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METHOD OF ELECTROLYTICALLY COATING MAGNESIUM AND ELECTROLYTE THEREFOR

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

The present disclosure is a continuation-in-part of my copending application, Serial No. 132,788, which was filed on December 13, 1949, now abandoned.

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. It also refers to the formation by such treatment of coatings having valuable abrasive and refractory properties.

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 high degree hitherto unknown 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, these prior art coatings have not offered 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 was 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 manganates.

A typical and preferred electrolytic bath may be made, in accordance with the present invention, from the constituents given in the following example:

Example A

	Grams per liter
Potassium manganate	20
Potassium fluoride (anhydrous)	35
Trisodium phosphate ($Na_3 Po_4 \cdot 12H_2O$)	35
Potassium hydroxide	100
Aluminum hydroxide (dried gel)	30

Although the formulation just set forth is a preferred one, it is possible to use wide ranges of each of the specified bath components and still get good coatings which have all the advantageous properties that characterize my present invention. For instance, the electrolytic bath may be made with the components in proper proportions suitably chosen from the ranges in the following example:

Example B

	Grams per liter [1]
Potassium manganate	1–60
Potassium fluoride (anhydrous)	1–300
Trisodium phosphate	[2]10–300
Potassium hydroxide	20–130
Aluminum hydroxide (dried gel))	1–100

[1] The constituents listed in the example have, by calculation, been adjusted to the basis of 100% purity. In actual practice, some of the ingredients are commercially available only at lower percentages of purity. Accordingly, correspondingly lesser amounts of each material must be employed.

[2] It should be noted that when more than approximately 100 grams per liter of trisodium phosphate is employed excessive precipitation of phosphate or other anions may result. Nevertheless, coatings may be obtained which have the desired attributes. The actual upper limit of trisodium phosphate in a particular bath will be that point at which the solubility limit of the phosphate or other anions is reached if precipitation is to be avoided.

It should be understood that the broad ranges of bath components given in Example B have been limited to those which give coatings having the unique abrasion and corrosion resistance properties that characterize my invention. However, by using the named constituents in quantities somewhat outside the preferred ranges of Example B, the resultant somewhat lesser quality coatings will be found to furnish excellent bases for paint or other subsequent treatment where an imperfection-free surface is not absolutely essential and where exceptionally high qualities of corrosion and abrasion resistance are not absolutely a requirement.

I have found, further, that the possible combination of concentrations (selected from the ranges indicated in Example B above) which may be employed with considerable success are quite numerous. For example, the named components were all put together in a bath at the lower limits of the indicated ranges, and a coating obtained which provides a good paint base although its corrosion resistance is not quite as satisfactory as that of coatings produced by the preferred bath described previously.

Other baths were tried in which each component was present in varying concentrations of its range as indicated in Example B, while the remaining constituents were maintained at the concentrations set forth in Example A. Baths also were tried in which all of the components were present in the maximum amounts (or less) stated in Example B, although it is probable that in some cases where the maxima were approached the components exceeded their particular solubility limits.

Further with respect to the use of aluminum hydroxide in the bath, it will be obvious that this material will react with the potassium hydroxide to form potassium aluminate which, I believe, is the active ingredient that contributes to the exceptional hardness of coatings made from baths that include that constituent. I have not yet been able to determine exactly how much of this aluminate is formed nor, because of its scarcity, has it been practical to test such a bath by direct introduction therein of potassium aluminate as a substitute for the aluminum hydroxide and potassium hydroxide. However, it should be understood that the present invention has within its purview this substitute use of the aluminate. Accordingly, based on the amounts of the various materials used to make of an Example B type bath containing aluminate, and calculating therefrom the aluminate believed then to be present therein as a reaction product, a suitable electrolytic bath could be made in accordance with my inven-

tion from the recommended ranges of the components given in the following example:

Example C

	Grams per liter
Potassium manganate	1–60
Potassium fluoride	1–300
Trisodium phosphate	10–300
Potassium hydroxide	20–85
Potassium aluminate	1–125

Wrought magnesium-rich articles to be given my protective coating are prepared for immersion in the electrolytic bath by thoroughly degreasing with a suitable organic solvent such as properly stabilizing carbon tetrachloride and/or a hot alkaline cleaner solution such as one containing sodium orthosilicate and a detergent. After the degreasing agent is rinsed off, the articles may be briefly pickled in a dilute nitric-sulfuric acid solution, followed by a water rinse and brush scrubbing to remove a fine powdery substance that forms on the metal surface as a result of the pickling operation. Castings of magnesium-rich articles may more suitably be given a sand-blasting treatment instead of pickling. Two of the thus cleaned articles are used as the electrodes in the above-described electrolytic baths 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. A. C. followed by D. C. and A. C. superposed on D. C. also were found to make coatings possible, although they were somewhat coarse and generally somewhat inferior to that obtained by simply using A. C. Optimum frequencies have been found to be between 50 and 13 cycles per second (C. P. S.) but frequencies ranging from 1 to 2000 C. P. S. have been tried with success, although it was noted that as the frequencies rose a thinner but smoother coating was obtained.

