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PROCESS AND COMPOSITION FOR IMMERSION PLATING OF ALUMINUM OR ALUMINUM ALLOYS WITH TIN

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ABSTRACT OF THE DISCLOSURE

A process for the immersion plating of aluminum and aluminum alloys with tin and the composition of the bath. The plating bath comprises an aqueous mixture of an alkali metal stannate and boric acid, or an alkali metal borate or mixtures thereof. The boric acid or alkali metal borate prevents precipitation of metastannic acid and allows the immersion tin plating bath to be operated under unusual pH conditions. The reaction products stabilize the bath and cause the bath to be self-regulating. The boric acid or alkali metal borate forms a complex with the alkali metal stannates in the plating bath.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a process for immersion plating of aluminum with tin and to the composition of the plating bath.

(2) Description of the prior art

Stannates have been used in the past for electroplating and immersion plating of tin under alkaline conditions with various substrates including aluminum and aluminum alloys. Problems, however, are encountered with the use of alkali metal stannates. All alkali metal stannate solutions are subject to hydrolysis in acordance with Equation I.

$$K_2Sn(OH)_6+2HOH\rightleftarrows H_2Sn(OH)_6\downarrow+2KOH \quad (I)$$

The hydrolysis is observed when an alkali metal stannate is dissolved in water. A turbid solution results unless the water is previously made alkaline with excess alkali metal hydroxide. Although the above reaction set forth in Equation I is reversible, the metastannic acid formed by the hydrolysis precipitates and it is difficult to return the precipitate to solution except under conditions which are not normally present in plating operations.

Carbon dioxide from the air also causes problems in the plating operation. The carbon dioxide reacts with water to form carbonic acid which, in turn, reacts with the stannate to form alkali metal carbonates and precipitate as metastannic acid or stannic hydroxide in accordance with Equations II and III.

$$CO_2+H_2O\rightarrow H_2CO_3 \quad (II)$$

$$H_2CO_3+K_2Sn(OH)_6\rightarrow Sn(OH)_4\downarrow+K_2CO_3+2H_2O \quad (III)$$

In the electroplating process, the hydrolysis reaction is severe at the anode. Excess alkali metal hydroxide is added

to the plating solution to shift the equilibrium of hydrolysis to the left and preventing formation of the metastannic acid.

The precipitate of stannic hydroxide forms a sludge in the plating tank and adversely affects the plating process. In installations of substantial size sludge losses of stannic hydroxide are substantial and increase the overall costs of the plating operation. The use of an alkali metal hydroxide to prevent the above discussed hydrolysis creates other problems in the immersion plating of aluminum. The high pH caused by the use of the alkali metal hydroxide reacts excessively with the aluminum metal and results in gassing or blistering and a dull, non-adherent plate. The reaction between the alkali metal hydroxide and aluminum is in accordance with equation IV.

$$NaOH+Al+H_2O\rightarrow NaAlO_2+1\tfrac{1}{2}H_2\uparrow \quad (IV)$$

The reaction of aluminum during the immersion plating process causes the stannate to react with the aluminum and generates free alkali metal hydroxide in accordance with Equation V.

$$3Na_2Sn(OH)_6+4Al\rightarrow 4NaAlO_2+3Sn\downarrow+2NaOH+8H_2\phi \quad (V)$$

The hydrolysis of the aluminate in the above equation also may generate excess alkali in accordance with Equation VI.

$$NaAlO_2+2H_2O\rightarrow Al(OH)_3+NaOH \quad (VI)$$

The reactions of the previously enumerated equations are dependent on temperature, concentration and pH. A low pH causes the reaction of Equation I to proceed rapidly to the right causing a substantial sludge formation and loss of tin for plating. A high pH causes Equations II and IV to proceed rapidly to the right again consuming substantial amounts of tin and severe gassing at the aluminum surface with the resulting blistering and nonadherent tin plate.

It has been suggested in the past to use acetic acid to control the free alkali in stannate baths. The use of mineral acids is not recommended since the action of the mineral acid is severe and precipitates stannic hydroxide sludge. Even with dilute acetic acid, some precipitation occurs as there are localized acetic conditions at the location where the acetic acid is added to the bath. The precipitate as stannic hydroxide with acetic acid is in accordance with Equation VII.

