

1

2,710,792

COMPOSITION AND PROCESS FOR TREATING ALUMINUM AND ALUMINUM ALLOYS PREPARATORY TO SPOT WELDING

Louis McDonald, Altadena, and Alfred E. Hawley, Long Beach, Calif., assignors to Kelite Products, Inc., Los Angeles, Calif., a corporation of California

No Drawing. Application March 30, 1953,
Serial No. 345,718

10 Claims. (Cl. 41—42)

This invention relates to a composition and to a process for treating aluminum and aluminum alloys preparatory to spot welding. Aluminum and aluminum alloys possess a surface coating of aluminum oxide. As marketed they are also usually coated with an oil. Before spot welding it is first necessary to remove the oil coating, for example with a caustic wash, and then to etch the surface of the metal to remove the aluminum oxide coating.

There have been a number of different commercial processes devised for etching aluminum but these have all been unsatisfactory in one or more respects. The effectiveness of a process of etching aluminum is in the art measured by the resistance of the etched sheet in certain standard testing apparatus. For good results the resistance should be below 100 micro-ohms and in some cases aircraft work requires aluminum etched to a resistance of below 50 micro-ohms. One process employed in the prior art comprises a treatment with a solution containing sulfuric acid, chromic acid and hydrofluoric acid. This process has both operational and toxic hazards. The solution may generate hydrofluoric acid gas vapors which are not only toxic but corrosive. Moreover, the etching time with such a solution for satisfactory results is very critical. A deviation of 10 seconds from the optimum period may produce unsatisfactory results. It is very difficult to operate a production line operation of spot welding aluminum and aluminum alloy parts with a process in which the etching is so critical as to time. As aluminum or aluminum alloys from such a process undergo very rapid reoxidization for satisfactory work they should be welded within a time period of the order of 30 minutes after the etching process.

A second process employed in the art is one carried out at a temperature of from 180° to 212° using acid salt solution, such as sodium bisulfate. This process is not as sensitive as to the time of treatment but is not as effective in etching the aluminum as on tests etched sheets of 90 micro-ohms resistance is about the limit of this process.

A third process is used comprising a treatment with phosphoric acid and formic acid. This process is not as critical in time of treatment but the process is subject to widely different results depending on the nature of the aluminum alloy process so that the time of treatment varies with different alloys and with some alloys the process is not effective in etching the aluminum to obtain an etched sheet with a micro-ohm resistance as low as 100.

It is a general object of the present invention to provide a process for etching aluminum which process is relatively free of operational hazards, free of toxic hazards, and which process is effective for producing satisfactory results on aluminum and aluminum alloys of different types.

By means of the present invention we have provided a composition and process for etching aluminum and aluminum alloys prior to spot welding which process

2

is relatively unaffected by the time or temperature of treatment and which process is capable of providing an etched sheet having a very low resistance, such as in the order of 3 to 5 micro-ohms.

Essentially this new composition and process embodies the discovery that a superior process of etching aluminum and aluminum alloys may be achieved by utilizing a composition in which the etching agent is a mixture of phosphoric acid and aryl sulfonic acid provided the composition also includes an effective sequestering agent for any aluminum compounds produced, which sequestering agent is preferably also an organic reducing agent. The aryl sulfonic acids employed are those containing less than 7 alkyl carbon atoms and include, for example, benzene, toluene and xylene sulfonic acids. These aryl sulfonic acids, in combination with phosphoric acid, are found to be very effective in etching or removing the oxide coating from aluminum or aluminum alloy sheets. Their effectiveness in the composition is found to reside in the fact that they hydrolyze in part to liberate free active sulfuric acid.

This mixture of phosphoric acid and aryl sulfonic acid does not provide as effective an etching agent in the absence of the sequestering agent.

In the process aluminum compounds or complexes are formed which interfere with the effectiveness of the etching process. By the addition of the sequestering agent, which preferably is also an organic reducing agent, the formation of aluminum compound is to some extent inhibited and moreover such compounds as are formed are maintained in solution so as to permit the acids to remain effective in accomplishing the desired etching. The sequestering agent employed may be any water soluble aliphatic hydroxy carboxylic acid or a sodium or ammonium salt thereof. Example of suitable sequestering agents are gluconic acid, glucono delta lactone, tartaric acid, citric acid and the ammonium and sodium salts thereof.

The etching of aluminum and aluminum alloys with such an admixture of phosphoric acid, aryl sulfonic acid and sequestering agent is found very effective while at the same time the operation is free of toxic hazards, and relatively insensitive to either time or temperature of treatment or nature of the alloys to be etched.

