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SURFACE TREATMENT OF MAGNESIUM AND MAGNESIUM BASE ALLOYS

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The invention relates to improvements in methods of producing adherent coatings on the surface of magnesium or magnesium base alloys; particularly to the production thereon of a coating having a high degree of resistance to chemical action and adapted to furnish an improved base for paints, varnishes, lacquers, etc.

It has been proposed in U. S. Patent 1,709,894 to treat light metals, particularly magnesium or magnesium base alloys, with a solution of a dihydrogen phosphate in order to form an adherent coating on the surface of such light metals whereby said surface is protected from the corrosive action of air, moisture, etc., and is better adapted to be varnished or painted. We have found that a distinct improvement in protective coatings on surfaces of magnesium and magnesium base alloys can be obtained by forming such coatings in situ on said surfaces through the use of a dihydrogen phosphate solution to which has been added a compound of tungstic, chromic or meta-vanadic acid, e. g. either the acid thereof or an alkali metal, alkaline earth metal, magnesium, or ammonium salt thereof. Further, we have found that the coating so produced on such surfaces affords a very superior base for paints, etc.

It is accordingly among the objects of the invention to provide an improved method and means whereby an integral coating having the aforementioned properties may be formed on magnesium surfaces. To the accomplishment of the foregoing and related ends, the invention, then, consists of the method and product hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail various ways in which the principle of the invention may be used.

As hereinbefore indicated, the improvements wherein our invention resides relate particularly to the production of an adherent protective coating on the surface of a magnesium or magnesium base alloy article. In effecting the formation of this coating, we prefer first to clean the article in a suitable manner, such as by immersing it in a mineral acid bath or by sand blasting or wire brushing. The method of cleaning will vary with the composition of the article being treated. For instance, articles of magnesium or of a magesium-aluminum alloy may be conveniently cleaned by dipping in a solution of nitric or sulphuric acid; while alloys of magnesium with the heavy metals, such as zinc, cadmium, tin, copper and the like, are preferably to be mechanically cleaned by sand blasting, etc. After cleaning, the article is treated, preferably by immersion, with an aqueous solution comprising a dihydrogen phosphate and an alkali metal, alkaline earth metal, or magnesium salt of chromic, tungstic, or meta-vanadic acid. Advantageously the treatment of the article is carried out at or near the boiling point of the solution of salts, since the reaction in a cold solution is much slower. Hydrogen will be evolved at the surface of the article when it is first immersed in the coating solution, due to chemical reaction between the metal and the solution, but after a few minutes the evolution of hydrogen will cease, indicating that the formation of the coating on the surface of the article is complete. The article may then be removed from the bath, rinsed with water and dried.

We may employ, in preparing the aforementioned coating solution, any water soluble dihydrogen phosphate; particularly the alkali metal, alkaline earth metal, magnesium, or ammonium compounds; and specifically the sodium or magnesium dihydrogen phosphates. In the preparation of the dihydrogen phosphate solution we may dissolve the phosphate compound in water, or use any other convenient method of obtaining the solution, e. g. dissolving calcined MgO in aqueous phosphoric acid. We may vary the amount of dihydrogen phosphate present in aqueous solution between 0.5 and 30.0 per cent by weight of such solution, more narrowly between 5 and 15 per cent, and specifically prefer to use about a 10 per cent solution. Among the alkali metal, alkaline earth metal, or magnesium salts of metallic acids which we have found may be advantageously used are the sodium, calcium, or magnesium salts of chromic, tungstic, and meta-vanadic acids. The following table shows the amounts in grams of the sodium salts of the aforementioned acids which we may add to 100 milliliters of an aqueous solution containing about 10 per cent by weight of sodium dihydrogen phosphate:—

Salt	Broad range	Preferred range	Specific amount
	Grams	*Grams*	*Grams*
$NaCr_2O_7$	Up to 30	1 to 20	10
$NaWO_4$	Up to 30	1 to 20	5
$NaVO_3$	Up to 2	0.1 to 1.5	1

In order to show the improved result attained by our invention we will describe the results of a series of tests showing the increase in the corro-

