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METHOD AND COMPOSITION FOR COATING ALUMINUM WITH TIN

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9 Claims. (Cl. 117—130)

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This invention relates to a method of coating metals on articles of aluminum or alloys thereof by immersion of the articles in aqueous solutions of suitable composition. More specifically the invention relates to a method of producing smooth and adherent deposits of tin on aluminum surfaces by immersion in aqueous baths without the use of electric current. The immersion deposits have a sound structure and such an unusually high degree of adhesion to the aluminum that they may be used as a base for the subsequent electrodeposition of other metals.

This application is a continuation-in-part of my copending application Serial No. 41,891 filed July 31, 1948, now Patent No. 2,580,773.

Tin may be deposited on aluminum by immersion from stannate solutions. This process is used commercially for tin coating aluminum automotive and airplane engine pistons. The lubricating qualities imparted by the tin serve to reduce seizing and scuffing and decrease engine break-in time.

The process using stannate solutions however is critical. The temperature must be maintained at 175 to 180° F. Allowing the temperature to rise above 180° F. causes blisters in the tin coating. Powdery tin coatings are encountered in present-day practice and this is objectionable because it scores the aluminum during the initial breaking-in period of engine pistons.

The stannate process is applicable only to some aluminum alloys such as castings; other alloys and pure aluminum (2S) yield powdery deposits. Even on the preferred alloys the adhesion of the tin is poor as may be readily shown by depositing copper on the tin coatings. The copper readily peels off; the separation is between the aluminum and the tin.

I have discovered that it is possible to produce smooth, extremely adherent and uniform coatings on aluminum surfaces of tin by immersion of the cleaned aluminum in aqueous baths containing water-soluble fluorides or fluoride complexes of tin. I may also use suitable water-soluble salts of tin with the addition of suitable amounts of hydrofluoric acid, sodium fluoride, ammonium fluoride, ammonium bifluoride, potassium fluoride, or potassium bifluoride to generate a fluoride anion in the bath.

The essential features of my invention are illustrated by the following specific examples for producing smooth, uniform adherent coatings of tin on aluminum articles. My process is suitable for producing metallic tin deposits on aluminum articles or alloys thereof containing aluminum as the essential component. The expression "aluminum" in the claims is intended to include articles made of commercially pure aluminum (2S) or aluminum alloys having aluminum as the essential component. The aluminum article is first thoroughly degreased and cleaned so as to remove any grease, dirt or other undesirable foreign materials on the surface of the aluminum article. For example, the aluminum article is first immersed in an organic solvent, such as trichlorethylene. The article is then treated to activate the surface. For this purpose the aluminum article may be immersed for about one to three minutes at room temperature in a bath containing 0.5 to 5.0 N hydrofluoric acid. In case the article treated is made of an aluminum alloy, a film may remain on the surface of the article which consists of the metals alloyed with the aluminum. It may be readily removed by dipping the article in 50% or more by volume of nitric acid at room temperature from ten to twenty seconds. This treatment is then followed by a cold water rinse. Warm or hot water should not be used to rinse the aluminum article because of the tendency to form a heavier oxide film on the aluminum surface which may interfere with the subsequent immersion process.

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Aluminum articles may also be satisfactorily cleaned preparatory to my immersion process by using suitable alkaline cleaners such as caustic soda or trisodium phosphate. For example, a solution of 50 g. l. of sodium hydroxide at a temperature of 65° C. is satisfactory. The aluminum article after preliminary cleaning treatment previously described is then immersed in an aqueous bath containing a tin cation and a fluoride anion.

Satisfactory deposits of tin on aluminum surfaces can be produced in accordance with the present invention. For example, a suitable bath for such purpose consists of:

$SnSO_4$	1.5 N (161.1 g./l.).
HF	2.0 N (70.0 ml./l. of 48% acid).
Hydrolyzed glue	1.0 g./l.
Goulac	0.2 g./l.
Purified residue acid	1.3 ml./l.

