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ETCHING OF ALUMINUM FOR BONDING

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ABSTRACT OF THE DISCLOSURE

Aluminum and aluminum-base alloys are treated by etching with an aqueous solution containing sulfuric acid, hydrofluoric acid and an alkali metal dichromate. This treatment prepares the surface of the metal for adhesive bonding.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85–568 (72 Stat. 435; 42 U.S.C. 2457).

This invention relates to an etchant process for the surface treatment of metals prior to bonding to non-metals, untreated metals, or other similarly treated metal units.

The aerospace as well as other industries are particularly interested in the etchant treatment of metals preliminary to adhesive bonding since relatively large numbers of components are adhesively bonded to each other to achieve the fabrication of a completed unit. Because of the quantity of bonded components produced the industries are further interested in an economic process which employs readily available and relatively inexpensive etchant materials which may be applied in a variety of ways to meet a variety of needs.

To insure obtaining optimum metal-to-metal or metal-to-nonmetal adhesive bond, the surface of the metal is required to be as clean as possible, but many metals have a surface which is too smooth or uniform to provide an optimum bond subsequent to cleaning. These metals, therefore, are chemically treated to provide an etched surface thereby producing more surface area which contributes to achieving a bond which provides the desired tenacity. Normally, etching metal requires the exercise of considerable control because an etchant reacting too rapidly will produce undesirable pits and cavities and a nonuniformly etched surface, while an etchant reaction proceeding too slowly will consume an excessive number of manhours.

Heretofore, one objection to the etching of metals was the etchant materials were limited in their scope of application, i.e., a heated immersion process was employed which restricted the use of the etchant to relatively large vat laboratory or factory application; the etchant materials could not be applied in the field or remote location. Another objection was the materials were relatively difficult to handle because of their toxicity and other undesirable reactions affecting personnel. Thus, the use of etchants requires considering the safety of the personnel employing the etchants, with the result the chemicals should be as free from objectionable properties as possible. Because etchant materials heretofore were required to be heated to achieve acceptable results, careful temperature control was required to prevent obtaining the aforementioned undesirable results.

The process of this invention employs a solution comprising a pair of acids, and an alkaline salt admixed with water. By the discreet use and blending of the chemical compounds comprising the etchant, the etchant may be: (1) sprayed onto the metal, (2) applied with a brush or

wiped on, and (3) an immersion bath may be employed. The basic composition of the etchant for all three applications is substantially the same, but by adjusting the quantity of two chemical components the viscosity of the etchant may be varied so as to achieve the aforementioned modes of application at ambient temperature, and etching of the metal may be achieved relatively rapidly when contrasted with the prior art.

On the other hand, one of the most widely accepted etchants and processes heretofore employed consists of sulfuric acid, sodium dichromate and water, the combination being relatively difficult to use since the metal to be treated must be immersed in the etchant, and the etchant must be employed at a carefully controlled elevated temperature for a relatively extended period of time. Varying the concentration of the three components will not enable etching of metal by brushing or spraying, two of the modes mentioned as being applicable to the instant invention, and further, the heated immersion process restricts etching of metal relatively rapidly at ambient temperature. Thus it becomes quite apparent this prior art process for etching metal is restricted in application.

The deficiency of the immediately preceding process may be further emphasized by relating an example. It is occasionally desirable to achieve an adhesive bonding of two or more metal components while working in the field, i.e., in a locale remote from the etchant baths. The prior art process does not provide the latitude whereby this may be accomplished, whereas the process of brushing, spraying or wiping on the etchant in the aforementioned manner will provide this latitude with a resultant savings of manhours.

Additionally, the prior art etchant material employs concentrations of quantities of components which renders the etchant relatively expensive whereas the etchant to be hereinafter described in more extensive detail employs quantities of components which significantly reduces the cost of the material, an item of considerable important when large quantities of the etchant is used.

There are other known etchants, but they display deficiencies such as being toxic, excessively reactive, controls necessary to achieve acceptable results are too rigid and costly, and the components comprising the etchants are not similar to the aforementioned components of this invention.

Epoxy adhesives and adhesive derivatives thereof exhibit superior bonding properties contributed materially to establishing a considerable interest therein by the aerospace industry. When it was determined metal could be bonded to metal or non-metal and an acceptable tenacious bond could be achieved, engineers began to design aerospace products requiring the use of adhesive bonding. It was further determined the use of adhesive would contribute to a reduction in weight of the product which in the aerospace industry is very often critical. For instance, some space operations require an additional 150 pounds of fuel for every additional pound of hardware. Thus, it may be seen weight reduction is a factor to be carefully considered, and the use of adhesives as contrasted with mechanical fasteners contributes to weight reduction.