It is desirable to maintain the current density throughout the electrolysis between 10–20 amperes per square foot; however, I have found that my process will operate satisfactorily with a current density of 5 amp./ft.^{2} 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 voltage throughout the electrolysis. 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 about 80–85 volts generally will indicate sufficient time of electrolysis. Using the indicated preferred current density and voltage, the process usually may be completed in about 60–90 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 I was able to employ the upper limit of current density indicated above, 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° C., all the way up to 65° C., at which point the coatings start to get somewhat irregular and patches were formed on the test panels. Even lower temperatures can be employed but some of the ingredients start to crystallize out of the bath.

Upon conclusion of the electrolysis, the work is rinsed in water and then dipped for about 30 seconds into a solution comprising hydrofluoric acid and water in the ratio of 1:1. The acid used may suitably be the commercially available material consisting of 48–52% HF by weight. After this dip, the work is removed, water rinsed and dried, and then placed in an oven where it is

heated at a temperature of about 85 to 105° C. and at a relative humidity of about 95% for approximately two to six hours. This conditioning can be eliminated if the coating is to be used as a base which is to be painted.

The described electrolytic treatment results in the formation of a coating possessing the superior properties which now will be described. The coating will be found to have all the abrasion resistant attributes and corrosion resisting properties of the coating formed by my original process described in co-pending application Serial No. 132,788. That is to say, the coating of the process herein described has met or exceeded the qualifications of my original coating when submitted to the test described in the above-mentioned co-pending application. By the processes herein described there is produced upon the magnesium or magnesium alloy article a coating which, from microscopic examination, has been found to be integral with the underlying base metal. By properly controlling the electrolysis, the film thickness of the coating may be varied, but it has been found that a film of 0.0010 to 0.0012 inch will give the desired properties. The coating, which is extremely resistant to abrasion, corrosion and erosion, is dense, hard and non-porous, adheres very well to the base metal and has excellent refractory characteristics. It is insoluble in dilute and concentrated nitric and sulfuric acids; it is not affected by dilute and only slightly reactive with concentrated hydrochloric acid. Although the coating provides ample protection for magnesium articles without the necessity of painting thereover, it will readily accept paint or varnish.

An appreciation of the just-described superior properties will be had from the following description of actual tests given my novel coating. Using a CS–17 abrasive wheel and 1000 gram weight on an abrasive testing machine magnesium articles bearing said coating were subjected to over 8000 cycles without noticeably affecting the coating. By comparison a number of prior art coatings, reputedly the best available, lasted from 10 to 500 cycles before resulting in failure (i. e. the point when electrical conductance through the metal can be established).

To test the new coating's corrosion resistance, salt spray exposures were conducted in accordance with Method B–117 of the American Society for Testing Materials. The exposures were conducted at a temperature of 92–97° F., using a solution of 20% sodium chloride. On a number of test panels it required 800 hours to produce an average of 11 small corrosion spots on the coating of my invention, whereas a like effect was caused in only 18 hours upon the best-known prior art coated article. In addition to this salt spray comparison test, panels covered with the novel coating were immersed in ocean water 4 hours each day for 7 successive days. When not immersed the panels were kept above the ocean water level. No deterioration resulted from this test.

The coating's hardness is attested to by the fact that when steel having a hardness equivalent to C–65 on the well-known Rockwell scale was rubbed with considerable pressure over the coating, no apreciable damage to the protective film resulted.

In another test, a heavy blow with te rounded head of a hammer was applied to a panel of 0.025 inch thickness bearing the coating of this invention and resting on a rigid surface but no spalling of the coating was noticed at the indentation.

Further advantages of my novel coating include a high dielectric strength, adhesion and an ability to resist high temperatures. A film thickness of between 0.0008 to 0.001 inch will hold back an electric potential of some 550 volts (60 C. P. S.), and this dielectric strength remains undiminished even after subjecting the coating to the flame of a Meeker burner for about three minutes. A magnesium alloy sheet bearing the novel coating can be bent appreciably and straightened without damaging the coating on the tensile surface, showing unusual adhesion. Very thin sheets can even be bent into a cylinder

without impairing the coating. None of the various properties of the coating described above are in any way diminished even after subjecting the coating to a temperature of 800° F. for one hour and a second hour at 900° F.

The coating resulting from the practice of my process normally has a durable, light brown color which makes it possess utility in the case of military material because it need not be given any special camouflaging treatment. Nevertheless, if it is desired to obtain coatings of different colors, dyes may be added to the coating in accordance with well-known procedures.