sion resistance of specific coatings obtained by practicing our improved method. Other alloys of magnesium may be employed instead of the one specifically hereinafter disclosed, for instance, the commercial alloys of magnesium with aluminum, zinc, tin, copper, manganese, and silicon. We treated a magnesium base alloy, consisting of 95.7 per cent magnesium, 4 per cent aluminum, and 0.3 per cent manganese, with certain coating solutions having concentrations of the various salts within the ranges set forth in the preceding table. Small panels of the alloy, about ¼ x 1" x 4" in dimension, were treated with the various coating solutions and then subjected to an alternate immersion test in a 3 per cent aqueous sodium chloride solution. The alternate immersion cycle was 15 seconds in the solution and 105 seconds out of the solution exposed to ordinary room atmosphere. All of the tests were run in triplicate and the results shown are the average obtained by comparing three similarly treated panels. The arbitrary numerical value 7 was assigned to measure the amount of corrosion of the coating obtained by treatment of the said alloy with a 10 per cent aqueous solution of sodium dihydrogen phosphate without the addition of any other salt. The values shown in the table as less than 7 indicate less corrosion, hence a comparative increase in the corrosion resistance of the coating formed on the alloy by treatment thereof with aqueous solutions containing 10 per cent of NaH_2PO_4, and the amount of other salts per 100 milliliters shown by the table:—

10 per cent NaH_2PO_4 solution containing—	Value
1.0 gram of $Na_2Cr_2O_7$	5
5.0 grams of $Na_2Cr_2O_7$	4
10 grams of $Na_2Cr_2O_7$	3
20 grams of $Na_2Cr_2O_7$	2
1.0 gram of Na_2WO_4	4
5.0 grams of Na_2WO_4	3
10 grams of Na_2WO_4	4
20 grams of Na_2WO_4	5
1.0 gram of $NaVO_3$	4

It will be noted from the results shown in the preceding table that the corrosion resistance of the coating increases progressively in accordance with the amount of sodium bichromate used in the coating solution. However, we have determined that a coating having a corrosion resistance value of 3 affords sufficient protection to magnesium surfaces to be commercially desirable, and for this reason our preferable amount of $Na_2Cr_2O_7$ to be used is about 10 grams per 100 milliliters of a 10 per cent NaH_2PO_4 solution. It will be seen that the value of the tungstate salt is progressively better up to a certain point as the amount thereof used increases but that past the optimum point the value of this salt in aiding the formation of a protective coating apparently decreases. The vanadate does not appear to have quite as beneficial a total action as the other salts, due probably to its being less soluble than the others, but per gram of salt added its action is more pronounced than other salts.

Instead of the sodium bichromate herein specifically disclosed we may use potassium bichromate, or any of the soluble chromates, which are probably converted to the bichromates in the acid phosphate solution, as equivalents for the sodium salt. Satisfactory results can also be obtained by using combinations of the various salts hereinbefore set forth, in admixture with a dihydrogen phosphate solution. Instead of adding compounds of the various acids, which is the preferable mode of procedure, we may add the acids themselves with equally advantageous results, therefore, where the word "compound" occurs in the claims it should be taken to mean the salts of the acids and/or the acids as well.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method and products herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

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

1. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of a solution of a dihydrogen phosphate and a compound of an acid from the group consisting of chromic, tungstic, and meta-vanadic acids.

2. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of a solution of a dihydrogen phosphate and a compound from the group consisting of the alkali metal, alkaline earth metal, and magnesium, salts of chromic, tungstic, and meta-vanadic acids.

3. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of a solution of a dihydrogen phosphate and a salt of chromic acid.

4. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of a solution of a dihydrogen phosphate and a salt of tungstic acid.

5. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of a solution of a dihydrogen phosphate and a compound selected from the group consisting of an alkali metal, alkaline earth metal, magnesium, or ammonium salt of chromic acid.

6. A method of treating the surfaces of magnesium or magnesium base alloys which comprises subjecting said surfaces to the action of an aqueous solution of mono-sodium phosphate and an alkali metal bichromate.

7. A magnesium or magnesium base alloy article having on its surface an adherent coating formed integrally therewith by the reaction of a solution of a dihydrogen phosphate and a compound of an acid selected from the group consisting of chromic, tungstic, and meta-vanadic acids.

8. A magnesium or magnesium base alloy article having on its surface an adherent coating formed integrally therewith by the reaction of a solution of a dihydrogen phosphate and a compound from the group consisting of the alkali metal, alkaline earth metal, magnesium, and ammonium salts of chromic, tungstic, and meta-vanadic acids.

9. A magnesium or magnesium base alloy article having on its surface an adherent coating formed integrally therewith by the reaction of a solution of a dihydrogen phosphate and a compound selected from the group consisting of an alkali metal, alkaline earth metal, or magnesium, salt of chromic acid.

10. A magnesium or magnesium base alloy ar-

ticle having on its surface an adherent coating formed integrally therewith by the reaction of an aqueous solution of mono-sodium phosphate and sodium tungstate.

11. A magnesium or magnesium base alloy article having on its surface an adherent coating formed integrally therewith by the reaction of an aqueous solution of mono-sodium phosphate and an alkali metal bichromate.

12. A composition of matter consisting of an aqueous solution of mono-sodium phosphate and sodium tungstate.

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