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

In commercial installations under normal operating conditions, the stannic hydroxide cannot be redissolved and is lost as a sludge. The formation of the sludge in the plating bath reduces substantially the plating operation that takes place in the bath and necessitates frequent cleaning and occasionally discarding of the bath. Again, this sludge within the bath represents substantial losses in both time and material. This is particularly true in the immersion tinning of aluminum alloy pistons in the automotive industry where large numbers of pistons are processed and down-time for cleaning or replacing the bath is a critical factor in the plating operation.

U.S. Pat. No. 2,947,639 suggests a method of minimizing this sludge problem. It is suggested in this patent to add compounds which react with the free alkali as it is formed to thus prevent the formation of the sludge within the bath. It is suggested in this patent that condensed phosphates such as pyrophosphates and polyphosphates be used to control the alkalinity of the bath. The reaction of the additive compounds depends upon the slow reversion to acid phosphate in water solution and subsequent reaction with free alkali as it is formed. The reaction between the phosphates and the alkali is in accordance with equations VIII and IX.

$$Na_5P_3O_{10}+2H_2O \rightarrow NaH_2PO_4+2Na_2HPO_4 \quad (VIII)$$

$$Na_2HPO_4+NaOH \rightarrow Na_3PO_4+H_2O \quad (IX)$$

The use of the polyphosphate as an additive compound does not prevent the hydrolysis of the stannate as set forth in Equation I and the additive compounds must also be used in relatively high concentrations to be effective for the severe conditions existing in operating baths.

Other prior patents, as for example, U.S. Pat. No. 3,338,725, suggest the use of a combination of additive compounds including polyphosphates, alkylene polyamines or aminomonocarboxylic acids. Again, the combination of additive compounds does not prevent the hydrolysis of the stannate and, further, requires the use of solids in combination with liquids which presents problems in formulation and increases the complexity of the plating operation.

In another patent, 3,274,021, it is suggested to use chelates to prevent the hydrolysis of the aluminate that is formed. In this process the salts of polyhydroxycarboxylic acids, such as sodium gulconate has not proven satisfactory. The additive compounds are expensive and upon continued use and addition to the plating bath results in the solution becoming viscous and the viscous plating solution is difficult to remove from the plated parts by the conventional washing operation.

SUMMARY OF THE INVENTION

We have discovered a novel plating bath composition for immersion plating wherein the excess alkali produced is consumed without the precipitation of metastannic acid. The plating bath composition includes an aqueous admixture of alkali metal stannate and a compound containing a boric oxide anion preferably in the form of boric acid or an alkali metal salt of boric acid. The boric oxide appears to form a complex with the stannate and the complex reacts with the aluminum and is converted to metallic tin and boric oxide that consumes the alkali formed during the process and prevents the precipitation of metastannic acid even if added in excess to saturation. Thus, the two major deficiencies present in known immersion plating processes of aluminum and aluminum alloys with tin have been eliminated by the hereinafter described immersion plating bath composition and the process of immersion plating with the novel plating bath.

In accordance with the hereinafter described invention, a novel aqueous immersion tinning bath is disclosed comprising a stannate salt selected from the group, consisting of alkali metal stannates and a compound containing a boric oxide onion selected from the group consisting of boric acid, alkali metal salts of boric acid and the hydrates of alkali metal salts of boric acid. The preferred molar ratio of stannate to boric acid or alkali metal borates is 8:1.

The process for treating aluminum to form a surface layer of tin thereon includes immersing the aluminum or aluminum alloy in an aqueous bath containing a stannate salt and a soluble compound containing a boric oxide anion, maintaining the aluminum in the bath for a sufficient period of time to deposit a surface layer of tin thereon, preventing the hydrolysis of the alkali metal stannates in the aqueous bath and neutralizing the excess alkali produced during the plating operation.

It is, therefore, a primary object of this invention to provide an improved immersion tinning bath for aluminum and aluminum alloys wherein the alkali generated during the plating process is consumed and the stannate metal hydroxides are not hydrolyzed.

Another object of this invention is to provide an immersion plating bath that does not require an alkali metal hydroxide in the initial makeup of the bath and does not require an acid or neutralizing agent or alkali to be used during the immersion plating process.

It is a further object of this invention to provide a process for immersion plating aluminum and aluminum alloys with tin in a plating bath without the use of organic acids to control the alkali formed during the plating process.

A still further object of this invention is to provide a novel process for immersion tinning of aluminum and aluminum alloys in a bath without precipitating metastannic acid due to hydrolysis of the alkali metal stannates.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The aluminum that may be plated with tin in the hereinafter described immersion plating process may be commercially pure aluminum or aluminum alloys. Typical of such alloys may be those aluminum alloys containing copper, magnesium or both copper and magnesium. A common alloy contains approximately 3% copper, 1.5% magnesium, 10% silicon, minor quantities of iron, zinc and nickel, and aluminum. Such alloys are commonly used for the fabrication of aluminum pistons for the automotive industry and may be identified as permanent mold casting alloy D–132.

