United States Patent Office 3,274,021 Patented Sept. 20, 1966

3,274,021

STANNATE COATING BATH AND METHOD OF COATING ALUMINUM WITH TIN

Jan C. Jongkind, Roseville, and Peter G. Kenedi, Detroit, Mich., assignors, by mesne assignments, to M & T Chemicals Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 27, 1962, Ser. No. 190,805
17 Claims. (Cl. 117—130)

The present invention relates to a process for immersion plating of aluminum 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 hydrozide 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 heretofore reduced the amounts of acid required. However because of the absence of any satisfactory techniques for solving the problem, acetic acid

is commonly employed, the addition being accompanied by vigorous agitation.

It is an object of this invention to provide an improved process for the immersion tinning of aluminum. It is a further object of this invention to provide novel aqueous alkali metal stannate baths useful for the immersion tinning of aluminum. It is another object of this invention to provide novel compositions of matter useful for making up and maintaining aqueous alkali metal stannate baths. Other objects of this invention will be apparent to those skilled in the art on inspection of the following description.

In accordance with certain of its aspects, the method of this invention for treating aluminum to form a surface layer of tin thereon may comprise immersing said aluminum in an aqueous bath consisting essentially of water, an anion of a polyhydroxy carboxylic acid, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereon; and withdrawing said aluminum from said bath.

The immersion baths may be typically 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 intially added to form a bath containing about 4 g./l. of the metal hydroxide to prevent precipitation of tin due to low pH during make-up. 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.

In accordance with this invention there may be added to the solution an anion of a polyhydroxy carboxylic acid. In the preferred embodiment, this anion may be an anion having less than about 8 carbon atoms. The preferred anion may be an anion of a polyhydroxy monocarboxylic acid, typified by the gluconate ion, the glucoheptonate ion, the glycerate ion, or of a polyhydroxy polycarboxylic acid typified by the saccharate ion or the tartrate ion. The preferred anions which may be employed may be gluconate, glucoheptonate, glycerate, and saccharate.

The anions may be added as sodium or potassium salts e.g. sodium gluconate, potassium gluconate, sodium saccharate, potassium saccharate, sodium glucoheptonate, potassium glucoheptonate, sodium glycerate, potassium glycerate, sodium tartrate, and potassium tartrate. The anion may alternatively be added as acid, typically gluconic acid, saccharic acid, etc. or as lactone, typically glucono-delta lactone, the delta-lactone of glucoheptonic acid, etc.; etc. Mixtures of these compounds may be employed.

The hydroxy acid salts may be added, preferably with agitation, to the aqueous stannate bath independently or jointly with the stannates which are used to make up and also to maintain the baths.

Preferably, the anion of the polyhydroxy carboxylic acid may be employed as the salt in amounts of 0.01 mole to 0.25 mole, say 0.1 mole/l. Equivalent amounts of acid or lactone may be employed. Smaller amounts may be

employed, but they do not substantially control the thickness of the immersion plate or the formation of sludge. Greater amounts may be employed but no substantial additional improvement may be obtained 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 is usually between 1–6 minutes, say 4 minutes. During this time, the aluminum may be coated with a layer of tin of desired thickness.

For make up and maintenance of the baths, preferred compositions may contain 80%–99% by weight of potassium stannate and/or sodium stannate and 1%–20% of at least one compound containing an anion of a polyhydroxy carboxylic acid. Preferred compositions of matter may contain 90%–98% of the stannate and 10%–2% of at least one compound containing an anion of a polyhydroxy carboxylic acid. The compositions containing lower percentage of the anion e.g. 2%–5% may be preferred for replenishment or maintenance while the compositions with the higher anion content e.g. 5%–20% may be preferred for the make up of new baths. Illustrative of these are the following compositions:

(1)

	Percent
Potassium stannate	95
Potassium gluconate	5

(2)

Sodium stannate	96
Sodium gluconate	4

(3)

Potassium stannate	98
Sodium gluconate	2

(4)

Sodium stannate	85
Sodium gluconate	15

(5)

Potassium stannate	97
Potassium glucoheptonate	3

(6)

Sodium stannate	96
Sodium glucoheptonate	4

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

EXAMPLE 1

Four solutions were made up containing 70 g./l. of potassium stannate each and respectively 0, 4, 8 and 12 g./l. of potassium hydroxide. The solutions were held at a temperature of 60° C. In each of the solutions, one of four identical discs of piston aluminum alloy (D–132 Alcoa) was immersed for exactly 4 minutes during which time a layer of tin was deposited on the disc.