By the process etched aluminum or aluminum alloy products are produced having as low as 2 to 3 micro-ohms resistance and satisfactory etching is obtained at a temperature range which may vary from 25° to 45° C.

The composition and process of the present invention for etching aluminum and aluminum alloy and further objects and advantages of the present invention will be fully understood from the following description of a preferred example of the present invention.

In the following description the preferred example of the cleaning composition is given in the form it is delivered to the user where it is normally diluted with an equal weight of water. Therefore, the composition in the etching operation contains in the order of about one-half the percentages of the ingredients given in the following example.

The preferred composition comprises:

7.9% citric acid
7.1% 28° Baumé ammonia
10% xylene sulfonic acid
37½% phosphoric acid
37½% water

In the above composition the sequestering agent, which is also an organic reducing agent, is a citric acid or citric acid combined with ammonia. This composition diluted with an equal weight of water was used for etching an aluminum alloy known as Aluminum 61 ST 0.04", one of

the more difficult aluminum alloys to etch. The following results were obtained:

Using only two minutes of treatment at a temperature of 25° C. the etched aluminum alloy sheets tested a micro-ohm resistance of 55. Maintaining the same time of treatment and increasing the temperature the etching becomes progressively more effective until at a temperature of 35° C. the etched sheets exhibited a micro-ohm resistance of about 3.2. Further raising the temperature of treatment to about 45° C. maintaining the same two minutes of treating time the effectiveness of the treatment decreased slightly but only to about a micro-ohm resistance of 3.7 at the temperature of 45° C. By increasing the time of treatment from two minutes it is found that the effectiveness of the treatment is improved at the lower temperatures and becomes more consistent or independent of the temperature of treatment. Thus, for example, using the treating time of eight minutes at a temperature of 25° C. the etched sheets tested 7 micro-ohms resistance. Using eight minutes treatment at 35° C. the etched sheets tested 7 micro-ohms resistance and at 45° C. and eight minutes of treatment the etched sheets tested 3 micro-ohms resistance. Increasing the treating time to fifteen minutes the micro-ohms resistance of the etched sheet was 4.5 at 25° C., 4.3 at 35° C., and 3.9 at 45° C.

It is to be noted that throughout the entire range of time of treatment of from two to fifteen minutes and throughout the entire temperature range of from 25° to 45° C. satisfactory etching was obtained and that at the longer period of treatment, fifteen minutes, the etching is much superior to that obtained with prior processes and at the same time substantially independent of time.

It is further found that the aluminum and aluminum alloy sheets etched by the process of the present invention have a property of remaining free of aluminum oxide for a longer period of time than those etched by other processes. Satisfactory welding may be carried out on sheets etched by the process of the present invention as late as forty-eight hours after the etching process.

In the foregoing preferred example of the present invention it is understood that citric acid is to be considered but one example of a water soluble aliphatic hydroxy carboxylic acid which may be employed as a sequestering agent.

The use of ammonia in the composition is beneficial but not essential. Ammonia, in combination with the citric acid or other water soluble aliphatic hydroxy carboxylic acid, has a property of improving the sequestering of any aluminum compounds produced in the etching operation. Likewise, xylene sulfonic acid is but one example of an aryl sulfonic acid containing less than 7 alkyl carbon atoms including, for example, benzene, toluene, as well as xylene sulfonic acids.

While in the preferred composition it is shown that the sequestering agent present as 7.9% of the composition may vary from 1% to 20% with satisfactory results, in the final diluted bath in which the aluminum and aluminum alloys are etched it may vary from 1/2% to 10%.

The preferred composition contains ammonia in the order of 2.4% but where ammonia is employed it may vary from 1/2% to 5% in the concentrated material or 1/4% to 2 1/2% in the bath in which etching is performed. The aryl sulfonic acid, which in this example is also an alkyl aryl sulfonic acid, may vary from 5% to 25% in concentrated solution, or from 2 1/2% to 12 1/2% in the etching bath. Phosphoric acid may vary from 22 1/2% to 52 1/2% in the concentrated solution or from 11 1/4% to 26 1/4% in the etching bath, the balance of the composition in most cases being water, although the composition may include higher percentages or other non-essential ingredients.

Thus the process of the present invention consists essentially of the treatment of aluminum or aluminum alloys preparatory to spot welding at a temperature pref-

erably from 25° to 45° C. inclusive, and at a time of treatment preferably from within 2 to 20 minutes using a composition which includes essentially a sequestering agent, an aryl sulfonic acid and phosphoric acid within the ranges specified.

