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METHOD FOR CONVERTING ALUMINUM AND ALUMINUM BASE, AND COPPER AND COPPER BASE MATERIAL SURFACES FROM A HYDROPHOBIC TO A HYDRAPHILIC STATE

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ABSTRACT OF THE DISCLOSURE

A method of converting an aluminum or aluminum base article surface from a hydrophobic to a hydrophilic state comprising the steps of making the surface to be converted the anode in a bath comprising an acid-free aqueous borax solution at a temperature between 100 and 200° F., and maintaining an applied anode current at a current density not exceeding 5 amperes/square foot for a total current application maximum of 300 coulombs/square foot. The hydrophilic surface produced is exceptionally amenable to subsequent coating by various paints such as epoxy base, melamine base, latex, oil base, etc.

Copper and copper base surfaces are similarly made hydrophilic in the same bath but with the difference in that the copper surface is made the cathode, the current density is at least 1 ampere/square foot, and minimum total current application of 30 coulombs/square foot is utilized. The bath need not be acid-free. The hydrophilic surface so made is extremely amenable to subsequent electroplating, resulting in improved adhesion.

FIELD OF THE INVENTION

This invention relates to electrochemical methods of preparing a surface for subsequent coating, particularly aluminum and copper surfaces, by use of a heated bath comprising an aqueous borax solution acid-free in the case of aluminum.

BACKGROUND OF THE INVENTION

Aluminum and aluminum base materials, and copper and copper base materials are two of the most widely used materials as bases for plating and painting, and for general coating applications. The surfaces of such materials can generally be prepared in the case of copper for subsequent plating, and in the case of aluminum for subsequent painting, by use of electrochemical methods. In particular, aluminum surfaces may be anodized utilizing sulphuric acid or chromic acid treatments, preparatory to subsequent coating by epoxy resin base paints, latex base paints, oil base paints, or polyurethane base paints, for example. Similiarly, copper surfaces are often prepared for subsequent coating by electroplating by use of ammonium persulfate activation, or by copper cyanide electrolytic strikes. While these are roughening treatments, the use of these is to assure good adhesion of subsequent electrodeposits such as those from a Watts nickel bath, sulfamate nickel bath, acid copper bath, etc.

Common to both aluminum and copper surface preparations above, is the problem of safety due to the corrosive nature of the baths used, waste disposal problems, the ecological problems caused by use of such corrosive materials, the cost of the materials involved, the stability of the solutions and particularly the bath and shelf life stability, and most particularly the fact that these baths have a tendency to roughen and attack the surfaces which are being prepared for subsequent coating.

Prior art baths for aluminum have also utilized borax in solution with the addition of acids. These baths re-

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quired high voltages and were self-limiting in that amperage dropped off to close to zero current density during operation, compared to a desired constant current operation.

Thus, it is an object of this invention to provide a method of preparing both aluminum and copper surfaces for subsequent coating that is (1) safe, (2) provides minimal waste disposal problems, (3) minimizes ecological difficulties, (4) is non-hazardous, (5) is low in cost, (6) offers great solution stability, (7) offers great bath and shelf life stability, (8) does not roughen the surface of the materials being prepared (9) does not attack the surfaces involved, and (10) results in excellent adhesion of the subsequent coating.

SUMMARY OF THE INVENTION

These and other objects are met by the method of this invention, which comprises the process of utilizing an aqueous borax solution (acid-free for aluminum) maintained at a temperature of substantially 100–200° F., placing two electrodes in the bath, one of which is the article surface to be converted to a hydrophilic state, and applying a current across the electrodes through the bath. In the case of aluminum, the article surfaces must be the anode, and the current density does not exceed 5 amperes/square foot for a total current application not exceeding 300 coulombs/square foot. In the case of copper, copper is made the cathode, with a current density of at least one ampere/square foot for a minimum current application of at least 30 coulombs/square foot.

Wetting and complexing agents may also be utilized in this bath.

A detailed description of the process, and preferred embodiments utilized, toward a better understanding of the scope and advantages of this invention will best be understood in relation to the general description below.

