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[54] ETCHING OF ALUMINUM BASE ALLOYS

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[51] **Int. Cl.**.....**C23g 1/22**, C23g 1/26

[58] **Field of Search**.....252/135, 156, 157, 192, 79.5; 156/22, 23, 21

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[57] **ABSTRACT**

Treating aluminum base alloys with a cleaning-etching solution made up of a caustic and a soluble pyro- or polyphosphate to inhibit formation of an undesirable film thereon.

4 Claims, No Drawings

ETCHING OF ALUMINUM BASE ALLOYS

BACKGROUND OF THE INVENTION

This invention relates to use of a cleaning-etching solution on aluminum base alloys. More particularly, it relates to an improved cleaning-etching step for aluminum base alloys which results in significant etching without producing an undesirable film on the alloy. By aluminum base alloys I mean aluminum and alloys of aluminum containing at least 50 percent by weight aluminum.

A conventional method for production of paint-coated aluminum or aluminum base alloys for various uses, for example, building panels, beverage cans, or the like, includes generally the steps of cleaning the aluminum, rinsing, chemically treating with what is conventionally referred to as a phosphate or chromate conversion coating, rinsing and then applying the appropriate paint or lacquer, for example, a vinyl organosol, which may be cured, for example, in an oven or other appropriate device for application of heat, such as an electron beam (electromagnetic) curing system. In such a process, the alkaline cleaning step may be performed by using cleaners such as tribasic sodium phosphate or sodium carbonate. However, such cleaners or etchants sometimes result in an etching which is too mild. Furthermore, on occasions they produce an undesirable film which has to be removed prior to the conversion coating step. Accordingly, development of a cleaning-etching solution which will produce significant etching without causing an undesirable film by reaction in some way with the alloy being treated represents a highly desirable result.

SUMMARY OF THE INVENTION

It is accordingly one object of this invention to produce an improved cleaning-etching step for use on aluminum base alloys. A further object is to develop a process for treating aluminum base alloys with a cleaning-etching solution which will substantially prevent formation of an undesirable film thereon while at the same time promoting the adhesion thereto of subsequent conversion-type and/or lacquer or paint-type coatings. Further objects will be apparent hereinafter from the description and claims which follow.

In its broader aspects my invention involves treating aluminum base alloys, especially aluminum base alloys with a content of magnesium, with a caustic solution which contains a soluble pyro- or polyphosphate. The pyro- or polyphosphate is preferably alkaline. Preferred alkaline pyro- or polyphosphates are ammonium, lithium, sodium and potassium pyro- or polyphosphates. Most effective according to my invention are the sodium and potassium pyro- or polyphosphates. Especially useful are the tetrapotassium and tetrasodium pyrophosphates and the sodium and potassium tripolyphosphates.

In addition to causing the desirable etching and cleaning action, the pyro- or polyphosphate, in conjunction with the caustic, substantially prevents formation of any undesirable film on the surface of the aluminum base alloy being treated therewith. Use of this particular etching and cleaning solution also promotes adhesion of subsequently applied phosphate and chromate films and also of paints or lacquers, for example, the phosphates used in conversion coatings and lacquers such as vinyl organosols.

While I do not wish to be bound by any particular theory as to how the caustic poly- or pyrophosphate solution works according to my invention, when applied to aluminum base alloys, particularly aluminum base alloys containing magnesium, it appears that the substance in the alloy which might otherwise react with the etching-cleaning solution to form an insoluble precipitate is solubilized, in the case of an aluminum base alloy containing magnesium, the magnesium. This is believed brought about by association of the highly charged pyro- or polyphosphate anion with a metal cation through

electrostatic attraction by forming covalent bonds with certain polyvalent ions. It appears that the appropriate excess of pyro- or polyphosphate ion in the caustic solution produces a soluble product which does not form an undesirable film on the surface of the alloy being treated. Apparently the combination of ionic bonding ties up certain polyvalent metal ions in the form of soluble phosphate complexes.

The treating solution must be caustic. Preferred caustic solutions are those containing sodium hydroxide, potassium hydroxide, tribasic sodium phosphate (Na_3PO_4) and sodium carbonate (Na_2CO_3).

