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(54) **Corrosion resistant coating composition and process and coated magnesium**

(57) A chromate-free, phosphate-fluoride conversion coating, with or without vanadate, formed on a magnesium or a magnesium alloy substrate, includes an active corrosion inhibitor selected from the group consisting of organo-phosphonic acids. The phosphonic acid group reacts with the magnesium metal of the substrate to form an insoluble salt.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a corrosion resistant, chromate-free, phosphate-fluoride conversion coating, with or without vanadate, for a product formed from magnesium or a magnesium alloy and to a coating solution for use in a coating process.

[0002] Magnesium alloys are light and strong, but very vulnerable to corrosion due to the reactive nature of magnesium. Magnesium alloys are protected from corrosion in all practical applications. A commonly used, low cost, corrosion resistant treatment for magnesium alloys is a dichromate based conversion coating. While dichromate based conversion coatings provide good corrosion protection, they are based on a chemical compound (hexavalent chromium) that has many occupational exposure risks. A non-chromate, corrosion resistant magnesium conversion coating is required to meet industry demands.

[0003] Another treatment for protecting magnesium or magnesium alloy products is shown in U.S. Patent No. 5,683,522 to Joesten. In this treatment, a paint adherent and corrosion resistant coating of magnesium phosphate and magnesium fluoride is applied to a product formed from a magnesium alloy. The process for applying the coating involves immersing the magnesium alloy product in a solution having phosphate and fluoride ions. This treatment while providing a barrier film and very good paint adhesion, does not include electrochemically active ingredients to suppress corrosion. U. S. Patent Application Publication No. 2003/0150525 discloses an improved phosphate-fluoride corrosion coating for magnesium and process for applying same.

[0004] It is an object of the present invention to provide an improved chromate-free corrosion resistant conversion coating for magnesium and magnesium alloy products.

[0005] It is a further object of the present invention to provide a coating solution for forming the chromate-free corrosion resistant coating.

SUMMARY OF THE INVENTION

[0006] The foregoing objects are attained by the present invention.

[0007] In accordance with the present invention, a chromate-free, phosphate-fluoride conversion coating, with or without vanadate, formed on a magnesium or a magnesium alloy substrate, includes an active corrosion inhibitor selected from the group consisting of organo-phosphonic acids. The phosphonic acid group reacts with the magnesium metal of the substrate to form an insoluble salt. The preferred organo-phosphonic acids used as corrosion inhibitors in accordance with the present invention are selected from the group consisting of straight chain or branched amino alkyl phosphonic acids, straight chain or branched alkyl phoshonic acids, and triphosphonic acids, particularly, nitrilotris (methylene) triphosphonic acid (NTMP). When the corrosion inhibitor includes amino alkyl phosphonic acids, the amine group can interact with vanadate ions in the coating solution to increase the vanadate incorporation into the conversion coating.

[0008] Other details of the magnesium-magnesium alloy conversion coating of the present invention, as well as objects and advantages attended thereto, are set forth in the following detailed description.

DETAILED DESCRIPTION

[0009] In accordance with the present invention, a solution for forming a chromate-free, corrosion resistant coating on a magnesium or magnesium alloy substrate comprises a solution having phosphate and fluoride ions and, an active corrosion inhibitor selected from the group consisting of organo-phosphonic acids.

[0010] The solution of the present invention may optionally include vanadate anions. The active corrosion inhibitor is selected from the group consisting of straight chained or branched amino-alkyl phosphonic acids, straight chained or branched alkyl phosphonic acids, triphosphonic acids, and mixtures thereof. A particular useful triphosphonic acid comprises nitrilotris (methylene) triphosphonic acid (NTMP).

[0011] As noted above, the chromate-free solution include phosphate and fluoride ions. Phosphate and fluoride ions are present in an amount of between about 1 g/L to 50 g/L and 1 g/L to 10 g/L, respectively, preferably between 10 g/L to 25 g/L and 3 g/L to 5 g/L, respectively. It is important in the present invention to control the pH of the solution and this is achieved by the amount of phosphate ions and fluoride ions in the solution. The pH of the solution is preferably in the range of 5 to 7. The particular phosphate and fluoride compounds employed in forming the solution having the appropriate pH is disclosed in detail in U.S. Patent Application Publication No. 2003/0150525 to which suitable reference can be made. As mentioned therein, suitable phosphate compounds include monobasic potassium phosphate (KH_2PO_4), dibasic potassium phosphate (K_2HPO_4), tribasic potassium phosphate (K_3PO_4), or phosphoric acid (H_3PO_4), or combinations of these alternatives. A preferred embodiment is a combination of monobasic potassium phosphate and dibasic potassium phosphate. Suitable fluoride compounds include sodium bifluoride ($NaHF_2$). In a preferred embodiment, the concentration is provided at about 0.3-0.5% by weight sodium bifluoride. Other fluoride compounds, such as potassium fluoride or hydrofluoric acid, may also be used.