The immersion bath which may be used in the practice of this invention is prepared by dissolving either potassium or sodium stannate in water to form a bath containing between approximately 17 grams per liter of the stannate to a saturated solution typically 35 grams per liter. This solution contains about 15 grams per liter of tin. The solution also contains at least one mole of boric oxide anion for 8 moles of alkali metal stannate and preferably one mole of boric oxide for each 6.6 moles of alkali metal stannate. The boric oxides may be added as boric acid, borax, potassium tetraborate, or one of the sodium or potassium condensed borates. The borates, boric acid are preferred and may be present in the solution in a concentration of about 1.5 grams per liter. Larger amounts of borate may be used but little, if any, improvement is obtained by increasing the concentration above about 1.5 grams per liter.

The immersion bath preferably has an initial pH of about 11.5 and is maintained at a pH of below about 12.8 at 140° C. The bath does not require alkali metal hydroxide in its initial makeup nor does the immersion bath require an acid or neutralizing agent or alkali to be added during the operation of the plating process. It appears that the boric acid prevents the hydrolysis of the stannate and also stabilizes the solution at the desired operation pH. It is believed that the boric oxide forms a complex with the stannate to provide the above desirable properties for the plating bath.

Stannate salts may be added to the bath at a rate sufficient to compensate for the tin loss occurring by the plating process and the tin loss experienced by drag-out with the plated articles. The borate may be added to compensate for the boric oxide removed on the plated articles by drag-out and for the boric oxide that reacts with the alkali metal hydroxide formed during the plating operation. The stannate salt and the boric oxide can be added separately but are preferably added together to the bath as a dry mixture.

It has been found that a desired plating bath composition may be maintained by adding to the aqueous solution a composition comprising about 80 to 98 parts by weight potassium stannate and between about 20 to 2 parts by

weight of boric acid. Preferably the composition employed to maintain the desired properties of the plating bath may comprise a dry mixture of 97 parts by weight potassium stannate and 3 parts by weight boric acid.

The following examples are typical of the compositions that may be added to the immersion tinning baths of this invention to make up for the tin losses and the boric oxide losses. The parts set forth are parts by weight.

EXAMPLE I

	Parts by weight
Potassium stannate	85
Boric acid	15

EXAMPLE II

Potassium stannate	90
Sodium tetraborate	7
Boric acid	3

EXAMPLE III

Potassium stannate	86
Sodium tetraborate	14

EXAMPLE IV

Sodium stannate	96
Boric acid	4

EXAMPLE V

Potassium stannate	80
Potassium tetraborate	20

An "ad hoc" test procedure was devised to provide a close proximity to the actual operating conditions experienced in commercial trading operations and to further accelerate into hours the solution conditions that would exist after days or weeks of commercial in-plant operation. The procedure was intended to simulate a large through-put of surface area to be plated for a given quantity of solution. The procedure also minimized drag-out and therefore increased the concentration of reaction products in the solution to a level that would require an extensively long period of actual operation to achieve.

The test procedure also simulated the accumulation of metallic aluminum in the bath as experienced under actual operating conditions where there is a carryover of turnings and the loss of aluminum parts that fall from the plating rack during the plating operation and remain in the bath for extended periods of time.

The tinning baths were made up in 500 ml. quantities and kept in a constant temperature bath at 140° F. To each bath was added 10 grams of D–132 aluminum alloy in the form of fine turnings and shavings. These particles of aluminum have a large surface area available for plating relative to their weight. After eight hours the turnings were removed and the bath allowed to stand overnight at room temperature. This simulated the shut-down periods in a commercial plating operation. The process was then repeated and the baths were analyzed frequently and maintained at about 15 grams per liter of tin. Every four hours a piece of freshly machined D–132 alloy, measuring 2" x 1" x ¼" was immersed in the solution for a period of four minutes, and the quality of the plate observed and noted.

Both the aluminum turnings and the aluminum test plates were cleaned prior to plating in a non-etching aluminum cleaner for a period of four minutes at 140° F., rinsed in cold water and dipped in a 5% by volume nitric acid solution at room temperature. This was followed by a water rinse, then placed in the plating bath.

