United States Patent Office 3,379,628 Patented Apr. 23, 1968

3,379,628

DECORATIVE ETCHING OF ALUMINUM

Glen M. Burdick, Wichita, Kans., and James R. Dafler and Richard L. Every, Ponca City, Okla., assignors to Continental Oil Company, Ponca City, Okla., a corporation of Delaware

No Drawing. Filed Apr. 21, 1965, Ser. No. 449,887
9 Claims. (Cl. 204—141)

This invention relates to a method for decoratively etching aluminum. More particularly, it relates to a method for anodic etching an aluminum object in an anhydrous electrolyte to effect decorative etching of the surface of said object.

Anodic etching of aluminum or aluminum alloy surfaces has been practiced extensively heretofore. While this process in its broadest sense contemplates passing a low density current through an electrolyte in which an aluminum electrode serves as an anode, it is more usually thought of as a method for electrolytically producing a decorative and/or protective oxide film on the surface of the aluminum anode. Another variant of the anodic etching process which has been investigated off and on in the past involves the anodic etching of an aluminum electrode in an anhydrous electrolyte free of oxygen-containing compounds to effect electrodeposition of aluminum onto the cathode. The purpose of the latter variant is to produce a thin uniform coating on a non-aluminum cathode surface; although the method has been proposed as one for the production of pure aluminum from an impure source thereof.

In our initial work directed to the anodic etching of aluminum for the purpose of coating cathodic objects with aluminum, we unexpectedly found that such an electrodeposition process will result in a mild erosion of the anode surface and that under controlled conditions, the entire exposed surface can be transformed to a pleasing crystalline pattern.

It is therefore the object of this invention to provide the process for decoratively etching an aluminum surface.

In accordance with this invention, aluminum is anodically etched in an electrolyte consisting essentially of a homogeneous melt of an aluminum alkyl and a compound capable of forming a complex therewith in an inert atmosphere under conditions of current density flow and temperature conventionally applicable in the anodic etching art referred to hereinabove. The present anodic etching process is carried out for a length of time sufficient to produce a bright decorative crystalline pattern over the entire surface of the aluminum object in contact with the electrolyte. Pleasing uniform patterns can be obtained in this manner without materially altering the thickness of the object being anodically etched. Thus, our process is suitable for etching relatively thin plates or other thin wall structures without adversely affecting the structural strength properties thereof.

The electrolytes useful in the practice of this invention are the relatively heat-stable complexes of an aluminum alkyl and a variety of compounds capable of coordinating therewith to yeld such addition compounds. These complexes are depicted by the following general formula:

$$A\cdot(AlR_3)_{1-2.1}$$

As indicated by the formula given, the molar amount of aluminum trialkyl present in the members of this broad class of complexes varies depending upon the nature of the complexing agent (a mole of the latter being represented in the above formula by the letter A). Suitable complexing agents include the alkali metal fluorides, the alkali metal cyanides, the alkali metal azides and the tetraalkyl ammonium halides. The compounds embraced by

each of the classes of complexing agents enumerated have the ability to combine with aluminum alkyl to provide two complexed forms thereof. The fluoride salts, as well as the quaternized ammonium compounds yield, in one form, a complex containing two moles of the aluminum trialkyl per mole of the complexing agent. The fluoride salts will also yield a stable 1:1 complex, i.e., a complex composed of one mole each of the complexing agent and aluminum trialkyl. The combining ratios for either the azides or the cyanides are somewhat different from those of the quaternary ammonium salts and the fluorides. For example, an alkali metal azide will combine with 1.8 moles of the aluminum alkyl to result in one form of complex; whereas, in the other stable form the molar ratio of aluminum alkyl to an azide is in the order of 2.1. On the other hand, the two stable forms of complexes derived from the cyanides respectively contain 1.5 and 2 moles of aluminum alkyl. Obviously, numerous complex mixtures exist in which the aggregate amount of aluminum alkyl present ranges between the respective amounts associated with the two stable forms thereof. Both of the stable forms of the complexes formed from a given complexing agent as well as the various intermediate compositions referred to are relatively low melting materials. In fact, a plurality of these compositions are liquid within the temperature range ordinarily used in anodic etching practices. As indicated, these complex compositions in a liquefied state are electrical conductors.

Any of the aluminum alkyls are satisfactory for preparing the electrolytes useful herein. Generally it is preferred to use a lower aluminum alkyl such as aluminum trimethyl, aluminum triethyl, aluminum tripropyl, aluminum tributyl, aluminum triamyl and aluminum trihexyl. Likewise, one can use mixtures of said aluminum alkyls such as obtained by growing aluminum triethyl in the presence of ethylene in accordance with the Ziegler condensation process. From the standpoint of availability, triethyl aluminum is particularly preferred. About the only governing factor in the selection of the complexing agent concerns the temperature contemplated for carrying out the etching process. This aspect will be elaborated upon hereinbelow.

The anode etching process is carried out in an atmosphere of an inert gas. The primary purpose of using an inert gas atmosphere is to obviate the combustion of any free aluminum alkyl that might be generated during the electrolytic process. As is well known, aluminum alkyls in the free state readily and spontaneously burn in the presence of either oxygen, a free oxygen containing gas such as air or moisture.

