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METHOD OF TREATING MAGNESIUM AND ITS ALLOYS

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The invention relates to methods of producing protective coatings upon magnesium and alloys thereof in which magnesium is the predominant constituent. It more particularly concerns an improved method of producing on articles of the aforesaid metals a coating which is highly resistant to corrosion and adapted to be used as an improved base for paints, varnishes, and the like.

Various methods have been proposed heretofore for producing protective coatings upon articles of magnesium and its alloys by subjecting them to the action of chemical solutions, among which the aqueous solutions of alkali metal chromates or bichromates are the most widely used.

I have now discovered that by dissolving in the aqueous chromate treating solution a relatively small concentration, less than 1 per cent, of a fluoride, greatly improved coatings are produced on articles of magnesium and its alloys by treatment in the solution. The invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims.

In carrying out the method, the solution or bath may be prepared by dissolving a soluble chromate or bichromate in water to produce a solution having a concentration above about 2 per cent, but preferably below the point of saturation. In general, a concentration of 8 to 10 per cent is suitable, although other concentrations may be used if desired. A fluoride, such as an inorganic fluoride, is added to the bath so as to produce therein a relatively small concentration of dissolved fluoride, that is, an amount less than about 1 per cent and preferably less than 0.6 per cent. Beneficial results have been obtained with concentrations of fluoride in solution as low as 0.0005 per cent, and excellent results are obtained if the fluoride concentration is from 0.001 per cent to 0.01 per cent. The advantage of the presence of a fluoride in the bath appears to decrease slowly as the concentration of the fluoride in solution therein is increased to 0.3 per cent, and more rapidly thereafter until when the concentration passes through about 0.9 per cent and approaches 1 per cent most of the beneficial effects are no longer obtained. By using a relatively insoluble fluoride, such as magnesium fluoride or calcium fluoride, the amount which goes into solution is automatically regulated in accordance with the solubility of the fluoride chosen and has the advantage that a relatively large amount may be added to the bath without increasing the amount of dissolved fluoride beyond the proper limit. Magnesium fluoride, for example, automatically provides a soluble fluoride concentration of approximately 0.009 per cent, which is within the optimum range, for best results. Calcium fluoride, which has a solubility on the order of 0.002 per cent, may be used similarly.

While the coating can be produced at ordinary temperatures by immersing the article to be treated in the solution, it is preferable to heat the solution to 50° C. or more, best results being obtained usually between 90° and 100° C. The duration of the treatment can be varied to suit the thickness of coating it is desired to produce, one hour generally being sufficient at temperatures between 90° and 100° C. At lower temperatures, correspondingly longer times are required as, for example, at 50° C. an immersion of from two to three hours is required to produce about the same coating effect as that obtainable at 100° C. in one hour. The following examples are illustrative of suitable modes of carrying out the invention.

Example 1

A treating solution was made by dissolving 10 per cent by weight of sodium bichromate in water, and into this was stirred 0.5 per cent by weight of powdered magnesium fluoride, a portion of which dissolved, leaving the remainder as undissolved particles. An article of a magnesium alloy consisting of 6 per cent of aluminum, 3 per cent of zinc, and 0.2 per cent of manganese was immersed for one hour at 100° C. in the solution, then withdrawn, rinsed and dried. Upon subjecting the article to the usual alternate immersion test in a 3 per cent salt solution for resistance to corrosion, it was found, after one month of such treatment, to have not more than 5 per cent of its surface attacked by the salt solution. In comparison with this, a similar treatment in a conventional 10 per cent solution of sodium bichromate at 100° C. for one hour without the addition of a fluoride produced a protective coating which showed more than 70 per cent of its surface area attacked in one month when subjected to the same alternate immersion test.

