United States Patent Office 3,692,583 Patented Sept. 19, 1972

3,692,583

DESMUTTING ETCHED ALUMINUM ALLOYS

Paul R. Mucenieks, Trenton, and Dirk J. Muyskens, Princeton Junction, N.J., assignors to FMC Corporation, New York, N.Y.

No Drawing. Filed Mar. 1, 1971, Ser. No. 119,885
Int. Cl. C23g 1/22
U.S. Cl. 134—3 4 Claims

ABSTRACT OF THE DISCLOSURE

Aluminum alloys which are covered with an insoluble smut due to alkali or other treatment are cleaned and brightened by aqueous compositions containing mineral acids and peroxydiphosphate ions.

BACKGROUND OF THE INVENTION

When aluminum alloys are etched with aqueous alkali, the resultant etched surfaces carry on their surfaces a black smut which contains the alkali-insoluble components of the alloy (e.g. copper, magnesium, silicon). Smuts which are very similar in appearance are formed by chemical exchange, electroplating and even by simple boiling with water alone. These smuts are conventionally removed by an aqueous acid containing an oxidizing agent such as nitrate, dichromate, persulfate or hydrogen peroxide. However, each one of these oxidizing agents has at least one major disadvantage. Nitrates evolve corrosive toxic fumes; dichromates are toxic, deposit a film and are difficult to dispose safely; hydrogen peroxide attacks the aluminum; and persulfate acts very slowly, and attacks the metal unless carefully monitored.

STATEMENT OF THE INVENTION

We have discovered that smut can be removed from aluminum alloy surfaces which are smutted as a result of treatment with an aqueous treating bath rapidly and effectively, and without damage to the aluminum, to produce bright surfaces, by using an aqueous solution containing enough mineral acid to get a pH of about 3.0 or lower, and preferably 0.2 to 0.7 (about 2 to 60% by weight of acid, preferably 10 to 30%), and 0.1 to 10% (and preferably 1 to 54%) by weight of a soluble peroxydiphosphate (calculated as potassium peroxydiphosphate). The solutions will clean and brighten typical caustic-etched or otherwise smutted surfaces in a short time, of the order of a few seconds to a few minutes, at temperatures from about ambient to the boiling point, preferably 40 to 60° C.

DETAILED DESCRIPTION OF THE INVENTION

In practicing our invention, we can use any mineral acid which is not oxidized by the peroxydiphosphate ion. Of the common mineral acids, sulfuric acid is the cheapest and optimum; phosphoric acid may also be used. Hydrochloric acid is readily oxidized, and should not be used; nitric acid is both reactive with the peroxydiphosphate and fume-producing and should be avoided.

The peroxydiphosphate ion may come from any soluble peroxydiphosphate, but is preferably the potassium salt $K_4P_2O_8$, since this is commercially available.

We use about 0.1 to 10% of peroxydiphosphate calculated as $K_4P_2O_8$. As the amount of this oxidizer is increased, desmutting time is reduced. Optimum results are obtained in the 1 to 5% range; below 1%, times tend to be longer than desirable, and above 5% the increase in speed is not sufficient to make larger quantities economic.

Acid concentrations vary from about 2 to 60% by weight, preferably 10 to 30%. The concentration should be high enough to give a pH of not higher than about

3.0, with optimum speed being obtained in the range of 0.2 to 0.7.

The concentration and time needed will of course vary with the depth of smut deposit on the aluminum, with higher concentration and greater time being required to treat heavier deposits.

The compositions may contain wetting agents to improve wetting of the surface, surface-treating agents such as fluoride, and even organic solvents if they are desired to treat the metal surface.

The cleaning reaction will go at ambient temperatures or lower, but is facilitated by mild heat. About 40 to 60° C. is the preferred temperature range. We prefer to avoid higher temperatures because they produce uncomfortable working conditions, but temperatures up to the boiling point may be used without interfering with the cleaning.

The process produces bright, smooth surfaces, free of residual films, in very short time, from as low as about 2 seconds under optimum conditions to about 5 minutes with heavy deposits and weaker solution. Other advantages are lack of attack on the metal surface, and absence of toxic or corrosive fumes. The solution is nontoxic, and can readily be sewered after filtering out and neutralizing.

SPECIFIC EXAMPLES OF THE INVENTION

The following specific examples of the invention are given by way of illustration, and not by way of limitation.

EXAMPLES 1, 2 AND 3

The tests were made with 2024 alloy (4.5% copper, 0.6% manganese, 1.5% magnesium, balance alumiuum). The panels were etched at 60 to 70° C. with an 18% sodium hydroxide solution for 10 to 20 minutes until they were covered with a black coating, rinsed and treated with the test solutions at 25 and 50° C. The test solutions were the following:

Solution A—10 ml. concentrated H_2SO_4 2.3 g. H_2O_2 (as 100%) water to make 100 ml.

Solution B—10 ml. concentrated H_2SO_4 2.5 g. $Na_2Cr_2O_7$ water to make 100 ml.

Solution C—10 ml. concentrated H_2SO_4 2.5 g. $(NH_4)_2S_2O_8$ water to make 100 ml.

Solution 1—10 ml. concentrated H_2SO_4 2.5 g. $K_4P_2O_8$ water to make 100 ml.

Nitrate containing solutions were excluded from the test because of heavy evolution of nitric oxides.

EXAMPLE 1

Results of tests at 50° C. for 10 seconds

Solution A—Hydrogen peroxide containing solution removed the black coating incompletely, leaving grey spots.

Solution B—Chromate containing solution removed the black deposit, however, the surface remained dull and yellowish.

Solution C—Peroxydisulfate containing solution removed the black deposit incompletely. A layer of red deposit remained.