As indicated previously, the relatively low temperatures ordinarily observed in the anodic etching art are applicable in the practice of this invention. Accordingly, suitable temperatures range from about room temperature to 200° C. Since many of the complex compositions described above melt at an elevated temperature, it is necessary to form a solution of such complexes in an inert solvent when adoci etching temperatures near room temperature or somewhat higher are employed. Suitable solvents include the normally liquid hydrocarbons, especially the aromatics. When using a solution of the complex, it is desirable not to dilute the complex more than is necessary since the conductivity of the solution decreases as it becomes more dilute.

All of the complex compositions described above containing more than a mole of the aluminum compound are subject to pyrolysis. In the pyrolysis process said complexes break down into free aluminum alkyl and the complex form containing a lower amount of aluminum alkyl. This is to be avoided and consequently, a maximum temperature should be observed which does not result in such pyrolysis. The temperature at which the various

complexes are pyrolyzed depends primarily upon the particular salt component of the complex. For example, the complexes of sodium fluoride will commence to decompose at a temperature range from about 80 to 90° C. The complexes based on the potassium salt decompose at considerably higher composition temperatures, e.g., in the order from about 150 to 180° C. The stated decomposition temperature ranges are given for the respective complexes of aluminum triethyl. By using higher aluminum alkyls one can obtain electrolyte compositions which will be satisfactory for use at temperatures somewhat above the maximum decomposition temperatures noted.

An applicable current density for obtaining etching in accordance with the instant process is from about 100 to 500 milliamperes per square inch. A preferred range of current densities is from about 150 to 200 milliamperes per square inch. Voltage differentials which will provide the aftermentioned current densities depend on the given complex and the temperature. The potential of the system should desirably be maintained constant throughout any particular anodic etching process. The constant potentials can be readily maintained by employing suitable controller for this purpose.

A variety of metals serve as suitable cathodes in the etching process of this invention. The preferred metals include aluminum, magnesium and any of the noble meals. The time required to obtain etching is dependent upon the degree of etching desired in conjunction with the particular current density employed. However, as mentioned hereinabove, under properly selected conditions it is possible to obtain uniform decorative crystalline patterns without materially altering the thickness of the aluminum object subjected to etching.

The following example is illustrative of a mode in which the novel etching process of this invention can be carried out. As indicated, this example is given primarily by way of illustration and accordingly, any enumeration of detail contained therein is not to be interpreted as representing a limitation on the invention except as otherwise indicated in the appended claims.

EXAMPLE I

A conventional glove or dry-box served as the anodic etching chamber in this example. Argon was used to purge the air from the dry-box. Aluminum triethyl was charged to the purged box and after heating to approximately 120° C., an amount of sodium fluoride was mixed with the aluminum triethyl to provide a homogeneous melt of a complex composed of two moles of ATE and one mole of NaF.

A specimen coupon of 99.997 cold rolled aluminum measuring about 1" x 3" x ⅛" was partially immersed in the electrolyte. A coupon of magnesium corresponding in size approximately to that of the aluminum coupon served as the cathode. A voltage differential of approximately 2.5 volts was established between the aluminum and magnesium coupons. The voltage potential was maintained constant throughout the etching process by means

of a commercially available potentiostat. The foregoing conditions resulted in a current density of about 175 milliamperes per square inch at a temperature of about 90° C. The etching process was carried out for a period of approximately two hours. After the stated period, the aluminum specimen was wtihdrawn and cleaned. The immersed porton exhibited a bright decorative crystalline pattern. The etched portion did not show any evidence of tarnish or aging upon exposure to air for an extended period.

A comparative example was run employing essentially the same conditions as outlined above but utilizing 96% sulfuric acid as the electrolyte instead of the complex of aluminum triethyl and sodium fluoride. Upon such treatment the immersed portion of the aluminum specimen exhibited a smooth, shiny surface.

We claim:

1. A method for decoratively etching the surface of an aluminum object which comprises anodically etching said object in an electrolyte consisting essentially of a homogeneous melt of an aluminum alkyl and a compound capable of forming a heat-stable complex therewith selected from the group consisting of alkali metal fluorides, alkali metal cyanides, alkali metal azides and tetraalkyl ammonium halides under an inert gas atmosphere to the extent that a bright decorative crystalline pattern is produced on the surface of the object.

2. A method in accordance with claim 1 wherein said homogeneous melt is a liquefied complex of from about 1 to 2 moles of the aluminum alkyl per mole of the alkali metal fluoride.

3. A method in accordance with claim 1 wherein said homogeneous melt is a liquefied complex of from about 1 to 2 moles of the aluminum alkyl per mole of the tetraalkyl ammonium halide.

4. A method in accordance with claim 1 wherein said homogeneous melt is a liquefied complex of from about 1.8 to 2.1 moles of the aluminum alkyl per mole of the alkali metal azide.

5. A method in accordance with claim 1 wherein said homogeneous melt is a liquefied complex of from about 1.5 to 2.0 moles of the aluminum alkyl per mole of the alkali metal cyanide.

6. A method in accordance with claim 2 wherein said alkyl metal fluoride is sodium fluoride.

7. A method in accordance with claim 6 wherein said aluminum alkyl is triethyl aluminum.

8. A process in accordance with claim 7 wherein the anodic etching is effected at a current density of from about 100 to 500 milliamperes per square inch.

9. A process in accordance with claim 7 wherein the anodic etching is effected at a current density of from about 150 to 200 milliamperes per square inch.

References Cited

UNITED STATES PATENTS

2,849,349 8/1958 Ziegler ..... 204—14

ROBERT K. MIHALEK, *Primary Examiner.*