin may precipitate from these baths at pH below about 11.5, normal operation of these baths may be at pH above this point and preferably at pH of at least 12. This pH may normally be maintained automatically by the hydroxide generated and it may not normally be necessary to add hydroxide to the baths.

The baths of this invention may contain an alkali metal polyphosphate. Typical alkali metal polyphosphates which

may be employed include sodium hexametaphosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, potassium hexametaphosphate, tetrapotassium pyrophosphate, potassium tripolyphosphate, etc. Sodium tripolyphosphate and potassium tripolyphosphate may be preferred. The alkali metal polyphosphate may preferably be present in the plating bath in the concentration of about 1.5–5 grams per liter (g./l.).

The novel baths may also contain at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids, and amino-alcohols. Alkylene polyamines may include alkylene diamines, alkylene triamines, alkylene tetra-amines, etc. Suitable illustrative alkylene polyamines may include ethylenediamine, propylenediamine, butylenediamine, ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, diethylenediamine (piperazine), diethylenetriamine, etc.

Illustrative aminomonocarboxylic acids suitable for use in this invention may include glycine, alanine, valine, leucine, isoleucine, phenylalanine, proline, tryphophan, arginine, lysine, histidine, β-alanine, α-aminobutyric acid, γ-aminobutyric acid, α,γ-diaminobutyric acid, ornithine, etc. If desired, these materials may be employed in the form of their salts, typically as sodium or potassium salts.

Illustrative aminoalcohols which may be employed may include ethanolamine, diethanolamine, triethanolamine, 2-amino-2-methyl-1-propanol, 2-amino-1-butanol, propanolamine, dipropanolamine, tripropanolamine, butanolamine, etc.

Typically, the soluble organic compound will be present in the bath in the amout of about 0.01–0.25 mole per liter, preferably about 0.1 mole/l. Smaller amounts may be used, but may not provide as great an improvement in these baths. Larger amounts may also be used, but little or no additional improvement may be realized thereby.

Immersion plating in accordance with this invention may be carried out between room temperature of e.g. 20° C. and 90° C., and preferably between 40° C. and 80° C., say 60° C. Immersion time may be as little as 30 seconds, but it is usually between 1–6 minutes, say 4 minutes. During this time, aluminum may be coated with a layer of tin of desired thickness, typically of the order of 1–4 microns.

The novel baths of this invention may typically be prepared initially by dissolving about 1.5–5 grams of alkali metal polyphosphate, say sodium tripolyphosphate; 0.01–0.25 mole, say 0.1 mole of the hereinbefore described soluble organic compound, say ethylenediamine or triethanolamine; 0.5–12 grams, say 4 grams of alkali metal hydroxide, say potassium hydroxide; and 15 grams to saturation, say 70 grams of stannate salt, say potassium stannate in sufficient water to give one liter of solution. Because of drag-out and depletion of tin through plating, it will be necessary periodically, to make additions to the bath during operation.

Since the novel baths of this invention maintain a pH at the desired operating level, it may not be necessary to add either additional alkali metal hydroxide or neutralizing agent during operation.

Stannate salt may be added at a rate sufficient to make up for the loss of stannate in the bath through plating and because of drag-out. The soluble organic compound and alkali metal polyphosphate may be added at a rate sufficient to compensate for drag-out. Each of these components may be added separately, but preferably they may be added together. It may be found that the desired balance may be maintained in the bath by adding thereto a composition comprising about 70–98 parts by weight stannate salt, 1–17 parts by weight of the noted soluble organic compound, and 1–14 parts by weight of the alkali metal polyphosphate. Preferably the composition employed to maintain the novel baths may comprise 80–96 parts by weight stannate salt, 2–10 parts by weight soluble organic compound, and 2–10 parts by weight alkali metal polyphosphate.

Typical examples of compositions which may be employed to maintain the novel baths of this invention may include the following wherein the parts are parts by weght.

(1)

Potassium stannate	85
Ethylene diamine	10
Potassium tripolyphosphate	5

(2)

Sodium stannate	87
Butylenediamine	8
Sodium tripolyphosphate	5

(3)

Potassium stannate	93
Diethylenediamine	4
Tetrapotassium pyrophosphate	3

(4)

Sodium stannate	74
Diethylenetriamine	15
Tetrasodium pyrophosphate	11

(5)

Potassium stannate	79
Glycine (K salt)	16
Potassium hexametaphosphate	5

(6)

Sodium stannate	88
β-Alanine (Na salt)	6
Sodium tripolyphosphate	6

(7)

Potassium stannate	94
Leucine	3
Sodium hexametaphosphate	3

(8)

Sodium stannate	97
Proline	2
Potassium tripolyphosphate	1

(9)

