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METHOD FOR REJUVENATION OF ALUMINUM TREATING SOLUTIONS

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In a copending application for patent, Ser. No. 445,196, filed July 22, 1954, now Patent No. 2,762,694, I have disclosed the conditioning of aluminum surfaces preparatory both to masking with surface coating compositions and also as a preconditioning operation to improve the uniformity of etching of the aluminum surfaces with alkali etching agents.

I have found that the use of water solutions of acids other than hydrochloric acid, and acid salts of acid having a pH of 4 or less, may be used to remove the aluminum oxide film, which covers surfaces of aluminum and alloys of aluminum, to improve the adherence of masking coatings, and also to improve the uniformity of etching attack by alkaline etching reagents on the exposed elemental metal surface.

I have also found such acidic solutions are useful for the removal of the so-called smut which appears on surfaces of aluminum alloys, particularly when aluminum is alloyed with elements, such as for example, copper, iron, silicon and carbon, etc. Such aluminum alloys, when etched with caustic soda, produce a film which is black and highly adherent to the surface. It is conventionally referred to as smut in this art. These smuts are insoluble in water and in most acids. They are soluble in HNO_3, mixtures of HNO_3 and H_2SO_4, and in mixtures of chromic acid and sulfuric acid. Such acids are extremely hazardous to use industrially.

It has been found that the addition of a fluoride ion yielding compound, that is, hydrofluoric acid, alkali metal or ammonium fluoride or equivalent acid fluoride salts, to the acid salts when dissolved in water produces a relatively mild acidic solution which, however, has the property of dissolving smut.

The acidic solutions employed above for these various purposes have all in common the property of dissolving aluminum oxide, or where the acidic salt solutions contain fluorides or acid fluorides they will dissolve smut readily but have an unsubstantial rate of attack on the elemental aluminum. They are all acid or acid salt solutions of pH of 4 or less and they are used at temperatures at which the attack rate on the elemental aluminum is substantially less than its attack on smut or aluminum oxide film and may be substantially entirely inactive to dissolve the aluminum metal for exposure times sufficient to remove the oxide or smut. These acidic solutions may be those made by a solution of HNO_3, H_2SO_4, phosphoric acid, and mixtures of these acids, or acid salts, such as sodium dihydrogen phosphate, sodium dihydrogen pyrophosphate, sodium acid sulfate, or sodium nitrate acidified with sulfuric acid, or the equivalent potassium and ammonium salts, all having a pH less than about 4 to which I may, and preferably do, add sodium, potassium or ammonium chromate or dichromate or chromic acid, adding the agents, when alkaline or neutral, in amount insufficient to raise the pH above 4. When I use the acid salts for smut removal, I preferably add a small amount of hydrofluoric acid or an alkali metal fluoride or alkali metal acid fluoride or ammonium acid fluoride. All of these solutions will remove smut or aluminum oxide film or film of other compounds produced in the etching process without any substantial attack on the elemental aluminum surface and may be classified as "acidic solutions safe on aluminum."

It has been found that their usefulness, in conditioning the surfaces of the aluminum prior to etching or in clearing up the etched surfaces to clean them of films or layers of compounds of aluminum such as smut or aluminum oxide film or film of other compounds which may be formed in the etching process, gradually diminishes during continued use so that longer and longer exposure times are required for the acidic solution to do its work. The solutions are said to be exhausted. A time comes when it is no longer economical to continue the use of such solutions and they are discarded and fresh solutions are made up.

I have found that such solutions may be revivified and their activity restored by adding hydrofluoric acid or a water soluble fluoride and preferably an alkali metal fluoride or an alkali metal acid fluoride or the equivalent ammonium salts which for this purpose are equivalent in action to the alkali metal fluorides or acid fluorides.

