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METHOD FOR PROTECTING MAGNESIUM AND MAGNESIUM ALLOYS FROM CORROSION

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This invention relates to a composition and method for treating articles of magnesium and magnesium alloys to produce thereon a protective coating which comprises subjecting such articles to an aqueous acidic solution comprising water, a chromium compound selected from the group consisting of chromic acid and salts thereof, e. g., sodium, potassium and ammonium salts, a nitrate compound selected from the group consisting of nitric acid and salts thereof, e. g., sodium, potassium and ammonium salts, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof, e. g., sodium, potassium and ammonium salts. The said solution should be adjusted to a pH of between 0.0 and 2.0. It should be noted that this method of treatment is useful both in connection with castings, wrought products and coatings of these metals.

The coatings resulting from the use of the foregoing composition and method exhibit corrosion-resistant properties of a far better character than realized heretofore in the art. In addition, operational advantages are afforded as will be fully discussed hereinafter.

The principal object of the invention is to produce a corrosion-resistant coating on the surface of a magnesium or magnesium alloy article by subjecting the same to a single immersion treatment in an aqueous acidic solution containing a hexavalent chromium compound, a nitrate compound and a chloride compound.

Another object of the invention is to provide such a treating solution and method as will enable the above mentioned results to be uniformly obtained on a commercial scale.

A further object of the invention is to provide such a treating solution and method as to shorten the treatment time for producing the enhanced protective coating noted heretofore.

A more specific object of this invention is to provide a method and composition of stipulated character so as to produce improved corrosion-resistant coatings on magnesium-aluminum, magnesium-manganese and magnesium-zinc-zirconium alloys.

An additional object of the invention is to provide a treating solution and method as will render the metal surface being coated suitable for the reception of paint and dye.

Still another object of this invention is to provide a treating solution and method and producing a corrosion-resistant coating on the surface of a magnesium or magnesium alloy article comprising providing an aqueous acidic solution containing from 14 to 37% by weight of a hexavalent chromium compound, 32 to 70% by weight of a nitrate compound and 4 to 50% by weight of a chloride compound, these ranges being calculated on the total weight of active ions present in the said aqueous acidic solution.

An additional object of this invention is to provide a treating solution and method as noted heretofore, said solution having a pH of between 0.0 and 2.0.

Still further objects and the entire scope of applicability

of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

The foregoing objects are accomplished, according to the present invention, by the use of an aqueous acidic solution comprising water, a chromium compound selected from the group consisting of chromic acid and salts thereof, a nitrogen-containing compound selected from the group consisting of nitric acid and salts thereof, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof. We have found that such solutions can be utilized to produce, on a magnesium or magnesium alloy metal, a coating having great corrosion resistance. In addition, a method of the character to be described has other commercially practical aspects. For example, by our invention we obtain economy in the use of the chemicals making up the solution and speed and facility with which desired results may be obtained. With the present invention, a single dip in the solution is sufficient to produce the improved corrosion-resistant film, thus facilitating commercial operations.

A further advantage is that room temperatures (75–80° F.) of operation of the dipping bath are made possible. This factor is also of great significance with respect to operating features in view of the fact that the effectiveness of the dipping bath is maintained over a longer period of time than realized at higher operating temperatures.

In addition to the above, it should be noted that the dry constituents of the dipping composition can be made up for sale as a powdered mixture. Such mixture may then be dissolved in water and prepared for use by the suitable adjustment of pH within the above noted range. As can be appreciated, this affords a substantial saving in shipping costs since the powdered mixture takes up much less space than in actual working solution.

A typical mixture of the composition utilized for our novel dipping solution would contain about 14 to 37% chromic compound, about 32 to 70% nitrogen-containing compound and about 4 to 50% chloride compound, the foregoing percent ranges being calculated on the basis of total weight of active ions, i. e., chromium, nitrate and chloride radicals, present in an aqueous solution containing said composition. The foregoing radicals can be obtained from the respective acids or salts. It should be stressed that a critical qualification relating to use of this composition is that the pH of the resulting dipping solution must be within a range of 0.0 to 2.0 and the preferred range is 0.2 to 1.6.

Of course, it can be appreciated that, if necessary, the above percentage ranges which are based on the total weight of active ions in solution, can be easily converted to grams per litre, for example, by suitable physical-chemical calculations based on the particular acids or salts utilized.

For carrying out the dip treatment, the solutions may be maintained at a temperature ranging from 50 to 150° F., with room temperature (75–80° F.) being preferred. The period of immersion varies, depending on freshness of the solution, concentration, pH, type of alloy and temperature of the solution. A preferable range for immersion time is between about 5 seconds to 5 minutes, with 15 seconds to 2 minutes being typical.

