

UNITED STATES PATENT OFFICE

2,276,286

METHOD OF TREATING PROTECTIVE COATINGS ON MAGNESIUM AND ITS ALLOYS

Robert W. Buzzard, Kensington, Md.

No Drawing. Application July 26, 1937,
Serial No. 155,699

6 Claims. (Cl. 204—35)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

The invention relates to the corrosion resistant coatings on magnesium and its alloys and has for one of its objects to increase the durability and the protective characteristics of the coating.

The method specifically relates to the treating of protective coatings on magnesium and its alloys with a chemical solution or seal in the presence of heat, followed by a heat treatment in a liquid inert to magnesium so as to not only dehydrate the coating but also to form a seal and surface coating, thus increasing the durability of the article treated to wear and improving its resistance to corrosion.

The invention disclosed and claimed herein is an improvement on and extension of the subject matter of my copending applications, Serial No. 150,932, filed June 29, 1937, now Patent No. 2,203,670 of June 11, 1940, and Serial No. 151,514, filed July 1, 1937, now abandoned.

The anodized article to be treated according to this invention is washed free of anodizing solution, providing the electrolytic bath is basically different from the chemical solution used in my method and is then immersed in a hot solution of chemical sealing compounds, preferably at or above the boiling point of water, but below the fusion point of the metal. After suitable treatment in this solution, the article is removed, washed and then introduced directly into a hot bath of liquid comprising a waterproofing or drying agent which, after the article is removed from the bath, is permitted to dry thereon.

The chemical sealing solution should contain a corrosion inhibiting ion such as either a chromate or dichromate and a second salt as a reacting ion such as manganese, chromium, molybdate, borate, sulphate, phosphate, fluoride or a combination of any of the said second salts. The concentration of the salts is limited only by their solubility, but may be varied to conform with time of application and quality of seal. Good chemical seals of coated metal have been obtained by subjecting the coatings to treatment for periods varying from five minutes to one hour.

The bath of liquid comprising a waterproofing or drying agent should contain one or more materials selected from the following groups, namely, petroleum base oils, waxes, resins, synthetic resins or drying oils. Anodized and chemically sealed magnesium and its alloys, when placed in a bath of this type, have the peculiar property of evolving a comparatively large volume of gas on heating to or above the boiling point of

water. Thus, the article in the hot bath will evolve gas vigorously on coming to the temperature of the bath. This action appears to be primarily a dehydration of the film and, with this action, the liquid of the bath is absorbed by the coating. In practice, it has been found that the gas evolves for a short period of time, about five to thirty minutes in a bath heated to 150° C. and then subsides. The article should remain in the bath until the evolution of gas ceases. It is then removed and either forced dried or allowed to dry in the air. The bath may be heated to varying temperatures, slightly below, at, or above the boiling point of water, but must be limited to below the fusion point of the metal.

Specifically, as an example, if an anodic coating be formed on magnesium or its alloys in a bath of 10 per cent dichromate and 2 per cent phosphate and the coating has been washed free of anodizing solution, its corrosion resistance will be greatly improved if it be first immersed for a period of about 20 minutes in a solution of 10 per cent dichromate and 10 per cent manganous sulphate heated to a temperature between 90° and 150° C., removed, washed and then introduced into a second bath of tung oil heated to a temperature between 90° and 150° C. The article is allowed to remain in the second bath until all evolution of gas has ceased, thus, the time period is dependent upon the temperature of the bath. The material is then removed from the bath and allowed to drain and/or dry.

As further examples of compositions which can be used as chemical seals for electrolytic coatings on magnesium, the following are cited.

- (a) 1 to 30 per cent dichromate
0.25 to 10 per cent (salts of chromium)
- (b) 1 to 30 per cent dichromate
1 to 30 per cent borate
- (c) 1 to 30 per cent dichromate
1 to 30 per cent sulphate
- (d) 1 to 30 per cent dichromate
0.25 to 20 per cent fluoride
- (e) 1 to 30 per cent dichromate
1 to 30 per cent phosphate
- (f) 1 to 30 per cent dichromate
1 to 30 per cent salt of manganese

In the above compositions, chromate or a suitable corrosion inhibiting ion can be substituted for dichromate and in various basic solutions, one or more of the following have been added with very good results, namely, chromium fluoride, sodium fluoride, chromium phosphate, sodium borate, manganous sulphate, zinc phosphate, zinc chromate, ammonium and other salts.

Baths of the following materials have been used very satisfactorily as waterproofing or drying agents in my improved method of sealing magnesium and its alloys:

(a) Petroleum base oils of the heavy type as used in high temperature heat treatment baths.

(b) Waxes, including paraffin, ceresin and carnauba wax.

