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METHOD OF ETCHING ALUMINUM

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The present application relates to a method and to a fluid solution for etching metal. It more particularly relates to the etching of aluminum and its alloys with an acidic etching fluid.

This application is a continuation-in-part of my earlier application Serial No. 196,502 filed May 8, 1962, now abandoned.

Both metal sheets and a metal lamination or laminations over one or both sides of a backing sheet are chemically etched in the production of various industrial articles. Examples include, but are not limited to, perforated masks, metal gridworks, flat springs, engravings, and etched printed circuits. Metal in the places where it is desired to be removed from the article is attacked by the etchant because the surface is left exposed in those places, whereas the balance or image area on the metal surface is protected with an applied etchant-resist coating, usually an organic coating.

Aluminum and its alloys are an example of metals having a highly exothermic character of reaction when the sheets are etched. A caustic etchant solution is commonly employed, e.g., sodium hydroxide. Acid etching solutions have been tried and particularly aqueous ferric chloride has been tried in effort to improve the operation, but these acidic agents encounter a self-impeding difficulty which slows and sometimes stops the action. The difficulty is due to deposited films from acid salts and similar deposits from substitutions, side reactions, and otherwise, and they block the aluminum surface from contact with the solution.

In any case, the temperature of the acid solution must be closely regulated or the exothermic reaction tends to get out of control. If the temperature is allowed to accelerate, there are serious local disparities so that overheated areas develop and the etching rate is not uniform. Because of this difficulty, it is important that the etching rate proceed generally uniformly over all surfaces affected. This difficulty is further increased due to areas of smutting on the article resulting from the random film and acid deposits above indicated.

According to the present invention, I add, to a ferric chloride ($FeCl_3$) etching fluid, an amount of a suitably soluble persulfate. I have discovered that, in etching aluminum and aluminum alloys with a fluid having this mixture, the smut ordinarily formed from the aluminum-ferric chloride reaction either never enters or leaves the solution or else is dissolved at about the same rate it is formed; in any case the solution encounters no self impeding difficulty from smut and the action is one that is not perceptibly impeded in its process. Thus, through an acidic process, the etching of the aluminum sheet proceeds smut-free without appreciable impairment.

It is therefore an object of this invention to provide an acidic, persulfate-containing solution of aqueous ferric chloride, and a process of dissolving metallic aluminum rapidly and in enhanced manner.

It is a further object to provide such a persulfate-containing, ferric chloride solution which does not produce solid reaction products during dissolution of the aluminum and which proceeds continuously in its action until the strength of the solution is spent.

The persulfates are active oxygen containing salts of persulfuric acid. It is desirable for present purposes to employ ammonium, sodium, or potassium persulfate,

preferably the ammonium persulfate because of the economy of more available persulfate ion (S_2O_8) per given weight, and also because of its commercial availability and ready and high degree of solubility in water. However other persulfates, for example lead persulfate, or mixtures of persulfates, having the requisite commercial availability can be employed.

The present deposit-free process of aluminum dissolution operates through coaction of the ferric chloride and the persulfate, both being present throughout the etching process. Hence I provide a single stage or single step etch, in contrast to prior procedures involving two or more bath stages in which the respective baths employed are of differing compositions. My solution affords a definite precipitation retarding action to the existing solutes and to the resulting solutes therein, particularly dissolved ferric ion, preventing them from depositing from the solution. The active oxygen containing persulfate is compatible with the ferric chloride and is believed to retard and to overcome the tendency of the solutes to precipitate.

No reason is known for this unique behavior. A working hypothesis has been advanced, however, regarding the failure of smut to manifest itself. The smut is normally black in color, powdery in consistency, and is thought to be wholly or in large part finely-divided elemental iron. The identification is based on its ferromagnetism and on qualitative tests of a solution which was prepared by nitric acid dissolution. Such a solution gave a negative test for aluminum.

The persulfate present in my solution exhibits a definite retarding action to hold the smut in solution and prevent the smut after it accumulates, from reducing to a state capable of precipitating out of the solution. This explanation is not submitted as necessarily valid or as essential to the present invention, but is offered merely in an effort to provide better understanding.

In general, a regular aqueous ferric chloride solution is made having its strength appropriate for the metal etching rate desired. The broad range is from approximately 0.500 mole to 1.500 moles of the ferric chloride per liter of water, i.e., 0.7 pound per gallon to 2.0 pounds per gallon. Although the persulfate can be added prior to the ferric chloride, it is preferably added subsequent thereto. The quantity of persulfate added is, in the general instance of ammonium persulfate, in the range from 0.12 pound of ammonium persulfate per gallon of water to a saturated solution. Ammonium persulfate is highly soluble and, as a practical matter, the rough limit 12 pounds to the gallon of water would probably never be exceeded and is certainly unlikely to be reached commercially.

