This invention relates to a novel method of providing strongly adherent coatings of fluorocarbon resins on the surfaces of aluminum and aluminum base alloys. More particularly the invention concerns a method for coating aluminum or an aluminum base alloy with a thin resistant layer of a fluorinated olefin polymer.

The drawing shows a flow sheet of the process. It is herein known whereby the surfaces of metals such as aluminum or copper may be coated with a thin layer of polytetrafluoroethylene, a fluorocarbon resin which is sold commercially under the name "Teflon." These known methods involve a preparatory treatment in which the surface of the metal is subjected, to chemical attack by one or more strong inorganic acids, such as, for example, hydrochloric, sulfuric, or chromic acid. The action of the acid results in the formation of small surface cavities or holes which have an entrance of slightly smaller diameter than the cavity itself, enabling the resin to enter the cavity and to be anchored thereby. The formation of such cavities is known as keyholing and it is intended to overcome the inherent nonadhesiveness of the polytetrafluoroethylene to the metal surface. A method of this kind is disclosed in U.S. Patent 2,944,917. The polytetrafluoroethylene is applied to the treated surface in the form of an aqueous dispersion.

Experience with the known methods of coating metals with fluorocarbon resins has demonstrated certain shortcomings and difficulties and led to a search for new and improved coating methods which would overcome or minimize these difficulties. Thus, the use of a wholly acid chemical or etching agent results in a tendency toward violent reaction, because of the presence of suspended particles of undissolved reaction products. This foaming forces the interruption of the treatment and removal of the work to allow the solution to reach equilibrium by cooling and dissolution of the suspended particles by the acid solution. This violent foaming limits the area of aluminum or other metals which can be conveniently handled with a given volume of acid solution and affects the time of transfer to the rinse bath which precedes the coating. During the transfer the foam adheres tenaciously to the metal surface, constituting a still active etching agent, difficult to remove by rinsing and quickly contaminating the rinse bath.

In the use of an inorganic acid etching pretreatment in accordance with known methods, the attack is slow initially, owing to passivity phenomena, thus resulting in a lengthened induction period, the etching velocity increasing as the metal oxide film is broken down. This tends to slow the process when applied industrially.

In connection with known methods of coating with fluoro-carbon resins the etching pattern obtained requires repeated applications of the polymers in order to obtain a coating which will be of sufficient thickness and adhesion and evenness, but nevertheless known types of coatings are usually applied by brushing agents and sharply etched.

In accordance with the present invention there is provided a novel method for coating of fluorocarbon resins upon the surface of metals, and particularly upon aluminum and aluminum base alloy surfaces, in the form of thin, strongly adherent layers or films. The novel method of the invention includes the steps of applying to the metal surface an etchant comprising an aqueous solution of a lower aliphatic carboxylic acid or a halogenated lower aliphatic carboxylic acid, and a salt of a metal which is lower in the electromotive force series of metals than aluminum. In accordance with a preferred embodiment of the invention, there is also incorporated in the etchant an alkali metal halide. The etchant solution is applied to the surface of the aluminum or aluminum base alloy at a moderately elevated temperature, ranging from about 140° F. to about 180° F. The time of the etching treatment depends upon the nature of the aluminum or aluminum alloy surface, and the thickness of the polymer film which is to be applied. In general, the period of etching is such that an average depth is attained which is approximately that of the film thickness. Thus, if a 2 mil film is to be applied, the etching time is such that an average depth of openings or micropores of approximately 2 mils is attained.

It is a characteristic of the novel etchants of the invention that they act upon the metal surface so as to penetrate and attack along the grain boundaries and into the grains themselves, thereby forming micropores or minute cavities which present numerous relatively broad, necked openings, but which in contrast, exhibit in section or profile, the general outlines of a multibarbed fish hook. In other words, the etchants of the invention produce a sectional pattern, resulting from attack along the grain boundaries and undercutting of the grains, having as a feature thereof a branching or dendritic structure. This provides numerous branching and hook-shaped zones into which the coating polymer may penetrate and thus obtain anchorage of extraordinary firmness and tenacity. These zones may range in depth, for example, from 0.001 to 0.002 inch, and vary in width from about 0.00001 to 0.0001 inch, permitting deep penetration and absorption of the dispersed polymer particles, which may range in size from 0.05 to 0.25 micron, depending upon the polymer applied. This penetration and absorption of the resin particles, when the resin is polymerized or fused, results in a strong hooking of the polymer coating onto the subsurface of the metal.

Following the etching step, the metal article is rinsed in water, advantageously at room temperature, for a period sufficient to remove all traces of acidity, for example from 5 to 10 minutes.

