

UNITED STATES PATENT OFFICE

2,332,487

SURFACE TREATMENT FOR ARTICLES OF MAGNESIUM AND ALLOYS THEREOF

William S. Loose, Midland, Mich., assignor to
The Dow Chemical Company, Midland, Mich.,
a corporation of Michigan

No Drawing. Application November 14, 1938,
Serial No. 240,343

7 Claims. (Cl. 204—29)

The invention relates to methods of providing a protective coating upon articles of magnesium and its alloys.

It has been proposed to produce protective coatings upon articles of magnesium and its alloys by immersion in an aqueous solution of a soluble fluoride, such as hydrofluoric acid, potassium fluoride, and the like, the article being preferably made the anode, whereby a deposit or film of magnesium fluoride is formed on the article. I have found that, when this process is carried out with acid fluoride solutions, the coatings produced are subject to considerable deterioration which permits corrosion to occur of the underlying metal. This is due, according to my observations, to the presence in the deposited coating of dilute hydrofluoric acid formed by the rinsing operation following the treatment and this acid readily attacks magnesium. I have now found that by treating the article with an aqueous solution containing a soluble alkali subsequent to the treatment in a soluble fluoride bath and before rinsing that greatly improved results are obtained as regards the resistance to corrosion of the protective coating. The invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims.

In carrying the invention into effect the article is treated with an aqueous solution, as for example, one containing a fluoride having an acid reaction, whereby there is produced a coating of the character generally known as a fluoride coating. For this purpose a solution is made containing hydrofluoric acid or a soluble compound containing free hydrogen fluoride, as for example, by dissolving in water a bifluoride. Besides hydrofluoric acid numerous bifluorides are available that are suitable for the purpose, such as sodium, potassium, and ammonium bifluoride. Similar solutions can be made by dissolving a neutral fluoride in water and adding hydrofluoric acid. The complex acid fluorides may be used as, for example, fluosilicic acid (H_2SiF_6) and hydrofluoboric acid (HF_4). The concentration at which to employ the fluorine compound may vary over a wide range from as little as about 0.25 per cent by weight of the equivalent of HF up to the saturation point of the compound employed. A preferred range of concentration is between about 10 and 30 per cent provided the fluoride selected may have such solubility. A convenient bath is one containing about 20 per cent of hydrogen fluoride, although solutions can be used containing 52 per cent or more of HF. The fluoride solution may be employed at any ordinary temperature up

to the boiling point of the solution, the higher the temperature employed the faster the initial coating is produced. The time of such treatment may be from one-half minute to 10 minutes or more depending upon the temperature and the thickness to which it is desired to build up the coating. If desired, the article may be anodically electrolyzed while being treated in the solution, whereby the production of the coating is facilitated. A suitable voltage to employ is between 90 and 100, using a magnesium cathode.

After having produced the fluoride coating in the manner described, the article is subjected to the action of an aqueous solution containing a suitable alkali whereby any residual fluorine acidity in the pores of the coating previously produced is neutralized, such step being taken without rinsing off the previously used solution. For this purpose, I may employ any of the soluble bases of the alkali and alkali earth metals, such as sodium or potassium hydroxide, calcium hydroxide, sodium carbonate, barium hydroxide, and the like. I prefer to use those bases which produce insoluble fluorides, such as calcium hydroxide, strontium hydroxide, etc., by reaction with a soluble fluoride in a concentration of from about 0.1 of a percent to 30 per cent or more in water solution depending upon the solubility of the selected alkali. In general, I prefer to use a concentration of about 10 per cent by weight and at the boiling temperature when an alkali metal alkali is used. The process may be carried out, however, at any ordinary temperature, the higher the temperature the less the time required. In general, the duration of the contact between the solution and the article should be from one-half to five minutes or more. In a preferred embodiment of the invention, I may use a saturated solution of calcium hydroxide or lime water for the second step, by immersing the article in it for 3 minutes at room temperature.

If desired, the article may be anodically electrolyzed in the alkaline solution. This has the effect generally of enhancing the resistance to corrosion of the finished article. A potential of about 15 volts or more may be used and preferably about 50–60 at a temperature of about 50° C. although other temperatures may be used. The bath is sufficiently alkaline for this anodic treatment when the pH is about 12 or above which is readily obtainable by adding from 2 to 6 per cent of sodium hydroxide to water.

The following examples are further illustrative of the invention:

Example 1

A magnesium alloy article, the alloy consisting of 6 per cent aluminum, 3 per cent of zinc, and 0.2 per cent of manganese, and the balance magnesium, was subjected to the action of a 30 per cent solution of hydrogen fluoride for 12 minutes at 30° C. and then to the action of a saturated solution of calcium hydroxide for 5 minutes at room temperature. The article was then rinsed and dried.

Example 2

A similar magnesium alloy article was immersed in a 52 per cent solution of hydrofluoric acid at 45° C. and anodized at a potential of 60 volts for 12 minutes. The article was then removed from the solution and subjected to the action of a 5 per cent solution of sodium hydroxide for 1 minute at 20° C. The article was then rinsed and dried.

Example 3

A similar magnesium alloy article was immersed in a 30 per cent solution of hydrofluoric acid at 30° C. for 12 minutes. The article was then removed from the solution and subjected to the action of an aqueous solution containing 5.0 per cent of sodium hydroxide at room temperature for 5 minutes. The article was then rinsed and dried.

As an illustration of the improvement resulting from the treatment with the alkali solution subsequent to the treatment in a solution of a soluble fluoride, comparative data was obtained of the resistance to corrosion as measured by the usual alternate immersion test in 3 per cent salt solution at 95° F. The percentage of the surface area which was attacked was measured and this was used to express the amount of corrosion.

The articles treated as described in the above examples and subjected to the test for corrosion resistance showed an average per cent surface attack in a week of approximately 9 per cent. In comparison with this, the average per cent surface attack of similar articles treated in conventional manner with a fluoride solution alone and then similarly tested was approximately 100 per cent. Treatment of similar mag-

nesium articles only in an alkaline solution, such as those used above, does not produce a significant amount of protective coating.

It is to be understood that the method may be used with other magnesium alloys than those illustrated.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A method of treating articles of magnesium and its alloys comprising subjecting the article to the action of an aqueous solution consisting essentially of acid fluoride, and thereafter, without rinsing off the fluoride solution, subjecting the treated article to the action of an aqueous solution of an alkali.

2. A method, according to claim 1 in which the acid fluoride is selected from the group consisting of hydrofluoric acid, ammonium bifluoride, and alkali metal bifluorides.

3. A method of treating articles of magnesium and its alloys comprising subjecting the article to the action of a solution consisting essentially of water and from about 0.25 to 50 per cent of HF, and thereafter, without rinsing off the fluoride solution, rinsing the treated article in an aqueous solution of a soluble hydroxide.

4. A method, according to claim 3, in which the soluble hydroxide is one producing an insoluble fluoride by reaction with a soluble fluoride.

5. A method, according to claim 3, in which the soluble hydroxide is calcium hydroxide.

6. A method of treating articles of magnesium and its alloys comprising subjecting the article to the action of an aqueous solution consisting essentially of a soluble acid fluoride and then, without rinsing off the fluoride solution, anodically electrolyzing the treated article in an aqueous solution of an alkali.

7. A method, according to claim 6, in which the alkali is an alkali metal hydroxide.

WILLIAM S. LOOSE.