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METHOD OF AND COMPOSITION FOR TREATING ALUMINUM AND ALUMINUM ALLOYS

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The present invention relates to the surface preparation of aluminum and aluminum alloys for subsequent metal finishing operations such as painting, anodizing, plating, bright dipping, welding, chromating, etc.

It is an important procedure in the aluminum finishing industry, prior to the finishing operations mentioned above, to remove the ever-present oxide film which forms on the surface of aluminum alloys on atmospheric exposure. A typical method employed in the past by which this is achieved is to immerse the previously degreased aluminum object in a suitable deoxidizing solution, which usually contains oxidizing agents such as chromic acid, chromates or dichromates, nitric acid or a mixture of these materials in well defined proportions. Their function is to replace this tenacious oxide film on the aluminum alloy by another film more suitable for subsequent treatments.

The use of chromic acid or any other chrome base deoxidizing solution in the finishing industry creates waste disposal difficulties since these formulations must be treated chemically before they can be disposed of safely. Also the use of chromic acid in certain finishing shops may cause contamination of rinsing waters, bright dips, anodizing and plating solutions. Furthermore, the use of nitric acid is always accompanied by obnoxious fumes which makes for uncomfortable and health hazardous conditions as well as corrosive action in many plating installations.

Another procedure frequently used heretofore in the aluminum finishing industry as a preparatory step, prior to the finishing treatments, consists of etching the aluminum alloy in a suitable alkaline solution, thereby removing substantial amounts of surface metal. During this etching process, certain alloying elements of the aluminum, which are insoluble in the etching solution, will cover the surface in the form of a loose coating forming an unsatisfactory basis for further treatment, and care must therefore be taken to see that this loose coating is completely removed. This phenomenon is known in the industry as smut formation, and removal of the smut is also covered by the term "deoxidizing" as it is used in practice and in the present specification and appended claims.

It is therefore a primary object of this invention to provide a novel deoxidizing solution which is free of waste treatment difficulties and wherein the ingredients are readily controllable at the room operating temperature of the solution; also to provide a solution compatible with bright dip and anodizing solutions. It is a further object of the invention to eliminate adherent films on the articles undergoing treatment and the production of offensive fumes and insoluble residues in the bath, which disadvantages have inherently characterized prior aluminum deoxidizing and desmutting operations. Among other advantages of the treatment herein disclosed is the fact that the bath components used are physiologically safe, which makes them well suited for treating aluminum objects to be used in the food industry. It is found that the deoxidizing action of the novel bath composition here disclosed is considerably faster than with existing chrome-type deoxidizers. Other features and advantages of the invention will be discussed as the description proceeds.

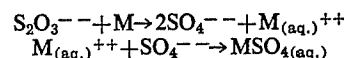
According to the present invention, a solution of a strong inorganic acid, and especially sulfuric acid, containing ammonium persulfate or persulfates of alkaline

and alkaline earth metals, at concentrations of from one gram per liter to saturation, is employed and provides excellent deoxidizing properties at room temperature on all aluminum alloys except those with high silicon content.

However, high silicon alloys can be handled with this system by adding a fluoride anion.

In the acid solution, as described above, the persulfate reacts with the aluminum or its alloying elements and is reduced to sulfate. Thus, unlike other deoxidizing baths, the exhausted solution of this invention contains no objectionable ingredients and can be disposed of after neutralization as in the case of any other spent acid.

While I do not intend to be limited thereby, it is believed that the reaction involved in the desmutting process is as follows:



where M is one or several of the alloying elements contained in the aluminum smut, and herein assumed to yield divalent ions in solution. A similar reaction can be formulated with aluminum or other trivalent ions.

One of the significant advantages of this discovery lies in the ability to achieve both cleaning and deoxidizing of aluminum objects in a single operation by the further incorporation of a suitable wetting agent. Any of several well-known surface tension depressing ionic or nonionic materials may be used for this purpose. Thus, it is found to be of great assistance in removing obnoxious oxide films from aluminum strip processed in continuous operation, wherein the aluminum strip is moved at high speed through a trough containing the deoxidizing solution and then through a rinsing trough. Large quantities of aluminum strip can be processed during short periods of time in such manner. Such treatments are impossible with chrome type deoxidizers which require very abundant rinsing that cannot be provided in a continuous operation.