The treating solution for best results contains from about 0.1 to about 5 percent by weight caustic material and from about 1 to about 30 percent by weight pyro- or polyphosphate. The preferred ranges for these two components are respectively from about 0.5 to about 1 percent by weight and from about 2.0 to about 5.0 percent by weight. In addition to the caustic material and the soluble pyro- or polyphosphate, the treating solution may also contain one or more emulsifying agents, one or more chelating agents, and one or more foam-control agents. Preferably these agents are not contained in a total amount exceeding about 5 percent Examples of such agents are polyoxyethylene-polyoxypropylene glycol, from about 0.1 to about 0.2 percent being preferred, polyoxyethylene lauryl ether, from about 0.2 to about 0.4 percent being preferred, and sodium gluconate, from about 0.2 to about 0.5 percent being preferred.

Representative aluminum base alloys which have shown best results in having the undesirable film removed therefrom according to my invention are aluminum-magnesium alloys especially those of the 5000 series such as 5052, 5082, 5086 and 5182 (Aluminum Association number designation). Aluminum-magnesium-manganese alloys such as 3004 and 3005 are similarly responsive to treatment with caustic pyro- and polyphosphates according to my invention. Other alloys which may be treated according to my invention are heat-treatable aluminum-magnesium-silicon alloys such as 6061. Additional alloys which do not contain appreciable amounts of magnesium such as 1100 and 3003 may also be treated according to the invention.

According to the process of this invention the aluminum base alloy to be treated is subjected to treatment according to any standard fashion, for example, by conventional spraying, dipping or the like, preferably for from 2 to 60 seconds and at a temperature of from about 120° to 180° F.

One of the principal advantages of my invention is that the soluble pyro- or polyphosphate treating solution functions simultaneously as a cleaning and etching solution and also as a solution which removes any undesirable film from the aluminum base alloy being treated. By my invention I eliminate the necessity for an intermediate acid treatment heretofore generally required to obtain a surface properly conditioned for accepting conversion coating or subsequent lacquer or paint films. A further advantage is that the soluble pyro- and polyphosphates used according to my invention also possess emulsifying, peptidization and water-conditioning properties necessary and desirable in a cleaning operation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are illustrative of my invention and some of its advantages over the prior art.

EXAMPLE 1

This example is illustrative of the prior art formation of an undesirable film during the etching step when the cleaner/etchant is a sodium hydroxide solution with no soluble pyro- or polyphosphate additive. The following table gives the results of etching various aluminum base alloys, reporting the weight loss due to etching and the amount of a reaction product film formed by the etching step.

TABLE I.—ETCHING VARIOUS ALUMINUM ALLOYS IN SODIUM HYDROXIDE SOLUTION

Alloy	Cleaner/etchant, percent by wt. in solution	Immersion time, sec.	Temp., ° F.	Weight loss due to etching, mg./ft.²	Reaction product film [1], mg./ft.²
1100	1½% NaOH	30	140	290	4.8
3003	1½% NaOH	30	140	244	7.2
6061	1½% NaOH	30	140	298	10.2
5052	1½% NaOH	30	140	309	47.4

[1] Determined by stripping 15 seconds in 1:1 nitric acid at ambient temperature.

EXAMPLE 2

This example illustrates etching an aluminum base alloy with various additional illustrative caustic solutions used as cleaner/etchants according to the prior art. Table II, which follows, reports results from use of the specified cleaner/etchants for the time and at the temperature indicated.

TABLE II.—ETCHING ALUMINUM-MAGNESIUM ALLOY 5052

Cleaner/etchant, percent by wt. in solution	Immersion time, sec.	Temp., °F.	Weight loss due to etching, mg./ft.²	Reaction product film, [1] mg./ft.²
1% NaOH	30	140	251	34.2
1% KOH	30	140	268	21.0
4% Na_3PO_4	30	140	133	8.4
1% Na_3PO_4	30	140	46	6.0
1% Na_2CO_3	30	140	33	5.4

[1] Determined by stripping 15 seconds in 1:1 nitric acid at ambient temperature.

EXAMPLE 3

This example is illustrative of use of soluble pyro- and polyphosphates in caustic pyro- or polyphosphate solution according to the instant invention. The following table (III) shows the results of etching a typical aluminum base alloy, one containing magnesium, Aluminum Association Alloy 5052.