(c) Resins, synthetic resins of the straight hydrocarbon type as Santo-resins, the glyceryl phthalate type or alkyd type and the phenolic type as Bakelites.

(d) Drying oils including tung or China-wood oil, linseed oil, and fish oil.

While the aforestated chemical solutions with the waterproofing baths are described as seals, they may be used directly together to produce a combination corrosion resistant coating and seal on magnesium or its alloys.

The sealing method herein described not only greatly improves the characteristics of electrolytic coatings on magnesium and magnesium alloys, but also improves protective coatings produced by the various dip or immersion methods wherein the coating is produced by reaction with the magnesium. In other words, resistance against corrosion of protective coated magnesium or its alloys can be greatly increased by treating the coated metal in a solution containing a corrosion inhibiting ion such as either chromate or dichromates in the presence of one or more reacting agents selected from the groups of fluorides, manganese, chromium, molybdates, borates, sulphates and phosphates. This treatment may or may not be followed by immersing the metal in a bath containing a waterproofing agent. However, if both the chemical seal and the waterproofing bath are used resistance against corrosion of the coated metal is increased accordingly.

In comparative corrosion tests, the benefits of sealing were evinced in that coated articles of identically the same type of magnesium, comprising dipped unsealed specimens, dipped chemically sealed specimens, dipped specimens chemically and waterproofed sealed, unsealed anodized specimens, chemically sealed anodized specimens, waterproofing sealed anodized specimens and anodized specimens sealed by the chemical solution followed by the waterproofing bath, immersed in a tank containing 3 per cent NaCl solution, disclosed that the unsealed dip coated metal failed within 5 hours, the chemically sealed dip coated specimens and the unsealed anodized metal failed 50 per cent within 100 hours, the chemically and waterproofed sealed dip coated specimens failed within 150 hours, the chemically sealed and the waterproofing sealed anodized specimens withstood 300 hours, while the anodized specimens sealed by the chemical solution followed by the heated waterproofing bath were in good condition in excess of 700 hours.

The above mentioned substances used in the magnesium treatments are mentioned by way of illustration and not limitation, since the invention comprehends treatments of the character indicated broadly above and is not to be limited except by the appended claims.

The invention herein described and claimed may be used and/or manufactured by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

I claim:

1. A method of producing corrosion resistant coatings on magnesium or magnesium alloys comprising anodizing the metal in a bath containing the phosphate and chromate radicals, the pH of the bath being on the acid side, subjecting the coated metal to a treatment with an aqueous solution containing manganous sulphate and a water soluble compound selected from the group consisting of the chromates and dichromates, and then immersing the metal in a drying oil selected from the group consisting of tung oil, linseed oil and fish oil.

2. A method of producing corrosion resistant coatings on magnesium or magnesium alloys comprising anodizing the metal in a bath containing the phosphate and chromate radicals, the pH of the bath being on the acid side, subjecting the coated metal to a treatment with an aqueous solution containing chromium fluoride and a water soluble compound selected from the group consisting of the chromates and dichromates, and then immersing the metal in a bath of tung oil heated to and maintained during treatment at a temperature substantially equivalent to or above the boiling point of water.

3. A method of sealing a protective coating on articles of magnesium or magnesium base alloys, produced by chemical reaction with the metal, to increase the corrosion resistance thereof, which comprises first treating the coated article in a hot solution containing a water soluble compound selected from the group consisting of the chromates and dichromates and also a water soluble salt selected from the group consisting of the sulphates, phosphates, molybdates, borates and fluorides, the pH of such solution being on the acid side, and then immersing the treated article in a bath of a waterproofing agent selected from the group consisting of petroleum base oils, waxes, resins and drying oils at a temperature not substantially below the boiling point of water, the latter treatment being continued until the evolution of gas from the treated article substantially ceases.

4. A method of producing protective coatings of improved corrosion resistance on articles of magnesium or magnesium base alloys which comprises forming on the metal an anodic coating produced by reaction with the magnesium, subjecting said coating to a non-electrolytic treatment in a hot solution containing a water soluble compound selected from the group consisting of the chromates and dichromates and also a water soluble salt selected from the group consisting of the sulphates, phosphates, molybdates, borates and fluorides, the pH of such solution being on the acid side, and then immersing the treated article in a liquid bath of a waterproofing agent selected from the group consisting of petroleum base oils, waxes, resins and drying oils at a temperature not substantially below the boiling point of water, the latter treatment being continued until the evolution of gas from the treated article substantially ceases.

5. A method according to claim 4 in which the waterproofing agent is a drying oil.

6. A method according to claim 4 in which the waterproofing agent is tung oil.

ROBERT W. BUZZARD.