The solution, at a temperature from about 90° F. to 140° F., is applied to the surface of the articles to be etched and the process proceeds until the proper depth is reached or until perforations to the right dimension result. The articles are then rinsed free of the etching solution, the resist on the image is removed, and the operation proceeds in the regular way to make the final article desired.

A listing, along with their respective molecular weights, of examples of the persulfate salts which are satisfactorily employed according to this invention is as follows:

Ammonium persulfate, $(NH_4)_2S_2O_8$	228.21
Sodium persulfate, $Na_2S_2O_8$	238.13
Potassium persulfate, $K_2S_2O_8$	270.32
Barium persulfate, BaS_2O_8	401.56
Lead persulfate, PbS_2O_8	453.39
Persulfate ion, S_2O_8	192

From the foregoing it will be seen that it requires, on the basis of the gram-molecular weight of the persulfate

ion appearing above, approximately 228/192 or $^{136}/_{192}$ grams of the $(NH_4)_2S_2O_8$ to yield 1 gram of the ion.

The cost per unit weight of $(NH_4)_2S_2O_8$ approximately equals the cost of the persulfates of sodium and potassium, and the enhanced results obtained with the $(NH_4)_2S_2O_8$ make it somewhat preferable as well as commercially more desirable in the present etching solutions.

If sodium persulfate is substituted in the solution in place of the $(NH_4)_2S_2O_8$, the amount employed is in the range between approximately 0.12 and 2 pounds of sodium persulfate per gallon of water, and preferably about 1 pound per gallon. The persulfate ion that results will follow according to the proportion whereby 238/192 or $^{146}/_{192}$ units of sodium persulfate by weight yield 1 unit weight of the ion. Sodium persulfate offers nearly as good concentration requirements as the $(NH_4)_2S_2O_8$ and the results are satisfactory in producing relatively smut-free, rapid acid etching.

If potassium persulfate is substituted, the range of concentration is from about 0.19 pound to somewhat more than 1 pound per gallon of water, preferably being about 1 pound per gallon. The ion that results will be in the proportion of 1 unit weight of S_2O_8 ion from approximately 270/192 or $^{178}/_{192}$ units of potassium persulfate by weight.

If the persulfate of barium or the persulfate of lead is substituted for the $(NH_4)_2S_2O_8$, each of the former will product only slightly more than half the available S_2O_8 ion as the $(NH_4)_2S_2O_8$. Moreover, it is difficult to obtain those two persulfates commercially. Use of the persulfates of potassium, barium, and lead nevertheless produces satisfactory results.

The following specific example of ways of operating according to the foregoing method and the solutions is intended to illustrate the invention for a better understanding. The example is not exhaustive of the ways possible, being disclosed with the desired purpose of a fuller description and not of limitation.

Example

For requirements of the 60 gallon nominal capacity of the tank of one commercially available spray etching machine, I first provide 50 gallons of tap water, which can be introduced directly into the machine or else the solution can be prepared elsewhere and then introduced into the machine. I then add crystals of ferric chloride in sufficient quantity into the water to raise the specific gravity to a reading generally between approximately 2° Bé. and 18° Bé., and preferably between approximately 13.7° Bé. and 18° Bé., this latter addition in terms of pounds to the gallon being 1.106 and 1.525 pounds, respectively.

If concentrated ferric chloride solution of a type commercially available is employed, I cut the solution with plain tap water until the specific gravity is in the foregoing range. One of such solutions, having the proprietary designation RCE solution, is available from Phillip A. Hunt, Palisades Park, New Jersey. As sold, the density of this solution is 1.40 originally, it has a Baumé reading of 41° to 43°, and contains one or more additives effective to speed up the etching rate.

Irrespective of whether ferric chloride is introduced as a liquid or in crystalline form, the percentage of ferric chloride in the solution at this point is from about 12 percent to about 16 percent by weight, ferric chloride being readily soluble in water.

To the foregoing solution, I add from about 0.8 to 1.2 pounds of ammonium persulfate to the gallon of water. The simplest means for carrying out this step within the stated range is, in the fifty gallon quantity referred to, merely to weigh out about 50 pounds of the white ammonium persulfate crystals and introduce this readily soluble addition into the solution. This procedure keeps the amount of ammonium persulfate at or below 13 percent by weight in the solution and the specific gravity of the solution rises to a reading of about 20° Bé.

Aluminum sheet or aluminum surface boards are fed into the etcher. The etch solution attacks the non-image surfaces and is satisfactorily applied, for example, in pressure induced sprays from spray nozzles. I have discovered that, by means of a cooling coil provided in the tank of the etcher, the temperatures of this exothermic reaction are entirely capable of being controlled so that the temperature ranges from about 100° F. to about 110° F. The etching thus proceeds in a controlled uniform manner despite the collective exothermal character of the aluminum, ferric chloride, and ammonium persulfate.

