

UNITED STATES PATENT OFFICE

2,580,773

METHOD AND COMPOSITION FOR COATING
ALUMINUM WITH ZINCSamuel Heiman, Philadelphia, Pa., assignor to
Philadelphia Rust-Proof Co., Philadelphia, Pa.,
a firmNo Drawing. Application July 31, 1948,
Serial No. 41,891

6 Claims. (Cl. 117—130)

1

2

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 metals nobler than aluminum 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. For example, zinc, cadmium, tin, and other metals may be deposited on aluminum in accordance with the present invention which have a greater bond to the aluminum than the cohesive strength of the aluminum base metal itself.

Hitherto, electroplated coatings upon aluminum have assumed an important place among the finishes for this metal because the light weight and low cost of aluminum are combined with the specific desirable properties of the plated coating. Thus, aluminum is plated with silver for increased surface conductivity on contacts and electronic parts, with cadmium and nickel for improved solderability, brass for bonding to rubber, heavy chromium for wear resistance and decorative chromium on nickel for improved appearance and abrasion resistance. The applications are manifold and continually increasing. The difficulty in plating on aluminum results from the high potential of the metal which ordinarily tends to produce loosely adherent immersion deposits and the ever-present surface oxide film. The problem has been attacked previously by five general methods:

1. *Etching the surface.*—Aluminum may be etched in a mixture of nitric and hydrofluoric acids and then nickel plated. The adhesion of the nickel to the aluminum depended to a large extent on the keying action of the nickel deposit in the pits in the aluminum surface.

2. *Deposition of a bonding metal by electrochemical displacement.*—The aluminum oxide film may be replaced by a metal deposited on the aluminum by electrochemical displacement. The immersion coating then serves as a base for the subsequent electrodeposition of other metals. Several processes have been proposed for depositing iron, manganese, nickel, and cadmium from hydrochloric acid solutions. In these processes, however, the aluminum was pitted by the hydrochloric acid and the adhesion attained was more the result of a mechanical keying action in the

pits in the aluminum than a true adhesion of the two metals. The process involving the deposition of zinc by immersion on the aluminum from a highly alkaline zincate solution has been much more successful in securing the highest degree of adhesion without pitting the base metal.

3. *Anodic treatment.*—The natural oxide coating on aluminum may be replaced by a relatively thick, porous, anodic oxide coating. The electroplated metal adheres to the aluminum by virtue of filling the pores of the oxide coating.

4. *Special plating solutions.*—Various methods have been proposed for plating zinc, cadmium, copper and nickel directly on aluminum, usually from solutions of various compositions, but none of these coatings has the degree of adhesion required.

5. *Miscellaneous methods.*—Copper has been deposited by immersion on aluminum from molten cuprous chloride at 450° C. A high degree of adhesion is obtained but the physical properties resulting from heat treatment of the aluminum are adversely affected and the process, in general, is more difficult than those described above.

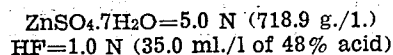
Of all the methods which have been devised and studied, only two produce smooth and adherent deposits and are used commercially today. They are the zinc immersion process and the anodic coating process. The former process is much more widely used because it is applicable to more alloys, requires less equipment and time, and the conditions are less critical.

I have discovered that it is possible to produce smooth, extremely adherent and uniform coatings on aluminum surfaces of metals nobler than aluminum by immersion of the cleaned aluminum in aqueous baths containing water-soluble fluorides or fluoride complexes of the metal desired to be deposited, such as zinc, cadmium, tin, iron, nickel, cobalt or manganese, or alloys thereof. It is also possible to produce uniform coatings of silver, gold, copper and antimony, or alloys thereof, on aluminum in accordance with my invention, although the coatings of these metals are not quite as adherent as in the case of the metals previously mentioned. I may also use suitable water-soluble salts of these metals with the addition of suitable amounts of hydrofluoric acid, sodium fluoride, ammonium fluoride, or ammonium acid fluoride, or ammonium 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 zinc on aluminum articles. My process is suit-

able for producing metallic 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 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 trichloroethylene. The article is then treated to remove the surface oxide film in order 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 alu-

acid may be increased up to a maximum of 2.5 N with increase in the zinc sulfate concentration. For general plating purposes, a very satisfactory bath composition well within the preferred range is for example:



The zinc immersion deposits obtained in the preferred range have a clean, uniform gray color. Spotty or streaked deposits were obtained from solutions containing excess hydrofluoric acid and were an indication of inferior adhesion of the plated coating.

Various fluoride salts in combination with zinc sulfate were evaluated as immersion dip solutions. The aluminum panels were treated by the procedure previously described, and the plated coatings evaluated for adhesion by the bend and furnace tests. The results of these tests are given in the table. The zinc sulfate concentration in all cases was 5 normal. In the furnace test, the coated panel was heated in a furnace at 300° C. for 2 hours according to the procedure given by Ferguson, Monthly Rev. Electroplaters' Soc., vol. 33, 295 (1946).