While I do not wish to be bound by any theory of the process, I believe that the hydrofluoric acid or the fluoride salts cause the precipitation from solution in the spent acidic reagent of dissolved metallic ions which have gone into solution as a result of the treatment of the aluminum body with the acidic material. I have found that by adding an amount of fluoride ions stoichiometrically equivalent to the Al^{+++} ion and other metallic ions, for example Cu and Fe, in solution in the spent acid solution, that I can substantially quantitatively precipitate the aluminum and other metallic ions dissolved from the aluminum surface in the removal of smut (that is, those metallic ions lower than Al in the electromotive series which are present in the acidic solution) and substantially completely revivify, the acidic solution to reestablish in substantial effect its original activity as when freshly prepared.

A convenient reagent for the purpose is ammonium acid fluoride $NH_4F.HF$, or I may use sodium acid fluoride NaF.HF, or potassium acid fluoride KF.HF. Thus, for example, the addition of the $NH_4F.HF$ to the spent acidic solution results in the precipitation of a white silky flock, which rapidly settles to the bottom of the vessel, and which contains Al, F, Na, as well as Fe and Cu, if these be present in solution in the spent acidic solution.

Illustrating the usefulness of my process is the application of the acid fluorides for the revivification of acid solutions employed in removal of smut which have become exhausted because of their use in the removal of smut.

Aluminum may be etched with solutions of sodium or potassium hydroxide, tri sodium or tri potassium phosphate, sodium or potassium carbonate, or a similar reagent having an alkalinity equivalent to that of .1 to 10 normal NaOH solution. The result is a solution of the elemental aluminum from the surface exposed to the alkali. The surface will be contaminated by the smut if the aluminum is one which is alloyed as described above.

As stated above, such smut contaminated aluminum may be cleaned of the contaminating smut by washing the aluminum surface with an acidic solution containing nitric acid or nitric sulfuric acid or sulfuric acid mixed with chromic acid. Such mixtures are hazardous to handle.

I have found that the dry mixture may be used in place of the above acids. Such dry mixtures may be mixtures of the acid salts of sulfuric acid and chromic

acid to which may be added suitable non-ionic or anionic acid stable wetting agents.

I may employ solid mixtures of the following composition:

50–99% of the acid salts referred to above
0.1–2% fluoride, or acid fluoride described above
0–1.0% of an anionic or non-ionic acid stable wetting agent
1–50% sodium or potassium or ammonium chromate or dichromate or chromic acid

using them in amount to add up to 100%.

An example of such mixture is as follows:

77.1% $NaHSO_4$ (sodium acid sulfate)
1% $NH_4F.HF$ (ammonium bi fluoride)
0.1% of an anionic or non-ionic wetting agent, for example, Nacconol Z, which is an alkyl aryl sulfonate sold by National Aniline, Div. Allied Chemical & Dye Corp., N. Y. C.
21.8% $K_2Cr_2O_7$ potassium dichromate

The acid stable anionic and non-ionic wetting agents referred to are a well recognized class of wetting agents. Examples of anionic wetting agents, in addition to Nacconol Z, are: "Dupanol M.E" or "C" (sodium lauryl sulfate) or "Areskap" (monobutylphenylphenol sodium sulfonate) sold by Monsanto Chemical Co., or "Santomerse D" (decyl benzene sodium sulfonate) sold by Monsanto Chemical Co. of St. Louis, Missouri. Examples of non-ionic wetting agents are alkyl aryl polyoxyethylene alcohols (Triton X–45 and Triton X–100, sold by Rohm and Haas Co. of Philadelphia), alkyl phenoxy polyoxyethylene ethanols (Igepol CO–630, Igepol CO–730 and Igepal CO–850, sold by Antara Chemicals, Div. General Dyestuff Corp. of N. Y.), polyoxyethylene thioether (Sterox SK, sold by Monsanto Chemical Co. of St. Louis, Mo.).

The mixtures may be used in concentration of from 4 oz. of the mixture per gallon of water to 32 oz. per gallon of water. A preferred acid concentration is about 16 oz. per gallon water.

