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

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This invention relates to a process for the immersion plating of aluminum and aluminum alloys and to novel compositions and baths for this purpose. It especially relates to the tin immersion plating of cast aluminum and aluminum alloy structures such as pistons.

Immersion tin plating as heretofore practiced has involved the use of a bath consisting of an aqueous solution of sodium stannate ($Na_2SnO_3 \cdot 3H_2O$), into which the parts have been immersed to be tin plated. The following reaction occurs when the aluminum parts are immersed in the bath, some of the aluminum going into solution to replace the tin of the bath and the tin forming a plate on the aluminum:

$$H_2O+3Na_2SnO_3+4Al \longrightarrow 4NaAlO_2+\underset{\downarrow}{Sn}+2NaOH$$

In using this bath in production operations it has been found to have a number of disadvantages. Surface blistering occurs in the tin plate on the parts. This is a characteristic of this process which has been tolerated where moderate but it has often been so extensive as to be objectionable. In the case of aluminum pistons such blistering has been severe enough to interfere with air gauge inspection of the wrist pin holes. In the reaction shown above taking place in the bath, free caustic in the nature of sodium hydroxide (NaOH) is produced. Unless immediately controlled, the bath becomes out of balance and some of this free caustic reacts as follows with some of the aluminum and water to form sodium aluminate and hydrogen gas:

$$NaOH+Al+H_2O \rightarrow NaAlO_2+3H\uparrow$$

It is the hydrogen which is believed to form the blisters.

It has heretofore been attempted to control the free caustic by making periodic additions of acetic acid (CH_3COOH) with or without retarders such as sodium acetate whenever the free sodium hydroxide content exceeded about 0.5 oz. per gallon of solution. This was not entirely effective, was cumbersome and not always done in time to avoid sub-standard plating. Moreover, whenever the pH of the sodium stannate solution (normally about 12.5 for a solution of C.P. sodium stannate and distilled water) dropped even slightly, as it did where controlled by acetic acid, tin dioxide SnO_2 was precipitated out as a sludge thus lowering the tin content of the bath and necessitating frequent additions of sodium stannate. Similar results occurred using potassium stannate in the bath.

My invention provides a process and composition for the immersion tin plating of cast aluminum and aluminum alloys employing an alkali metal stannate type aqueous salt bath by which surface blistering of the tin plate may be substantially if not virtually eliminated and the need for control of the bath by acetic acid be avoided thus minimizing sludge formation and frequent tin additions.

Another object is to provide an aqueous alkali metal stannate type immersion tin plating bath and process with a control agent or compound capable of acting upon

the free caustic as it is produced during operation of the bath and of maintaining the free caustic content below the maximum allowable concentration (about 0.2 oz. per gallon of solution) that will cause unbalance.

A further object is to provide a sodium or potassium stannate type immersion tin plating bath and process with a control agent capable of substantially reducing the formation of tin dioxide sludge and thereby making fewer, if any, additions of sodium stannate to the bath necessary.

Still another object is to provide an alkali metal stannate type bath such as one containing sodium and/or potassium stannate, with a free caustic and sludge control agent selected from alkali metal phosphates and mixtures thereof whose alkali to acid salt ratio ($Na_2O:P_2O5$) is not greater than 2 to 1.

An additional object is to provide an alkali metal stannate type bath with a sludge and caustic control agent selected from the alkali metal polyphosphates and mixtures thereof.

A specific object is to provide a composition consisting essentially of sodium and/or potassium stannate and sodium or potassium tripolyphosphate ($Na_5P_3O_{10}$) from which a low cost highly efficient aqueous bath may be obtained for the immersion tin plating of aluminum and aluminum alloy parts and in the operation of which bath free caustic is automatically controlled such that a tin plate may be produced that is free of objectionable blistering.

Another object is to provide a composition of the character of the preceding objects comprising dry discrete ingredients which are compatible when mixed together and have a satisfactory shelf life when packaged.

