

1

2

Example "A"

2,880,148

METHOD AND BATH FOR ELECTROLYTICALLY
COATING MAGNESIUM

Harry A. Evangelides, Chalfont, Pa.

No Drawing. Application November 17, 1955
Serial No. 547,590

14 Claims. (Cl. 204—35)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon.

The present disclosure is a continuation-in-part of my now abandoned co-pending application, Serial No. 132,788, which was filed on December 13, 1949, and of my co-pending application, Serial No. 318,536, which was filed on November 3, 1952, and has since issued as Patent No. 2,723,952, dated November 15, 1955, for Method of Electrolytically Coating Magnesium and Electrolyte Therefor.

This invention relates to processes for protecting magnesium and magnesium base alloys against corrosion and erosion by treatment of the metal with a solution which electrochemically reacts with the metal to produce a protective coating on the metal's surface.

Broadly stated, the primary object of my invention is to provide means for acquiring such a coating that will have the indicated desired attributes to a very high degree not generally known to the art.

A secondary object is to produce such a coating by means which are simple, rapid and inexpensive.

Because of their many valuable characteristics, particularly their strength-to-weight ratio, magnesium-rich alloys have long been desired by metal users. But employment of such alloys has been considerably restricted due to low resistance to corrosion and erosion, and as a result many treatments have been devised to produce coatings on the metal which will diminish such deteriorative effects.

However, the prior art coatings have not furnished sufficient protection to make magnesium alloys suitable for all their otherwise possible uses. One reason for this is that the prior art coatings have not been very resistant to abrasion so that the coatings often were damaged and the base metal left unprotected. My invention overcomes these deficiencies by providing a caliber of protection against corrosion, erosion and abrasion which has tremendously expanded the possible applications of magnesium-rich alloys.

According to the present invention a protective coating is produced on magnesium and magnesium base alloys by treating the metal in an alkaline electrolytic bath preferably containing fluorides, phosphates, alkali metal hydroxides and a compound selected from the class consisting of chromates, selenates, stannates, tungstates, vanadates, molybdates, silicates and borates.

In Example "A" which follows, there are identified the constituents of an electrolytic bath made in accordance with the present invention. In one column opposite those constituents, the quantities thereof are listed in what may be considered a typical and preferred composition. In an adjacent column the quantities are listed in accordance with ranges of constituents which may be employed with acceptable results.

	Preferred Formulation, grams/liter of water	Ranges, grams/liter of water
Potassium chromate.....	20	1-60
Potassium fluoride (anhydrous).....	35	1-300
Tri-potassium phosphate.....	35	10-300
Potassium hydroxide.....	100	20-130

A number of modifications to this bath may be employed, each consisting of a straightforward substitution of one constituent for another listed above. To list each as a separate example would be unnecessarily repetitive. In the interests of conciseness, as well as accuracy, the following explanation of the specific details should be sufficient. In lieu of potassium chromate there may be employed, in the same preferred amount or within the same ranges indicated, either potassium selenate, or stannate, or tungstate, or vanadate, or molybdate, or silicate, or borate. Furthermore, in each instance where a potassium compound has been called for, a sodium compound of the chromate, etc., fluoride, phosphate, and hydroxide may be employed instead, without requiring any change in the quantities shown therefor in the preferred amounts or broad ranges of constituents. Each of the substitution compounds for the ones listed under the above example has been tried (in the preferred amounts and at the upper and lower limits stated) without varying the conditions of use as hereinafter described, and all have led to essentially equivalent and successful results. That is to say regardless of which of the substitution compounds mentioned is employed, for the corresponding substances in the example, if the amounts thereof and the operating conditions are maintained the same, the results will be substantially duplicative of each other.