Another advantage of this formulation is that it will not dimensionally alter or affect aluminum objects that are immersed, even for very prolonged periods of time. Furthermore, bright dipped objects immersed in this composition do not undergo dulling or loss of luster.

The following examples are given for illustration purposes but it will be understood that they do not define the limits of the invention which are set out in the claims.

Example No. 1

Aqueous solutions were prepared with the following concentrations and employed at the indicated conditions:

H ₂ SO ₄ , 66° Baumé	1-10%.
Ammonium persulfate	30 grams per liter.
Temperature	50 to 90° F.
pH	2.0 max.

Aluminum objects, previously etched in high temperature alkaline baths until the formation of a heavy dark smut appears, were then immersed in the above solution for periods of 10 seconds to 2 minutes. A light and smut-free surface is obtained which forms an excellent base for further finishing operations such as anodizing, painting, bright dipping, dyeing, chromating, etc. Also, aluminum objects treated in the above solution show excellent protection against dulling on subsequent atmospheric exposure.

Example No. 2

Aqueous solutions as in Example 1 were modified by replacing ammonium persulfate with potassium persulfate at concentrations from 1 gram per liter to saturation. Aluminum alloys, previously etch-cleaned in commercial alkaline cleaning mixtures, were then dipped in the above solution for periods of 10 seconds to 3

minutes. The resulting surface forms a very satisfactory basis for further finishing operations.

Example No. 3

The following aqueous solution was prepared:

Sodium bisulfate	50 grams per liter.
Ammonium persulfate	30 grams per liter.
Temperature	50 to 90° F.
pH	2.0 max.

Aluminum objects previously cleaned in commercial cleaning solutions and then dipped in the above formulation are of excellent appearance and are well suited for further finishing treatments. The formulation given in Example No. 3 has the further advantage of eliminating handling of liquid acids during shipping and subsequent preparation for use, which always is somewhat hazardous in the case of liquid materials.

The solutions of the foregoing examples are suitable for use on aluminum and all alloys thereof except those containing silicon as a significant alloying element, in amounts for example of 1% or more. In such case the inclusion of a fluoride ion in the bath composition is necessary and the following is typical of satisfactory formulations for this purpose.

Example No. 4

Aqueous solutions were prepared, as given in Examples 1-3 and to these was added from .1 to 20 grams per liter of ammonium bifluoride to provide the equivalent of from about 0.067 to 13.2 grams per liter of fluoride ion in solution. Aluminum objects containing silicon immersed in the above solutions at room temperature for periods of 20 seconds to 3 minutes formed highly satisfactory bases for further treatment such as phosphating, anodizing, bright dipping, painting, dyeing, spot welding, etc.

Although the above example uses ammonium bifluoride, other inorganic fluorides can be conveniently used.

Dry compositions comprising admixtures in proper proportion of soluble persulfate salts and the acid salts of strong inorganic acids may be prepared such that when these dry compositions are dissolved in an appropriate volume of water, a desmutting solution of the desired concentration is obtained. Such dry compositions have advantages over the liquid form, more especially from the safety standpoint because of better chemical stability and the consequent reduction of explosion hazards, elimination of handling of corrosive liquids, as well as in respect to simplifying shipment and storage as mentioned above in connection with the composition described in Example No. 3. For the dry composition, the soluble persulfate salts may be any of the alkali, alkaline earth and ammonium compounds; any of the soluble acid salts of sulfuric or other strong inorganic acid may be employed as the other component.

Each of the foregoing examples is directed to the use of sulfuric acid or the acid salt, since these are found in practice to be the most practical and economical to employ and are therefore definitely preferred. The system is operative with other strong acids; however, most of the others, with the possible exception of phosphoric acid, introduce problems of waste disposal, noxious fumes and/or greater cost. In all cases, however, it is critical that the acid employed create a solution pH equal to or less than 2.0.