The discs were removed from the solution, dried, and weighed. Then the tin deposit was stripped from the disc by immersion in a mixture of 3 parts of water and one part of concentrated nitric acid and the discs weighed again. From the loss of weight, the thickness of the coating was calculated.

Then to each of the solutions 8 g./l. of sodium gluconate was added, the immersion tinning process was repeated, and the plating thickness determined as before. Successively at intervals, additional aliquots of sodium gluconate were added, until each of the four solutions contained 39 g./l. of sodium gluconate; and after each addition, the plating thickness obtained by use of the solution was determined. The results are shown in Table I.

Table I

Na gluconate, g./l.	KOH concentration			
	0 g./l.	4 g./l.	8 g./l.	12 g./l.
	(Tin thickness in millionths of an inch)			
0	91	105	205	239
8	99	100	162	189
16	106	94	126	165
24	98	90	108	120
39	81	114	113	117

From this table it may be seen that the thickness of tin deposited from baths containing only stannate and alkali hydroxide and no gluconate, varies greatly with free alkali content. It may be noted for example that the tin deposit increased almost threefold as the potassium hydroxide increased from 0 to 12 g./l. In baths containing sodium gluconate, the plating thickness is much less dependent on the free KOH content and remains essentially constant over the wide range of potassium hydroxide content. The deposits from the baths containing gluconate had a better appearance with less streaking than did the deposits from baths without gluconate, particularly at the high caustic values of 8 and 12 g./l.

EXAMPLE 2

Another series of examples was conducted in a similar manner with other compounds having anions of polyhydroxy carboxylic acids; the results are shown in Table II.

Table II

Additive	g./l.	KOH concentration						
		1.5 g./l.	2 g./l.	4 g./l.	6 g./l.	8 g./l.	9 g./l.	12 g./l.
		(Tin thickness in millionths of an inch)						
None			92	150		205	206	239
Na glucoheptonate	24		74	103				146
Na glucoheptonate	39		84	100				110
K Na tartrate	39		113	143		180		211
K saccharate	11.6			87		155		103
Na glycerate	8		84	141		195		202
Na lactate	39		94	100				239
K citrate	39		106	114		198		251
Na acetate	40	76			137		213	

From Table II which shows tin thickness in millionths of an inch, it can be seen that as the potassium hydroxide content increases from 2 to 12 g./l., the thickness of tin plated on aluminum may undesirably increase 147 millionths from 92 to 239, a factor of 2.6, when the technique of this invention is not employed. Practice of this invention using sodium glucoheptonate may reduce this undesirable increase in thickness to e.g. 26 millionths from 84 to 110, which represents an increase by a factor of only 1.3. From Table II, it will be apparent that the lactate, citrate and acetate ions (which are not within the scope of this invention) do not permit attainment of

results which are better than the standard, but in contrast are less effective in that the tin deposit at e.g. 12 g./l. of KOH is higher than for the standard.

EXAMPLE 3

In this example, which is typical of prior art practice, a bath was made up containing 70 g./l. of potassium stannate and 4.0 g./l. of potassium hydroxide by dissolving first the potassium hydroxide and then the potassium stannate. The bath was analyzed for free potassium hydroxide, and brought to 60° C.

Three pieces of aluminum 3 x 6 x ¼" were 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 two liters of the stannate solution for 4 minutes to deposit a layer of tin. The aluminum parts were then withdrawn, rinsed, and the tin deposit stripped from the aluminum parts by immersing for one minute in the nitric acid solution, and rinsing under a stream of cold water. The parts were then ready for the second dip in the stannate solution. A series of 10 successive dips and strippings is designated as a cycle in the table below. At the end of each cycle, the bath was analyzed for free hydrooxide and tin, and the tin content brought up to 28 g./l. by addition of potassium stannate. At the beginning and end of each cycle, the thickness of the immersion coating was determined by means of difference in weight on a disc as described in Example 1. The surface area plated during one cycle was 15 square feet per gallon of plating solution. The results are given in Table III.