GENERAL DESCRIPTION

While the copper preparation and aluminum preparation techniques described below differ in certain aspects, a common analysis of equipment is utilizable in both cleaning methods. In both systems, an aqueous borax solution is utilized in a tank that is non-corrosive and non-reactive with the borax solution, when the solution is heated in a temperature range of substantially 100–200° F. Thus, such common tanks such as stainless steel or polypropylene are quite acceptable. The borax solution may vary in concentration from a quarter ounce per gallon to saturation amounts at the temperature involved. The solution is maintained acid-free for aluminum. Acid use does not appear to affect the copper bath.

Both for copper and aluminum, an additional electrode is necessary utilizing the borax bath as the electrolyte. Again, the electrode should be non-corrosive or non-reactive with the bath at the temperature involved, and may be copper, stainless steel, lead or gold, as examples. Similarly, is is evident that both materials, the aluminum or aluminum base materials on the one hand and the copper and copper base materials on the other hand, should be precleaned prior to the treatment to be described. This essentially means eliminating grease and dirt from the surfaces of the materials. For aluminum, cleaning methods are known in the art, such as vapor degreasing, acid dipping in nitric acid, inhibited alkaline cleaning, and the use in general of deoxidizers and desmutters. Where a freshly machined surface is utilized, only vapor decreasing may be necessary. In the case of copper and copper base materials, general acid dips such as in hydrochloric acid, is sufficient. Other techniques for copper also well known in the art.

ALUMINUM

Thus, a pre-cleaned aluminum surface may be placed into a heated bath comprising an acid-free aqueous borax solution, heated to a temperature of between substantially 100–200° F. The aluminum surface is made one of two electrodes in the bath, the other electrode being one of the common materials above. A current is applied across the electrodes through the bath acting as the electrolyte, with the aluminum surface being made the anode, and the current density controlled not to exceed 5 amperes/square foot at the article surface. The current is maintained for a time not exceeding a total current application of 300 coulombs/square foot. Then, the current is discontinued the article removed from the bath, and rinsed by use of water, alcohol, etc. and dried by spin drying, forced air drying, or other known methods.

It has been found that surfaces of aluminum or aluminum base materials prepared in this manner are extremely hydrophilic and have excellent adhesion properties for subsequent coating by epoxy resin base, epoxy phenolic, epoxy melamine, melamine, latex base paints, oil base paints, polyurethane base paints, and other commonly known paints.

To improve the bath properties, wetting agents and complexing agents may be added. Wetting agents are utilized for promoting uniformity of surface activation by the current and to act as supplementary cleaning agents in the removal of trace amounts of residual contaminations from the surface. The complexing agents are utilized to reduce the processing time and current requirements by their activating activity. In the case of aluminum, this particular treatment causes no loss of surface brightness, as opposed to other anodizing treatments that tend to dull the surface. For aluminum, the preferred operating temperature range is within 140–170° F., with a particular preferred temperature of 150° F. While one quarter ounce per gallon to saturation amount of borax at the operating temperature is utilizable, for aluminum, one quarter to ten ounces per gallon of borax is a preferred concentration range. Still more preferred is the use of a range of 3–6 ounces per gallon of borax, and most preferably 4 ounces per gallon. A current density not exceeding 5 amperes/square foot is utilized, with a preferred range of 1–3 amperes/square foot, and still more preferably 2.5 amperes/square foot. The total current application should not exceed 300 coulombs/square foot, with 40–75 coulombs/square foot preferred and 50 coulombs/square foot most preferred. Wetting agents may be utilized, particularly sodium lauryl sulphate, and most particularly sodium lauryl sulphate in a percentage of .1% on a weight/volume basis. Similarly, a complexing agent may be utilized, particularly tetrasodium salt of ethylene diaminetetraacetic acid (EDTA), or sodium gluconate, Rochelle salts, sodium citrate, or other known complexing agents may be utilized. In particular, optimum operating conditions have been found in a situation utilizing a borax concentration of 4 ounces per gallon at 2.5 amperes/square foot for 20 seconds at substantially 150° F.