The first rinse may be followed by a treatment with a mild acid to remove emut or to remove metal ions present from the metal salt component of the etchant. This acid treatment is then followed by another water rinse. After drying, the metal article to be coated is subjected to treatment with an aqueous dispersion of the fluorocarbon resin by any conventional step, such as spraying, brushing, dipping, or flow coating. The concentration, viscosity, and application time will depend upon the particular resin employed, but such conditions are conventional and are well known to those skilled in the art. The fluorocarbon resin coat is then sintered or baked, for a period of time which depends upon the baking or fusion temperature selected. Thus, for example, the baking temperature may range from about 650° F. to about 740° F., and the length of time will vary inversely as the baking temperature, ranging, for example, from about 10 to 60 minutes.

The dispersing coating and baking steps are repeated until a smooth even coating is obtained. Usually only two applications are required. However, where a mechanical pretreatment of the metal prior to etching has been employed, as explained more fully below, a further application of resin may be indicated.

The method of the present invention is particularly
adapted for the etching and coating of aluminum and aluminum base alloys. The aluminum base alloys which can be coated by the method of the invention include Nos. 1100, 3003, 5052, 5182, 5754, 5657, and 6061, the designation numbers being those of the Aluminum Association Designation System. The term aluminum itself refers to metal having a purity of 99.0% or greater.

As indicated above, the novel etchant of the invention comprises an aqueous solution of a lower aliphatic carboxylic acid or a halogenated lower aliphatic carboxylic acid and a salt of a metal which is lower in the electromotive force series than aluminum, with or without addition of an alkali metal halide.

The lower aliphatic carboxylic acids which are suitable for the preparation of the etchant include acetic acid, propionic acid, and butyric acid, acetic acid (obtained commercially as glacial acetic acid) being preferred. The halogenated lower aliphatic carboxylic acids which are suitable include trichloroacetic acid, monochloroacetic acid and 2-chloropropionic acid, but trichloroacetic acid is preferred. Although trichloroacetic acid has approximately the same electromotive force as acetic acid, the latter is preferred for this purpose, because of its minimal foaming tendency. These acids are preferably employed in concentrations of about 3 to 50 percent by weight.

In accordance with the invention, there is also present in the etchant a salt of a metal which is lower in the electromotive force series than aluminum. The function of the metal ions furnished by these salts is to act as depolarizing agents and as a means of promoting preferential attack at the grain interstices.

Metal salts which are suitable for this depolarizing function include the water-soluble salts of copper, nickel, cobalt, zinc, tin, and the like in the highest state of their valence. Thus, there may be employed the chlorides, nitrates, sulfates, or acetates of the metals mentioned. Examples of preferred metal salts include cupric chloride, ferric chloride, and nickel chloride. The metal salt is present in the bath in an amount ranging between about 0.1% and 1.5%.

The etchant bath may also include as an ingredient thereof an alkali metal halide, such as, for example, sodium chloride, potassium chloride, or lithium chloride, which also serves as an etchant, but which in addition provides a gentle etching action and minimizes or eliminates foaming tendencies. The amount of alkali metal halide may range from about 5% to about 20% by weight.

In accordance with one aspect of the invention, there is employed as an etchant a preferential embodiment which is an aqueous solution of acetic acid, sodium chloride, and cupric chloride, having the following ranges of composition:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid, glacial</td>
<td>25-30</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>5-20</td>
</tr>
<tr>
<td>Cupric chloride</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

In accordance with a second form of the invention, there may be employed as an etchant an aqueous bath having the following ranges of composition:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloroacetic acid</td>
<td>0.25-0.5 lb. per gallon (3-6% by weight)</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>0.05-0.1 lb. per gallon (0.6-1.2% by weight)</td>
</tr>
<tr>
<td>Chloroplatinic acid</td>
<td>0.001-0.002 ounce per gal. (0.00075-0.0015% by wt.)</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The etching method of the invention possesses numerous advantages compared with known methods. These include ease of control, economy of operation, the fact that the coated metal can be cold worked following coating with unimpaired adhesion of the fluorocarbon resin coating, and the deposit of a more adherent, tough, and resistant coating with fewer coating steps than before. The formation of the multilayered fish hook type of cavity resulting from penetration of the metal surface by the etchant which then cuts in and acts parallel to the surface at several levels, increases the tenacity of the polymer deposited within these hook shaped zones and surrounding the barbed hooks, requiring great force to dislodge the coating, and bringing into play the internal cohesive forces of the resin coating itself.