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, in the electrolysis a lesser current density and a lower voltage than those above described may be perfectly satisfactory in coating certain magnesium alloys. Instead of operating the bath within the time limits above indicated, the electrolysis can be run for as much as two hours or more, the increased time allowing the coating to become even more uniform. The dip in hydrofluoric acid after the electrolysis followed by the two-hour treatment under elevated temperature and humidity conditions, is advantageous because it increases the coating's resistance to corrosion, but if only high abrasion resistance is sought, then this acid dip and conditioning may well be eliminated. Moreover, when this dip is employed, even concentrated acid will be suitable and the time may be increased considerably over the suggested 30 seconds, if desired. Instead of the named alkali metal compounds, i. e. the potassium components described for use in the bath, use may be made of equivalent sodium compounds and vice versa.

As examples of other modifications, instead of employing manganate in the electrolytic bath, it is possible to obtain coatings with titanates, chromates, arsenates, molybdates, selenates, stannates, tungstates and vanadates. The results with titanates, arsenates and molybdates are not quite as satisfactory as when manganates are employed, but the chromates, selenates, stannates, tungstates and vanadates produce coatings whose abrasion resistance compares favorably with the coating obtained with manganates, although the corrosion resistance is not quite as good.

Still another modification is to substitute silicates or borates for the phosphate in the preferred formulation. Phosphate can, if used carelessly, cause pits or craters in the coating, but its value lies in its effectiveness in lowering voltage requirements for the process. Silicates and borates, however, will cause no harm to the coating under almost any conditions, and will actually cause a better looking coating, one which is smooth and has no pits. Of course, when silicates are employed, the aluminum hydroxide or aluminate must be omitted as otherwise the bath will become fouled with gel.

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 will protect the base metal against corrosion and erosion; and that I have produced such a coating by means which 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 by way of illustration.

I claim:

1. An electrolytic bath for forming a coating on the surface of articles of magnesium and magnesium base alloys consisting essentially of 1 to 60 gms. per liter of a manganate selected from the class consisting of sodium and potassium manganates, 1 to 300 gms. per liter of any anhydrous fluoride selected from the class consisting of sodium and potassium fluorides, 10 to 300 gms. per liter of a phosphate selected from the class consisting of sodium and potassium phosphates, 20 to 130 gms. per liter of an alkali metal hydroxide from the class consisting of sodium and potassium hydroxides, and 1 to 125 gms. per liter of an aluminum compound selected from the class consisting of aluminum hydroxide potassium aluminate and sodium aluminate.

2. The bath of claim 1 in which the manganate is a sodium manganate.

3. The bath of claim 1 in which the manganate is a potassium manganate.

4. The bath of claim 1 in which the fluoride is a sodium fluoride.

5. The bath of claim 1 in which the fluoride is a potassium fluoride.

6. The bath of claim 1 in which the phosphate is a sodium phosphate.

7. The bath of claim 1 in which the phosphate is a potassium phosphate.

8. The bath of claim 1 in which the alkali metal hydroxide is potassium hydroxide.

9. The bath of claim 1 in which the alkali metal hydroxide is sodium hydroxide.

10. The bath of claim 1 in which the aluminum compound is aluminum hydroxide.

11. The bath of claim 1 in which the aluminum compound is potassium aluminate.

12. The bath of claim 1 in which the aluminum compound is sodium aluminate.

13. An electrolytic bath for forming a coating on the surface of articles of magnesium and magnesium base alloys consisting essentially of 10 to 25 grams per liter of a manganate selected from the class consisting of sodium and potassium manganates, 30 to 40 gms. per liter of an anhydrous fluoride selected from the class consisting of sodium and potassium fluorides, 30 to 50 gms. per liter of a phosphate selected from the class consisting of sodium and potassium phosphates, 100 to 130 gms. per liter of an alkali metal hydroxide selected from the class consisting of sodium and potassium hydroxides, and 25 to 35 gms. per liter of an aluminum compound selected from the class consisting of aluminum hydroxide, potassium aluminate and sodium aluminate.

14. 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 1, passing an electric current of at least 5 amps. per square foot through said bath while maintaining said bath at a temperature between —10° and 65° centigrade.

15. The method of claim 14 in which the bath is maintained at a temperature between 20° and 30° centigrade.

16. 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 13, passing an electric current of at least 5 amps. per square foot through said bath while maintaining said bath at a temperature between —10° and 65° centigrade.

17. The method of claim 16 in which the bath is maintained at a temperature between 20° and 30° centigrade.

18. 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 1, passing an electric current of at least 5 amps. per square foot through said bath while maintaining said bath at a temperature between —10° and 65° centigrade, and thereafter conditioning said article against corrosion by dipping in a solution containing equal pro-

portions of hydrofluoric acid and water, and then heating to from 85° to 105° centigrade at a relative humidity of about 95 per cent from 2 to 6 hours.

19. The method of claim 18 in which the bath is maintained at a temperature between 20° and 30° centigrade.

20. 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 13, passing an electric current of at least 5 amps. per square foot through said bath while maintaining said bath at a temperature between —10° and 65° centigrade, and thereafter conditioning said article against corrosion by dipping in a solution containing equal proportions of hydrofluoric acid and water, and then heating to from 85° to 105° centigrade at a relative humidity of about 95 per cent from 2 to 6 hours.

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

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