Still another object is to provide a process and composition for the immersion tin plating of aluminum and aluminum alloys that will permit a substantial saving in material and labor over known processes and compositions.

Other objects of my invention will appear from the following description.

I have discovered that the difficulties enumerated above may be overcome and that aluminum and aluminum alloy parts may be expeditiously and satisfactorily immersion tin plated by the use of an aqueous bath in which an alkali metal stannate salt such as sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) or potassium stannate ($K_2SnO_3 \cdot 3H_2O$) and mixtures thereof furnish the tin to be deposited on the aluminum, and an alkali metal polyphosphate in which the alkali to acid salt ratio ($Na_2O:P_2O_5$) is no greater than 2 to 1, for example those corresponding to the higher alkali metal phosphates higher than orthophosphate and mixtures of any of such polyphosphates furnish control of caustic and sludge. Examples of the polyphosphates I may use are sodium hexametaphosphate also known as polymetaphosphate $(NaPO_3)_6$, tetrasodium pyrophosphate ($Na_4P_2O_7$), sodium tripolyphosphate ($Na_5P_3O_{10}$), potassium hexametaphosphate $(KPO_3)_6$, tetra potassium pyrophosphate ($K_4P_2O_7$) and potassium tripolyphosphate ($K_5P_3O_{10}$) and mixtures thereof. I preferably use sodium tripolyphosphate as the control agent because it appears to have the ability of providing the essential control over longer periods of time than other polyphosphates and because of its favorable pH value.

Sodium tripolyphosphate ($Na_5P_3O_{10}$) and potassium tripolyphosphate ($K_5P_3O_{10}$) are molecularly dehydrated metal acid phosphates, each having a pH of approximately 9.80 in a 1% solution.

Tetrasodium pyrophosphate ($Na_4P_2O_7$) and potassium pyrophosphate ($K_4P_2O_7$) are molecularly dehydrated metal acid phosphates each having a pH of about 10.2 in a 1% solution.

Sodium hexametaphosphate and potassium hexametaphosphate are molecularly dehydrated metal acid phosphates each having a pH of about 7.2 to 7.9 in a 1% solution.

A bath containing the foregoing two essential ingredients not only effectively tin plates parts of the above character but produces a tin plate coating of ample thickness, somewhat dependent upon the bath employed and time and temperature of plating, in the order of 0.00004″ to 0.000120″ that shows substantially uniformly good adhesion, substantially uniform color, and that is substantially free of surface blistering. Moreover, the ingredients essential to this composition are compatible in the bath, for example the pH of about 9.8 of sodium tripolyphosphate in solution being most compatible with the desired pH range of about 12.5 to 13.5 of the alkali metal stannates in solution. The ingredients are likewise compatible when mixed dry and packaged for use for preparing a new bath or as an addition to an old solution.

The alkali metal stannates operate in their customary capacity to react with the aluminum as shown above forming a plate on the aluminum. The alkali metal polyphosphates act to control the tendency of the deposited plate to surface blister by acting on the free caustic of the bath as it is formed during the plating operations thus maintaining its concentration at a safe value believed an amount below about 0.2 oz. per gallon of solution and substantially inhibiting reaction of the free caustic with aluminum to produce the free hydrogen gas described above believed to be the cause of blistering. In so doing it also serves to avoid the formation of tin dioxide (SnO_2) sludge which is a characteristic where acetic acid control was employed and thereby also reduces the number of additions of sodium stannate necessary to keep the tin content of the bath at a proper level. A substantial saving in the cost of plating is thus possible.