Although the formulations set forth above are very satisfactory, still more beneficial results are obtained with the inclusion in the bath of aluminum hydroxide, or sodium or potassium aluminate. However, these aluminum compounds are incompatible with the use of silicates as the bath will become fouled with a gel when the two are mixed together. Hence, the aluminum compounds are to be used in baths which do not contain those silicates, as illustrated in the following examples:

Example "B"

	Preferred Formulation, grams/liter of water	Ranges, grams/liter of water
Potassium chromate.....	20	1-60
Potassium fluoride (anhydrous).....	35	1-300
Tri-potassium phosphate.....	35	10-300
Potassium hydroxide.....	100	20-130
Aluminum hydroxide.....	30	1-100

Example "C"

	Preferred Formulation, grams/liter of water	Ranges, grams/liter of water
Potassium chromate.....	20	1-60
Potassium fluoride (anhydrous).....	35	1-300
Tri-potassium phosphate.....	35	10-300
Potassium hydroxide.....	65	20-85
Potassium aluminate.....	40	1-125

As was mentioned with regard to Example "A," the two columns of figures in Examples "B" and "C" will be seen to represent a preferred composition in the one, and in the other are listed ranges of the constituents which may

3

be successfully employed in practicing the present invention. Here, too, the same sort of modifications have been tested with the same degree of success, as explained above. That is, in lieu of potassium chromate there may be substituted potassium selenate, stannate, tungstate, vanadate, molybdate, or borate. Furthermore, in each instance where a potassium compound has been called for, a sodium compound of the chromate, etc., fluoride, phosphate, and hydroxide may be employed as a direct substitution without changing amounts or conditions of use.

Wrought magnesium-rich articles to be given the protective coating of the present invention are prepared for immersion in the electrolytic baths described above by thoroughly degreasing with a suitable organic solvent such as properly stabilized carbon tetrachloride and/or a hot alkaline cleaner solution, such as one containing sodium orthosilicate and a detergent. Two of the thus cleaned articles are used as the electrodes in the electrolytic baths of the present invention which preferably are kept between 20° to 30° C. When the connections are properly made, the current is turned on and the process operated as described below.

Either alternating (A.C.) or direct (D.C.) current may be employed, although the former appears to effect a better coating. It is possible, also, to use A.C. followed by D.C., and A.C. superposed on D.C. Optimum frequencies have been found to be between 50 and 133 cycles per second (c.p.s.) but frequencies ranging from 1 to 2,000 c.p.s. have been tried with success.

It is desirable to maintain the current density throughout the electrolysis between 10–20 amperes per square foot. However, the process will operate satisfactorily with a current density of 5 amperes per square foot and at least up to a current density of 500 amperes per square foot (which was the limit of the apparatus that I had available for use in testing the present invention). The required current density is achieved by appropriately adjusting the electrolytic conditions, including the voltage, in a manner well known to the art.

The voltage and time requirements appear to vary somewhat with the nature of different magnesium alloys given the novel treatment, but on the average it has been found that an upper limit of 50–85 volts generally will indicate sufficient time of electrolysis. The process can, in some cases, be operated satisfactorily as high as 100 volts, or more, and acceptable results have also been achieved with low voltages on the order of 7–13 volts.

Using the preferred current density and voltage indicated above, the process usually may be completed in about 20–60 minutes. Of course, as the current density is increased, it is possible to reduce the amount of time of the operation. In some cases where the upper limit of current density mentioned above was employed, satisfactory coatings were obtained in about three minutes.

With respect to the temperature requirement, although the above-mentioned temperature of 20–30° C. is preferred, I have found it possible to get good coatings from –10 to 65° C.

Upon conclusion of the electrolysis, work which has been treated at the indicated higher voltages (60 v. or more) is rinsed in water and then dipped for about 1 to 2 minutes in a solution which preferably comprises approximately 20 grams of sodium or potassium dichromate, approximately 100 grams of ammonium bifluoride, and enough water to make up 1 liter. This solution preferably is kept at room temperature. After this dip, the work is removed and dried without rinsing, and then placed in an oven where it is heated at a temperature of about 85 to 95° C., and at a relative humidity of 95% for approximately 7–16 hours. This oven conditioning may be eliminated if the coating is to be used as a base which is to be painted.

