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TREATING ALUMINUM SURFACES

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This invention relates to the treatment of aluminum surfaces, and more particularly to imparting a decorative finish to such surfaces. As used herein, the word "aluminum" includes pure aluminum, commercial aluminum containing the usual impurities, and aluminum base alloys.

Subjecting annealed aluminum to a small, critical amount of mechanical working and subsequent heat treatment, especially at recrystallization temperatures, produces large grains or crystals, and their size may even be abnormally large if desired for decorative purposes. Etching the treated metal reveals the surface crystal faces, and thereby imparts a decorative pattern to an otherwise plain metal surface. This invention is particularly applicable to those aluminum articles or panels possessing relatively large grains or crystals, but is not limited thereto.

Prior known solutions for etching aluminum surfaces to reveal the grain boundaries have included aqua regia solutions. Aqua regia is formed by mixing one part concentrated nitric acid with 3 to 4 parts hydrochloric acid. Such a solution is desirably employed in a diluted form for economy, and for ease in handling, but is not as active as the undiluted solution.

The hydrochloric acid in the aqua regia etching solution appears to be the essential etching component in that a solution of hydrochloric acid alone will reveal the grain boundaries on an etched metal surface. However, by also employing nitric acid in the etching solution a sharper contrast among grain boundaries and a brighter overall appearance may be produced on the treated surface under certain conditions, this result apparently being attributable to the presence of a nitric acid reaction product. This reaction product is believed to be nitrosyl chloride, represented by the formula NOCl.

Etching of aluminum articles proceeds slowly and inconsistently in aqueous solutions of aqua regia diluted by more than about 25% by volume water when maintained at about room temperature or slightly above. Striations or marks resulting from working operations will not be smoothed or obscured, thus distracting from the brilliance and decorative appearance of the article. Etching the aluminum surface in such solutions substantially above 100° F. also results in a loss in brilliance. Temperatures in excess of 125° F. produce a dull finish which is undesirable from a decorative standpoint. Preliminary heating of the aqueous acid solution to about 150° F. appears to accelerate production of the desired nitric acid reaction product, but the solution must be cooled to below about 100° F. for use. Further, the nitric acid reaction product formed is dissipated on standing and must be replenished periodically. Preheating and cooling for this purpose is extremely inconvenient, uneconomical and time consuming. Furthermore, hot fuming acids always present additional problems and hazards.

Another solution for etching aluminum surfaces to reveal grains comprises concentrated hydrochloric acid, nitric acid, and hydrofluoric acid, the solution usually being diluted with about 25% by volume water. However, this etching solution has an exceedingly high rate of reaction and therefore is not a practical commercial means for decorating the metal surface. A further disadvantage is that the reaction is highly exothermic. Consequently, the temperature rises rapidly beyond the desired range for producing a bright surface thereby making it extremely difficult to control the etching operation. In addition, a bath of this nature produces excessive fumes which are corrosive to equipment and materials in the area, and detrimental to the health of workmen. Moreover, the necessity for handling hydrofluoric acid in itself presents numerous hazards, and requires special equipment.

A special pretreatment is usually required when either of the above known solutions are used for etching commercial aluminum. The aluminum article or panel is usually coated with a heavy, natural oxide film formed during fabricating and heat treating operations. This oxide film inhibits the consistent development of a sharp contrast between grains, and further prevents immediate action of the solution upon the metal. Consequently, it is necessary to remove the oxide film as by first immersing the aluminum article in a dilute solution of sulfuric acid-chromic acid maintained at a temperature of about 160 to 180° F. for about one to three minutes. The article is rinsed and subsequently treated in a 5% solution of sodium hydroxide for about one to five minutes at 150° F. Generally, these combined operations are necessary to insure the removal of the natural oxide film and to provide a uniform surface.

