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METHOD OF DEOXIDIZING AN ALUMINUM SURFACE

Nelson J. Newhard, Jr., Oreland, and James H. Thirsk, Meadowbrook, Pa., assignors to Amchem Products, Inc., a corporation of Delaware

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This invention relates to the art of treating metallic surfaces and is particularly concerned with the provision of an improved metal treating material and an improved method for deoxidizing surfaces of aluminum. For purposes of exemplification, the following disclosure will be directed to the treatment of aluminum and in this connection it should be understood that the word "aluminum" as used herein includes not only essentially pure aluminum but also such alloys thereof in which aluminum is the principal ingredient.

As is well known, upon exposure to air, aluminum surfaces tend to oxidize. Such an oxidized surface presents certain problems when it is desired to apply to the surface a corrosion resistant coating by treating it with known acidic solutions consisting principally of hexavalent chromium and fluorides with or without special additives for special purposes. For instance, if a uniform coating is to be produced by employing such an acidic solution, it is necessary to deoxidize the aluminum surface prior to subjecting it to the action of the coating solution. Unfortunately, the deoxidizing solutions heretofore employed, while removing the oxide film tend to objectionably etch the surface of the aluminum and, for some reason not fully understood by the inventors, quite often lead to an impairment of the corrosion resistance of the subsequently coated surface when contrasted with the corrosion resistance that can be secured by coating the surface without deoxidizing it.

We have found it possible to deoxidize aluminum surfaces which, in whole or in part, bear an oxide film without producing a heavy etch and without any apparent impairment in the corrosion resistance of the subsequently coated surface.

With the foregoing in mind, the principal objects of our invention may be stated as involving the provision of an improved metal treating material and a novel method by means of which an aluminum surface may be satisfactorily deoxidized without producing thereon a heavy etch and without impairment of the corrosion resistance of the surface when subsequently coated by the familiar acidic solutions of the art which consist primarily of hexavalent chromium and fluorides.

Our improved material consists essentially of an acid aqueous solution having a pH of between 0.5 and 1.0 and containing as its principal and essential ingredients hexavalent chromium and dissolved fluoride in certain proportions as will appear below.

With respect to the content of hexavalent chromium in the solution, we have found that this should lie between 10 and 100 grams per liter. Below 10 grams per liter the bath may tend to produce a conversion coating on the surface of aluminum which will interfere with the action of the subsequently applied regular coating producing bath. In general, we have found that optimum results have been secured where the content of hexavalent chromium per liter ranges somewhere between 20 and 30 grams per liter. The source of the hexavalent chromium appears to make little or no difference. For in-

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stance, it may be introduced as chromic acid or soluble salts thereof, such as potassium dichromate, ammonium dichromate, ammonium chromate, sodium chromate, etc.

The amount of fluoride present in the bath is critical.

5 The fluoride concentration must be made up and maintained at such a level that its activity as measured by the ability of a bath to etch, i. e., as measured by weight loss, a piece of lime-soda glass will be between the fluoride activity of a solution corresponding to A

10 Chromic acid-----grams-- 30
Hydrofluoric acid (48.8%)-----milliliters-- 0.25
Water, to make 1 liter.

and B

15 Chromic acid-----grams-- 30
Hydrofluoric acid (48.8%)-----milliliters-- 0.25
Water, to make 1 liter.

Should the fluoride activity of the bath be less than the activity of Solution A the bath will not deoxidize properly. Conversely, if the bath activity is greater than the activity of solution B, there will be a tendency of the bath to undesirably etch the aluminum surface. In order to determine the activity of the bath, it has been found 25 desirable and convenient to use ordinary commercial microscope slides of lime-soda glass. It has been found convenient to measure the activity of the bath by heating a convenient volume to approximately 120° F. and immersing enough microscope slides as is necessary to secure 26 square inches of surface in the solution for two 30 hours and measuring the weight loss of the glass at the end of the two hour immersion. Obviously, the measurements with solutions A and B are made under similar conditions.

