

# UNITED STATES PATENT OFFICE

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## ELECTROPLATING ON ALUMINUM

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This invention relates to methods of treating aluminum surfaces, including a novel pickling process followed by anodic oxidation and deposition of electroplates on such prepared surfaces.

In the preparation of aluminum articles for electroplating, it has long been a problem to secure adherent deposits. Electroplates of otherwise suitable metals were found to be non-adherent, in spite of multiple preliminary treatments to prepare the surfaces for receiving such electroplates. The formation of oxide coatings on aluminum by the so-called anodizing process improved the adherence of the electroplates. However, required operative controls were found to be critical, and the results were not uniform.

It has now been found that the latent difficulty in the treatment of aluminum to prepare the surfaces for the reception of truly adherent electroplates, and for other purposes, is due essentially to the high reactivity of the aluminum metal itself in plating baths. With this discovery, the problem has been attacked from the unorthodox viewpoint of cleaning the aluminum surface without corroding the aluminum basis metal. This was successfully accomplished by pickling aluminum surfaces in a special concentrated acid mixture, in which the aluminum was unattacked, and in which the associated alloying ingredients were selectively dissolved from the surface of the metal, without affecting the physical or molecular structure of the aluminum body. Such purified aluminum surfaces have been found to be susceptible of anodic treatment to give a very thin, permeable coating of oxide, which can be electroplated, by conventional electroplating methods, to give truly adherent electroplates.

The above and other desirable features of novelty and advantage of the present invention will be more clearly understood by reference to the particular process steps recited herein, wherein a preferred sequence of treatments is recited.

Considering the invention in its more specific aspects, an aluminum article, or surface to be treated, is first preliminarily cleansed, in the usual manner, to remove surface dirt and grease. This may be done by treating with solvents, or dipping in solutions of cleansing compounds. After rinsing, the articles are treated with a novel nitric acid-hydrofluoric acid pickle to remove any alloying ingredients present at the surface of the basis metal. The nitric acid-hydrofluoric acid pickle, utilized for this purpose,

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comprises a mixture of concentrated nitric acid and concentrated hydrofluoric acid. The concentrated acids are commercial grades, that is, 67% nitric acid, and 48% hydrofluoric acid.

5 The pickling composition which has been found to give most desirable results, when used with wrought or cast aluminum, comprises approximately 95% of the concentrated nitric acid solution, with the balance concentrated hydrofluoric acid. While a pickle containing 95% nitric acid is preferred, desirable results may be obtained with pickles in which the concentrated nitric acid may constitute at least 90% of the mixtures, with the balance concentrated hydrofluoric acid. The novel pickles should contain no added water.

While the values given for the acid components of the pickle are believed to be optimum, and the aluminum metal of the surfaces treated is unattacked, the most suitable mixture of components for a pickle to be used with any given aluminum alloy may be determined in the following manner: a coupon, or test piece, of the aluminum to be treated, is placed in a measured amount of concentrated nitric acid. Hydrofluoric acid is then added slowly, and with thorough mixing, to the nitric acid until evolution of gas begins at the surface of the test piece. Measured additions of concentrated nitric acid are then added until the gassing ceases. The relative amounts of the two acids used will determine the best composition for pickling the particular alloy.

The above pickle is generally suited for treating aluminum surfaces to purify the same, and has a particular value when treating cast aluminum surfaces, wherein the aluminum is usually alloyed with one or more ingredients, including silicon, manganese, copper and zinc. By selectively removing these alloying ingredients, a pure aluminum surface is obtained, and the effect of the alloying elements on the coatings is avoided at later stages of the treatment, and particularly in the anodizing step which follows.

The special acid pickle treatment described above will be run at ordinary room temperature, care being taken to provide proper equipment for handling the acid mixture, and for insuring proper ventilation of the working spaces. The time consumed in actual pickling is substantially negligible, as it is of the order of 10-30 seconds per treatment.

As noted above, it is found that, by the use of the special acid dip, there is obtained at least

a surface layer of pure aluminum, which surface is particularly receptive to that type of anodic oxide film suitable for plating, whereby the control of anodic oxidation is rendered much less critical. For anodizing it was now found that an alkaline bath was particularly suitable, not only because of its detergent effect on the surface of the pickled metal, but, also because of the fact that, with the purified base, the operative conditions were much less critical. As an electrolyte, solutions of sodium carbonate, in concentrations varying from a half of 1% up to saturation, and operated at temperatures ranging from slightly above freezing to boiling, were found to give substantially uniform results.

With such an electrolyte, the use of an alternating current was found to give the desired pervious anode film coating which was most desired for electroplates. With the use of alternating current, the oxide coating is formed only during the half-wave period when the aluminum is anodic. During this half-time anodizing, the oxide coating formed on the aluminum is undergoing a full-time dissolution in the alkaline carbonate bath. The result of the half-time anodizing, coupled with the full-time chemical dissolution, will be the formation of the special anodic oxide film on the surface of the aluminum.

By balancing the factor of voltage, temperature, time and concentration, aluminum has been successfully anodized, preparatory to plating, within these limits:

Concentration of  $\text{Na}_2\text{CO}_3$ , .01% to saturation  
 Temperature, 4° C. to 100° C.  
 Time, 2 minutes to 1 hour  
 Voltage, 5 to 160 volts A. C.