This invention has as its primary object to provide a method for imparting a decorative finish to aluminum articles by employing merely a simple chemical etching solution. It is another object of this invention to provide an efficient and effective solution for etching aluminum articles, particularly those having a large crystal structure. It is still a further object of this invention to provide a method for etching aluminum articles having a large crystal structure that requires a less critical pretreatment, that gives a brighter, more glittering overall appearance to the metal surface than heretofore has been possible by other known means, and that gives a more striking contrast between surface crystal faces.

In accordance with my invention, the aluminum article is etched by immersion in an aqueous solution of aqua regia containing a soluble nitrite ion. I have discovered that the nitric acid reaction product, which greatly increases the etching power of the solution, can be formed in the solution simply by the addition of a soluble nitrite salt to the solution. The nitrite ion of the salt apparently reacts with the hydrochloric acid to form nitrosyl chloride. The reddish-brown coloration of the solution caused by this reaction can be used as an auto-indicator, in that when the color fades another addition of the nitrite salt may be made thereby replenishing the reaction product in the bath.

In etching the surfaces of an aluminum article, particularly one having abnormally large crystals, an aqueous acid solution consisting essentially of hydrochloric acid, nitric acid and a compound introducing a soluble nitrite ion may be effectively employed. Thus, the use of solutions diluted with water reduces expense and eliminates the hazards, as well as the need for special equip-

ment, connected with handling concentrated acids. The acid solution preferably contains not less than about 25% by volume added water, and preferably not more than about 75% added water for practical purposes. Thus, a suitable etching solution for purposes of my invention may consist essentially of, by volume, about 20 to 60% hydrochloric acid, 5 to 15% nitric acid and 25 to 75% added water plus the soluble nitrite ion in an amount as indicated below. Reference is had herein, and in the appended claims, to hydrochloric acid containing about 38% by weight hydrogen chloride and to nitric acid containing about 70% by weight hydrogen nitrate. When acids of a different concentration are employed, the amount of water added should be adjusted accordingly.

The required concentration of the nitrite ion in the etching bath is somewhat dependent upon the acid concentration of the bath, the more dilute the solution the greater concentration of nitrite ion required to obtain the best results. The concentration of the nitrite ion preferably is no less than about 0.2 gram per liter, since solutions of a lower concentration result in a decrease in useful life and etching power. Generally, it is not necessary to exceed about 5 grams of nitrite ion per liter, even in cases of maximum dilution, for higher concentrations apparently do not accelerate the etching process nor develop a greater brilliance to the metal surface. Acid solutions containing the nitrite ion more readily penetrate the natural oxide film formed during fabrication and heat treatment thereby making the pretreatment less critical. In cases where the oxide film is not particularly thick, the pretreatment may be eliminated altogether.

According to my invention, a brilliant aluminum surface exhibiting a sharp contrast among grain boundaries of the large surface crystal faces can be obtained by etching the aluminum object in the above-described bath maintained at relatively low temperatures, i.e., room temperature or slightly above. The nitric reaction product is formed upon the addition of the nitrite salt to the acid solution. This obviates any need for heating the bath to elevated temperatures. Preferably, the bath should be maintained at a temperature of about 70 to 100° F., and more preferably from about 75 to 85° F. Operating the bath at temperatures substantially in excess of 100° F. results in a decrease in brilliance and luster which is generally undesirable from a decorative standpoint. Because the reaction is moderately exothermic, any excessive temperature rise beyond the described range can be readily prevented by circulating cold water through coils surrounding the bath container.

Immersing an aluminum article in the aqueous acid bath containing a soluble nitrite ion for about 2 to 30 minutes will produce the desired decorative finish when operating within the above described ranges. Prolonged immersions in the etching bath do not produce more brilliant surfaces or result in a greater contrast in grain boundaries. Also, excessively long immersions may consume an undesirable amount of aluminum. On the other hand, immersions for less than 2 minutes generally are not sufficient to produce a finish most desired for decorative purposes.