The smut contaminated aluminum alloy, such as 24S, when immersed or sprayed with this solution at a temperature of 60–180 degrees F. for about 2 to 10 minutes, depending on the degree of contamination by smut and the temperature employed, becomes smut free, the surface appearing clean and bright and without any substantial corrosive attack on the aluminum surface.

The higher the concentration of the mixture employed in the solution, the more critical becomes the time of immersion. Thus, the aluminum, after removal of the smut, begins to oxidize in the solution and an oxide film is developed. The time of immersion or other contact with the solution should be such that the smut is removed and the process discontinued before any substantial build-up of oxide film on the metal surface occurs.

The same precaution should be employed when the above solution is employed to remove an aluminum oxide film in addition to or in place of smut. The time of contact and preferred concentration may or may not be the same as in the above case depending on the nature of the oxide surface.

In both cases whatever time rate is established for desmutting or deoxidizing the metal at the temperature employed, it will be found that as more and more pieces of metal are treated with the solution, a point is reached when the solution will no longer desmut or deoxidize the aluminum at the temperature and the times chosen as above. They are spent solutions within the criteria set forth above.

In order to continue to use this solution, either the time must be prolonged or the temperature increased or the solution revivified.

I have found that I can revivify such solutions which have become spent by adding small amounts of alkali or ammonium acid fluoride, that is, $NH_4F.HF$, or KF.HF, or NaF.HF, or NaF, or KF, or HF, or other soluble fluorides. The addition of these materials causes the precipitation of the dissolved aluminum and other metallic ions higher in the electromotive series than aluminum, which have been dissolved, may be precipitated substantially quantitatively. A white silky flocculent precipitate is formed. This precipitate settles to the bottom of the container and when the container is cleaned the precipitate, which is not adherent, may be readily flushed out.

It is preferred that the acid fluoride or fluoride is added in an amount stoichiometrically equivalent to the Al ions in solution, 3 mols of acid fluoride or fluoride, for example 3 mols $NH_4F.HF$, being employed per mol of Al. It is believed that the fluoride precipitates the Al^{+++} as insoluble aluminum fluoride complex. If the acid fluoride is added in amount, so that after precipitating the metallic ions some of the acid fluoride or fluoride is present in excess then, on reuse, some solution of the aluminum from the aluminum object occurs. If a substantial excess of the acid fluoride or fluoride is employed this results in a corrosion of the surface of the aluminum which is undesirable. Some small excess of free fluoride or acid fluoride in the order of about 0.25% by weight of the solution may be tolerated, if care is taken in the treatment not to permit too great a length of time in the exposure of the aluminum to the solution.

Small amount of nitrate ions (in the order of about 0.04% or greater weight percentage of the solution) when added to the solution inhibits the corrosive attack of the free acid fluoride.

The solution, after having been treated with the fluoride, may be reused since its smut and oxide removal capacity is substantially completely restored.

The following is an example of the application of my process which is given as illustrating a preferred embodiment of my invention but not as a limitation of my invention:

Example 1

Parts which have been etched with caustic soda solutions, such as described above, and which are covered with dark adherent surface layers of smut are rinsed free of the etchant caustic. The rinsed part is introduced into a tank and sprayed with a solution or dipped into a solution, made up by dissolving 16 oz. per gallon of the mixture identified above, that is, 77.1% $NaHSO_4$; 1% $NH_4F.HF$; 21.8% $K_2Cr_2O_7$; and 0.1% of Nacconol Z (all percentages are by weight). The part is wetted for a period of 3 minutes, the solution having a temperature of 80 degrees F. The parts are then removed, rinsed and dried. They are cleaned of the adherent smut. When the solution is active, it will desmut such parts and may be repeatedly used on new parts to be desmutted. A time will be reached, depending on how many parts are desmutted and the volume of the solution employed, when the solution no longer will desmut parts at the above temperature and exposure time. The solution is thus termed exhausted under the condition as imposed by the time and temperature specified. It is to be noted that the prolongation of time of exposure or elevation of temperature would cause additional activity in smut removal until the chemical capacity of the solution to remove smut is chemically exhausted. However, I have found it more convenient to continue the treatment for the chosen times and temperature and to revivify the solution instead of increasing the time or temperature of treatment and to revivify the solution when it is substantially completely chemically exhausted.