The hydrolyzed glue is prepared by adding one cc. of 10% sodium hydroxide solution to 100 cc. of 10% bone glue solution and boiling under a reflux condenser for two hours. The excess alkali is neutralized with sulfuric acid and the solution then filtered to remove suspended matter. Goulac is a concentrated sulfite paper pulp process waste and contains lignin sulfonates. Purified residue acid is a mixture of high boiling coal tar phenols and had the following distillation range: I. B. P.—102°; 5%=212°; 10%=222°; 30%=232°; 50%=235°; 70%=238°; E. P.=276°.

Without the presence of addition agents, a heavy, black, pulverulent deposit of tin is precipitated on the aluminum which could be easily wiped off. The addition of glue and cresylic acid, to the stannous sulfate-hydrofluoric acid system results in sound, homogeneous tin deposits. Further improvement is effected by using a mixture of hydrolyzed glue, goulac and purified residue acid. These addition agents are added to the $SnSO_4$—HF solution in the order given above and with vigorous stirring. The solution is then filtered through coarse filter paper to remove suspended matter and excess purified residue acid. The presence of small amounts of phenolic type compounds and hydrophilic colloids in these solutions leads to smoother, brighter and harder deposits of smaller grain size and less ductility. These phenolic type of compounds are generally designated as hydroxy aromatic compounds.

Good agitation of the aluminum in the tin solution is essential for sound tin immersion deposits. Lack of agitation may result in dark streaks in the tin and subsequently poor adhesion of the copper plate.

The optimum time of immersion of the aluminum in the tin solution is important for good results and is relatively critical. The preferred time of immersion varies with the concentrations of stannous sulfate and hydrofluoric acid. The lower the $SnSO_4$ and the higher the HF concentrations, the shorter the time for good tin deposits. In general, the immersion time should not be longer than about ten seconds. The amount of stannous sulfate in the bath may range from 0.5 to 2.5 N and the hydrofluoric acid from 0.25 to 5 N.

According to the present invention it is possible to produce on aluminum articles deposits thereon of tin by immersion of the aluminum articles in an aqueous bath containing the cation of tin and a fluoride anion. The scientific basis of my invention is not fully known to me but it appears that the fluoride anion has a very high solvent action on the surface oxide which may be present on the aluminum, the presence of which normally prevents adherent immersion coatings on aluminum. My immersion bath acts to remove the oxide film present and permits the tin to be deposited on the aluminum surface in metal to metal contact before any substantial formation of an intervening oxide film. The present invention thus makes it possible to deposit tin on aluminum for any desired purpose, either for protecting the aluminum, for electrodeposition of other metals thereon, or for receiving other coatings such as paint, lacquer, plastic films and the like.

I have found that baths containing compositions of the following components and under conditions given are also suitable for depositing tin on aluminum surfaces:

Stannous sulfate	Varied from 0.05 N to 7.25 N.
Ammonium fluoride	Varied from 0.1 N to 14 N.
Hydrolyzed glue	1.0 g./l.
Goulac	0.2 g./l.
Purified residue acid	1.3 ml./l.
Temperature	20° C. to 60° C.
Time	2 to 60 seconds.
Agitation	Mild.

The wide range of compositions of stannous sulfate and ammonium fluoride within which good tin deposits may be obtained is very striking. In testing the deposits, copper was plated upon the tin immersion deposit to a thickness of 0.0005'' and the adhesion determined qualitatively by bending. The solubility of stannous sulfate in water at room temperature is 1.8 N. The increased solubility of stannous sulfate in the presence of ammonium fluoride is caused by the formation of a tin fluoride complex. I prefer to use baths containing 0.5 N to 9 N NH_4F and 0.25 N to 3 N $SnSO_4$ at a temperature of 25° C.

The fluoride in my bath appears to have two functions: (1) to dissolve the oxide film on the aluminum as previously discussed and (2) to form a tin fluoride complex and thereby greatly extend the range of concentrations of tin and fluoride constituents.

In regard to the operating conditions, the $SnSO_4$—NH_4F bath is preferred over the

$SnSO_4$—HF

solution. The time of immersion in the HF bath is very critical and ranges from 5 to 10 seconds. If the time is greater than about ten seconds, the HF attacks the aluminum through the pores in the tin and resulting gassing causes deterioration of the tin deposit. In the NH_4F bath there is no gassing, consequently the aluminum may be left in solution up to 1 or 2 minutes without deleterious effect.