[0012] In accordance with the present invention, the corrosion inhibitor is present in the solution in an amount of between about 1 ppm to 1 wt%, preferably 10 ppm to 0.5 wt%. The corrosion inhibitor is in the form of an organo-phosphonic acid. Preferred organo-phosphonic

acids include straight chained and branched amino-alkyl phosphonic acids, straight chained or branched alkyl phosphonic acids and triphosphonic acids. A particularly useful triphosphonic acid is nitrilotris (methylene) triphosphonic acid (NTMP).

[0013] In accordance with the present invention, the solution may optionally include vanadate anions. Sodium vanadate is a suitable source of vanadate ions for the solution of the present invention. In accordance with the present invention, the vanadate ions are present in an amount of between about 1.0 g/l to 5.0 g/l. It has been found that the vanadate anions interact with the amine group of the amino alkyl phosphonic acids increase incorporation of the vanadate into the conversion coating thereby improving the coating performance. In addition, the phosphonic acid groups of the corrosion inhibitor react with the magnesium metal substrate to form insoluble salts which improve corrosion performance.

[0014] The preferred chromate-free solution comprises phosphate ions in an amount of between 10 to 25 g/L, fluoride ions in an amount of between 3 g/L to 5 g/L, vanadate anions in an amount of between 1 g/L to 5 g/L, and the corrosion inhibitor in an amount of between 10 ppm to 0.5 wt%.

[0015] A magnesium or magnesium alloy substrate having a conversion coating in accordance with the present invention comprises mostly magnesium phosphate and magnesium fluoride. It is believed that the amino alkyl phosphonic acid will form insoluble magnesium salt as part of the conversion coating. This component will increase the interaction of vanadium with conversion coating, therefore increase vanadium content in the coating, should vanadium is used as corrosion inhibitor as well.

[0016] It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modification of form, size, arrangement of parts and details of operation. The invention rather is intended to encompass all such modifications which are within its scope as defined by the claims.

Claims

1. A solution for forming a chromate-free, corrosion resistant coating on a product formed from magnesium or a magnesium alloy, comprising:

   the solution having phosphate and fluoride ions; and
   an active corrosion inhibitor selected from the group consisting of organo-phosphonic acids.

2. A solution according to claim 1, wherein the organo-phosphonic acid is selected from the group consisting of straight chained amino-alkyl phosphonic acids, branched amino-alkyl phosphonic acids, straight chained alkyl phosphonic acids, branched alkyl phosphonic acids, triphosphonic acids, and mixtures thereof.

3. A solution according to claim 2, wherein the triphosphonic acids comprise nitrilotris (methylene) triphosphonic acid (NTMP).

4. A solution according to any one of the preceding claims, wherein the solution includes vanadate.

5. A solution according to any one of the preceding claims, wherein the solution comprises 1 ppm to 1 wt% of the corrosion inhibitor, preferably 10 ppm to 0.5 wt%.

6. A solution according to claim 5, wherein phosphate ions are present in an amount of between 1 g/L to 50 g/L, preferably between 10 g/L to 25 g/L, and the fluoride ions are present in an amount of 1 g/L to 10 g/L, preferably 3 g/L to 5 g/L.

7. A process for preparing a corrosion-resistant, chromate free, coating on a magnesium or magnesium alloy substrate comprising treating the substrate with a solution as defined in any one of the preceding claims, wherein the phosphonic acid group reacts with magnesium metal forming an insoluble salt.

8. An article comprising a magnesium or magnesium alloy substrate and a corrosion resistant coating obtainable by the process as defined in claim 7.

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EUROPEAN SEARCH REPORT

Application Number
EP 04 25 3681

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	17 September 2004	Torfs, F

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