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PROTECTIVE COATING ON MAGNESIUM

Roy Shawcross, Salina, Pa., assignor to Aluminum Company of America, Pittsburgh, Pa., a corporation of Pennsylvania

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7 Claims. (Cl. 204—56)

This invention relates to a method for improving the resistance of magnesium to corrosion, and more particularly it is concerned with a process for producing a protective coating upon the surfaces of articles of magnesium.

The term "magnesium" as used in this specification and in the appended claims includes alloys containing more than 50 per cent of magnesium as well as magnesium itself.

While magnesium and its alloys are well adapted for most ordinary uses in which that metal is generally employed, it quite often is desirable to provide a film or coating upon the surface of the metal in order to protect it from agents which otherwise have a corrosive effect upon the untreated magnesium. In some cases, however, magnesium articles being provided with such films undergo some dimensional change during the coating operation, the action of the film-forming agent causing some increase or decrease in their size. This dimensional change is one that is permitted by some dimensional tolerances, but it may become quite serious, as when coated articles must be supplied within a narrow range of dimensional tolerances. Moreover, it frequently happens that an article is treated which is made from two or more alloys of magnesium, and in such a case some difficulty is often encountered in causing the coating to adhere to the surface of that portion of the article made up of the alloy having the higher solution potential. While a satisfactory coating forms during the treatment upon the alloy having the lower potential, the film which forms upon the higher potential alloy in the assembly is not so thick and does not adhere to the surface of the alloy so readily.

The object of this invention is to provide an improved surface treatment for articles of magnesium whereby the resistance of such articles to corrosion is improved. More particularly, the object of the invention is to provide an improved treatment by which a protective coating may be formed upon articles of magnesium without effecting any substantial change in the dimensions of the articles treated.

The invention has for its specific object the provision of such a method for producing a protective coating upon the surface of an article constructed from a plurality of alloys of magnesium. Other objects will appear in the following description of the invention and in the appended claims.

I have found that these and related objects may be accomplished by treating the surfaces of mag-

nesium articles in an aqueous solution containing basic aluminum nitrate and at least one alkali metal chromate, which term as used herein includes the dichromate of any of the alkali metals, including ammonium. Preferably the solution also should contain a suitable wetting agent.

The basic aluminum nitrate, including whatever normal aluminum nitrate may be present, should comprise between about 10 and about 60 per cent of the weight of the coating solution and preferably should be maintained between about 40 and 60 per cent. The alkali metal chromate content should amount to about 1 to 10 per cent and the wetting agent, if used, to about 0.05 to 0.2 per cent of the total weight of the solution. Such a solution has a pH between about 0.75 and 3.8 during the coating operation.

A method for the production of basic aluminum nitrate suitable for use in the practice of my invention is described in considerable detail in Patent No. 2,127,504, granted August 23, 1938, to Derr and Stere. Such a nitrate may be prepared by melting normal aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, at a temperature of about 73°C . and gradually increasing the temperature to about 145°C . During this rise in temperature the normal aluminum nitrate melts, and then seems to decompose and nitric acid and water of crystallization are driven off, leaving alumina dissolved in the melt. This alumina appears to form a complex with the remaining undecomposed molecules of aluminum nitrate apparently corresponding to the formula



and this complex of the molecules of aluminum nitrate and of alumina is the basic nitrate of aluminum which I employ in the coating solution. It is not necessary that all of the normal aluminum nitrate be converted to the basic nitrate, but from about 1 to 60 per cent of the weight of the total alumina equivalent in the coating solution should be alumina in excess of the amount present as $\text{Al}(\text{NO}_3)_3$ and forming a complex with the aluminum nitrate, and this alumina is herein referred to as excess alumina. I have found that the most satisfactory results are obtained if the excess alumina forming the complex is between about 25 and 40 per cent of the total alumina equivalent.

The chromate of any of the alkali metals may be used, but I prefer to use the potassium salt. In the preferred practice of the invention a wetting agent is used in the solution, and this preferably is a sulfonated alcohol or a salt thereof

which is stable in the coating solution and at the temperatures employed during the coating operation. I have found a commercial sulfonated alcohol preparation sold as MPD 189 to be particularly adapted for this purpose.

The surface of an article of magnesium may be coated in such a solution either by immersion or electrolytically. The period of immersion in the solution is preferably between about 15 and 60 minutes and the temperature of the solution should be from about 95° to 100° C. If the article is to be coated electrolytically, it should be made the anode for a period of about 10 to 30 minutes in the solution at the same temperature. The cathode may be carbon and the current density should be from about 0.25 to 2.0 amperes per square inch of magnesium surface treated.