To revivify the solutions, I add $NH_4F.HF$, or NaF.HF, or KF.HF, or NaF, or KF, or HF, or other fluorides. For the procedure set forth above, that is, where treatment is for 3 minutes and at 80 degrees F. with the above acid salt solution, I have found that the addition of $NH_4F.HF$ in an amount equal to 0.2 oz. per gallon of

solution or 0.3 oz. of NaF.HF per gallon of solution, will revivify the solution to restore its original activity.

Since because of variations in operating conditions, where repeated revivification of the solution is desired, it may be found that the concentrations of acid fluorides or fluorides stated above may exceed the stoichiometric requirements of the spent solution and result in an excess of free acid fluoride in solution. At other times the above treatment will not completely revivify the solution since it may not be sufficient to completely precipitate the Al^{+++} ions in solution. In the latter case, no serious difficulty occurs and the solution merely becomes spent sooner on repeated use. However, in the former case, the solution may be corrosive to aluminum to give a white adherent coat to the desmutted aluminum.

In order to avoid this latter contingency, I may, and usually prefer to, add an inhibitor, such as NO_3^- ion. I have found that the addition of concentrated HNO_3 above about 0.1% to 1% by volume of the solution to be revivified, for example: one-half gallon of concentrated HNO_3 (67% HNO_3 by volume) per 1,000 gallons of solution (that is, .03% HNO_3 by volume) is sufficient to prevent corrosive attack by excess acid fluoride when the acid fluoride is added in the proportions given above, that is, 0.2 oz. per gallon where $NH_4F.HF$ is used or 0.3 oz. per gallon where NaF.HF is used. I may also use a soluble nitrate such as sodium, potassium or ammonium nitrate in amounts chemicaly equivalent to the HNO_3 as specified above in solutions sufficiently acid to give the above HNO_3 equivalent.

While I have described a particular embodiment of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. In a method of treating aluminum objects having a surface layer of metal compounds thereon to remove said compounds, wherein said compounds are removed by contacting said surface layer with an aqueous acidic solution containing fluoride ions, said solution being adapted to react with and dissolve said layer without appreciably corroding the aluminum objects; the improvement of revivifying said solution, after treatment and removal of said aluminum objects from the bath, by increasing the free fluoride concentration thereof above that existing during the metal compound dissolving procedure to a concentration corrosive to aluminum objects by adding to said solution a free fluoride ion yielding compound in an amount substantially equal to the amount of said compound stoichiometrically equivalent to the dissolved metal ions present in the solution, to precipitate substantially all the dissolved metal ions from said solution in combination with the additional fluoride ions.

2. In a method as set forth in claim 1, the added fluoride ion yielding compound being chosen from the group consisting of hydrofluoric acid, sodium acid fluoride, potassium acid fluoride, ammonium acid fluoride, sodium fluoride, potassium fluoride, and ammonium fluoride.

3. In a method as set forth in claim 2, the aqueous acidic solution containing fluoride ions containing about 4 oz. to 32 oz. per gallon of water of a mixture consisting essentially of about 50 to 99 percent of an acid salt chosen from the group consisting of sodium dihydrogen phosphate, sodium dihydrogen pyrophosphate and sodium acid sulfate, about 0.1 to 2 percent of a fluoride chosen from the group consisting of sodium, potassium, and ammonium fluorides, and equivalent acid fluorides, about 0 to 1.0 percent of a wetting agent, and about 1 to 50 percent of a compound chosen from the group consisting of potassium chromate, potassium dichromate, the equivalent sodium and ammonium salts thereof, and chromic acid, all percentages being on the basis of weight.

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