The concentration of the persulfate in solution can vary rather widely as indicated in the examples and still be operative, although of course the concentration will affect the processing time. As mentioned above, concentrations as low as 1 gram per liter are useful and they may go as high as the limit of solubility of the compound in solution. In general, however, the best results for the ammonium, sodium and potassium persulfates both operationally and economically are obtained

at concentrations of from around 20 to 50 grams per liter, with an optimum at around 30 grams per liter.

While the high solubility of the reaction products of the deoxidizing treatment makes rinsing a very simple matter, any of the foregoing baths may incorporate an acid-compatible surfactant, for example sodium lauryl sulfate, to facilitate run-off of adherent solution during transfer of the articles from the surface preparation treatment herein disclosed to a subsequent operation.

This not only substantially reduces solution drag-out, and the inherent replenishment problem, but it materially reduces or eliminates contamination of subsequent treatment baths. As already mentioned, the formulations here disclosed permit of continuous strip metal processing which is not possible in the conventional chromic-nitric acid formulations. Where it is desired to combine cleaning with deoxidizing as above indicated, the solution temperature should be higher than that employed for deoxidizing purposes alone. In such cases, temperatures of from 70° to 160° F. are recommended.

Processing time of course depends on the degree of oxidation of the metal surface and on the concentration of the active agents in solution. In the range of preferred concentrations mentioned, the solutions normally produce the desired deoxidizing action after immersion times of 20 seconds to 2 minutes. The upper limit however is not critical as the solutions will not dimensionally affect immersed parts even on very prolonged exposure. The lower limit is at least 10 seconds.

What is claimed is:

1. A deoxidizing solution for aluminum alloys containing silicon as a significant alloying element, which consists essentially, in addition to water, of a soluble persulfate selected from the group consisting of persulfuric acid and the ammonium, alkali and alkaline earth metal salts thereof in amount of from 1.0 gram per liter to saturation, a soluble fluoride providing a fluoride ion concentration in solution equivalent to that obtained from 0.1 to 20.0 grams per liter of ammonium bifluoride, and a supplemental acid component selected from the group consisting of sulfuric and phosphoric acids, the acid salts thereof, and nitric acid, in amount sufficient to provide a solution pH not over 2.0.

2. The process of deoxidizing and desmutting aluminum and aluminum alloy articles which comprises providing an aqueous solution consisting essentially, in addition to water, of a soluble persulfate in amount sufficient to give a persulfate ion concentration equivalent to that provided by from 1.0 gram per liter to saturation of ammonium persulfate, and a supplemental acid component selected from the group consisting of sulfuric and phosphoric acids, the acid salts thereof, and nitric acid, in amount sufficient to provide a solution pH not in excess of 2.0, treating said articles by immersing them in said solution for a period of at least 10 seconds at a temperature of at least 50° F.

3. The process of deoxidizing and desmutting aluminum and aluminum alloy articles as defined in claim 2, wherein said persulfate is selected from the group consisting of persulfuric acid and the ammonium, alkali and alkaline earth salts thereof in amount of from 1.0 gram per liter to saturation.

4. The process of treating aluminum and aluminum alloy articles as defined in claim 3, wherein there is also present in solution a surface tension depressant wetting agent, and the temperature of the solution is maintained at from 70° to 160° F.

5. The process of treating aluminum and aluminum alloy articles as defined in claim 3, wherein there is also present in solution a soluble fluoride in concentration sufficient to provide from about 0.067 to 13.2 grams per liter of fluoride ion in solution.

6. The process of treating aluminum and aluminum alloy articles to provide an oxide-and-smut-free surface on the articles which comprises the steps of immersing

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the articles, for a period of from 10 seconds to around 3 minutes, in a sulfuric acid solution containing at least one compound selected from the group consisting of ammonium, potassium and sodium persulfate in amount of from 1.0 gram per liter to saturation, the amount of acid in solution being sufficient to maintain the pH thereof not in excess of 2.0, and the solution temperature being maintained between about 50° to 90° F.

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