It is evident that depending upon the shape of the aluminum or aluminum base article, areas can be masked to expose limited areas of the entire article, or the entire article may be placed in the bath if it is desired to subsequently coat the entire surface. The amount of area exposed is a matter of choice, but is the effective area that must be utilized in calculating the amperage per square foot and total current applied.

COPPER

In the case of copper and copper base materials, the same bath is utilized. However, the acid-free requirement is waived. Acid use appears to have little or no effect upon the bath. The differences for copper is that the copper is made the cathode, whereas before, aluminum was

the anode. Thus, copper is utilized as the cathode in the same bath comprising an aqueous borax solution at a temperature between substantially 100–200° F. The preferred range, as with aluminum, is 140–170° F., with a still more preferred temperature of operation of 150° F.

It is preferred that the bath be acid-free. A preferred concentration of borax is between one quarter ounce per gallon to saturation at the operating temperature, with a preferred operating range of 3–6 ounces per gallon of borax, and still more preferably 4 ounces per gallon. A minimum of one ampere/square foot current density at the cathode surface is utilized, with a general range of 5–15 amperes/square foot preferred, with most preferably 10 amperes/square foot utilized. A minimum of 30 coulombs/square foot current application is utilized, with a preferred range being between 150–600 coulombs/square foot, with 300 coulombs/square foot preferred. The same wetting agents as utilized in the aluminum bath, and the same complexing agents as utilized with the aluminum baths are utilized here. Thus, optionally one may add sodium lauryl sulphate preferably in an amount of .1% on a weight/volume basis, and a complexing salt, preferably a tetrasodium salt such as EDTA, or the more common sodium gluconate, Rochelle salt, sodium citrate, etc. A preferred bath in general has 4 ounces per gallon borax concentration at 150° F. at 10 amperes/square foot current density for approximately 30 seconds operating time. Upon removal from the bath, the article is rinsed with water, and immediately electroplated without intermediate drying.

As in the case of aluminum, the surface is not attacked, and no measurable damage can be noted optically or with tracer (stylus type) instruments. The surface nonetheless is methodically activated and shows excellent adhesion for subsequent plating. Aluminum bronze materials, comprising essentially 95% copper plus aluminum, silicon and cobalt, as well as unalloyed copper, and other copper alloys have been particularly used in conjunction with this bath. There is no detectable stock removal or detectable surface damage. Subsequent electrodeposits such as nickel have excellent adhesion. For example, using the preferred conditions above, nickel from a nickel sulfamate bath was successfully plated upon the copper prepared in the above manner. The nickel sulfamate bath utilized a half hour treatment of 40 amperes/square foot at 120° F., as known in the art. Also copper from copper sulfate bath, 40 amperes/square foot, 90° F., ½ hour. Plating adhesion was excellent meeting the requirements of U.S. Federal specifications (e.g. QQ–P–416), as a standard.

Similarly, aluminum bronze prepared by a three minute treatment in a borax solution at a 4-ounce per gallon concentration, containing .1% sodium lauryl sulphate as the wetting agent, the piece being held at 10 amperes/square foot cathodic at a temperature of 140° F. was subsequently plated in a nickel sulfamate plating bath at 120° F., with a 20 amperes/square foot current density for one hour, to put on one mil of nickel, as in the prior example. The plating adhesion again was excellent, as measured by the above Federal standard.

Similarly, plating was achieved after a borax activation at four minutes at 100° F. at 10 amperes/square foot cathodic. Another example showed successful borox activation with one minute at 170° F. and ten amperes/square foot cathodic. The test adhesion, according to the above Federal specifications, was excellent. Unalloyed copper, brasses and other copper alloys are actually easier to prepare for good adhesion than the aluminum bronze above.

Thus, aluminum materials have been made extremely hydrophilic, for subsequent excellent adhesions of various commonly known coating materials, by the use of the borax bath under the conditions described above. Similarly, copper has been activated, including copper alloys, aluminum bronze, brass, and other copper materials, according to use of the bath above. Subsequently electroplating adhesions are excellent.