Potassium stannate	80
Lysine	10
Tetrapotassium pyrophosphate	10

(10)

Sodium stannate	96
α-Aminobutyric acid (K salt)	2.5
Sodium tripolyphosphate	1.5

(11)

Potassium stannate	86
α,γ-Diaminobutyric acid (Na salt)	8
Potassium hexametaphosphate	6

(12)

Sodium stannate	70
Ornithine	16
Tetrasodium pyrophosphate	14

(13)

Potassium stannate	78
Ethanolamine	10
Tetrapotassium pyrophosphate	12

(14)

Sodium stannate	98
Dipropanolamine	1
Sodium tripolyphosphate	1

(15)

Potassium stannate	90
Triethanolamine	5
Potassium tripolyphosphate	5

In order to give those skilled in the art a better appreciation of the invention, the following illustrative examples are provided.

Example 16

Four separate immersion tinning baths may be made up by dissolving 8 grams of potassium hydroxide and 140 grams of potassium stannate in about 1.5 liters of water, and diluting the resulting solutions to 2 liters with water. Prior to this dilution, the following materials are added to the solution and dissolved therein:

Bath: Added

A --- Nothing—control.
B --- Ethylenediamine—6 grams; sodium tripolyphosphate—5 grams.
C --- Triethanolamine—30 grams; potassium tripolyphosphate—7 grams.
D --- β-Alanine (Na salt)—30 grams; potassium hexametaphosphate—10 grams.

After dilution to 2 liters, all of the baths contain 70 g./l. potassium stannate, and 4 g./l. potassium hydroxide. Bath A, the control, contains no polyphosphate or soluble organic compound of this invention. Baths B, C and D are prepared in accordance with this invention to contain:

Bath: Added

B ------ Ethylenediamine—3 g./l. (0.05 mole/l.); sodium tripolyphosphate—2.5 g./l.
C ------ Triethanolamine—15 g./l. (0.1 mole/l.); potassium tripolyphosphate—3.5 g./l.
D ------ β-Alanine—15 g./l. (0.14 mole/l.); potassium hexametaphosphate—5 g./l.

Each of the baths may be heated to and maintained at 60° C. For each bath, three pieces of D–132 aluminum 3 x 6 x ¼" may be degreased in trichloroethylene vapor, dipped for 30 seconds in a solution of 30 g./l. of trisodium phosphate and 30 g./l. of sodium carbonate at 60° C., rinsed in cold water, dipped for 30 seconds in a mixture of one part of concentrated nitric acid and 3 parts of water, rinsed in cold water, and immersed in the two-liter bath for 4 minutes to deposit thereon a layer of tin. The aluminum panels may then be withdrawn, rinsed, and the tin deposit stripped from them by immersing for one minute in the nitric acid solution, and rinsing under a stream of cold water. The parts are then ready for the second dip in the baths. A series of 10 successive dips and strippings is considered as one cycle, and the surface area plated in each cycle is 36.8 square decimeters per liter. At the end of each cycle, the baths may be analyzed for free hydroxide and tin, and the tin content brought up to 28 g./l. by addition of the following maintenance compositions.

Bath	Maintenance Composition	Percentage
A	Potassium stannate	100
B	do	96.2
	Ethylenediamine	2.1
	Sodium tripolyphosphate	1.7
C	Potassium stannate	88.3
	Triethanolamine	9.5
	Potassium tripolyphosphate	2.2
D	Potassium stannate	87.5
	β-Alanine (Na Salt)	9.4
	Potassium hexametaphosphate	3.1

In each case, sufficient maintenance composition is added to bring the tin content of the bath back to 28 g./l. At the beginning and end of each complete cycle, the thickness of tin plated may be determined by weighing a panel before and after stripping in nitric acid.

Bath A, which is typical of prior art practice, shows a rapid increase in free hydroxide. After 2 cycles, the free hydroxide rises to 4.9 g./l.; after 5 cycles it is 8.5 g./l.; and after 6 cycles it is 9.8 g./l. The thickness of tin deposited also undesirably increases to 157×10^{-6} inches after 2 cycles, 167×10^{-6} inches after 4 cycles and 186×10^{-6} inches after 6 cycles. By the end of the fourth cycle, the tin plate is streaky, gray and of generally poor appearance. A large quantity of sludge is formed during the test.

Baths B, C, and D, which are operated in accordance with this invention, give smooth, adherent deposits with little streaking and good appearance throughout the test. The thickness of tin deposited may fall within the range of $70–115\times10^{-6}$ inches after each cycle. It may be found that the free hydroxide content of the bath reaches an equilibrium value in the range 1.6–3 g./l. Much less sludge is produced in these baths than in Bath A.