Example 2

To a 10 per cent solution of sodium bichromate 0.025 per cent by weight of powdered calcium fluoride was added and partly dissolved in the solution by stirring. An article of a magnesium alloy comprising 6 per cent of aluminum, 3 per cent of zinc, and 0.2 per cent of manganese, the balance being magnesium, was subjected to the action of the solution at 100° C. for one hour. It was then removed, rinsed and dried, and sub-

jected to the conventional alternate immersion test in a 3 per cent solution for resistance to corrosion for one month. As a result of this test, the article showed only 10 per cent of its surface area was attacked by the salt solution in comparison with 70 per cent attack when a similar article was treated in conventional manner in the same concentration of sodium bichromate solution without the addition of a fluoride.

Example 3

To a 10 per cent aqueous solution of sodium bichromate there was added 0.001 per cent of sodium fluoride. Into this solution there was immersed an article of a magnesium alloy comprising 6 per cent of aluminum, 3 per cent of zinc, 0.2 per cent of manganese, the balance being magnesium, for one hour at 100° C. It was then withdrawn, rinsed and dried, and subjected to the conventional alternate immersion test for resistance to corrosion in a 3 per cent salt solution. At the end of one week, as a result of this test, the area of the surface of the article which was attacked was found to be but 5 per cent of the total surface area of the article. A similar article treated in a 10 per cent solution of sodium bichromate for one hour at 100° C. but without the addition of a fluoride showed in a similar corrosion test more than 70 per cent of its surface area attacked in one week.

Although simple immersion in the solution, preferably while heated, suffices to produce the desired coating, if desired a potential may be applied to the article so as to bring about an anodic oxidation during the coating operation. This additional step has the advantage in some cases of decreasing the time required to produce the coating. Such anodic oxidation may be produced by applying from 0.2 to 10 volts or more on the article as anode in the solution, using a carbon or graphite cathode.

The pH value at which the bath may be used may be varied from that normally resulting from dissolving the bath ingredients in water by adding either an acid or alkali to the bath. In general, pH values below 6 are desirable and the best results require a pH value of about 4 to 4.5. In use, the bath tends to become more alkaline, and its pH value can be maintained at a suitable value by occasional additions of chromic acid.

In the claims, I have used the term "chromate" in the broad sense to include both normal chromate and bichromate.

I claim:

1. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in subjecting the article to the action of an aqueous solution consisting essentially of a soluble chromate and from about 0.001 to about 0.01 per cent of an inorganic fluoride.

2. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in subjecting the article to the action of an aqueous solution consisting essentially of an alkali metal chromate and a saturating amount of magnesium fluoride.

3. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in subjecting the article to the action of an aqueous solution consisting essentially of an alkali metal chromate and a saturating amount of calcium fluoride.

4. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in bringing the article into contact with an aqueous solution at 90° C. to 100° C. and consisting essentially of more than about 2 per cent of a soluble chromate selected from the group consisting of the alkali metal and ammonium chromates and bichromates, and from about 0.001 to about 0.01 per cent of an inorganic fluoride.

5. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in bringing the article into contact with an aqueous solution consisting essentially of more than about 2 per cent of a soluble chromate and from about 0.001 to about 0.01 per cent of a fluoride, said solution having a pH value between 6 and 4.

6. In a method of treating uncoated articles of magnesium and its alloys, the steps which consist in immersing the article in an aqueous solution consisting essentially of more than about 2 per cent of a soluble chromate and from about 0.001 to about 0.01 per cent of the fluoride in the dissolved state, and applying a potential to the article so as to make it anodic while immersed in the solution.

7. In a method of treating uncoated articles of magnesium and its alloys, the step which consists in subjecting the article to the action of an aqueous solution consisting essentially of a soluble chromate and from about 0.001 to about 0.3 per cent of an inorganic fluoride.

8. A solution for forming a protective surface coating on articles of magnesium and its alloys consisting essentially of water having dissolved therein at least 2 per cent of a soluble chromate selected from the group consisting of the alkali metal and ammonium chromates and bichromates, and from 0.001 to 0.01 per cent of an inorganic fluoride in the dissolved state.

9. A composition according to claim 8 wherein the fluoride is magnesium fluoride.

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