In contrast to prior fluorocarbon coatings, it has been found that preliminary mechanical working of the aluminum surface, as by rolling, scratching, brushing, abrasive blasting, belt sanding, and light embossing, sets up localized strains on the aluminum surface. These serve to activate and to direct the etchant, controlling its direction as the points of localized strains are preferentially etched. Further control of the etch is accomplished by the use of the aforementioned metal salts, the ions such as copper, iron, and platinum, acting as depolarizing agents and forming corrosion cells with the aluminum and the aluminum oxide. These mechanical treatments also enhance the effectiveness of the fluorocarbon coatings, the patterns thus produced are highlighted by the etch since the final coating is transparent, to yield interesting and attractive patterns. Thus an aluminum panel having a textured embossed finish will assume a wood grain pattern as the result of the treatment.

For the coating resin there may be employed any suitable fluorocarbon resin in the form of an aqueous dispersion. Typical examples of suitable fluorocarbon resins include tetrafluoroethylene (Teflon-TFE), trifluorochochloroethylene (Kol-F), and fluorine-containing polyethylene. These resins are obtainable commercially in the form of aqueous dispersions containing about 50%-60% solids, suitable for dip-coating applications.

The fluorocarbon resins are dispersed in water using a suitable dispersing agent, for example, sodium lauryl sulfate, providing a liquid coating composition which when applied to a metal substrate and fused by baking at or above the fusion temperature of the resin forms a continuous film of the polymerized resin. Thus, in the case of polytetrafluoroethylene the fusion temperature of the polymer is 621°F. For the purposes of the present invention it is preferred to use the fluorocarbon resins in dispersed form in a concentration of from about 30% to about 40% solids, and a baking temperature, in the case of polytetrafluoroethylene at 740°F. For about 10 minutes.

It has been found further, in accordance with the invention, that improved properties are obtained when the coated article is subjected to subsequent mechanical operations such as forming or drawing. This permits work hardening of most of the aluminum alloys to higher tempers and promotes rigidity. Another advantage of the present invention is that it permits matching of the baking cycle of the resin, the annealing cycle of the aluminum alloy used, and the work hardening rate of the alloy in accordance with the nature of the end product being coated.

Baking cycles may accordingly be selected which will bring the metal to the desired temper and condition for post-forming. For a forming operation where the metal has to be annealed between subsequent drawing operations, a treatment cycle, in accordance with the invention may consist of etching the alloy, applying a layer of the resin, polymerizing with heating cycle which anneals the aluminum, performing a first drawing operation, applying another layer of the resin, polymerizing and annealing to condition, performing a second forming operation, and so on. Most wrought aluminum alloys anneal at the baking temperature range of the fluorocarbon resins.

The method of the present invention is adapted for the production of superior fluorocarbon resin coatings on aluminum articles, particularly those intended for food
5 handling, such as food storage vessels, cooking utensils, and the like.

The method of the invention is illustrated by the following examples, which are, however, not to be considered as limiting:

Example 1

An aluminum 5005 alloy sheet suitable for use as a component of a cooking griddle was thoroughly cleaned so as to be free from all surface contamination in the manner conventionally employed in preparation for anodizing. A salt etching bath having the following composition:

Percent by weight
Acetic acid (glacial)............................................. 30
Sodium chloride.................................................. 10
Cupric chloride.................................................. 5
Water.................................................................. 40

was prepared. The sheet was dipped in this bath for 20 minutes at a bath temperature of 175° F. The bath etches gently with a scrubbing action, without the formation of foam or of suspended particles. The sheet was removed and the slight deposit of copper was removed by a dip in concentrated nitric acid for 10–20 seconds at room temperature. A photomicrograph of the resulting etch showed attack along the grain boundaries and undercutting the grain, to form multi-barbed hooks 0.001” to 0.002” deep, varying in width from 0.001” to 0.001”.

The bath was fortified with additional cupric chloride for subsequent use to replace copper lost through plating on the aluminum surface.

The article removed from the nitric bath was thoroughly rinsed in water for 5 to 10 minutes and dried.

An aqueous dispersion of tetrafluoroethylene containing 30% solids was applied to the etched sheet by spraying and the sheet was dried. The coating was then baked by heating the sheet in an electric oven for 10 minutes at 740° F. The spraying was then repeated and a second baking cycle performed under the same conditions. The article was finally subjected to hotpressing at 400–500 lbs. per sq. in. at a temperature of 550° to 600° F. to smoothen the surface of the formed polytetrafluoroethylene. A hard, dense, transparent, adherent coating of the polymer was obtained.