Table

Fluoride Salt	Concentration of Fluoride Salt mixed with 5 N $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at which—	
	Copper Deposits on Zinc Film passed Furnace Test	Precipitate Formed in $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ Fluoride Salt Mixture
Sodium Fluoride, NaF.....	0.2 N-0.4 N	0.4 N
Potassium Fluoride, $\text{KF} \cdot 2\text{H}_2\text{O}$	0.2 N-0.4 N	0.4 N
Ammonium Fluoride, NH_4F	0.2 N-1.0 N	1.0 N
Ammonium Acid Fluoride, $\text{NH}_4\text{F} \cdot \text{HF}$	0.2 N-1.0 N	1.0 N

minum article because of the tendency to form an oxide film on the aluminum surface which may interfere with the subsequent immersion process.

Aluminum articles may also be satisfactorily cleaned preparatory to my immersion process by using suitably inhibited 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 zinc cation and a fluoride anion. The bath for example may have zinc sulfate and hydrofluoric acid as its essential agents. According to my invention the ranges of these ingredients in the bath are 3 N to 7 N of zinc sulfate and 0.2 N to 2.5 N hydrofluoric acid. The aluminum article is immersed in this bath from 30 seconds to 5 minutes at about 20° C. room temperature or as high as 50° C. if desired to produce a clear, uniform gray color, strongly adherent zinc coating on the surface of the aluminum.

The cohesion of the zinc coating to the aluminum thus produced has been found to be greater than the cohesive strength of the aluminum base itself as determined by the Ollard Test. Iron Age, vol. 146, 17-20 (1940), Trans. Faraday Soc., vol. 21, 81 (1925).

There is a considerable range of concentrations of the two components of the immersion baths at which excellent zinc deposits may be obtained. The minimum hydrofluoric concentration is about 0.2 N. The concentration of hydrofluoric

From the above data, it is seen that the fluoride salts are just as effective as hydrofluoric acid. Neither hydrofluoric acid nor the fluoride salts were effective below a concentration of 0.2 normal and the plated coatings blistered in the furnace. While the zinc sulfate solutions and hydrofluoric acid were miscible in all proportions, there was a maximum solubility of the fluoride salts in the 5 normal zinc sulfate solution. The precipitate which formed at the fluoride salt concentrations given in the table was probably the zinc alkali fluoride complex or possibly zinc hydroxide or basic zinc sulfate. This fixes an upper limit to the fluoride range at which good deposits are obtained, and this is much narrower than that obtained with hydrofluoric acid. On the other hand, a convenient way of maintaining a fixed fluoride concentration is available by keeping the solution saturated with the fluoride salt. Furthermore, the salt is easier to handle than the acid both for preparing the solution and making additions.

The effect of varying the temperature and concentration of the hydrofluoric acid dip was studied for its effect on the quality of the zinc immersion coating as measured by the Furnace Test on the copper electrodeposits.

Tests were made with 0.5 N hydrofluoric acid at 40° C. and the results compared with those obtained at the standard 25° C. It was found that, in general, the activity of the reaction of hydrofluoric acid on aluminum at 40° C. was approximately twice that at 25° C., and the minimum time in the acid dip therefore could be halved.

5

The effect of acid concentration was studied with 0.5 N, 1.5 N and 3.0 N hydrofluoric acid solutions at 25° C. There was a considerable increase in the activity of the acid with increase in strength. With a fifteen second dip in 3.0 N acid, an aluminum panel plated according to the present method passed the Furnace Test.

The concentration temperature and time in the hydrofluoric acid dip for activating the aluminum surface are not critical and the dip is effective under a wide range of conditions. The optimum conditions must be determined for each article plated depending on its alloy composition and surface condition.

In general, the 0.5 N solution at room temperature is recommended and the time of dip should be sufficient to activate the surface and permit maximum adhesion without removing too much metal and possibly etching the aluminum.

The effect of variation in the time of immersion of the aluminum in the zinc immersion solution consisting of 5 N zinc sulfate and 1 N hydrofluoric acid was studied. It was found that the immersion time was not critical and that satisfactory deposits were obtained when the time varied from ten seconds to two minutes. The zinc films had a uniform gray color. There was a slight amount of gassing, which increased in amount with time, but which was dislodged from the panel by the mild agitation during the immersion. On the basis of this work, the preferred time in the zinc immersion solution is 30 to 60 seconds. The thickness of coating thus produced is self-limiting as soon as the entire aluminum surface is coated. However, if thicker zinc or other metal coatings are desired, the aluminum article may be connected as the cathode to a suitable source of direct current to produce excellent adherent deposits. When using current I prefer to use baths containing a fluoride salt to supply the fluoride anion rather than hydrofluoric acid so as not to develop too high acidity in the bath.

The temperature of the standard 5 N zinc sulfate-1 N hydrofluoric acid immersion solution was 25° C. in the previously noted work. The effect of raising the temperature of this solution to 45° C., on the quality of the final copper electroplate was studied and evaluated by the Furnace Test. The higher temperature had the effect of giving a heavier zinc coating and decreased the permissible immersion time from two minutes at 25° C. to 20 seconds. The immersion solution should therefore be kept at room temperature, preferably between 20° and 25° C. I prefer to use zinc sulfate in my baths but other zinc salts such as zinc chloride, zinc nitrate and zinc acetate may be used instead.

