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PROCESS FOR THE SURFACE TREATMENT OF ALUMINUM AND ITS ALLOYS

Hargovind N. Vazirani, Stirling, N.J., assignor to Bell Telephone Laboratories, Incorporated, Murray Hill and Berkeley Heights, N.J., a corporation of New York

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12 Claims

ABSTRACT OF THE DISCLOSURE

This is a method for the surface cleaning of aluminum and its alloys which yields an improved adhesive bond between aluminum and organic adhesives, and comprises treatment in a sulfochromate cleaning solution followed by treatment in a reducing solution.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the surface cleaning of aluminum and its alloy by use of a sulfochromate cleaning solution followed by use of a reducing solution.

Prior art

Sulfochromate is well known as a cleaner of aluminum surfaces. For example, in "Surface Treatment and Finishing of Aluminum and Its Alloys," Wernick and Pinner, Third Edition, 1964, Robert Draper, Ltd., page 175, several sulfochromate solutions were recommended to remove corrosion products, unsound surface layers, oxide films and burned-in oil. It was recommended that these treatments be preceded by vapor degreasing or emulsion cleaning to avoid excessive contamination of the sulfochromate solution.

Sulfochromate is also known to be used as a cleaner for the particular purpose of improving adhesive bonds between aluminum structural parts. In this regard, adhesive bonding is preferred over other bonding methods where it is desired to have high tensile strengths, close product dimensional control, and outstanding fatigue and damping capacity. However, there are several limitations involved in adhesive bonding. One limitation is the necessity of joining parts which have closely similar compositions, surface areas, and weight-per-unit length in order to minimize internal stress during thermal cycling. A further limitation is that close tolerances must be obtained on bond line thickness in order not to fall below acceptable tensile shear strengths. Likewise, the amount of overlap of joints must be closely controlled. Such limitations could be somewhat relaxed if higher initial bond strengths were obtainable. A further limitation is that bonds often degrade with time, resulting in bond failures after a certain period of time, the period depending on the stress, temperature, and humidity levels, and being in some cases as short as a few days. It is also important in certain applications to have the highest bond strengths possible as, for example, in electrical equipment racks and enclosures. This invention is a novel process for improving the adhesive bonding characteristics of the surfaces of aluminum and its alloys.

SUMMARY OF THE INVENTION

This is a method for improving adhesive bonding of aluminum and its alloys to organic adhesives which is a surface treatment comprising the prior art steps of preliminary cleaning, rinsing with water, and cleaning with a sulfochromate solution, followed by the novel step of

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treating with a reducing solution, followed by rinsing with water, and drying.

DETAILED DESCRIPTION

This process applies to aluminum and any of its alloys containing at least 50 percent aluminum, but also applies to any alloys which have sufficient aluminum to give rise to surface contamination which is characteristic of pure aluminum surfaces, and is sufficient to interfere substantially with adhesive bonding. Preliminary cleaning is by methods well known in the art and thus the following description of preliminary cleaning is intended to be exemplary and not limiting. Furthermore, preliminary cleaning is not essential to the practice of the invention but is included here because practically desirable, for reasons which are set out below. The first step is degreasing. The purpose of this step is to remove deposits of oils and grease, which is desirable in that it minimizes contamination of subsequent solutions, replacement of which by fresh solutions may be both costly and time-consuming. Degreasing may be carried out with the degreaser in either the liquid or vapor phase. The preferred method is vapor degreasing, because a solvent in the vapor phase is substantially free of contaminants which have already been removed, and thus the process proceeds as if a fresh solution were constantly being applied to the surface of the metal, whereas a liquid retains contaminants which are constantly in contact with the immersed metal surface. Degreasers may be selected from the group consisting of alcohols, ketones and chlorinated solvents, such as trichloroethylene or perchlorethylene. Of these, trichloro- and perchlorethylene are preferred for vapor degreasing because of their boiling points, which are about 187° F. and 234° F., respectively. These boiling points are desirable in that they are sufficiently high to allow substantial condensation on the cooler metal surface before the temperature of the metal approaches that of the vapor, at which time condensation becomes minimal. Perchlorethylene is preferred over trichloroethylene because it is more stable and a more effective remover of baked-in oils and grease. The next step is cleaning with surface active agents, such as alkyl aryl polyether alcohols, and alkaline cleaners, such as sodium metasilicate, trisodium phosphate or sodium borate. It has been found that an aqueous solution containing from 1 to 10 percent sodium metasilicate, from 1 to 10 percent trisodium phosphate, and from 1 to 10 percent of an alkyl aryl polyether alcohol, makes a more effective cleaning solution than any of these aqueous agents alone. This step is carried out at a temperature of from 70° F. to 180° F. for from 1 to 20 minutes. This step is also desirable in that it minimizes contamination of subsequent solutions and is more important than the degreasing step in that it removes substantially more of the surface contaminants. Even this step may be omitted, however, if the surface is substantially free of dirt and grease. It is then preferred to rinse the surface with water to remove any foreign ions or other contaminants left behind by the cleaners. Two other preliminary cleaning methods, either of which may be substituted for either of the above methods, include cleaning in a nitric-phosphoric acid solution, and sandblasting. The acid solution contains from 5 to 20 percent nitric acid, from 60 to 80 percent phosphoric acid, and remainder water. Immersion of the metal is at a temperature of from 70° F. to 150° F., for from 10 to 300 seconds. Sandblasting is done at an air pressure of from 5 to 100 p.s.i., with sand which passes a standard screen from No. 150 to 500. This concludes preliminary cleaning.