The Baumé reading keeps increasing with dissolution of the aluminum and as a practical matter is allowed to reach about 29° Bé. to 30 Bé. but not higher. The rate of etching has materially reduced at this point and the solution, which by then will have dissolved from between 7 and 8 pounds of aluminum, can be considered spent from the commercial standpoint.

The solution is replaced by a fresh solution as above and the operation is then repeated.

The proportions just set forth are considered optimum for aluminum and its usual alloys employed in etched metal articles. The amount of the persulfate salt has a critical value because the S_2O_8 ions available in the solution must exceed a minimum concentration. Thus in the examples of the persulfates of ammonium and sodium, smut begins to appear and impede the aluminum etching process when the concentration of either of these two persulfate salts, whichever one is present, is below approximately ⅛ pound per gallon of water in the solution. The recommended use of 1 pound more or less per gallon (0.52 mole per liter) of the selected one of these two salts or the other persulfate salts is, as indicated, the practical approach to insure adequate S_2O_8 ions at all times.

In the present solutions, the ion of the ferric chloride is in the 3+ condition and, being electronegative to the aluminum, assures rapid reaction in being substituted for the aluminum metal. It contrasts quite sharply to the persulfate of the solution, which is there primarily for the purpose already indicated. To some extent, however, the persulfate probably also attacks the aluminum and this behavior is believed accounted for due to an intereffect or coaction of the chloride ion Cl—.

Persulfate has been found to be a very reluctant etchant to aluminum in absence of the chloride ion, but its capability in etching aluminum can be demonstrated to a degree. Thus if the chloride is added as common sodium chloride, it will cause slight attack of a persulfate solution upon aluminum. The reaction is slow despite the presence of the chloride ion and the reason is felt in part to be due to the fact that the sodium of the salt is electropositive to aluminum.

While certain procedures have been set forth above for employing the present invention, it will be apparent to those skilled in the art that variations therefrom may be made without departing from the scope of the invention. For example, the etching solution may be applied by a splashing action in the machine as afforded by paddling. In place of the corresponding persulfate salts, persulfuric acid if available may be used. The salts are recommended, however, and particularly the salts indicated to be prererable herein inasmuch as it is known that they are fully compatible with and readily manageable in the bath solution in affording the desired action. The bath solution employed in the present invention is quite insensitive to minor changes in concentrations and may be used to etch a wide variety of aluminum and its alloys, especially those alloys which contain a very large proportion of aluminum and which are not readily etchable with enhanced results by known procedure.

I claim:

1. The method of etching aluminum with an aqueous ferric chloride solution, which includes the addition, to the gallon of the solution, of at least 0.12 pound of persulfate salt to prevent the formation of unwanted smut and to sustain the etching action by the ferric chloride in the solution, and applying such solution to aluminum to etch same.

2. The method according to claim 1, wherein the unwanted smut consists essentially of free iron, and wherein the persulfate salt constitutent of said solution is selected from the group consisting of ammonium, sodium, potassium, barium, and lead persulfate.

3. The method according to claim 1, wherein the ferric chloride is in sufficient concentration that the ferric chloride solution reads between approximately 2° Bé. and 18° Bé. in its specific gravity, the persulfate being ammonium persulfate and the addition thereof being about 0.8 to 1.2 pounds of the ammonium persulfate to the gallon of the ferric chloride solution.

4. The method according to claim 1, wherein the persulfate added to the gallon of the water provided for the aqueous ferric chloride solution is ammonium persulfate, and the addition thereof being about 0.12 to 12.00 pounds of ammonium persulfate to the gallon of the water, said solution then, after the last one of said ferric chloride and ammonium persulfate has been added thereto, being applied to the aluminum as aforesaid.

5. The method according to claim 4, wherein the addition of the persulfate added to the gallon of the water provided for the aqueous ferric chloride solution is in the range of about 0.8 to 1.2 pounds of ammonium

persulfate, and the application of the solution, after the last one of the ferric chloride and ammonium persulfate has been added to the water, is by spraying the solution against an aluminum-containing article, such solution being maintained, at least throughout the spraying of the article, at a temperature in the range of about 100° F. to 110° F.

6. The method according to claim 1, wherein the ferric chloride is limited in concentration to the extent that the ferric chloride solution does not exceed approximately 18° Bé. in its specific gravity, the persulfate addition being ammonium persulfate added in an amount raising the specific gravity of the solution to at least approximately 20° Bé., the etching of the aluminum being characterized by maintaining the solution, throughout etching, at a temperature from about 100° F. to 110° F. and discontinuing etching when the solution reaches an expended strength condition indicated by the Baumé reading increasing to approximately 30° Bé.

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