Work which has been treated at the indicated lower voltages (13 v. or below) is dipped for about 2 minutes or more in a solution preferably comprising approxi-

4

mately 2 grams of sodium or potassium dichromate and enough water to make up 1 liter. The temperature of this solution is kept at about 90° C. After this dip, the work is removed and dried without rinsing. No oven conditioning is required after this treatment.

The described electrolytic treatments result in formation of coatings possessing superior properties which were more fully described in the aforementioned parent applications and will be found in my aforementioned issued patent. It will be sufficient, therefore, to say at this point that the coatings produced by the present invention far surpass those of the prior art with respect to their ability to resist abrasion, corrosion and erosion, and that the present coatings are dense, hard and non-porous, adhering very well to the base metal and having excellent refractory characteristics. The novel coatings are insoluble in dilute and concentrated nitric and sulfuric acids as well as dilute hydrochloric acid, and are only slightly reactive with concentrated hydrochloric acid. The corrosion resistance of the present coatings is exceptional as proven by the fact that many hundreds of hours were required to produce corrosion spots on test panels exposed in accordance with M.B-117 of the American Society for Testing Materials, whereas an equivalent attack on the metal was caused in only a few hours upon the best known prior art coated article.

The present invention may be modified in a number of ways, some of which have already been indicated, without departing from its spirit and scope. For example, dyes may be added to the coating in accordance with well-known procedures in order to obtain coatings of different colors. Instead of spraying the paint within the time limits indicated above, the electrolysis can be run for as much as 2 hours or more, the increased time allowing the coating to become even more uniform. The oven conditioning, after the bifluoride-dichromate dip, can be eliminated if only high abrasion resistance is sought and high corrosion resistance is not material.

Still other obvious modifications will suggest themselves to workers skilled in the art, depending upon the particular magnesium coating problem which may confront them.

From the foregoing it will be seen that I have provided means for acquiring on the surface of magnesium and magnesium base alloys, by treating them with a solution that electrochemically reacts therewith, a coating that well protected the metals against corrosion and erosion; and that I have produced such a coating by means that are simple, rapid and inexpensive.

As previously pointed out, my invention is capable of wide application and hence is not to be restricted to the specific limits here described and illustrated.

I claim:

1. An electrolytic bath for forming a coating on the surface of articles of magnesium and magnesium base alloys having water as the solvent and consisting essentially of 1 to 60 grams per liter of a compound selected from the class consisting of sodium and potassium chromates, selenates, stannates, tungstates, vanadates, molybdates, and borates, 1 to 300 grams per liter of an anhydrous fluoride selected from the class consisting of sodium and potassium fluorides, 10 to 300 grams per liter of a phosphate selected from the class consisting of sodium and potassium phosphates, 20 to 130 grams per liter of an alkali metal hydroxide from the class consisting of sodium and potassium hydroxides, and 1 to 125 grams per liter of an aluminum compound selected from the class consisting of aluminum hydroxide, potassium aluminate, and sodium aluminate.

2. A method of producing an abrasion resistant and corrosion resistant coating upon magnesium rich articles which consists of forming a bath according to claim 1 and passing an electrical current of at least 5 amps per square foot through said bath while maintaining the bath at a temperature between –10° and 65° centigrade.

5

3. The method of claim 2 in which the bath is maintained at a temperature between 20° and 30° centigrade.

4. The method of producing a coating upon an article formed of magnesium and magnesium base alloys which consists of making said article an electrode in an electrolytic bath consisting of the composition of claim 2, passing an electric current of at least 5 amperes per square foot through said bath, obtaining said current at a voltage between about 7 and 85 volts, while maintaining said bath at a temperature between about -10° C. and 65° C., and thereafter conditioning said article against corrosion by dipping in a solution selected from the class consisting of sodium and potassium dichromate and sodium and potassium dichromate ammonium bifluoride which chemically reacts with the coating, allowing to dry without rinsing, and then ageing said article.