However, as engineers continued to study the advantages of using adhesives it was determined thoroughly cleaning the metal would contribute to producing reliable and tenacious bonds. Materials found to be effective cleaners are trichloroethylene, a volatile solvent, MEK (methyl-ethyl-ketone) and in certain instances alkaline detergents. Other cleaning agents which may be used are freons, ethers, esters, aromatics, chlorinated hydrocarbons, and many conventionally well known organic solvents. Some of these identified cleaning agents are more suitable for use with alumium and aluminum alloys, and

some are more applicable for cleaning beryllium and beryllium alloys. Additionally, certain of the cleaning agents may be found more effective for cleaning wrought aluminum or beryllium alloys while others are more effective for use with cast aluminum or beryllium alloys. However, it is to be understood the type of soil encountered in large measure dictates the cleaning agent used. However, any cleaning agent is applicable if it removes the soil and is non-reactive and non-corrosive.

Although a through cleaning of the metal will enhance the adhesive bond, adhesion of metal-to-metal or metal-to-nonmetal will be further increased by etching the metal to provide a greater surface area for bonding.

The hereinafter described etching composition of this invention has been found effective for etching various sheet aluminum alloys, also wrought aluminum alloys, and it is probably useful on cast aluminum alloys. Although the following description will be restricted to the application of the etching composition to sheet aluminum alloys, it is to be understood the composition is also applicable to beryllium and beryllium alloys as well as other metals and metal alloys.

In order to achieve etching of the aforementioned metals and alloys thereof, one of the acids, previously mentioned, is preferably sulfuric having, generally, a concentration of 98 percent, the amounts or quantities used being in the range between about 0.1–30.0 percent by weight, the optimum quantity being about 1.0 percent by weight.

Sulfuric acid serves as a solvent for aluminum and aluminum oxide, and in lower concentrations serves as a solvent for beryllium and beryllium alloys. Because of the solvent properties of sulfuric acid, it is virtually essential it be present in the composition. However, there is no particular advantage in using sulfuric acid in quantities exceeding about 30 percent, because the etchant materials become increasingly difficult to handle. This is so because of the corrosiveness and high heat of solution which develops in the presence of water.

Admixed with the sulfuric acid is the second of the acids mentioned which serves to accelerate or increase the reaction rate. The acid found to be most applicable and suitable is hydrofluoric, although a compound which will yield an adequate concentration of fluoride ions may be considered a suitable substitute. The entire effect of the chemical reaction is not entirely understood, but it apparently activates the etching composition in some way so an aggressive etching of the metal or metal alloys is produced. If no hydrofluoric acid is present the etching reaction is too slow at ambient temperature which ranges between about 60°–80° F. This temperature range is particularly applicable when the etching composition is wiped on, sprayed on or used in the field.

It is preferred the concentration of hydrofluoric acid be about 48 percent, and used in quantities between about 0.1–10.0 percent by weight, the preferred quantities being between 0.2–1.0 percent by weight depending on whether the composition is employed as a bath, a spray or is brushed on.

If hydrofluoric acid is not present in the etching composition, the etching reaction is too low or slow to be practicable, and if the quantity used exceeds ten percent by weight, the etching reaction is too rapid, and pitting is likely to occur.

To achieve optimum results with the etching composition, it has been found a corrosion inhibitor is beneficial to limit the rate of reaction. A rather extensive variety of chemical compounds are available which will display the aforementioned chemical properties. Such compounds are chromates, sodium bisulfate and the like. Compounds of this type are applicable so long as they yield the required concentration of sulfate ion and dichromate ion.

The preferred corrosion inhibitor is sodium dichromate (dihydrate) used in quantities between about 2.0–20.0 percent by weight, the preferred and optimum quantity being about 6.0 percent by weight; however, potassium and lithium are considered adequate and suitable substitutes. The dichromate of sodium also causes a formation of some type of coating on the surface of the metal which aids in the subsequent adhesive bonding. If the sodium dichromate is eliminated completely from the etching composition, pitting corrosion occurs, and if a quantity in excess of 20 percent by weight is used, the reaction of the composition with aluminum is slowed to an impractical rate.

Functioning as a solvent or carrier for the aforementioned components is distilled or deionized water which comprises the balance of the etching composition and is used in preferred quantities between about 90.0–94.0 percent by weight.

Except in those instances specifically mentioned, it is desirable to avoid materials which leave deposits or corrosive residues on the surface of the metal being treated. Tap water almost invariably includes undesirable mineral agents and chlorides, which leave undesirable residues, and, therefore, is not suitable as a solvent. Mineral deposits may form from the tap water and chlorides may affect chemical action of an etching composition bath in an unpredictable manner.

The deionized water in the composition leaves the cleanest surface possible with no water marks or other residues.

Another component which may be optionally included in the etching composition is a wetting agent which will help give a smooth surface to the metal after etching. It has been determined any wetting agent is applicable which is stable in the strongly oxidizing dichromate acid solution.

Following the etching of the metal or metal alloy, the treated material is thoroughly rinsed with distilled or deionized water. The purpose of this is to remove all the corrosive material of the etching composition from the surface of the metal. The reasons for using distilled or deionized rinse water is the same as those previously defined.