The coatings produced either by immersion or electrolytically in the solution are bronze to dark brown in color and they are relatively thick and adherent and are quite dense and non-porous. They offer good resistance to the attack of corrosive agents and provide excellent protection against corrosion for the underlying metal. In addition, the coatings may be applied to the surfaces of magnesium articles which are to be painted.

My coating treatment is particularly adapted for the treatment of articles which have been fabricated to very close tolerances. This is because there is usually no important dimensional change in the size of such articles as they are coated in the solution. For example, the loss in diameter of a cylinder of magnesium 0.946 inch in diameter while it is subjected to some of the various coating treatments now used commercially has been found to be as high as 0.05 inch. In contrast, such a cylinder of a magnesium base alloy containing 1.5 per cent manganese was found to have undergone a loss in diameter of only 0.0001 inch during a 30 minute coating treatment in an aqueous solution containing 24.1 per cent basic aluminum nitrate having an excess alumina content of 11.2 per cent, 5 per cent potassium dichromate, and 0.2 per cent MPD 189. Similar specimens of other alloys were coated in the same solution and these likewise became coated without any substantial dimensional changes.

My method of producing coatings upon magnesium has the further advantage that it may be used to coat the surfaces of articles constructed from more than one alloy of magnesium. The fact that there might be a difference in the solution potential of the different alloys making up the articles does not appear to hinder the formation by the method of this invention of a protective coating covering the surfaces of the alloys during the treatment. This may be shown by the following description of tests made in connection with the coating in the solution of composite articles made up from two alloys of magnesium, each having different solution potentials.

An article having portions made from a magnesium base alloy containing 10 per cent aluminum and 0.2 per cent manganese and remaining portions made from an alloy of magnesium containing 3 per cent aluminum was immersed for 30 minutes in an aqueous solution at a temperature of 100° C. and containing 24.1 per cent basic aluminum nitrate of which 11.2 per cent was excess alumina, and in addition 5 per cent potassium dichromate and 0.2 per cent MPD 189. At the end of that time, despite the difference in the solution potential of the two magnesium

base alloys from which the article was constructed, the entire article was provided with a hard adherent coating which showed excellent resistance to corrosion in an aqueous solution containing sodium chloride. Similar resistance to corrosion was displayed by the coating formed upon an article made anode in the same solution for period of 15 minutes at 10 volts and with a current density of 1 ampere per square inch.

These examples, in which all composition percentages are given by weight, are given for purposes of illustration and it will be understood that various changes may be made in the operation of my process without departing from the scope of my invention.

I claim:

1. A method for producing a protective coating on the surface of an article of magnesium which comprises treating said surface with an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate and between about 10 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between 1 and about 60 per cent forming a complex with said aluminum nitrate.

2. A method for producing a protective coating on the surface of an article of magnesium which comprises treating said surface with an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate, between about 0.05 and 0.2 per cent of a wetting agent, and between about 10 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between about 1 and about 60 per cent forming a complex with said aluminum nitrate.

3. A method for producing a protective coating on the surface of an article of magnesium which comprises treating said surface with an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate, between about 0.5 and 0.2 per cent of a wetting agent, and between about 40 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between about 1 and about 60 per cent forming a complex with said aluminum nitrate.

4. A method for producing a protective coating on the surface of an article made from a plurality of alloys of magnesium which comprises treating said surface with an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate, between about 0.05 and 0.2 per cent of a wetting agent, and between about 10 and about 60 per cent of aluminum nitrate, said basic aluminum nitrate having a content of between about 1 and about 60 per cent excess of alumina forming a complex with said aluminum nitrate.

5. A method for producing a protective coating on the surface of an article of magnesium which comprises immersing said article for a period of between about 15 and about 60 minutes in an aqueous solution at a temperature of about 95 to 100° C. and containing between about 1 and about 10 per cent of at least one alkali metal chromate and between about 10 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between about 1 and about 60 per cent forming a complex with said aluminum nitrate.

6. A method for producing a protective coating on the surface of an article of magnesium which

comprises making said article anode during electrolysis in an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate and between about 10 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between about 1 and about 60 per cent forming a complex with said aluminum nitrate.

7. A method for producing a protective coating on the surface of an article of magnesium which comprises making said article anode for a period

between about 10 and about 30 minutes during electrolysis at a current density from about 0.25 to 2.0 amperes per square inch of surface of said article treated, in an aqueous solution containing between about 1 and about 10 per cent of at least one alkali metal chromate and between about 10 and about 60 per cent of basic aluminum nitrate, said basic aluminum nitrate containing excess alumina in an amount between about 1 and about 60 per cent forming a complex with said aluminum nitrate.

ROY SHAWCROSS.

CERTIFICATE OF CORRECTION.

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June 15, 1943.

ROY SHAWCROSS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 43, claim 3, for "0.5" read --0.05--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of July, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.