Although the exact action of the polyphosphates in the bath is not exactly known, it is believed that they are slightly unstable in a water solution and revert in time and as required to acid salts of the orthophosphates from which they were prepared which react with the free alkali. The ratio of Na_2O to P_2O_5 in the polyphosphates will indicate the potential amount of hydrogen ion to be released during hydrolysis. For example, sodium tripolyphosphate having a Na_2O:P_2O_5 ratio of 5:3 is believed to revert to mono and dibasic phosphates (NaH_2PO_4 having a pH of about 5.5 and Na_2HPO_4 having a pH of about 7.9) which react as follows to produce trisodium phosphate (pH of about 12.2) and water thereby using up the free alkali (NaOH) formed in the coating process:

(*a*) $NaH_2PO_4 + 2NaOH \rightarrow Na_3PO_4 + 2H_2O$

(*b*) $Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$

The stannate and polyphosphate of the bath for instance, sodium stannate and sodium tripolyphosphate may be used in various concentrations and good results obtained. Preferably the concentration of alkali metal stannate salt will be sufficient to insure a tin content in the bath of between 2 to 4 oz. per gallon of solution, such in the case of sodium stannate for example requiring between about 4.5 to 9 oz. of sodium stannate per gallon. The upper value given for tin in the bath is important only from the standpoint of cost. Larger concentrations, even up to a saturated solution, may be used without effecting plating but such merely results in a waste of tin. The lower value allows for some further reduction in tin to about one ounce per gallon in operation of the bath while still assuring good plating. Still lower concentrations will effect the thickness and quality of plate obtained.

The concentration of polyphosphates for instance sodium tripolyphosphate will be sufficient in amount to effectively control the free caustic content of the bath below a concentration causing unbalance. The amounts will vary somewhat dependent upon the tin salt and control agent employed. Usually a small quantity between about ¼ to about 3 oz. for each 6 oz. of alkali metal stannate per gallon of solution, or stated otherwise about 1/24 to ½ part by weight of alkali metal polyphosphate for each part by weight of alkali metal stannate will suffice. These amounts are sufficient to produce tin deposits of adequate thickness and which are much brighter in appearance than any obtained by the conventional sodium stannate solution where acetic acid has been the control addition.

Consistent and excellent results over a long period of operation are obtainable for example with an aqueous bath in which the essential ingredients consist of 6 oz. per gallon of solution of sodium stannate and 1 oz. per gallon of solution of sodium tripolyphosphate. The tin concentration of such a bath may be easily maintained by adding as required the same mixture as used in the solution make-up. No additions of acetic acid are needed and there is no increase in free caustic concentration over that present in the newly prepared solution.

The immersion plating baths of my invention may be operated over a substantial temperature range depending upon the composition of the part being plated. For cast aluminum alloy parts it is preferably operated at a temperature between 165° to 175° to keep the amount of free alkali per gallon of solution to below 0.20 ounce and sludge to a minimum. For purer aluminum parts, lower temperatures are preferably employed even as low as 75° F. depending upon the tin salt employed. Potassium stannate permits the use of lower temperatures than for instance sodium stannate. Overheating effects a side reaction increasing the free alkali and producing excessive sludge. The reaction is illustrated by the following:

$$H_2O + Na_2SnO_3 \xrightarrow{\text{excessive heat}} SnO_2 + 2NaOH$$

For the purpose of illustration only, my invention will be described in connection with the application, by immersion plating, of a tin plate to the barrel of engine pistons made of a cast aluminum-silicon-copper alloy to provide them with added resistance to wear and scuffing. Thus a bath is prepared containing the following ingredients in the amounts indicated per gallon of solution:

	Oz.
Sodium stannate	6
Tripolyphosphate	1
Water	Balance

The bath will have a tin concentration of at least 2 ounces per gallon of solution.

The aluminum pistons are now first cleaned by immersion in a solution of a suitable aluminum cleaning composition, the following being by way of example:

	Percent
Sodium metasilicate $NaSiO_3 \cdot 5H_2O$	35
Sodium tripolyphosphate $Na_5P_3O_{10}$	40
Sodium bicarbonate $NaHCO_3$	21
Sodium lignosulfate	3
Pluronic L–62	1

They are then rinsed in cold water sufficiently that the parts are free of water breaks after rinsing. Next the pistons are immersed in a nitric acid solution made with commercial nitric acid (sp. gr. 1.42) and maintained at 5% (by volume). Following this step the parts are again rinsed in cold water and then immersed in the tin coating bath of my invention maintained at a temperature of between about 165° to 175° in which the parts are held for about four minutes.

