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METHOD OF PROVIDING A PROTECTIVE
COATING ON MAGNESIUM AND ITS AL-
LOYS

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The invention relates to methods of producing protective coatings on articles of magnesium and magnesium base alloys. 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 applying paints, varnishes, lacquers, and the like.

Various methods have been proposed heretofore for producing protective coatings on magnesium and its alloys by subjecting articles thereof to the action of chemical solutions, among which the aqueous solutions of certain of the oxygenated inorganic compounds which produce adherent coatings are the most widely used, such as aqueous solutions containing chromates or bichromates of the alkali metals.

We have now found that new and greatly improved results are obtained if, instead of subjecting the article of magnesium or an alloy thereof directly to the action of an aqueous solution of an oxygenated inorganic compound, the article is first subjected to the action of a solution containing a soluble fluoride. 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, according to the invention, subjected to the action of a solution containing a soluble fluoride by spraying the solution on the metal or by immersing the metal in the solution or in any other manner in which the solution and the article may be brought into contact for a sufficient length of time to bring about the formation of a coating. When the fluoride is used in aqueous solution, the coating is so thin as to be difficult to analyze in substance with certainty. It is believed, however, to be largely magnesium fluoride. Molten fluoride baths definitely yield a coating of magnesium fluoride. Various soluble fluorides may be used to make a solution or bath suitable for producing this coating. For example, there may be used 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 these, and some of the more complex fluorides may be used such as fluosilicic acid (H_2SiF_6) and hydrofluoboric acid (HBF_4). Of these fluorides we pre-

fer to use those having an acid reaction as is obtained by dissolving hydrofluoric acid or an acid fluoride in water in a concentration of about 2 per cent or more by weight. A generally useful fluoride solution is a 25 to 30 per cent solution of hydrofluoric acid. Other concentrations may be used, if desired.

In carrying out this step of the process, the article is brought into contact with preferably an aqueous solution of the soluble fluoride for from about 1 to 60 minutes or more at ordinary temperatures. If desired, however, the temperature may be as high as 80°C . or even higher, whereby the action of the solution will be expedited, provided excessive volatilization of HF from the solution does not occur. If the soluble fluoride bath contains mainly hydrogen fluoride, it is best to use the bath 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 also may be expedited, if desired, by applying a potential to the article, this being made the anode. A suitable voltage to employ is from 90 to 100 or more. At ordinary temperatures anodizing for from about 5 to 15 minutes in the fluoride bath as described will produce a satisfactory coating. Baths comprising a molten fluoride also may be used for depositing a fluoride coating, the article being made the anode, and electrolyzed to effect the deposition. Fused potassium or sodium fluoride, bifluoride, and mixtures of dehydrated boric acid with potassium bifluoride may be used at about 200°C . Voltages up to 220 may be used.

After having thus subjected the article to the action of the fluoride solution or bath, as described, it is preferably rinsed in water. The article is then ready for the next step. In this it is subjected, as by immersion, to the action of an aqueous solution of a salt of an oxy-acid of an element selected from the group consisting of chromium, molybdenum, phosphorus, selenium, titanium, tungsten, vanadium, especially the alkali metal and ammonium salts of such oxy-acids. The aqueous solutions of these compounds react with magnesium to produce insoluble compounds therewith either directly or upon the compound being reduced by the action of the metal to form an insoluble magnesium compound. The following are typical examples of such salts: sodium chromate and bi-chromate, ammonium molybdate, the sodium phosphates, ammonium selenate, sodium titanate, sodium tungstate, and sodium vanadate.