The next step is cleaning with a sulfochromate aqueous solution containing from .1 to 10 percent by weight of sodium dichromate or potassium dichromate, or from

.1 to 20 percent by weight of chromic trioxide, and from 10 to 50 percent by weight of sulfuric acid. The time and temperature are not critical and the clean surface can be visually detected, although immersion is usually at a temperature of from 70° F. to 150° F. for from 2 to 20 minutes. The higher amounts of sulfuric acid correspond to shorter immersion times and lower solution temperatures. Too high a concentration of sulfuric acid will attack the surface of the metal too rapidly, taking away substantial amounts of the pure metal. In addition, the solubility of chromate is reduced by too high a sulfuric acid concentration, and keeping the chromate salts in solution is difficult above the ranges specified, which are close to the respective solubility limits of the salts for a 50 percent sulfuric acid content.

If chromate falls below .1 percent and sulfuric acid falls below 10 percent, the solution is not as effective against severe contamination and requires excessively long cleaning times for moderate surface contamination.

The next step is reducing. This should follow immediately after the prior step in order to get optimum performance, but could be postponed as long as one hour. The reason for rapid reducing is not entirely understood, but is essential to optimum results. Any reducing agent which has an oxidation potential of up to 1.30 volt is sufficient, where oxidation potential is with reference to the hydrogen gas-hydrogen ion couple as zero, measured for salts at unit activities in a 1 molal sulfuric solution at a temperature of 25° C. However, it is preferred that the oxidation potential be below 0.80 volt in order for reduction to proceed rapidly. It is also preferred that the reducing agent be stable in an acid medium, of pH between 3 and 4 which is preferred because it prevents precipitation of reduced ions. Above a pH of 4 the solubility of reduced ions becomes too low, and such ions begin precipitating fairly soon after use of the solution is begun, and below a pH of 3 the acidity is such that the beneficial neutralizing of the remaining sulfochromate becomes minimal. Examples of preferred reducing agents are ferrous sulfate, sodium sulfite, sodium bisulfite and sodium thiosulfate. The reducing agent should be present in an amount of from .1 to 10 percent by weight, below which heavy agitation is needed and the benefit of rapid reducing is lost, and above which the concentration of reduced ions becomes so large as to begin precipitating out of solution before the reducer is used up. The reducing step is advantageously carried out at a solution temperature of from 70° F. to 150° F., for up to 60 seconds, and is preferably commenced within 10 seconds after treatment with the sulfochromate solution. The next step is rinsing and since this is the last step before adhesive bonding, rinsing with deionized water is preferred to insure that every possible contaminant is removed. Air drying is satisfactory. In this condition the material is ready for adhesive bonding. Since the method described is essentially directed toward improving bonding by improving the surface of the metal, it is not limited for use with certain adhesives, but is useful in preparing surfaces for application of any organic adhesive bonding materials, such as: epoxy and modified epoxy resins, such as nylon modified epoxy resins; nitrile rubber phenolics; polyvinyl butyral; and polyvinyl formals.

Likewise, the described method is not limited for use in preparing two or more similar metal surfaces for joining by means of organic adhesive materials, but applies also to preparing one or more metal surfaces, which are similar or dissimilar, for joinder, two or more of which are to be joined.