Table III

Cycle	Start of Cycle		End of Cycle	
	Thickness of Plate 10^{-6} inches	KOH, g./l.	Thickness of Plate 10^{-6} inches	KOH, g./l.
1	84	3.1	127	4.85
2	95	4.85	157	4.90
3	134	4.90	140	4.90
4	127	4.90	167	
5	136		170	8.5
6	224	8.5	186	9.8

The appearance of the tin deposit became streaky and gray and generally unsatisfactory after the fourth cycle, indicating an undesirably high caustic content. In order to maintain a satisfactory quality, neutralization would have been necessary after the fourth cycle. After the sixth cycle the bath was filtered, the recovered sludge dried at 100° C. overnight and weighed. The weight of the dried sludge was 43.2 g.

EXAMPLE 4

Two mixtures of potassium stannate and sodium gluconate were made up. Mixture A contained 85% potassium stannate and 15% sodium gluconate. Mixture B contained 97% potassium stannate and 3% sodium gluconate.

A bath was made up by dissolving 81 g./l. of mixture A and 1.5 g./l. of potassium hydroxide in two liters of water. Again a test was conducted using an identical technique as in Example 3, with the exception that the replenishment of the tin content of the bath after each cycle was accomplished by adding the appropriate quantity of mixture B instead of potassium stannate. The results are given in Table IV.

Table IV

Cycle	Start of Cycle		End of Cycle	
	Thickness of Plate 10^{-6} inches	KOH, g./l.	Thickness of Plate 10^{-6} inches	KOH, g./l.
1	79	1.5	99	1.6
2	73	1.6	107	1.6
3	66	1.6	82	1.6
4	84	1.6	101	1.3
5	81	1.3	95	1.3
6	90	1.3	102	1.7
7	72	1.7	81	1.0

In contrast to the results in Example 3, the quality of the deposit was good during the entire test with no streaking. The free potassium hydroxide content was constant during the test and even after seven cycles no need for neutralization existed. The sludge recovered from this bath, after drying, weighed 12.2 g.

Thus, it can be noted that a much smaller change in the thickness of the plate over the course of a cycle was obtained than was the case in Example 3; a better plate was uniformly obtained; neutralization was not needed to control the caustic and the sludging was decreased to almost 25% of that of Example 3.

EXAMPLE 5

This experiment was run, using mixtures and conditions identical to those of Example 4, except that the starting solution was made up with 8 g. of potassium hydroxide per liter instead of 1.5 g. of potassium hydroxide per liter. The results are given in Table V.

Table V

Cycle	Start of Cycle		End of Cycle	
	Thickness of Plate 10^{-6} inches	KOH, g./l.	Thickness of Plate 10^{-6} inches	KOH, g./l.
1	142	8.0	138	4.6
2	98	4.6	116	3.3
3	99	3.3	88	2.0
4	81	2.0	104	1.6
5	77	1.6	97	1.7
6	75	1.7	104	1.7
7	70	1.7	77	(1)

[1] Not determined.

The quality of the deposit was good throughout the test, even when starting with a high potassium hydroxide content of 8 g./l., which gave poor deposits in Examples 1 and 3 where gluconate was absent; the bath after a short time stabilized itself at a low free alkali content and after seven cycles no neutralization was necessary. The dried sludge obtained from this bath weighed 14.1 g.

The above examples show that the additives of this invention are capable of permitting attainment of uniform and satisfactory tin immersion deposits on aluminum over wide ranges of caustic concentration in the solution. This benefit minimizes the need for acid additions to neutralize free caustic. In life tests the baths could be used at least 50% longer than the control solutions without addition of acid. The amount of sludge was considerably less for the baths containing the novel compositions of this invention.

It is a particular feature of this invention that it permits operation of tin plating baths under conditions such that the thickness of the deposited tin plate is much more independent of the free alkali content of the bath than has been the case with prior art baths. It is another feature of the process of this invention that it minimizes or eliminates the need for addition to the bath of acid to neutralize the hydroxide formed.