The oxygenated compound may be employed

in aqueous solutions having various pH values, best results being obtained when the pH value of about 10.2 is avoided, which is the pH value corresponding to the formation of magnesium hydroxide by precipitation. For example, we have found that the pH value of the bath may lie advantageously either between about 0.5 and 8 or between about 12 and 14. The concentration in which to employ the oxygenated compound varies more particularly with the pH at which the solution is to be used and may also be limited by the solubility of the particular oxygenated compound employed. We have found that in the lower range of pH values a considerable concentration of the oxygenated compound may be employed as, for example, from about 5 to 40 per cent by weight, while at the higher range of pH values only a relatively low concentration is desirable, such as from about 0.1 to 4 per cent of oxygenated compound, although in some instances as much as 10 per cent may be used. The pH value of the solution may be lowered or raised, if desired or necessary, by adding either an acid such as sulphuric acid, or an alkali, preferably of the alkali metals, such as sodium hydroxide, respectively, thus regulating the pH of the solution of the oxygenated compound to a value between about 0.5 and 8 or between about 12 and 14, as desired. In the foregoing ranges of pH values, we prefer to use from 4 to 6 in the lower range and from 13 to 14 in the higher range.

The duration of the treatment in the solution containing the oxygenated compound varies with its temperature, concentration, and pH value. In general, a treatment of from 5 to 60 minutes and preferably from 30 to 45 minutes at or near the boiling temperature of the solution produces satisfactory results. Similar results can be obtained at temperatures up to 70° C. and in from 5 minutes to one hour by making the article the anode and electrolyzing in a solution having a pH between 0.5 and 8, with a current density of from 5 to 50 amperes of anodizing current per square foot of surface. When the pH of the solution is between 12 and 14, superior results are obtained, particularly if the voltage employed is above 15. If desired, an alkaline solution can be used for the anodization, as by adding about 2 per cent of sodium hydroxide to the solution containing the oxygenated compound. Suitable concentrations in which to employ the oxygenated compound for best results when the article is to be anodized vary with the specific compound used as follows: with chromates, the concentration may be about 0.2 per cent; with molybdates, about 5 to 6 per cent; phosphates, about 3 per cent; selenate, about 1 per cent; titanate, about 1 per cent; tungstate, about 3 per cent; and vanadate, about 5 per cent, although other concentrations may be used.

After the article has been subjected to the action of the solution of the oxygenated inorganic compound either with or without anodizing, as described, following the treatment with a fluoride, the article may be rinsed in water and dried.

The following examples are illustrative of modes of carrying out the invention.

Example 1

A casting of a magnesium alloy consisting of 6 per cent of aluminum, 3 per cent of zinc, 0.1 per cent of manganese, the balance being magnesium, was sand blasted, then cleaned by a 10 second dip in a water solution containing 8 per cent of nitric acid and 2 per cent of sulphuric

acid, as is the usual practice of preparation for a chemical finish. The cleaned casting was then immersed for 5 minutes in a 15 per cent solution of hydrofluoric acid at room temperature, followed by a cold water rinse. The so treated casting was then immersed for 45 minutes in a boiling 10 per cent solution of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), rinsed in cold water, and dried.

Example 2

A similar casting to Example 1 was sand blasted and then pickled in a 10 per cent solution of nitric acid to provide a clean surface thereon. The so cleaned casting was then immersed for 10 minutes in a 52 per cent solution of hydrofluoric acid at room temperature. The casting was removed from this solution and then immersed in a solution containing 0.25 per cent of sodium bichromate and 2 per cent of sodium hydroxide for 10 minutes at 50° C. while being anodically electrolyzed with a potential of 45 volts, the pH of the bath being 13.4. The casting was then removed from the solution, rinsed and dried. The ability to resist corrosion was then determined by subjecting the article to the usual alternate immersion test in a 3 per cent solution of salt at 95° F. for one week and measuring the area of surface attacked. Castings treated as above described showed only 3 to 6 per cent as much area corroded as similar castings treated in either the above solution of the oxygenated compound without initially treating the article in the fluoride solution or the above fluoride solution alone.

Example 3

An article of a magnesium base alloy consisting of 4 per cent of aluminum, 0.3 per cent manganese, the balance being magnesium, in the extruded condition, was immersed for 12 minutes in a 25 per cent solution of hydrofluoric acid at 25° C. After this treatment, the article was transferred to a boiling 10 per cent solution of sodium metavanadate for 10 minutes, then rinsed and dried. The resistance to corrosion of the so treated article was found to be from 5 to 7 times as great as the resistance to corrosion obtained upon treating similar articles in either of the two above described solutions.