5. The method of claim 4 in which the bath is maintained at a temperature between 20° C. and 30° C.

6. The method of claim 5 in which the current of at least about 5 amperes per square foot is maintained at a voltage above about 50 volts and said article is conditioned against corrosion by dipping for a period of about 1 to 2 minutes in an aqueous solution containing about 20 grams per liter of a dichromate selected from the class consisting of sodium dichromate, potassium dichromate and about 100 grams per liter ammonium bifluoride, said solution being kept at about room temperature, allowing said article to dry without rinsing, then ageing by heating to from about 85° to 95° C. at a relative humidity of about 95% from about 7 to 16 hours.

7. The method of claim 5 in which said current of 5 amperes per square foot is maintained at a voltage between about 7 and at least about 13 volts, and said article is conditioned against corrosion by dipping for at least 2 minutes in an aqueous solution containing about 2 grams per liter of a dichromate selected from the class consisting of sodium dichromate and potassium dichromate, said solution being kept at about 90° centigrade, allowing to dry without rinsing then ageing at about room temperature.

8. An electrolytic bath for forming a coating on the surface of articles of magnesium and magnesium base alloys having water as the solvent and consisting essentially of about 10 to 25 grams per liter of a compound selected from the class consisting of sodium and potassium chromates, selenates, stannates, tungstates, vanadates, molybdates and borates, about 30 to 40 grams per liter of an anhydrous fluoride selected from the class consisting of sodium and potassium fluorides, about 30 to 50 grams per liter of a phosphate selected from the class consisting of sodium and potassium phosphate, about 100 to 130 grams per liter of an alkali metal hydroxide selected from the class consisting of sodium and potassium hydroxide and about 25 to 35 grams per liter of an aluminum compound selected from the class consisting of aluminum hydroxide, potassium aluminate and sodium aluminate.

9. The method of producing a coating upon an article

6

formed of magnesium and magnesium base alloys which consists of making said article an electrode in an electrolytic bath consisting of the composition of claim 8, passing an electric current of at least about 5 amperes per square foot through said bath while maintaining said bath at a temperature between -10° and 65° centigrade.

10. The method of claim 9 in which said bath is maintained at a temperature between 20° and 30° centigrade.

11. The method of producing a coating upon an article formed of magnesium and magnesium base alloys which consists of making said article an electrode in an electrolyte bath consisting of the composition of claim 8, passing an electric current of at least about 5 amperes per square foot through said bath, obtaining said current at a voltage between 7 and 85 volts, while maintaining said bath at a temperature between -10° and 65° centigrade, and thereafter conditioning said article against corrosion by dipping in a solution selected from the class consisting of sodium dichromate and potassium dichromate and sodium dichromate and potassium dichromate ammonium bifluoride which chemically reacts with the coating allowing to dry without rinsing, then ageing said article.

12. The method of claim 11 in which the bath is maintained at a temperature between 20° and 30° centigrade.

13. The method of claim 12 in which the current of 5 amperes per square foot is maintained at a voltage above about 50 volts and said article is conditioned against corrosion by dipping for a period of about 1 to 2 minutes in an aqueous solution containing about 20 grams/liter of a dichromate selected from the class consisting of sodium dichromate and potassium dichromates and about 100 grams per liter ammonium bifluoride, said solution being kept at about room temperature, allowing said article to dry without rinsing, then ageing by heating to from about 85° to 95° centigrade at a relative humidity of about 95% from about 7 to 16 hours.

14. The method of claim 12 in which the current of at least about 5 amperes per square foot is maintained at a voltage between about 7 and 13 volts, and said article is conditioned against corrosion by dipping for at least 8 minutes in an aqueous solution containing about 2 grams per liter of a dichromate selected from the class consisting of sodium dichromate and potassium dichromate, said solution being kept at about 90° centigrade, allowing to dry without rinsing, then ageing at about room temperature.

References Cited in the file of this patent

UNITED STATES PATENTS

2,305,669	Budiloff et al.	Dec. 22, 1942
2,314,341	Buzzard	Mar. 23, 1943
2,766,199	Higgins	Oct. 9, 1956

FOREIGN PATENTS

543,726	Great Britain	Mar. 10, 1942
---------	---------------------	---------------