35 The source of fluoride may be hydrofluoric acid, simple salts such as sodium fluoride, ammonium fluoride, potassium fluoride, etc., or complex fluoride acid, such as fluoboric, fluosilicic or their soluble salts, such as sodium silica fluoride, potassium fluosilicate, ammonium silica 40 fluoride, etc. As a general rule, we prefer to use the complex fluorides as a source of fluoride because when so doing optimum results seem to be achieved.

The pH of the bath must be between 0.5 and 1.0 and, if desired, this pH may be secured in preparing the operating solution by adjusting the type and proportionate 45 content of fluoride and chromate so that the desired degree of acidity is secured. However, where this is not done the acidity of the bath may be secured by addition of a small amount of nitric acid. In general, large quantities of sulfate and chloride ions are to be avoided.

50 Insofar as temperatures are concerned, the solutions of the present invention may be used at practically any temperature although, in most instances, we prefer to employ the temperature of the room in which the operation is carried out, say, somewhere between 50 and 90° 55 F. The usual rule applies, namely, that the time of treatment may be shortened by elevation of the temperature or lengthened by a lowering of the temperature although between 50 and 90° F., as stated, the time element is not of too much importance. Within that range, 60 most alloys of aluminum can be satisfactorily deoxidized in from one to two minutes unless the surface bear an excessively heavy oxide film when as much as two to four minutes may be required.

Suitable but not necessarily limiting examples of useful 65 aluminum deoxidizing baths are as follows:

Example No. 1

Grams
Chromic acid----- 22
Potassium dichromate----- 7.5
70 Diammonium silica fluoride----- 0.75
Water, to make 1 liter.

Example No. II

Chromic acid.....	Grams
Hydrofluoric acid, 100% basis.....	40
Water, to make 1 liter.....	0.12

Example No. III

Potassium dichromate.....	Grams
Potassium zirconium fluoride.....	90
Water, to make 1 liter.....	1.2

NOTE.—The pH of this bath is adjusted to 0.85 with nitric acid.

In employing our improved solutions for the deoxidization of aluminum surfaces, the metal should first be cleaned and this cleaning can be accomplished by any conventional means such as the use of a solvent, a mild alkali, etc. After the cleaning operation the surface of the metal is brought into contact with the deoxidizing solution either by spraying or flowing the solution over the surface of the metal or by dipping the metal into a bath of the solution. The solution should be allowed to act upon the surface until deoxidization of the surface has occurred which may take place in a period of from approximately one to four minutes, as indicated above, where the temperature of the bath lies between 50 and 90° F.

After the deoxidizing action has been completed the metal is removed from further contact with the solution and is thereafter given a protective coating with any of the conventional fluoride-chromate coating solutions familiar to the art, as mentioned near the beginning of this disclosure.

We claim:

1. The method of treating an aluminum surface which

consists in subjecting the surface to the action of an aqueous acid solution consisting essentially of hexavalent chromium and fluoride, the quantity of hexavalent chromium being from 10 to 100 grams per liter and the quantity of fluoride being sufficient to give a bath activity at least as great as a solution of:

Chromic acid.....	grams..	30
48.8% hydrofluoric acid.....	milliliters..	0.25
Water, to make 1 liter.....		

but having no more activity than a solution of:

Chromic acid.....	grams..	30
48.8% hydrofluoric acid.....	milliliters..	1
Water, to make 1 liter.....		

the pH of the solution being between 0.5 and 1.0, and the treatment being continued until the surface is deoxidized.

2. The method of claim 1 wherein the time of treatment is from 1 to 4 minutes with the temperature of the solution being from 50 to 90° F.

3. The method of claim 1 wherein the content of hexavalent chromium in the solution is from 20 to 30 grams per liter.

4. The method of claim 3 in which the content of fluoride is supplied from the class of fluorides which consists of complex fluoride acids and soluble salts thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,867,514

January 6, 1959

Nelson J. Newhard, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 16, for "milliliters 0.25" read -- milliliters 1.0 --;
line 61, for "surface" read -- surfaces --.

Signed and sealed this 14th day of April 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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