Example 2

After pretreatment as in Example 1, a sheet of 5005 alloy was etched in the following bath:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Percent</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloroacetic</td>
<td>0.5</td>
<td>Ib.</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>0.1</td>
<td>Ib.</td>
</tr>
<tr>
<td>Chloroplatinic acid</td>
<td>0.002</td>
<td>Oz.</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>gallon</td>
</tr>
</tbody>
</table>

at a temperature of about 160° F. for 15 minutes. The addition of the small amount of chloroplatinic acid eliminates the induction period of the trichloroacetic acid and produces immediate attack. The deposition of metallic platinum has a depolarizing action. Photomicrographs of the metal showed deep hooking micro pores with a depth of etch of 0.001” or greater. The sheet was thoroughly rinsed for 5 minutes, and then dipped into a solution of 10% oxalic acid at 120° F. for 20–60 seconds to remove smut, then thoroughly rinsed in water for 10 minutes and dried. An aqueous dispersion of tetrafluoroethylene containing 30% solids was applied by spraying, the sheet was dried, and then baked for 10 minutes at 740° F. The spraying and baking steps were repeated. A firm transparent and strongly adherent coating of polytetrafluoroethylene was obtained.

It will be understood by those skilled in the art that metal surfaces prepared in accordance with the foregoing disclosure also provide the added advantages of mechanical adhesion when coated with dispersions or solutions of other resins suitable for coatings (e.g., vinyl, acrylic and alkyd resins).

While present preferred embodiments of the invention, and methods of practicing the same, have been illustrated and described, it will be recognized that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

What is claimed is:
1. Method of preparing aluminum and aluminum base alloy surfaces to adhere mechanically to coating films which comprises the steps of applying to the surface of the metal an etchant comprising an aqueous solution containing from about 3% to about 50% by weight of a member selected from the group consisting of a lower aliphatic carboxylic acid and a halogenated lower aliphatic carboxylic acid, and from about 0.1% to about 1.5% by weight of a salt of a metal lower in the electromotive force series than aluminum, at a temperature between about 140° F. and about 180° F., to form cavities in the metal surface having branching and hook-shaped zones, and rinsing the surface to remove the etchant.
2. The method of claim 1 in which the lower aliphatic carboxylic acid is acetic acid.
3. The method of claim 1 in which the etchant solution further includes from about 5% to about 20% by weight of an alkali metal halide.
4. Method for the coating of fluorocarbon resins upon aluminum and aluminum base alloy surfaces in the form of thin adherent films which comprises the steps of applying to the surface of the metal an etchant comprising an aqueous solution containing from about 1% to about 5% by weight of a member selected from the group consisting of a lower aliphatic carboxylic acid and a halogenated lower aliphatic carboxylic acid, and from about 0.1% to about 1.5% by weight of a salt of a metal lower in the electromotive force series than aluminum, at a temperature between about 140° F. and about 180° F., to form cavities in the metal surface having branching and hook-shaped zones, applying an aqueous dispersion of a fluorocarbon resin to the metal surface, and then baking at a temperature above the fusion point of the resin to effect polymerization and coating film formation.
5. The method of claim 4 in which the halogenated lower aliphatic carboxylic acid is trichloroacetic acid.
6. The method of claim 4 in which the etchant solution further includes from about 5% to about 20% by weight of an alkali metal halide.
7. The method of claim 4 in which the lower aliphatic carboxylic acid is acetic acid.
8. Method for the coating of fluorocarbon resins upon aluminum and aluminum base alloy surfaces in the form of thin adherent films which comprises the steps of applying to the surface of the metal an etchant comprising an aqueous solution of from about 25% to about 50% of acetic acid, from about 5% to about 20% of sodium chloride, and from about 0.1% to about 0.2% of cupric chloride, by weight, at a temperature between about 160° and about 180° F., to form cavities in the metal surface having branching and hook-shaped zones, then applying an aqueous dispersion of a fluorocarbon resin to the metal surface, and then baking at a temperature above the fusion point of the resin to effect polymerization and coating film formation.
9. The method of claim 8 in which the fluorocarbon resin is tetrafluoroethylene.
10. The method of claim 8 in which the fluorocarbon resin is fluorinated ethylene-propylene.
11. The method of claim 8 in which the metal surface is rinsed in concentrated nitric acid after etching to remove deposited copper.
12. Method for the coating of fluorocarbon resins upon aluminum and aluminum base alloy surfaces in the form of thin adherent films which comprises the steps of applying to the surface of the metal an etchant comprising an aqueous solution of from about 3% to about 6% of trichloroacetic acid, from about 0.6 to about 1.2% of ferric chloride and from about 0.00075% to about 0.0015% of
chiorplatinic acid, by weight, at a temperature between about 140° F. and about 160° F., to form cavities in the metal surface having branching and hook-shaped zones, applying an aqueous dispersion of a fluorocarbon resin to the metal surface, and then baking at a temperature above the fusion point of the resin to effect polymerization and coating film formation.

13. The method of claim 12 in which the fluorocarbon resin is tetrafluoroethylene.

14. The method of claim 12 in which the metal is dipped in a solution of oxalic acid after etching to remove smut formed.