In commercial use, the variation in the type of metal treated introduces no difficulty. One set of operating conditions can be used for all aluminum alloys, whether cast and wrought, and for assemblies of different alloys. As a specific instance, illustrating the flexibility of the processes herein, an aluminum casting, having a wrought aluminum alloy insert, was preliminarily cleaned, rinsed, and then pickled, for 30 seconds, in an acid pickle comprising 95% concentrated nitric acid and 5% concentrated hydrofluoric acid. After rinsing, it was anodizing for 10 minutes, at 45 volts A. C., at a temperature of 104° F., in an alkaline bath comprising an aqueous solution of sodium carbonate monohydrate, containing 6 ounces of the salt per gallon of solution. This particular item was then rinsed, and electroplated for 20 minutes in a standard acid cadmium bath. A smooth, adherent, highly corrosion-resistant electroplate was obtained.

Aluminum articles or assemblies, prepared as described herein, may be plated, not only in mildly acid baths, but also in neutral, or mildly alkaline baths, especially if the metal ion concentration of the bath is suppressed. Standard nickel plating solutions have been found to give desirable results, as have copper pyrophosphate baths. Copper-plated members may be soft-soldered to form composite structures. The copper or nickel plates may also be used as substrates or undercoats for electro-deposits of other metals from strong acid or alkaline baths, which metals are ordinarily not suited for direct plating on aluminum.

In tests carried out on the products prepared according to the teachings herein, there has been no case wherein the electro-deposit has been mechanically stripped from the basis aluminum,

although forces as great as 8300 p. s. i. have been applied to soldered joints. The electroplates will withstand any degree of bending or forming that the basis aluminum itself will tolerate. Articles prepared as taught above may be heated up to the melting point of the aluminum without previous separation of the electroplates.

A feature of great importance, which has made itself evident in the course of the research described herein, is the fact that an aluminum surface, once pickled and anodized, as described above, may be stripped and replated, a number of times, without requiring repickling or reanodizing. Thus, selected parts of aluminum articles may be copper-plated, soldered or brazed together into a unit, and the unsoldered copperized areas stripped by dipping in concentrated nitric acid. After rinsing, the unit can be directly plated in an acid cadmium plating bath. In this way, the dangerous galvanic couple between copper and aluminum is removed, and a structural unit of high surface corrosion resistance is assured.

Corrosion resistance is of prime importance in case of aluminum articles which are to be exposed to the elements. It has been found that cadmium, alone of all plating metals, affords a surface substantially equal in galvanic potential to aluminum. Thus, aluminum castings, prepared according to the present teachings, and then plated with 0.0005 inch of cadmium, have been exposed to the standard salt-spray test, for over 500 hours, without breaking down the plate, or exhibiting ascertainable corrosion of the aluminum. Such results are in very sharp contrast to the abrupt and severe corrosion of the aluminum basis metal, experienced when it is coated with electro-deposits of nickel, copper, silver or other metals customarily used for electroplating.

The process herein is essentially distinguished from other methods of preparing aluminum surfaces for plating, because it is simple, and does not require the multiplicity of cleaning and pickling operations necessary in prior art processes. In addition, it has wide operating limits, and the solutions are easily maintained. This is particularly true in the case of the anodizing solution where, due to the cheapness of the sodium carbonate, fresh solutions can be made daily and substantially no control analyses or steps are required.

A special feature of novelty has been found to reside in the fact that only one set of operating conditions is needed for all aluminum alloys, whether cast or wrought. Another highly advantageous result, flowing from the improvements herein, is the facile preparation of assemblies of different aluminum alloys for all plating procedures. The aluminum surfaces, prepared and plated, as taught above, have been found to be exceptionally stable and, once prepared and plated, may be stripped and replated over and over again without requiring either repickling or reanodizing.

The electroplates deposited on the improved aluminum surfaces have been found to be truly adherent, and no instance has been noted, after extensive tests, of any separation of an electroplate from the aluminum base, pickled and anodized as taught herein.

It will now be appreciated that there has been provided novel processes for specially preparing aluminous surfaces for the reception of truly adherent electroplates, which permit the formation

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of light-weight, corrosion-resistant structures, formed as single items, or which may be fabricated from assembled parts joined by solder or low-temperature brazes.

What is claimed is:

1. The method of plating aluminum alloys which consists of the step of producing a surface of substantially pure aluminum on the article to be plated by pickling the same in a nitric-hydrofluoric acid dip of 90% to 99% of concentrated nitric acid (67%) with the balance of concentrated hydrofluoric acid (48%), the dip being proportioned in accordance with the type of alloy selectively to dissolve associated alloying ingredients from the surface of the article while the hydrofluoric acid is present in an amount insufficient to cause the evolution of gas, then anodizing the article in a sodium carbonate solution by alternating current, and thereafter electroplating the anodized surface of the article.

2. The method of plating aluminum alloys which consists of the step of producing a surface of substantially pure aluminum on the article to be plated by pickling the same in a nitric-hydrofluoric acid dip by which the basis aluminum is unattacked, the dip being composed of substantially 95% of concentrated nitric acid 67% with the balance of concentrated hydrofluoric acid (48%), the dip being proportioned in accordance with the type of alloy selectively to dissolve associated alloying ingredients while the hydrofluoric acid is present in an amount insufficient to cause the evolution of gas, then anodically oxidizing the surface of the article under the influence of an alternating current in a sodium carbonate solution, whereby the

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oxide is formed only during half-wave periods while the surface of the article is continuously attacked by the solution resulting in the formation of an oxide film, and thereafter electroplating over the film.

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