TABLE III.—ETCHING ALUMINUM-MAGNESIUM ALLOY 5052

Cleaner/etchant, percent by wt. in solution	Time, sec.	Temp., ° F.	Weight loss due to etching, mg./ft.²	Reaction product film mg./ft.²
1% NaOH plus 3% $Na_4P_2O_7$ (tetrasodium pyrophosphate)	30	140	268	4.2
1% KOH plus 3% $Na_4P_2O_7$	30	140	251	3.0
1% KOH plus 3% $Na_5P_3O_{10}$ (sodium tripolyphosphate)	30	140	275	4.2
1% Na_3PO_4 plus 3% $Na_4P_2O_7$	30	140	108	1.2
1% Na_3PO_4 plus 3% $Na_5P_3O_{10}$	30	140	107	1.2
1% Na_2CO_3 plus 3% $Na_4P_2O_7$	30	140	36	0.6

EXAMPLE 4

This example illustrates use of representative concentrations of caustic poly- or pyrophosphate solutions according to the invention. Treatment was for 30 seconds at 140° F in each instance. Results are shown in Table IV, which follows. The alloy treated was a magnesium-containing aluminum base alloy.

TABLE IV

SUMMARY OF DATA - NaOH-TSPP (TETRASODIUM PYROPHOSPHATE) SOLUTIONS 30-SECOND IMMERSION AT 140°F

Percent by weight in solution NaOH	TSPP	Weight Loss due to etching mg./Ft.²	Reaction Product Film mg.Ft.²
	3.0	4.2	0.6
0.5	0	117.6	18.6
1.0	0	222.6	34.8
2.0	0	280.8	41.4
5.0	0	709.2	69.0
0.1	3.0	48.6	0.6
0.2	3.0	80.4	1.8
0.25	3.0	120.0	1.2
0.3	3.0	108.0	1.8
0.4	3.0	138.6	1.8
0.5	3.0	157.8	3.0
0.75	3.0	168.6	2.4
1.0	3.0	180.0	4.2
0.5	1.0	73.8	2.4
0.5	2.0	130.8	2.4
0.5	3.0	164.4	2.4
0.5	4.0	181.8	2.4
0.5	5.0	188.4	2.4
0.25	1.5	75.6	1.2
0.5	3.0	139.2	1.2
0.75	4.5	193.8	2.4
2.0	2.0	307.2	7.2
2.0	4.0	317.4	7.2
2.0	6.0	355.2	7.2
2.0	8.0	371.4	4.8
2.0	10.0	369.0	3.6
2.0	12.0	369.0	3.6
5.0	15.0	675.6	6.0
5.0	20.0	652.2	9.6
5.0	25.0	624.0	12.6
5.0	30.0	589.8	15.0

EXAMPLE 5

The following table (V) illustrates treatment of other aluminum base alloys according to the process of this invention as well as with a conventional prior art caustic solution.

TABLE V

REACTION PRODUCT FILM

Alloy	Cleaner/Etchant (30-second) immersion at 140°F) 1½% Sodium Hydroxide	3% TSPP + 1 ½% NaOH
1100	4.8 mg/ft²	4.0 mg/ft²
6061	10.2 mg/ft²	9.0 mg/ft²
3003	2.4 mg/ft²*	2.4 mg/ft²*

* 1% sodium hydroxide instead of 1 ½%

While the invention has been described in terms of preferred embodiments, the claims appended hereto are intended to encompass all embodiments which fall within the spirit of the invention.

Having thus described my invention and certain preferred embodiments thereof, I claim:

1. In a process for etching an aluminum base alloy, the improvement comprising treating said alloy with a solution consisting essentially of from about 0.1 to about 5 percent by weight caustic, from about 1 to about 30 percent by weight soluble pyro- or polyphosphate salt and not exceeding about 5 percent by weight of at least one substance from the group consisting of emulsifying agents, chelating agents and foam control agents at from about 120° F to about 180° F, thereby through a solubilizing action minimizing formation of a reaction product film on said alloy.

2. The improvement of claim 1 wherein the caustic is sodium hydroxide, potassium hydroxide, tribasic sodium phosphate, or sodium carbonate and the soluble pyro- or polyphosphate is an alkaline pyro- or polyphosphate.

3. The improvement of claim 1 wherein the caustic is sodium hydroxide, potassium hydroxide, tribasic sodium phosphate, or sodium carbonate and the soluble pyro- or

polyphosphate is a tetrapotassium or tetrasodium pyrophosphate or sodium or potassium tripolyphosphate.

4. The improvement of claim 1 wherein the aluminum base alloy contains magnesium, the caustic is sodium hydroxide, potassium hydroxide, tribasic sodium phosphate or sodium carbonate and the soluble pyro- or polyphosphate is tetrasodium pyrophosphate, sodium tripolyphosphate, tetrapotassium pyrophosphate or potassium tripolyphosphate.

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