It appears that in tin plating baths, reaction (I) supra may occur together with reaction (III), the latter acting to neutralize the excess caustic generated in reaction (I):

$$Al+NaOH+H_2O \rightarrow NaAlO_2+1.5H_2 \quad (III)$$

If the bath initially contained a low free alkali content, reaction (I) may produce more alkali than is consumed by reaction (III); in a bath with an initially high alkali content, reaction (III) may consume more alkali than is produced by reaction (I). In either case, the bath may reach an equilibrium at an intermediate level due to these reactions which may occur at the surface of the aluminum. The additives of this invention allow the production of a satisfactory tin deposit even in the presence of an excess of caustic and thus provides a bath which is operable over a wide range of conditions.

After the bath has been operating for a considerable period of time, the aluminate produced by reactions (I) and (III), which may be distributed throughout the bath, may react with water to produce sodium hydroxide and sludge in accordance with reaction (IV):

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

It is believed that the presence in the bath of the compounds of this invention may reduce this reaction and thereby minimize the formation of caustic, sodium hydroxide, and sludge including aluminum hydroxide.

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.

We claim:

1. The method of treating aluminum by immersion plating to form a surface layer of tin thereon which comprises immersing said aluminum in an aqueous bath containing water, an anion of a polyhydroxy carboxylic acid in amount of 0.01–0.25 mole per liter calculated as salt, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate; 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 method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is an anion of a polyhydroxy monocarboxylic acid.

3. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is an anion of a polyhydroxy polycarboxylic acid.

4. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is selected from the group consisting of gluonate, glucoheptonate, saccharate, and glycerate.

5. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is present in the form of a salt.

6. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said stannate is present in amount of 15 grams per liter to saturation.

7. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is gluoconate present in the form of a salt.

8. The method of treating aluminum by immersion plating to form a surface layer of tin thereon as claimed in claim 1 wherein said anion is an anion of a polyhydroxy carboxylic acid having less than about eight carbon atoms.

9. The method of treating aluminum by immersion plating to form a surface layer of tin thereon which comprises immersing said aluminum in an aqueous bath containing water, potassium stannate, and from 0.01–0.25 mole per liter sodium gluconate; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereon; and withdrawing said aluminum from said bath.

10. The method of treating aluminum by immersion plating to form a surface layer of tin thereon which comprises immersing said aluminum in an aqueous bath containing water, an alkali metal hydroxide, an anion of a polyhydroxy carboxylic acid in amount of 0.01–0.25 mole per liter calculated as salt, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate; maintaining said aluminum in said bath for time sufficient to deposit a surface layer of tin thereon; and withdrawing said aluminum from said bath.

11. An alkaline aqueous immersion tinning bath comprising an anion of a polyhydroxy carboxylic acid in amount of 0.01–0.25 mole per liter calculated as salt, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate.

12. An alkaline aqueous immersion tinning bath comprising an anion of a polyhydroxy monocarboxylic acid in amount of 0.01–0.25 mole per liter calculated as salt, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate.

13. An alkaline aqueous immersion tinning bath comprising an anion of a polyhydroxy polycarboxylic acid in amount of 0.01–0.25 mole per liter calculated as salt, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate.

14. An alkaline aqueous immersion tinning bath comprising an anion selected from the group consisting of gluconate, glucoheptonate, saccharate, and glycerate in amount of 0.01–0.25 mole per liter; and a stannate salt selected from the group consisting of sodium stannate and potassium stannate.

15. An alkaline aqueous immersion tinning bath comprising an anion of a polyhydroxy carboxylic acid having less than about eight carbon atoms in amount of 0.01–0.25 mole per liter, and a stannate salt selected from the group consisting of sodium stannate and potassium stannate.

16. A novel immersion plating composition of matter comprising a stannate salt selected from the group consisting of sodium stannate and potassium stannate; and 1%–20% by weight of the total of a compound containing an anion of a polyhydroxy monocarboxylic acid.

17. A novel immersion plating composition of matter comprising 80%–99% by weight of a stannate salt selected from the group consisting of sodium stannate and potassium stannate and 1%–20% sodium gluconate.

References Cited by the Examiner

UNITED STATES PATENTS

694,658	3/1902	Meurant	204—54
2,377,606	6/1945	Blackmum	117—130
2,947,639	8/1960	Balden	117—130

OTHER REFERENCES

Stout et al.: Transactions of the Electrochemical Society, vol. 68, 1935, pp. 483–492.

ALFRED L. LEAVITT, *Primary Examiner.*

RICHARD D. NEVIUS, *Examiner.*

R. S. KENDALL, *Assistant Examiner.*