What is claimed is:

1. A method for converting the surface of an aluminum and aluminum base article from a hydrophobic to a hydrophilic base comprising the steps of:
heating a bath comprising an acid-free aqueous borax solution to a temperature between substantially 100–200° F.;
placing two electrodes in the bath, one of which is the article surface to be converted to a hydrophilic state; applying a current across the electrode through the bath, the article surface being made the anode, the current density not exceeding 5 amperes per square foot at the article surface;
maintaining the applied current for a time not exceeding a total current application of 300 coulombs per square foot, and removing the article from the bath.

2. The method of claim 1 wherein the bath is heated to a temperature range of 140–170° F.

3. The method of claim 1 wherein the bath is heated to a temperature of substantially 150° F.

4. The method of claim 1 wherein the bath contains a borax concentration of between one quarter to ten ounces per gallon.

5. The method of claim 1 wherein the borax concentration in the bath is between 3–6 ounces per gallon.

6. The method of claim 1 wherein the borax concentration is 4 ounces per gallon.

7. The method of claim 1 wherein the current density is between one to three amperes per square foot at the article surface.

8. The method of claim 1 wherein the current density is 2.5 amperes per square foot at the article surface.

9. The method of claim 1 wherein the applied current is maintained for a total time application of between 40–75 coulombs per square foot.

10. The method of claim 1 wherein the applied current is maintained for a time of a total current application of 50 coulombs per square foot.

11. The method of claim 1 wherein the bath includes a wetting agent.

12. The method of claim 11 wherein the wetting agent is sodium lauryl sulphate.

13. The method of claim 12 wherein the sodium lauryl sulphate is present in .1% on a weight/volume basis.

14. The method of claim 1 wherein the bath includes a complexing agent.

15. The method of claim 14 wherein the complexing agent is tetrasodium salt of ethylenediaminetetraacetic acid.

16. A method for converting the surface of a copper and copper base articles from a hydrophobic to a hydrophilic state comprising the steps of:
heating a bath comprising an aqueous borax solution to a temperature between substantially 100–200° F., placing two electrodes in the bath, one of which is the article surface to be converted to a hydrophilic state;
applying a current across the electrodes through the bath, the article surface being the cathode, the cur- density being at least one ampere per square foot,
maintaining the applied current for a time at least exceeding a total current application of 30 coulombs per square foot, and
removing the article from the bath.

17. The method of claim 16 wherein the bath is heated to temperature range of 140–170° F.

18. The method of claim 16 wherein the bath is heated to a temperature of substantially 150° F.

19. The method of claim 16 wherein the bath contains a borax concentration of between one quarter ounce per gallon to saturation.

20. The method of claim 16 wherein the borax concentration in the bath is between 3–6 ounces per gallon.

21. The method of claim 16 wherein the borax concentration is 4 ounces per gallon.

22. The method of claim 16 wherein the current density is between 5 to 15 amperes per square foot at the article surface.

23. The method of claim 16 wherein the current density is 10 amperes per square foot at the article surface.

24. The method of claim 16 wherein the applied current is maintained for a total time application of between 150–600 coulombs per square foot.

25. The method of claim 16 wherein the applied current is maintained for a time of a total current application of 300 coulombs ped square foot.

26 The method of claim 16 wherein the bath includes a wetting agent.

27. The method of claim 26 wherein the wetting agent is sodium lauryl sulphate.

28. The method of claim 27 wherein the sodium lauryl sulphate is present in .1% on a weight to volume basis.

29. The method of claim 16 wherein the bath includes a complexing agent.

30. The method of claim 29 wherein the complexing agent is tetrasodium salt of ethylenediaminettetraacetic acid.

31. The method of claim 16 wherein the aqueous borax solution is an acid-free aqueous borax solution.

References Cited

UNITED STATES PATENTS

1,314,839	9/1919	Weeks	204—129.75
2,958,610	11/1960	Ramierz	204—33

FOREIGN PATENTS

518,733	3/1940	Great Britain	204—33

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204—33, 129,75