Solution 1—Peroxydiphosphate containing solution removed the smut completely, leaving a bright surface.

EXAMPLE 2

Results of tests at 25° C. for 10 seconds

Solution A—Hydrogen peroxide containing solution removed the black deposit, but the surface remained dull.

Solution B—Chromate containing solution did not remove the copper deposit completely. The deposit was removed when the surface was rinsed with running water.

Solution C—Peroxydisulfate containing solution did not remove the smut. The deposit was not removed even by rubbing the surface after rinsing.

Solution 1—Peroxydiphosphate containing solution did not remove the deposit completely. The deposit was removed by rubbing slightly after rinsing.

EXAMPLE 3

Results of tests at 25° C. for 1 minute

Solution A—Hydrogen peroxide containing solution removed the deposit, surface was coated with reddish deposit.

Solution B—Chromate containing solution removed the deposit, surface was coated with heavy yellowish film.

Solution C—Peroxydisulfate containing solution did not remove the deposit. The deposit was removed when the surface was rinsed with running water.

Solution 1—Peroxydiphosphate containing solution removed the smut completely, leaving a bright surface.

EXAMPLE 4

Tests were made with 6063 alloy, nominal composition of which is 0.4% silicon, 0.7% magnesium, balance aluminum. Panels were etched at 60 to 70° C. with 8% NaOH solution for 10 minutes, until they were covered with black coating, rinsed and treated with the test solutions of Example 1 at 50° C. for 20 seconds.

Solution A—Hydrogen peroxide containing solution removed the black coating incompletely, leaving a dark film.

Solution B—Chromate containing solution removed the black coating incompletely, leaving a dark film.

Solution C—Peroxydisulfate containing solution removed the black deposit incompletely, leaving grey spots.

Solution 1—Peroxydiphosphate containing solution removed the smut completely, leaving a clean surface.

EXAMPLE 5

Tests were made with 6061 alloy, nominal composition of which is 0.6% silicon, 0.25% copper, 1% magnesium, 0.25% chromium, balance aluminum; etching and treating as in Example 4.

Solution A—Hydrogen peroxide containing solution removed black coating, however some dark film was left.

Solution B—Chromate containing solution removed the black deposit, however the surface remained covered with a yellowish grey film.

Solution C—Peroxydisulfate containing solution removed the deposit incompletely, surface remained with grey spots.

Solution 1—Peroxydiphosphate containing solution removed the black coating completely, leaving a clean and bright surface.

EXAMPLE 6 AND 7

The test solutions were the following:

Solution D—18 g. H_3PO_4 (as 100%) 2.5 g. H_2O_2 (as 100%) water to make 100 ml.

Solution E—18 g. H_3PO_4 (as 100%) 2.5 g. $Na_2Cr_2O_7$ water to make 100 ml.

Solution F—18 g. H_3PO_4 (as 100%) 2.5 g. $(NH_4)_2S_2O_8$ water to make 100 ml.

Solution 2—18 g. H_3PO_4 (as 100%) 2.5 g. $K_4P_2O_8$ water to make 100 ml.

Panels were etched at 60 to 70° C. with 8% NaOH solution for 10 minutes, rinsed and treated with test solution at 50° C. for 20 seconds.

EXAMPLE 6

Tests were made with 5254 alloy, nominal composition of which is 3.5% magnesium, 0.25% chromium, balance aluminum. After etching with sodium hydroxide, this alloy had a dull greyish-white film.

Solution D—Hydrogen peroxide containing solution removed the film, leaving a shiny surface.

Solution E—Chromate containing solution removed the film, however the surface remained with yellow-grey spots.

Solution F—Peroxydisulfate containing solution removed the film, however the surface remained dull.

Solution 2—Peroxydiphosphate containing solution removed the film, leaving a shiny surface superior to that obtained with hydrogen peroxide.

EXAMPLE 7

Tests were made with 1060 alloy (99.60% aluminum, 0.25% silicon, 0.35% iron, 0.05% copper, 0.03% manganese, 0.03% magnesium, 0.05% zinc, 0.03% titanium). After boiling with tap water for 8 hours, the surface was covered with a black deposit. The cleaning solutions were applied at 50° C. for 20 seconds.

Solution D—Hydrogen peroxide containing solution did not remove the coating.

Solution E—Sodium chromate containing solution did not remove the coating.

Solution F—Ammonium persulfate containing solution removed the coating partially.

Solution 2—Peroxydiphosphate containing solution removed the black deposit completely.

Obviously, the examples can be multiplied indefinitely without departing from the scope of the invention as defined in the claims.

What is claimed is:

1. The method of desmutting an aluminum alloy which has been treated with an aqueous liquid and carries on its surface a resultant black smut, which comprises heating the smutted alloy with an aqueous solution containing in solution from 0.1 to 10% of a peroxydiphosphate calculated as $K_4P_2O_8$ equivalent, and a mineral acid which is not attacked by the peroxydiphosphate, in quantity sufficient to get a pH of 3.0 or less, for a time sufficient to desmut the alloy.

2. The method of claim 1, in which the acid is sulfuric or phosphoric.

3. The method of claim 2, in which the amount of acid used is sufficient to produce a pH of 0.2 to 0.7, and the peroxydiphosphate is from 1 to 5%.

4. The method of claim 1, in which the aqueous heating bath is a caustic etch.

References Cited

FOREIGN PATENTS

1,809,799 7/1969 Germany.

ROBERT F. BURNETT, Primary Examiner

R. J. ROCHE, Assistant Examiner

U.S. Cl. X.R.

156—22, 23; 134—41; 252—79.1, 79.2