In the HF bath, vigorous agitation of the aluminum is essential. Lack of agitation results in dark streaks in the tin and subsequently poor adhesion of the copper plate. In the NH_4F bath, the agitation need be only mild in accordance with good plating practice for deposition by immersion.

The above differences between the HF and the NH_4F baths appear to result from the difference in pH of the two types of solution. The pH of the HF baths ranges from 0.2 to 1.0 whereas the pH of the NH_4F solutions ranges from 5.0 to 6.5. The pH was measured by Accutint pH papers, which are manufactured by Anahemia Co., New York.

As previously explained, it is the fluoride ion which is the solvent for the oxide film on aluminum and the fluoride salts of ammonium, sodium and potassium are just as effective for this purpose as hydrofluoric acid.

The results obtained with NH_4F were also obtained with either sodium fluoride or potassium flouride. The pH of all three types of solutions were from 5.0 to 6.5. This further appears to establish that the important conditions for the deposition of adherent tin deposits are (1) presence of fluoride ion and (2) relatively high pH in the range of 5.0 to 6.5.

It will be apparent that the novel and essential features of my invention may be utilized to prepare a large number of immersion baths depending upon the metal desired to be coated, the aluminum article to be coated and the operating conditions under which the coating is to be carried out. The specific examples given herein are intended to be illustrative embodiments of the basic essential features of my invention as defined in the appended claims.

I claim:

1. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film

and immersing the cleaned aluminum article in an aqueous bath consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, a water-soluble tin salt and a water-soluble fluoride, the concentration of tin salt in said bath being in the range of 0.05 N to 7.25 N and the concentration of fluoride being in the range of 0.1 N to 14 N.

2. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film and immersing the cleaned aluminum article in an aqueous bath consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.05 N to 7.25 N and the concentration of ammonium fluoride being in the range of 0.1 N to 14 N.

3. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film and immersing the cleaned aluminum article in an aqueous bath consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and hydrofluoric acid, the concentration of stannous sulfate in said bath being in the range of 0.5 N to 2.5 N and the concentration of hydrofluoric acid being in the range of 0.25 N to 5 N.

4. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film and immersing the cleaned aluminum article in an aqueous bath consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.25 N to 3 N and the concentration of ammonium fluoride being in the range of 0.5 N to 9 N.

5. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film and immersing the cleaned aluminum article from 2 to 60 seconds in an aqueous bath at a temperature from 20 to 60° C. consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.05 N to 7.25 N and the concentration of ammonium fluoride being in the range of 0.1 N to 14 N.

6. The method of coating aluminum articles with an adherent, smooth deposit of tin which comprises cleaning the aluminum article to remove substantially all of the surface oxide film and immersing the cleaned aluminum article in an aqueous bath having a pH from 5.0 to 6.5 and consisting essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.05 N to 7.25 N and the concentration of ammonium fluoride being in the range of 0.1 to 14 N.

7. An immersion aqueous bath for depositing metallic tin on a clean aluminum surface substantially free of surface oxide film which consists essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.05 N to 7.25 N and the concentration of ammonium fluoride being in the range of 0.1 N to 14 N.

8. An immersion aqueous bath for depositing metallic tin on a clean aluminum surface substantially free of surface oxide film which consists essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.25 N to 3 N and the concentration of ammonium fluoride being in the range of 0.5 N to 9 N.

9. An immersion aqueous bath for depositing metallic tin on a clean aluminum surface substantially free of surface oxide film which consists essentially of water, an organic addition agent consisting essentially of a water-soluble glue and a hydroxy aromatic compound, stannous sulfate and ammonium fluoride, the concentration of stannous sulfate in said bath being in the range of 0.05 N to 7.25 N and the concentration of ammonium fluoride being in the range of 0.1 N to 14 N, said bath having a pH from 5.0 to 6.5.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,580,773	Heiman	Jan. 1, 1952