The parts are then removed, rinsed in cold or hot water and given a final rinse in hot water at not less than 175° F.

The plate formed on cast aluminum alloy pistons will be found to be uniform in character and color, will possess good adhesion, and will have a thickness in excess of 0.00004". For example at temperatures respectively of 130° F., 160° F. and 190° F. the thickness of coatings will be in the order respectively of about .000091", .000085" and .000083" respectively. These coatings are believed to be heavier than those obtained with conventional baths.

The following are additional examples of baths that may be used for example in plating cast aluminum alloy pistons. The alloy plated being in each instance aluminum alloy SAE 332. It will be noted that when using potassium stannate as the tin providing salt, lower temperatures should be used. This is to avoid blistering.

Example	Tin Salt	Polyphosphate	Temperature, ° F.	Time, min.	Thickness, inches	Adhesion
2	6 oz. Na_2SnO_3/gal	1 oz. $Na_5P_3O_{10}$/gal	160	10	0.000122	good.
3	6 oz. Na_2SnO_3/gal	¼ oz. $Na_5P_3O_{10}$/gal	160	4	0.000078	good.
4	12 oz. Na_2SnO_3/gal	1 oz. $Na_5P_3O_{10}$/gal	160	4	0.000028	good.
5	6 oz. K_2SnO_3/gal	1 oz. $Na_5P_3O_{10}$/gal	135	4	0.000065	good.
6	6 oz. K_2SnO_3/gal	2 oz. $Na_5P_3O_{10}$/gal	135	4	0.000064	good.
7	8 oz. K_2SnO_3/gal	1 oz. $Na_5P_3O_{10}$/gal	135	4	0.000077	good.
8	6 oz. Na_2SnO_3/gal	1 oz. $(NaPO_3)_6$	160	4	0.000103	good.

Corresponding potassium polyphosphates will give comparable results. Moreover, where purer aluminum alloys are plated, the immersion time may be substantially decreased, two minutes and even less sufficing in many cases.

The novel immersion bath of my invention is highly efficient in operation and because the polyphosphates control the concentration of free caustic in a safe range, no additions for such control are ordinarily required and losses of tin by sludge are kept at a minimum. These factors reduce materially the cost of materials and operating labor in the processing over prior immersion processes.

From the foregoing description of my invention it will be apparent that I have provided a new and novel composition and process for producing a tin plate on aluminum and aluminum alloy parts and that is productive of a highly satisfactory and inexpensive plate. It will be apparent to those skilled in the art that various changes in the composition and specific steps of processing may be made without, however, departing from the spirit or intent of my invention. All changes and modifications and equivalent compositions and processes as may come with the purview of the appended claims are therefore contemplated.

The present application is a continuation in part of my copending application Serial No. 611,772, filed September 24, 1956, now abandoned.

I claim:

1. A dry composition for preparing an aqueous tin coating bath for aluminum and aluminum alloys consisting essentially of alkali metal stannate and alkali metal polyphosphate the latter in amount sufficient to effectively control the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

2. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of alkali metal stannate and including a small quantity of alkali metal polyphosphate whose alkali (Na_2O) to acid salt (P_2O_5) ratio is no greater that 2:1 for controlling free caustic and sludge said polyphosphate being in amount sufficient to control the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

3. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of alkali metal polyphosphate whose alkali (Na_2O) to acid salt (P_2O_5) ratio is no

greater than 2:1 and alkali metal stannate, said polyphosphate being present in amount sufficient for effectively controlling the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

4. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of alkali metal stannate and alkali metal polyphosphate comprising alkali metal tripolyphosphate, in amount sufficient for effectively controlling the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

5. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys comprising a small quantity of an alkali metal polyphosphate and a major amount essentially the remainder of said composition of alkali metal stannate, said polyphosphate being in sufficient amount to provide free caustic and sludge control said polyphosphate being in amount sufficient to control the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

6. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of an alkali metal stannate salt and an alkali metal polyphosphate in amount between about 1/24 to about ½ part by weight for each part by weight of the alkali stannate salt.

7. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of sodium stannate and alkali metal tripolyphosphate in amount between about 1/24 to about ½ part by weight for each part by weight of sodium stannate.

8. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of potassium stannate and alkali metal tripolyphosphate in amount between about 1/24 to about ½ part by weight for each part by weight of potassium stannate.

9. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of sodium stannate and sodium tripolyphosphate in amount between about 1/24 to about ½ part by weight for each part by weight of sodium stannate.

10. A dry composition for preparing an aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of potassium stannate and sodium tripolyphosphate in amount between about 1/24 to about ½ part by weight for each part by weight of potassium stannate.

11. An aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of water, alkali metal stannate and alkali metal polyphosphate the latter in amount sufficient to substantially control the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

12. An aqueous immersion tin coating bath for alumi-

num and aluminum alloys consisting essentially of water, alkali metal stannate and alkali metal polyphosphate in amount between ¼ to 3 oz. by weight thereof for each 6 ounces of stannate.

13. An aqueous immersion tin coating bath for aluminum and aluminum alloys consisting essentially of water, alkali metal stannate and alkali metal tripolyphosphate, said tripolyphosphate being present in amount of about one part by weight thereof for each six parts by weight of said alkali metal stannate per gallon of solution.

14. An aqueous immersion tin coating bath consisting essentially of water, alkali metal stannate in amount to provide a concentration of at least about 1 oz. of tin per gallon of solution and alkali metal polyphosphate the latter in amount sufficient to control the free caustic concentration of the bath during operation thereof below about 0.2 oz. per gallon of solution.

15. An immersion tin plating process for tin plating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, alkali metal stannate salt and alkali metal polyphosphate in amount sufficient for effectively controlling the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

16. An immersion tin plating process for tin plating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, alkali metal stannate salt in amount between about 4.5 to 9 oz. per gallon of solution and alkali metal polyphosphate, whose alkali (Na_2O) to acid salt (P_2O_5) ratio is no greater than 2:1, in amount between about $1/24$ to ½ by weight for each part by weight of alkali stannate.

17. An immersion tin plating process for tin plating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, alkali metal stannate salt in amount to provide a concentration of at least about 1 oz. of tin per gallon of solution and alkali metal tripolyphosphate in amount sufficient for effectively controlling the free caustic content of the bath below such a concentration causing release of hydrogen in amount to produce objectionable blistering at the aluminum-tin interface.

18. An immersion tin plating process for tin coating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, an alkali metal stannate salt in amount sufficient to provide in the bath a tin concentration of at least one oz. of tin per gallon of solution and an alkali metal polyphosphate in amount by weight at least about $1/24$ of the weight of said stannate salt.

19. An immersion tin plating process for tin coating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, an alkali metal stannate salt in amount sufficient to provide in the bath a tin concentration of at least about one ounce of tin per gallon of solution and alkali metal polyphosphate in amount sufficient to control the free caustic concentration of the bath during operation thereof below about 0.2 oz. per gallon of solution.

20. An immersion tin plating process for tin coating aluminum and aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, sodium stannate in amount sufficient to provide a tin concentration in the bath of between one to four ounces of tin per gallon of solution, and sodium tripolyphosphate in amount by weight of between one-half to three ounces thereof for each six ounces of sodium stannate.

21. An immersion tin plating process for tin coating aluminum alloy parts comprising immersing the parts in an aqueous bath consisting essentially of water, an alkali metal stannate salt in amount sufficient to provide in the bath a tin concentration of at least about one ounce of tin per gallon of solution and alkali metal polyphosphate in amount sufficient to control the free caustic concentration of the bath during operation below about 0.2 ounce per gallon of solution, maintaining said bath at a temperature between about 130° F. and 190° F. and keeping said parts immersed for a period at least about two minutes.

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