Example 1.—A sample of aluminum 2024-T3, .1 inch thick, was vapor degreased with trichloroethylene and cleaned in a solution containing sodium metasilicate and an alkyl aryl polyether alcohol for 15 minutes at 150° F. It was then rinsed in warm tap water for 5 minutes at 160° F. It was then acid-cleaned in a mixture of sodium dichromate, concentrated sulfuric acid and water in the

ratio of 1:10:30 by weight for 5 minutes at 140° F. It was then immersed in a .1 normal solution of ferrous sulfate in a .1 percent solution of sulfuric acid in distilled water for ½ minute. It was then rinsed in tap water for 5 minutes at 55° F., then in deionized water for ½ minute and dried in an oven for ½ hour at 140° F. It was then bonded with another identically treated sample by means of a modified epoxy resin, using a standard ½ inch lap joint and a bond thickness of 3 mils, as called for by ASTM procedure D-1002. Fatigue was then measured by observing the time to fail when a static load was applied. The time for failure when a static load of 4500 p.s.i. was applied in an ambient atmosphere of 95° F. and 90 percent relative humidity was 57 days, as compared to 11 days when the reducing step was omitted.

Example 2.—A sample of aluminum 2024-T86, .063 inch thick was used. It was vapor degreased with trichloroethylene, acid-cleaned in a solution whose composition was identical to that in Example 1, for 8 minutes at 150° F., and then reduced and rinsed as in Example 1. The surface water was then blown off with forced air, and the sample was oven-dried at 150° F. for 10 minutes. Tensile strength was measured according to ASTM procedure D-1002. A tensile shear value of 7835 p.s.i. was obtained as compared with a value of 6874 p.s.i. when the reducing step was omitted.

The invention has been described with reference to particular embodiments thereof, but it is intended that variations therefrom which basically rely on the teachings of the invention are to be considered as within the scope of the description and the appended claims.

While the examples have been limited to the illustration of the joinder of particular aluminum alloys and adhesives for the sake of uniformity of testing procedures, it is to be understood that the invention is not limited to the use of such alloys and adhesives, nor to the joinder of similar metals and alloys.

What is claimed is:

1. A method for cleaning a surface comprising a material selected from the group of surfaces consisting of aluminum and its alloys containing at least 50 percent aluminum, comprising the step of contacting said surface with a first aqueous solution containing dichromate ions and sulfate ions, characterized by the step of contacting the surface with a second aqueous solution containing a reducing agent having an oxidation potential of up to 1.30 volt subsequent to the step of contacting the surface with the said first solution.

2. The method of claim 1 in which the pH of said second solution is between 3 and 4.

3. The method of claim 1 in which the oxidation potential of the reducing agent is of a value up to 0.8 volt.

4. The method of claim 3 in which said second solution consists essentially of an aqueous solution of from 0.1 to 10 percent by weight of a material selected from the group consisting of ferrous sulfate, sodium sulfite, sodium bisulfite, and sodium thiosulfate.

5. The method of claim 1 in which the step of contacting said surface with said second solution is carried out at a temperature of from 70° F. to 150° F. for up to 60 seconds.

6. The method of claim 1 in which the step of contacting said surface with said second solution is carried out within one hour after the step of contacting the surface with said first solution.

7. The method of claim 6 in which the step of contacting said surface with said second solution is carried out within ten seconds after the step of contacting the surface with said first solution.

8. The method of claim 1 in which said first solution contains a member selected from the group consisting of sodium dichromate, potassium dichromate and chromic trioxide, sodium dichromate and potassium dichromate being present in an amount of from 0.1 to 10 percent by weight and chromic trioxide being present in an

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amount of from 0.1 to 20 percent by weight, and contains from 10 to 50 percent by weight of concentrated sulfuric acid.

9. The method of claim 1 in which the step of contacting said surface with said first solution is carried out at a temperature of from 70° F. to 150° F. for from 2 to 20 minutes.

10. The method of claim 1 in which the step of contacting said surface with said first solution is preceded by preliminary cleaning.

11. The method of claim 1 in which the treatment of said surface is followed by adhesive bonding of an organic adhesive material to said surface for the purpose of bonding it to one or more other metal surfaces.

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12. Product produced by the method of claim 1.

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ALFRED L. LEAVITT, Primary Examiner
J. A. BELL, Assistant Examiner

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