The following examples illustrate useful compositions and operating conditions which have been utilized to coat magnesium and magnesium alloys. The advantageous

results obtained were substantially as those described, both in operating factors and in the enhanced corrosion-resistance of the final coating.

Example I

Chromic acid.....	g./l.	19.2
Nitric acid (C.P.).....	ml./l.	24.0
Hydrochloric acid (C.P.).....	ml./l.	46.0
Temperature.....	°F.	75
pH.....		0.2
Immersion time.....	seconds	30

Example II

Chromic acid.....	g./l.	15.0
Sodium nitrate.....	g./l.	22.5
Hydrochloric acid (C.P.).....	ml./l.	46.0
Temperature.....	°F.	75
pH.....		0.4
Immersion time.....	seconds	30

Example III

Chromic acid.....	g./l.	19.2
Nitric acid (C.P.).....	ml./l.	37.0
Sodium chloride.....	g./l.	36.0
Temperature.....	°F.	75
pH.....		0.5
Immersion time.....	seconds	30

Example IV

Sodium bichromate.....	g./l.	30.0
Sodium nitrate.....	g./l.	36.0
Hydrochloric acid (C.P.).....	ml./l.	60
Temperature.....	°F.	75
pH.....		0.2
Immersion time.....	seconds	30

Example V

Sodium bichromate.....	g./l.	30
Zinc chloride.....	g./l.	46
Nitric acid (C.P.).....	ml./l.	27
Temperature.....	°F.	75
pH.....		0.4
Immersion time.....	seconds	30

Example VI

Potassium bichromate.....	g./l.	40
Sodium nitrate.....	g./l.	36
Hydrochloric acid (C.P.).....	ml./l.	60
Temperature.....	°F.	75
pH.....		.2
Immersion time.....	seconds	30

Example VII

Chromic acid.....	g./l.	15
Potassium nitrate.....	g./l.	27
Hydrochloric acid (C.P.).....	ml./l.	46
Temperature.....	°F.	75
pH.....		.3
Immersion time.....	seconds	30

The solution of Examples I through VII are preferably used for alloys composed mainly of magnesium and aluminum or of magnesium and manganese and the preferred pH varies between pH 0.2 to pH 1.6. The examples VIII and IX which are noted hereinafter have been found particularly applicable to alloys composed mainly of magnesium with zinc and zirconium, and the pH may vary between pH 0.6 and pH 1.0. In other words, it has been found that a specific pH range is more particularly suited to the latter class of magnesium alloys.

Example VIII

Chromic acid.....	g./l.	15
Sodium nitrate.....	g./l.	22.5
Hydrochloric acid (C.P.).....	ml./l.	6.0
Temperature.....	°F.	75

pH.....		0.8
Immersion time.....	seconds	30

Example IX

5 Sodium bichromate.....	g./l.	30
Sodium chloride.....	g./l.	23
Nitric acid (C.P.).....	ml./l.	24
Temperature.....	°F.	75
pH.....		0.8
10 Immersion time.....	seconds	30

In connection with the above noted Examples I through IX, it should be noted that the preferred percentage ranges of compounds is, for Example I through VII, 14 to 26% chromic compound, 32 to 47% nitrogen-containing compound, and 33 to 50% chloride compound. For Examples VIII and IX the preferred range is 22 to 37% chromic compound, 50 to 70% nitrate compound, and 4 to 19% chloride compound. Of course, all of the foregoing weight ranges are based on percent by weight of active ions present in an aqueous solution containing such composition.

In carrying out the actual coating process, the uncoated metal surface is first cleaned in alkaline and acid solutions in order to remove contaminating material. The immersion treatment is then carried out,

After the immersion treatment, the parts must be thoroughly rinsed to obtain optimum results. For example, a water rinse may be employed, and its primary function is to remove any excess dipping solution. The coated part may then be dried by air blast, centrifuge or other practical means.

It is preferred to immerse the articles of magnesium or magnesium alloy, or the articles coated with such metal, in a dipping bath. However, the coating treatment may, in some cases, be carried out by other means, e. g., by spraying or brushing the aqueous solution upon the surfaces to be treated.

The uncoated metal surfaces are initially introduced into the aqueous bath until the desired protective coating is formed, slight agitation of the bath or the parts being dipped, or both, being advantageous. Articles treated with the solution in the manner above set forth exhibit an enhanced resistance to salt spray.