The preferred period of time for leaving the etching composition in contact with the metal being etched is between 30 seconds and 30 minutes, the time depending on: (a) whether the metal is immersed in an etching bath, (b) is sprayed on, (c) is brushed or wiped on, (d) the concentration of the components, and (e) whether heat is being applied. Time is not necessarily critical except a dark "smut" deposit appears after a prolonged application. It is believed the smut comprises metallic materials which have been redeposited on the surface of the metal, particularly does this occur when the metal is immersed in an etching bath. Included in the smut are probably some oxides or hydrated oxides, but it is unlikely aluminum oxide is present since this material is soluble in the etching bath. This smut does not reduce the efficiency of the process and is removed during the rinsing step.

Although the etchant is an acidic composition, no particular dangers have been noted in the use of the formulation aside from the general corrosiveness of acid solutions having concentrations as high as described.

Immersion processing is the most common prebond surface conditioning technique, and the following acidic etchant composition has been found particularly suitable for this purpose.

	Weight, percent
Hydrofluoric acid (48%)	0.5
Sulfuric acid (98%)	1.0
Sodium dichromate (dihydrate)	6.0
Water, distilled or deionized	92.5
	100

Aluminum and alloys thereof are to remain immersed in the bath for a period of about 5 minutes when the temperature of the etchant is ambient or room temperature, i.e., about 70° F. However, the temperature of the bath may range between about 50°–90° F., and accordingly the

period of immersion of the metal will vary in accordance with the temperature of the bath. For instance, the period of immersion will be greater if the bath is cooler than the optimum 70° F., whereas it will be less if the temperature exceeds the optmium. If the temperature of the bath is below the stated minimum, the etchant reaction is inordinately slow, and above the maximum temperature related, the etchant reaction becomes so rapid as to give uneven action over the entire surface of the metal being etched.

For applications where a spray method is applicable and needed, the following etchant composition is preferred:

	Weight, percent
Hydrofluoric acid (48%)	0.2
Sulfuric acid (98%)	1.0
Sodium dichromate (dihydrate)	6.0
Water, distilled or deionized	92.8
	100

The metal component being sprayed is treated for about ten minutes at the aforementioned optimum room temperature.

For applications of etchant composition where a manual wipe-on or brush-on is applicable the surface of the metal may be first abraded using either hand or power-driven sanders and abrasive paper.

After abrasion, the following etchant composition may be applied by wiping on the metal or by brushing it on:

	Weight, percent
Hydrofluoric acid (48%)	1.0
Sulfuric acid (98%)	1.0
Sodium dichromate (dihydrate)	6.0
Water, distilled or deionized	92.0
	100

This etchant is to remain on the surface of the metal for about two minutes at room temperature before being removed by the aforementioned rinse water.

Of course, rinse water is to be applied in the other two examples after expiration of the related time period.

Attention is directed to the quantities of hydrofluoric acid and water used in the three examples. In the example applicable to the spray, the viscosity of the etchant composition is reduced by reducing the quantity of hydrofluoric acid used, and increasing the quantity of water when this example is contrasted with the viscosity of the bath etchant. In contrast, the viscosity of the etchant is increased in the example illustrating the brush-on or wipe-on etchant when contrasted with the previous two by increasing the quantity of hydrofluoric acid and reducing the quantity of water.

While the present invention has been described herein in what is considered to be preferred embodiments thereof, it should be recognized departures may be made therefrom within the scope of the invention, and it should therefore not be limited to the details of the within disclosure but should be accorded the full scope of the appended claims.

What is claimed is:

1. The method of treating the surface of an article formed of aluminum or an aluminum alloy to prepare the same for adhesive bonding which comprises:
   (a) cleaning said surface;
   (b) contacting the cleaned surface with an aqueous etchant solution containing 0.1 to 30.0 weight percent sulfuric acid, 0.1 to 10 weight percent hydrofluoric acid, 2.0 to 20.0 weight percent alkali metal dichromate, the balance of the etchant being deionized water; and
   (c) washing the etched surface with deionized water.

2. The method of claim 1 wherein said article is contacted with said etchant by immersion in an etchant bath for five minutes at a temperature of about 50 to 90° F. and the etchant bath consists of about 0.5 weight percent hydrofluoric acid having a concentration of about 48 percent, about 1.0 weight percent sulfuric acid having a concentration of about 98 percent, about 6.0 weight percent sodium dichromate and about 92.5 weight percent deionized water.

3. The method of claim 1 wherein said article is contacted with said etchant by spraying the etchant thereon and said etchant consists of about 0.2 weight percent hydrofluoric acid having a concentration of about 48 percent, about 1.0 weight percent sulfuric acid having a concentration of about 98 weight percent, about 6.0 weight percent sodium dichromate and about 92.8 weight percent deionized water.

4. The method of claim 1 wherein said article is contacted with said etchant by wiping the etchant thereon and said etchant consists of about 1.0 weight percent hydrofluoric acid having a concentration of about 48 percent, about 1.0 weight percent sulfuric acid having a concentration of about 98 percent, about 6.0 weight percent sodium dichromate and about 92.0 weight percent deionized water.

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