It was found that the best indication of the quality of the tin plate on the aluminum alloy was its visual appearance. When the plate was bright white, it was fine grained, free of blisters and tightly adherent. As the quality of the plate diminished, the plate became dull, then slightly grey. As the plate appeared grey, small blisters were evident and the plate was not adherent and was unacceptable.

EXAMPLE VI

Four known bath compositions were prepared for comparative purposes in accordance with the above procedure and maintained at concentrations as follows:

Composition A:	Grams/500 ml.
Potassium stannate	25.7
Composition B:	
Potassium stannate	25.7
Sodium tripolyphosphate	4.2
Composition C:	
Potassium stannate	35.0
Sodium tripolyphosphate	1.25
Ethylenediamine	1.50
Composition D:	
Potassium stannate	16.7
Sodium gluconate	3.0
Potassium hydroxide	0.75

Two baths were prepared according to the herein described invention:

Composition E:	Grams/500 ml.
Potassium stannate	25.7
Boric acid	0.78
Composition F:	
Potassium stannate	25.7
Potassium tetraborate	4.2

The relative concentrations of the stannates and the additive compounds were maintained in the above baths by adding the following compositions to the bath in the following proportions expressed as weight percent.

Composition A:	Percent
Potassium stannate	100.0
Composition B:	
Potassium stannate	86.0
Sodium tripolyphosphate	14.0
Composition C:	
Potassium stannate	96.2
Sodium tripolyphosphate	2.1
Ethylenediamine	1.7
Composition D:	
Potassium stannate	97.0
Sodium gluconate	3.0
Composition E:	
Potassium stannate	97.0
Boric acid	3.0
Composition F:	
Potassium stannate	86.0
Potassium tetraborate	14.0

The properties of the plated surfaces were compared and classified according to the following designation:

Condition or appearance of the plated surface:

Very bright	VB
Bright	B
Dull	D
Light grey	LG
Grey	G

The properties of the plating bath solutions were compared and classified according to the following designation:

Condition or appearance of the bath:

Clear	CL
Turbid (no precipitate)	TB
Precipitate	PPT
Light green	LTG
Viscous	VS

The condition of the bath and the quality of the plating was observed during eight hour periods continuing through 104 hours. The designation "Discarded" indicated that the plating was below minimum standards. The color of the solution correlates with the condition of the plated product. Table I compares the six baths and the plating efficiency by the quality of the plate and by the appearance of the bath.

TABLE I

Bath		Elapsed time, hours														
		0	8	16	24	32	40	48	56	64	72	80	88	96	104	
A	Solution	TB	TB	PPT	PPT	(1)										
A	Plate	VB	B	D	G											
B	Solution	TB	TB	TB	PPT	PPT	PPT	PPT	PPT	PPT	PPT	PPT	(1)			
B	Plate	VB	VB	VB	VB	VB	B	B	B	D	LG	G				
C	Solution	TB	TB	PPT	PPT	PPT	PPT	PPT	(1)							
C	Plate	VB	VB	VB	B	B	LG	G								
D	Solution	TB	TB	TB	TB	TB, LG	TB, LG	LG, TB	LG, TB	LG, TB	LG, VS	LG, VS	(1)			
D	Plate	VB	VB	VB	VB	VB	VB	VB	VB	B	D	D				
E	Solution	CL	CL	CL	CL	CL	CL	TB	TB	PPT	PPT	PPT	PPT	PPT	PPT	(2)
E	Plate	VB	VB	VB	VB	VB	VB	VB	VB	VB	VB	VB	B	B	B	(2)
F	Solution	CL	CL	CL	TB	TB	PPT	PPT	PPT	PPT	PPT	PPT	PPT	PPT	PPT	(2)
F	Plate	VB	VB	VB	VB	VB	VB	VB	VB	VB	B	B	B	B	B	(2)

[1] Discarded. [2] Discontinued test.

It is evident from the above table that bath A consisting of potassium stannate in aqueous solution was totally unacceptable after an eight hour period and was discarded after 24 hours. The bath produced unacceptable platings at 20 hours and was discarded after 24 hours. Baths B, C and D, which included additive compounds to the potassium stannate solution, illustrate an improvement over the use of potassium stannate alone in the plating bath. Bath B, however, that included the sodium tripolyphosphate, plated inferiorly after 64 hours, and was unacceptable at 78 hours, and discarded after 80 hours. Bath C that included as additives sodium tripolyphosphate and ethylenediamine plated inferiorly after 44 hours and was unacceptable by 50 hours and discarded. Bath D, which included as additives sodium gluconate and potassium hydroxide, provided acceptable though inferior plating at 80 hours. The bath however was foul smelling and viscous and the plates were difficult to wash and the bath was discarded. With bath D the plates had a dull appearance after the bath had been in use for 72 hours.