By this process we obtain etched aluminum and aluminum alloys having lower micro-ohm resistance than those generally produced by prior processes, the process is relatively noncritical with respect to time or temperature of treatment, is free of toxic hazard, and the etched sheets have the property of retaining themselves free of aluminum oxide coating for longer periods of time.

While the particular examples of the composition herein described are well adapted to carry out the objects of the invention, this invention is of the scope set forth in the appended claims.

We claim:

1. A composition for etching aluminum and aluminum alloys preparatory to spot welding, said composition comprising, phosphoric acid, a sequestering agent, and an aryl sulfonic acid having less than 7 alkyl carbon atoms.

2. A composition as in claim 1 in which the sequestering agent is a water soluble aliphatic hydroxy carboxylic acid.

3. A composition as in claim 1 in which the sequestering agent is a water soluble aliphatic hydroxy carboxylic acid selected from the group comprising citric acid, tartaric acid, glucono delta lactone and the ammonium and sodium salts thereof.

4. A composition as in claim 1 in which the sequestering agent is a water soluble aliphatic hydroxy carboxylic acid in proportions of 1/2% to 20%, the aryl sulfonic acid in proportions of 2 1/2% to 25%, and the phosphoric acid in proportions of 11 1/4% to 52 1/2%, the balance being essentially water.

5. A composition as in claim 1 in which the sequestering agent is a water soluble aliphatic hydroxy carboxylic acid in proportions of 1/2% to 20%, the aryl sulfonic acid in proportions of 2 1/2% to 25%, and the phosphoric acid in proportions of 11 1/4% to 52 1/2%, the composition also including ammonia from 1/4% to 5%, the balance being essentially water.

6. A process of etching aluminum and aluminum alloys preparatory to spot welding, which process comprises, subjecting the same to etching with a composition comprising essentially a sequestering agent, an aryl sulfonic acid containing less than 7 alkyl carbon atoms, phosphoric acid, and water.

7. A process of etching aluminum and aluminum alloys preparatory to spot welding, which process comprises, subjecting the same to etching with a composition comprising essentially a sequestering agent, an aryl sulfonic acid containing less than 7 alkyl carbon atoms, phosphoric acid, and water, the sequestering agent being a water soluble aliphatic hydroxy carboxylic acid.

8. A process of etching aluminum and aluminum alloys preparatory to spot welding, which process comprises, subjecting the same to etching with a composition comprising essentially a sequestering agent, an aryl sulfonic acid containing less than 7 alkyl carbon atoms, phosphoric acid, and water, the time of treatment being from 2 to 20 minutes and the temperature of treatment being from 25° to 45° C.

9. A process of etching aluminum and aluminum alloys preparatory to spot welding, which process comprises, subjecting the same to etching with a composition comprising essentially a sequestering agent, an aryl sulfonic acid containing less than 7 alkyl carbon atoms, phosphoric acid, and water, the sequestering agent being in proportion of 1/2% to 10%, the aryl sulfonic acid being in the proportion of 2 1/2% to 12 1/2%, and the phosphoric acid being in the proportion of 11 1/4% to 26 1/4%.

5

10. A process of etching aluminum and aluminum alloys preparatory to spot welding, which process comprises, subjecting the same to etching with a composition comprising essentially a sequestering agent, an aryl sulfonic acid containing less than 7 alkyl carbon atoms, phosphoric acid, and water, the sequestering agent being in proportion of $\frac{1}{2}\%$ to 10%, the aryl sulfonic acid being in the proportion of $2\frac{1}{2}\%$ to $12\frac{1}{2}\%$, the phosphoric acid being in the proportion of $11\frac{1}{4}\%$ to $26\frac{1}{4}\%$, the composition also including from $\frac{1}{4}\%$ to $2\frac{1}{2}\%$ ammonia.

References Cited in the file of this patent

UNITED STATES PATENTS

1,994,500 Boller ----- Mar. 19, 1935 15

2,186,579
2,287,050
2,318,559
2,413,365
2,446,060
2,465,750
2,674,523

6

Dubpernell et al. ----- Jan. 9, 1940
Miller ----- June 23, 1942
Percival ----- May 4, 1943
McCoy ----- Dec. 3, 1946
Pray ----- July 27, 1948
Reid ----- Mar. 29, 1949
McDonald et al. ----- Apr. 6, 1954

FOREIGN PATENTS

France ----- July 11, 1951

OTHER REFERENCES

Prescott et al.: Sequestering Agents in Aluminum Etching, Metal Finishing, October 1953, pp. 65 to 67.
Martel et al.: Metal Chelate Compounds, Prentice-Hall, Inc. 1952, pp. 471 to 473.