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METHOD OF TREATING MAGNESIUM AND ITS ALLOYS

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The invention relates to protective coatings for articles of magnesium and its alloys. It more particularly concerns an improved method of increasing the resistance to corrosive attack of articles of the aforesaid metals.

It has been proposed heretofore to subject articles of magnesium and its alloys to the action of an aqueous solution of hydrofluoric acid or the water-soluble fluoride salts by immersing the article in such solution either with or without the application of electrolysis. The protective coatings thereby produced, I have found, are subject to considerable deterioration when exposed to either the atmosphere or aqueous salt solutions, particularly those of the nature of sea water. I have now found that by subjecting articles thus treated with a solution of a fluoride to the action of aqueous solutions containing an arsenic compound, even though it be relatively insoluble therein, a greatly increased resistance to corrosion is obtained. The invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims.

In carrying the method into effect the article to be treated is first cleaned, if necessary, as by wire brushing or pickling in a dilute mineral acid which is capable of forming water-soluble salts of magnesium such as nitric or sulphuric acid. The cleaned article is then subjected to the action of a bath comprising a fluoride for a sufficient length of time to bring about the formation of a coating. Suitable fluoride baths may be either aqueous, such as water solutions of soluble fluorides, or non-aqueous, such as molten fluorides. When the fluoride is used in aqueous solution, the coating thus produced is relatively thin and difficult to analyze with certainty. It is believed, however, to be largely magnesium fluoride. Molten fluoride baths, on the other hand, definitely yield a coating of magnesium fluoride. Various fluorides may be used to make a solution or bath suitable for producing this coating. For example, there may be used the water-soluble fluorides such as hydrofluoric acid, the acid fluorides or bi-fluorides such as potassium bi-fluoride, ammonium bi-fluoride, and the like. The neutral alkali metal fluorides such as sodium and potassium fluoride and combinations of all of the above, as well as some of the more complex fluorides, may be used such as fluosilicic acid (H_2SiF_6) and hydrofluoboric acid (HBF_4). I generally prefer to use an aqueous solution of a fluoride having an acid reaction as by dissolving hydrofluoric acid or an acid fluoride in water, a suitable concentration being

about 2 per cent or more by weight. A 25 to 30 per cent solution of hydrofluoric acid is satisfactory. Other concentrations may be used, if desired, those above-mentioned being merely illustrative.

In treating the article with aqueous solutions, it is brought into contact therewith for from about 1 to 60 minutes or more at ordinary temperatures, although temperatures as high as 80° or more may be employed, provided excessive volatilization of hydrogen fluoride from the solution does not occur. Baths containing mainly hydrogen fluoride are best used at about room temperature, so as to avoid incurring a loss of HF which is fairly easily volatilized from the solution at higher temperatures. The action of the solution may be expedited either by raising the temperature or by anodically electrolyzing the article employing voltages up to 100 volts or more. Such anodizing may be carried out at ordinary temperatures for 5 to 15 minutes or more.

Baths comprising a molten fluoride may be used similarly for depositing a fluoride coating, the article being made the anode and electrolyzed to effect the deposition of magnesium fluoride. Fused potassium or sodium fluoride or bi-fluoride, and mixtures of dehydrated boric acid with potassium fluoride may be used at about 200°C . employing an anodizing voltage up to about 220.

After a coating has been produced by means of a bath or solution comprising a fluoride, the coated article is then subjected to the action of an arsenic compound in an aqueous medium, as by boiling the article with water to which has been added a compound of arsenic. It is preferable to employ a relatively insoluble arsenic compound such as a sulphide of arsenic, although other arsenic compounds which are relatively soluble may likewise be employed such as arsenic acid, arsenous acid, arsenic fluoride, arsenic iodide, arsenous bromide, arsenous chloride, arsenous fluoride, arsenous iodide, arsenous oxychloride, the alkali metal and ammonium arsenates and arsenites, etc. A relatively small amount may be added to the water in which the article is to be treated such as 1 per cent, although other quantities may be employed. Best results appear to be obtained when the pH of the solution is between about 5 and 8, but effective action can be obtained at other pH values such as those lying between about 3 and 14. If the pH is below about 3, the magnesium of the article tends to decompose the arsenic compound in the bath with excessive rapidity

causing a rapid loss of effectiveness of the bath. The pH of the bath may be regulated by adding either an acid such as sulphuric acid or an alkali such as sodium hydroxide according to whether it is desired to maintain the bath in acid, neutral, or alkaline condition, respectively. The solution may be employed at any ordinary temperature including the boiling point. The duration of the treatment may be varied according to the depth of coating it is desired to produce, from 5 minutes to 1 hour being generally effective.

By my improved method I have found that the extent to which articles treated according to my method is corroded is from $\frac{1}{3}$ to $\frac{1}{2}$ of that of similar articles treated by immersion in the known fluoride baths or solutions of arsenic compounds alone.

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 steps stated by any of the following claims or the equivalent of such stated steps be employed.

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

1. The method of producing a protective coating upon articles of magnesium and magnesium-base alloys which consists in subjecting the article to the action of a bath comprising a fluoride selected from the class consisting of hydrofluoric acid, fluosilicic acid, hydrofluoboric acid, acid fluorides, and neutral alkali metal fluorides to form a coating on the surface of the article, and then subjecting the coated article to the action of a bath comprising water and an arsenic compound, whereby the fluoride-formed coating is altered to increase the corrosion resistance thereof.
2. A method according to claim 1 wherein the fluoride bath is a non-aqueous bath.
3. A method according to claim 1 wherein the fluoride bath is an aqueous solution.
4. A method according to claim 1 wherein the fluoride bath is an aqueous acid solution of an alkali metal fluoride.

5. A method according to claim 1 wherein the fluoride bath comprises an acid fluoride.

6. A method according to claim 1 wherein the fluoride bath comprises hydrofluoric acid.

7. In a method of producing a protective coating upon articles of magnesium and its alloys, the steps which comprise subjecting the article to the action of an aqueous acid solution of a fluoride, whereby a coating is formed on the surface of the article, and then subjecting the coated article to the action of a bath comprising water and a relatively insoluble arsenic compound, whereby the fluoride-formed coating is altered to increase the corrosion resistance thereof.

8. A method according to claim 7 wherein the arsenic compound is a sulfide of arsenic.

9. The method of producing a protective coating upon articles of magnesium and its alloys which consists in subjecting the article to the action of an aqueous acid solution of a fluoride, whereby a coating is formed on the surface of the article, and then subjecting the coated article to the action of an aqueous solution comprising an arsenic compound, said solution having a pH value between 3 and 14, whereby the fluoride-formed coating is altered to increase the corrosion resistance thereof.

10. A method according to claim 9 wherein the article is anodically electrolyzed in the fluoride solution.

11. A method according to claim 9 wherein the arsenic solution has a pH value between 5 and 8.

12. In a method of treating articles of magnesium and its alloys which have previously been subjected to the action of a bath comprising a fluoride to form a coating on the surface of the articles, the step which consists in subjecting the coated articles to the action of a bath comprising water and an arsenic compound, whereby the fluoride-formed coating is altered to increase the corrosion resistance thereof.

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