Baths E and F both exhibited surprisingly superior properties when compared with baths A through D. Baths E and F, prepared according to the present invention, were still functioning properly, yielding a bright, tightly adherent plate at 104 hours when the tests were discontinued. It should be noted from the color of the solution and the plating characteristics of Baths E and F as compared with Bath A that the boric oxide added to the bath with the potassium stannate did not function as a brightening agent. It is believed that the boric oxide forms a complex with the stannate and this complex reacts with the aluminum to form a plate of tin thereon without the hydrolysis of the complex and without the forming of excess alkali metal hydroxide in the bath during the plating process. It is believed that the alkali metal stannates and the compound containing the boric oxide anion form a stable complex in solution and the complex reacts with the aluminum metal. During the reaction the complex is converted to metallic tin on the aluminum surface and the boric oxide anion reacts with the alkali metal hydroxide to maintain the bath at an operating pH level.

According to the provisions of the patent statutes we have explained the principle, preferred construction and mode of operation of our invention and have illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

We claim:

1. An aqueous immersion tin plating bath for aluminum and aluminum alloys comprising water, between about 80 and 98 parts by weight of an alkali metal stannate and between 20 and 2 parts by weight of at least one compound containing a boric oxide anion being present in an amount sufficient to prevent the hydrolysis of the alkali metal stannate solution and prevent the formation of excess free alkali metal hydroxide, said bath having a pH of between about 11.5 and 12.8 at a temperature of 140° C.

2. An aqueous immersion tin plating bath for aluminum and aluminum alloys consisting essentially of water, alkali metal stannate and at least one compound containing a boric oxide anion, said compound and said alkali metal stannate being present in a molar ratio of at least one mole of boric oxide for each 8 moles of alkali metal stannate.

3. An aqueous immersion tin plating bath as set forth in claim **2** in which said compound containing a boric oxide anion is at least one compound selected from the group consisting of boric acid, alkali metal borates and hydrates of alkali metal borates.

4. An aqueous immersion tin plating bath as set forth in claim **2** in which said compound containing a boric oxide anion is boric acid and said boric acid is present in a concentration of about 1.5 grams per liter of said bath.

5. An aqueous immersion tin plate bath as set forth in claim **1** in which said compound containing a boric oxide anion is boric acid, said alkali metal stannate salt being present to provide in the bath a concentration of at least 17 grams of alkali metal salt per liter of bath and said boric acid being present to provide in the bath a concentration of at least 1.5 grams boric acid per liter of said bath.

6. The process for maintaining an aqueous immersion tin plate bath which comprises adding thereto a composition comprising between about 80 and 98 parts by weight of an alkali metal stannate salt and between 20 and 2 parts by weight of at least one compound containing a boric oxide anion, said composition added to the bath in an amount sufficient to compensate for the loss of tin by the plating process and by the loss of the alkali metal stannate salt by drag-out with the plated article and the loss of the boric oxide anion by reaction with the alkali metal hydroxide formed during the plating process and the loss of the bosic oxide anion by drag-out with the plated articles, said bath having a pH of between about 11.5 and 12.8 at a temperature of 140° C.

7. The process for maintaining an aqueous immersion tin plate bath as set forth in claim **6** in which said composition comprises a dry mixture of about 97 parts by weight of potassium stannate and about 3 parts by weight of boric acid.

8. A process for immersion plating of aluminum and aluminum alloys with tin by immersing said aluminum in an aqueous immersion tinning bath containing between about 80 and 98 parts by weght of an alkali metal stannate salt and between about 20 and 2 parts by weight of at least one compound having a boric oxide anion, said bath having a pH of between 11.5 and 12.8 at a temperature of about 140° C., and adding to said bath during the plating process a sufficient amount of alkali metal stannate to compensate for the loss of tin by the plating process

and a sufficient amount of said compound having a boric oxide anion to compensate for the loss of the boric oxide anion by reaction with the alkali metal hydroxide formed during the plating process.

9. A process for immersion plating of aluminum and aluminum alloys as set forth in claim **8** which includes adding a sufficient amount of said compound containing a boric oxide anion to maintain the pH of the bath between 11.5 and 12.8 during the plating process.

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