From this comparison, it is readily seen that operation of Bath A, in accordance with prior art techniques, is characterized by streaky, gray plate, build-up of free hydroxide, excessive sludging, and lack of control over the thickness of tin plated. Baths B, C and D illustrate the advantages obtained by use of the baths and processes of this invention, including good control of deposit thicknesses, little sludging, control of free hydroxide content, and smooth deposits of good appearance.

Although this invention has been illustrated by reference to specific examples, numerous changes and modifications thereof which clearly fall within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. The process for treating aluminum to form a surface layer of tin thereon which comprises immersing said aluminum in an aqueous bath containing a stannate salt selected from the group consisting of sodium stannate and potassium stannate, an alkali metal polyphosphate, and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereon; and withdrawing said aluminum from said bath.

2. The process for treating aluminum to form a surface layer of tin thereon which comprises immersing said aluminum in an aqueous bath containing 15 g./l. to saturation of a stannate salt selected from the group consisting of sodium stannate and potassium stannate, 0.5–12 g./l. alkali metal hydroxide, 1.5–5 g./l. alkali metal polyphosphate, 0.01–0.25 mole/l. of at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols, maintaining said bath at 40–80° C. during said immersion; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereon; and withdrawing said aluminum from said bath.

3. A novel alkaline aqueous immersion tinning bath comprising a stannate salt selected from the group consisting of sodium stannate and potassium stannate; an alkali metal polyphosphate; and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols.

4. The novel alkaline aqueous immersion tinning bath of claim **3** which comprises 1.5–5 g./l. of said alkali metal polyphosphate.

5. The novel alkaline aqueous immersion tinning bath of claim **3** which comprises 0.01–0.25 mole/l. of said soluble organic compound.

6. The novel alkaline aqueous immersion tinning bath which comprises 15 g./l. to saturation of a stannate salt selected from the group consisting of sodium stannate and potassium stannate; 0.5–12 g./l. alkali metal hydroxide; 1.5–5 g./l. alkali polyphosphate; and 0.01–0.25 mole/l. of at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols.

7. The novel alkaline aqueous immersion tinning bath of claim **6** wherein said soluble organic compound is ethylenediamine.

8. The novel alkaline aqueous immersion tinning bath of claim 6 wherein said soluble organic compound is triethanolamine.

9. The novel alkaline aqueous immersion tinning bath of claim 6 wherein said soluble organic compound is β-alanine.

10. The novel alkaline aqueous immersion tinning bath of claim 6 wherein said alkali metal polyphosphate is alkali metal tripolyphosphate.

11. A novel composition for use in maintaining alkaline aqueous immersion tinning bath which comprises a stannate salt selected from the group consisting of sodium stannate and potassium stannate; an alkali metal polyphosphate; and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols.

12. The novel composition for use in maintaining alkaline aqueous immersion tinning bath which comprises 70–98 parts of a stannate salt selected from the group consisting of sodium stannate and potassium stannate; 1–14 parts of an alkali metal polyphosphate; and 1–17 parts of at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols.

13. The novel composition for maintaining alkaline aqueous immersion tinning bath claimed in claim 12 wherein said alkali metal polyphosphate is alkali metal tripolyphosphate.

14. The novel composition for use in maintaining alkaline aqueous immersion tinning bath which comprises 80–96 parts of a stannate salt selected from the group consisting of sodium stannate and potassium stannate; 2–10 parts of an alkali metal polyphosphate; and 2–10 parts of at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohols.

15. The novel composition for maintaining alkaline aqueous immersion tinning bath as claimed in claim 14 wherein said alkali metal polyphosphate is alkali metal tripolyphosphate.

16. The novel alkaline aqueous immersion tinning bath claimed in claim 15 wherein said soluble organic compound is ethylenediamine.

17. The novel alkaline aqueous immersion tinning bath claimed in claim 15 wherein said soluble organic compound is triethanolamine.

18. The novel alkaline aqueous immersion tinning bath claimed in claim 15 wherein said soluble organic compound is β-alanine.

19. The process for maintaining an alkaline aqueous immersion tinning bath which comprises adding thereto, a composition comprising a stannate salt selected from the group consisting of sodium stannate and potassium stannate; an alkali metal polyphosphate; and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohol.

20. In the process for treating aluminum to form a surface layer of tin thereon by immersing said aluminum in an alkaline aqueous immersion tinning bath containing a stannate salt selected from the group consisting of sodium stannate and potassium stannate, the improvement which comprises adding to said bath an alkali metal polyphosphate and at least one soluble organic compound selected from the group consisting of alkylene polyamines, aminomonocarboxylic acids and aminoalcohol.

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