In certain instances it may be desirable to provide the etched metal surface with a protective coating, such as a lacquer or varnish. For example, a clear methacrylate lacquer may be applied to the treated aluminum surface. Or the etched article may be subject to an anodic treatment to give a protective, artificial oxide film. In such a case, the aluminum article is made the anode in an electrolytic solution such as a sulfuric acid solution or chromic acid solution. Of course, an artificial oxide film may be produced by other means, for example by treating the aluminum article with a solution of an alkaline carbonate, usually a sodium carbonate-chromate solution. Etched aluminum articles or panels possessing an artificial oxide film have the added advantage in that they may

be further decorated by coloring with an appropriate dye or pigment.

My invention is illustrated by the following example wherein an aluminum panel 0.064" gauge having a large crystalline structure was cleaned with an organic solvent to remove the fabricating oils. The panel was then immersed in a 5% sodium hydroxide solution maintained at 150° F. for about 30 seconds. The aluminum panel was rinsed with water and immersed in an etching solution consisting of 4 parts hydrochloric acid, 1 part nitric acid and 5 parts water, and containing 5 grams per liter of sodium nitrite. The panel was immersed in the etching solution for 5 minutes at a temperature of 80° F. A brilliant, glittering surface was formed, the surface face crystals exhibiting a sharp contrast in grain boundaries and reflecting different degrees of brightness. No striations resulting from rolling operations were noticeable. When viewed from different directions, the panel always gave a new impression.

An alkali metal nitrite, an alkaline earth metal nitrite, or any nitrite salt soluble in the etching solution may be substituted for the sodium nitrite in the above example. The active ingredient is the soluble nitrite ion. For example, potassium nitrite, calcium nitrite, and barium nitrite may be employed with equally satisfactory results.

Articles made in accordance with my invention are decorative in appearance, and are particularly useful in architectural applications such as wall, ceiling and door panels, display counters and in automotive trim, lighting fixtures, jewelry and novelty items, and the like.

I claim:

1. A method of imparting a decorative finish to surfaces of aluminum articles by revealing their surface crystal faces comprising immersing said articles in an aqueous solution consisting essentially of aqua regia and a soluble nitrite ion and maintained at a temperature of about 70 to 100° F., said nitrite ion being present in an amount causing a reddish-brown coloration of said solution at the aforesaid temperature.

2. A method of imparting a decorative finish to surfaces of aluminum articles by revealing their surface crystal faces comprising immersing said article in an aqueous solution consisting essentially of aqua regia, not less than 25% added water and not less than 0.2 gram per liter of a soluble nitrite ion and maintained at a temperature of about 70 to 100° F.

3. A method of imparting a decorative finish to surfaces of aluminum articles by revealing their surface crystal faces comprising immersing said article in an aqueous solution consisting essentially of aqua regia, not less than 25% added water and not less than 0.2 gram per liter of a soluble nitrite ion and maintained at a temperature from about 70 to 100° F. for a period of about 2 to 30 minutes.

4. A method of imparting a decorative finish to surfaces of aluminum articles by revealing their surface crystal faces comprising immersing said article in a solution consisting essentially of 20 to 60% by volume hydrochloric acid (on the basis of 38% by weight hydrogen chloride), 5 to 15% by volume nitric acid (on the basis of 70% by weight hydrogen, nitrate), said acids being present in about the proportions in aqua regia, 25 to 75% by volume added water, and not less than 0.2 gram per liter of soluble nitrite ion, said solution being maintained at a temperature of about 75 to 85° F.

5. A method of imparting a decorative finish to surfaces of aluminum articles by revealing their surface crystal faces comprising immersing said article in a solution consisting essentially of 20 to 60% by volume hydrochloric acid (on the basis of 38% by weight hydrogen chloride), 5 to 15% by volume nitric acid (on the basis of 70% by weight hydrogen nitrate), said acids being present in about the proportions in aqua regia, 25 to 75% by volume added water and from about 0.2 to 5 grams per liter of soluble nitrite ion and maintained at a tem-

perature from about 70 to 100° F. for a period of about 2 to 30 minutes.

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