As noted above, the significant features of the invention are the maintenance of the critical weight proportions of the active ions in solution and the maintenance of the stipulated pH range. We have discovered that such controlled ranges are responsible for the enhanced corrosion-resistance and the advantageous operating conditions that have been discussed heretofore. In this respect, it is noted that at least one of the ingredients making up the composition must be an acid in order to impart the desired acidic characteristic to the solution. Of course, an all-salt composition would not fall within the desired pH range.

The dipping solution of this invention needs no venting. In addition, it can be maintained for an indefinite period by a periodic replenishment of the chemicals in their original proportions with a necessary adjustment of pH.

In the appended claims, the expression "magnesium" and "magnesium alloy articles" is intended to cover castings, wrought products and coatings of magnesium and magnesium alloys, as well as mixtures in which the alloys are present in substantial amount.

The novel principles of this invention are broader than the specific embodiments recited above and rather than unduly extend this disclosure by attempting to list all the numerous modifications which have been conceived and reduced to practice during the course of this development, these novel features are defined in the following claims.

We claim:

1. A composition for use in aqueous solution to impart a protective coating to magnesium and magnesium alloy articles consisting essentially of a hexavalent chromium

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compound selected from the group consisting of chromic acid and salts thereof in amount of about 14 to 37%, a nitrogen-containing compound selected from the group consisting of nitric acid and salts thereof in amount of about 32 to 70%, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof in amount of about 4 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of active ions present in an aqueous solution containing said composition and having a pH of from about 0.0 to 2.0.

2. A composition according to claim 1 wherein said hexavalent chromium compound is chromic acid, said nitrogen-containing compound is sodium nitrate and said chloride compound is hydrochloric acid.

3. An aqueous acidic solution to impart a protective coating to magnesium and magnesium alloy articles consisting essentially of water, a hexavalent chromium compound selected from the group consisting of chromic acid and salts thereof in amount of about 14 to 37%, a nitrogen-containing compound selected from the group consisting of nitric acid and salts thereof in amount of about 32 to 70%, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof in amount of about 4 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of active ions present in said aqueous solution containing said composition and having a pH of from about 0.0 to 2.0.

4. An aqueous acidic solution according to claim 3 wherein said hexavalent chromium compound is chromic acid, said nitrogen-containing compound is sodium nitrate and said chloride compound is hydrochloric acid.

5. An aqueous acidic solution according to claim 3 containing said hexavalent chromium compound in amount of from about 14 to 26%, the nitrogen-containing compound in amount of about 32 to 47%, and the chloride compound in amount of 33 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of the active ions present in the said aqueous acidic solution, and said solution having a pH of from about 0.2 to 1.6.

6. An aqueous acidic solution according to claim 3, containing said hexavalent chromium compound in amount of from about 22 to 37%, the nitrogen-containing compound in amount of about 50 to 70%, and the chloride compound in amount of 4 to 19%, the foregoing percent ranges being calculated on the basis of the total weight of the active ions present in the said aqueous acidic solution, and said solution having a pH of from about 0.6 to 1.0.

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7. The method of treating magnesium and magnesium alloy articles to produce thereon a protective coating which comprises subjecting the same to an aqueous acidic solution consisting essentially of water, a hexavalent chromium compound selected from the group consisting of chromic acid and salts thereof in amount of about 14 to 37%, a nitrogen-containing compound selected from the group consisting of nitric acid and salts thereof in amount of about 32 to 37%, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof in amount of about 4 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of active ions present in said aqueous solution containing said composition and having a pH of from about 0.0 to 2.0.

8. A method according to claim 7 wherein the hexavalent chromium compound is present in amount of about 14 to 37%, the nitrogen-containing compound is present in amount of about 32 to 70%, and the chloride compound is present in amount of 4 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of the active ions present in the said aqueous acidic solution, and wherein the said aqueous solution has a pH of from about 0.0 to 2.0.

9. A method according to claim 7 wherein the treatment is conducted with the solution at a temperature of about 50° to 150° F., the immersion time is from five to three hundred seconds and the immersion is followed by a water rinse.

10. The method of treating magnesium and magnesium alloy articles to produce thereon a protective coating comprising immersing the same in an aqueous acidic solution consisting essentially of water, a hexavalent chromium compound selected from the group consisting of chromic acid and salts thereof in amount of about 14 to 37%, a nitrogen-containing compound selected from the group consisting of nitric acid and salts thereof in amount of about 32 to 37%, and a chloride compound selected from the group consisting of hydrochloric acid and salts thereof in amount of about 4 to 50%, the foregoing percent ranges being calculated on the basis of the total weight of active ions present in said aqueous solution containing said composition and having a pH of from about 0.0 to 2.0, rinsing in cold water, and drying in an air blast.

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