Example 4

A magnesium base alloy article of rolled sheet, the alloy consisting of 4 per cent of aluminum 0.3 per cent manganese, the balance being magnesium, was subjected to the action of a 25 per cent solution of hydrofluoric acid for 15 minutes at 28° C. and then to the action of a boiling aqueous solution containing 12 per cent each of sodium bichromate and sodium dihydrogen phosphate. The resistance to corrosion was found to be more than twice as great as similar articles treated in either of the two above solutions.

The coating produced according to the method provides an excellent base for the application of paint, varnish, or the like in that the varnish is made to adhere better and in combination with the chemical coating generally provides additional protection against corrosive attack.

Other modes of applying the principle of the 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.

We therefore particularly point out and distinctly claim as our invention:

1. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of a bath, the active constituent of which is a fluoride, to produce a coating on the article, and then subjecting the coated article to the action of an aqueous solution of a water-soluble salt of an oxy-acid of an element selected from the group consisting of chromium, molybdenum, phosphorus, selenium, titanium, tungsten, and vanadium to increase the corrosion resistance of the coating thereon.

2. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing a soluble fluoride as active constituent, to produce a coating upon the article, and then subjecting the coated article to the action of an aqueous solution of a water-soluble salt selected from the class consisting of the alkali metal and ammonium salts of the oxy-acid of the elements chromium, molybdenum, phosphorus, selenium, titanium, tungsten, and vanadium to increase the corrosion resistance of the coating thereon.

3. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing a soluble fluoride as active constituent, to produce a coating upon the article, and then subjecting the coated article to the action of an aqueous solution of a soluble salt of chromic acid to increase the corrosion resistance of the coating thereon.

4. A method according to claim 3 wherein the soluble chromate is an alkali metal chromate.

5. A method according to claim 2 wherein the oxy-acid salt is sodium vanadate.

6. A method according to claim 2 wherein the oxy-acid salt is a phosphate.

7. A method according to claim 2 wherein the fluoride is an acid fluoride.

8. A method according to claim 3 wherein the fluoride is hydrofluoric acid and the soluble chromate is an alkali metal chromate.

9. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing hydrofluoric acid to produce a coating on the article, and then subjecting the coated article to the action of an aqueous solution containing sodium bi-chromate and having a pH value between 0.5 and 8 to increase the corrosion resistance of the coating thereon.

10. In a method of producing a protective coating upon articles of magnesium and magnesium

base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing hydrofluoric acid to produce a coating on the article, and then subjecting the coated article to the action of an aqueous solution containing sodium chromate and having a pH value between 12 and 14 to increase the corrosion resistance of the coating thereon.

11. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing a soluble fluoride while anodically electrolyzing the same to produce a coating on the article, and thereafter subjecting the coated article to the action of an aqueous solution containing an alkali metal chromate to increase the corrosion resistance of the coating thereon.

12. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing a soluble fluoride to produce a coating on the article, and thereafter subjecting the coated article to the action of an aqueous solution containing an alkali metal chromate while anodically electrolyzing the same to increase the corrosion resistance of the coating thereon.

13. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of an aqueous solution containing a soluble fluoride while anodically electrolyzing the same to produce a coating on the article, and thereafter subjecting the coated article to the action of an aqueous solution containing an alkali metal chromate while anodically electrolyzing the same to increase the corrosion resistance of the coating thereon.

14. In a method of producing a protective coating upon articles of magnesium and magnesium base alloys, the steps which consist in subjecting the article to the action of a solution containing hydrofluoric acid at room temperature to produce a coating on the article, and thereafter subjecting the coated article to the action of an aqueous solution containing sodium bi-chromate at the boiling temperature to increase the corrosion resistance of the coating thereon.

15. In a method of improving the corrosion resistance of an article of magnesium and magnesium base alloys, said article having a magnesium fluoride coating thereon, the step which consists in subjecting the article to the action of an aqueous solution of a soluble alkali metal chromate.

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