Excellent deposits of tin on aluminum surfaces can also be produced in accordance with the present invention. A suitable bath for such purpose consists of:

$\text{SnSO}_4 = 1.5 \text{ N (161.1 g./l.)}$
 $\text{HF} = 2.0 \text{ N (70.0 ml./l. of 48\% acid)}$

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

6

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° C.; E. P. = 90% = 276° C.

Without the presence of addition agents, a heavy, block, 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 hydrophilic colloids in these solutions leads to smoother, brighter, and harder deposits of smaller grain size and less ductility.

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. As previously stated, other metals nobler than aluminum can be successfully deposited on aluminum by immersion in a bath containing the cadmium cation and the fluoride anion. For example, satisfactory deposits can be obtained on aluminum articles which have been first pre-cleaned as previously described and then immersing the aluminum articles in a bath containing cadmium sulfate in amount 0.02 N to 0.055 N and hydrofluoric acid in amount 0.5 N to 12 N. It is advantageous to add a small amount of glue to improve the structure of the coating. A preferred bath for general purposes contains 3 N hydrofluoric acid, 0.035 N cadmium sulfate and 2 g./l. hydrolyzed glue. Agitation of the aluminum article during immersion for about 5 to 15 seconds at room temperature is desirable to obtain deposits of uniform sound structure.

I may produce alloy coatings of metals on aluminum in accordance with my invention by utilizing a bath containing two or more metal cations. For example, a zinc-cadmium alloy coating on aluminum can be produced by immersing the aluminum article as cathode in a bath having 5 N zinc sulfate, 1 N cadmium sulfate, and 1 N hydrofluoric acid and passing direct current for about ten minutes using a current density 10 amps. per sq. ft. Satisfactory alloy coatings with or without the use of current can be obtained particularly when the metals are close to each other in the electromotive series, such as zinc and cadmium, nickel and iron, nickel and cobalt, etc.

According to the present invention it is possible to produce on aluminum articles deposits thereon of zinc, cadmium, tin and other metals nobler than aluminum and alloys thereof by immersion of the aluminum articles in an aqueous bath containing the cation of the metal or metals desired to be deposited 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 metal to be deposited on the aluminum surface in metal to metal contact before any substantial formation of an intervening oxide film. The metal to metal contact of zinc and aluminum produced by my immersion bath is so intimate that the bond between the zinc deposit and the aluminum surface is greater than the cohesive strength of the aluminum base metal itself. The present invention thus makes it possible to deposit metals 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.

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 zinc 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, a water-soluble zinc salt and a water-soluble fluoride, the concentration of the zinc salt in said bath being in the range of 3 N to 7 N and the concentration of the fluoride being in the range of 0.2 N to 2.5 N.

2. The method of coating aluminum articles with an adherent, smooth deposit of zinc 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,

zinc sulfate and hydrofluoric acid, the concentration of zinc sulfate in said bath being in the range of 3 N to 7 N and the concentration of hydrofluoric acid being in the range of 0.2 N to 2.5 N.

3. The method of coating aluminum articles with an adherent smooth deposit of zinc which comprises cleaning the aluminum article to remove substantially all of the surface oxide film, immersing the cleaned aluminum article from 30 seconds to about 5 minutes in an aqueous bath at a temperature from 20 to 50° C., said bath consisting essentially of water, zinc sulfate and hydrofluoric acid, the concentration of zinc sulfate in said bath being in the range of 3 N to 7 N and the concentration of hydrofluoric acid being in the range of 0.2 N to 2.5 N.

4. The method of coating aluminum articles with an adherent smooth deposit of zinc 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, zinc sulfate and hydrofluoric acid, the concentration of zinc sulfate in said bath being about 5 N and the concentration of hydrofluoric acid being about 1 N.

5. An immersion aqueous bath for depositing metallic zinc on a clean aluminum surface substantially free of surface oxide film which consists essentially of water, a water-soluble zinc salt and a water-soluble fluoride, the concentration of the zinc salt in said bath being in the range of 3 N to 7 N and the concentration of the fluoride being in the range of 0.2 N to 2.5 N.

6. An immersion aqueous bath for depositing metallic zinc on a clean aluminum surface substantially free of surface oxide film which consists essentially of water, zinc sulfate and hydrofluoric acid, the concentration of the zinc sulfate in said bath being in the range of 3 N to 7 N and the concentration of the hydrofluoric acid being in the range of 0.2 N to 2.5 N.

SAMUEL HEIMAN.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,045,718	Marino	Nov. 16, 1912
1,607,676	Jirotka	Nov. 23, 1926
1,723,067	Pacz	Aug. 6, 1929
1,984,624	Bagley	Dec. 18, 1934
2,217,921	Saukaitis	Oct. 15, 1940
2,297,241	Perner	Sept. 29, 1942