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[54] **COATING FOR MAGNESIUM AND ITS ALLOYS AND METHOD OF APPLYING**
12 Claims, No Drawings

[52] **U.S. Cl.** ..... **204/56 M**
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[50] **Field of Search** 204/56.1

[56] **References Cited**

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ABSTRACT: The surface of magnesium and its alloys is provided with a protective coating, both decorative and resistant to corrosion, when subjected to an ammonium bifluoride and an ammonium metavanadate aqueous solution which preferably contains in addition water-soluble organic compounds, water-soluble permanganate ions, or water-soluble nitrate ions. The coating is conveniently and efficiently applied to the metal which is the anode in the coating solution.

COATING FOR MAGNESIUM AND ITS ALLOYS AND METHOD OF APPLYING

BACKGROUND OF THE INVENTION

Magnesium metal and its alloys are attractive for structural materials; however, because of its reactivity and tendency to deteriorate by corrosion, the metal and its alloys most generally must be provided with a protective coating. Existing coatings have provided a certain degree of protection by delaying the onset of corrosion. The best state-of-the-art coatings offer no protection at points where the substrate metal is exposed by penetration such as by scratching, scribing through the coating, incomplete covering or failure of the coating to provide a physical barrier to the environment. Imperfections in the coatings such as those which may be present after the most careful application procedure of the prior art or those resulting from mechanical abuse after application, serve as a focal point for the onset of corrosion. Once begun, this corrosion accelerates rapidly due to the lack of inhibitive properties in the coating other than a barrier to the atmospheric conditions by its physical presence. Thus, a need exists for a coating which, in addition to providing a physical barrier to the environment, will provide an inhibiting influence to counteract corrosion both at breaks in the coating and at porosity sites where moisture or other constituents present in the atmosphere eventually penetrate through to the substrate metal.

Therefore, an object of this invention is to provide a coating which is attractive and which provides a high degree of protection from corrosion to a substrate of magnesium and its alloys.

Another object of this invention is to provide a protective coating for magnesium and its alloys which coating will extend its protective influence over minor points of penetration through the coating.

A further object of this invention is to provide a method for producing an anodic reaction on the surface of magnesium and its alloys to thereby produce thereon a hard brown to gray colored uniform coating of high protective value.

A still further object of this invention is to provide a novel aqueous solution of chemicals for use in coating magnesium and its alloys.

SUMMARY OF THE INVENTION

This invention relates to a method for electrochemically applying a protective coating to magnesium and its alloys. A decorative and corrosion-resistant coating is formed on magnesium and its alloys by an anodic reaction in a solution or aqueous bath containing ammonium bifluoride, ammonium meta-vanadate, and preferably containing a third ingredient selected from polar organic compounds, sodium or potassium permanganate, and sodium or potassium nitrate. The solution is used in conjunction with an impressed potential of approximately 135–175 DC volts or 140–190 AC volts.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The coating process of this invention works best with magnesium alloys which do not contain a large amount of lithium (e.g. 13–15 weight percent, such as alloy LA141XA of table II below).

Magnesium alloys are those alloys which contain a major portion of magnesium, generally those containing at least about 50 percent by weight magnesium. Magnesium alloys may be substantially all magnesium except for trace amount of additives required to impart certain desired mechanical or chemical properties. Magnesium alloys which are representative of the alloys especially suitable for use in this invention are listed in table I. The minor constituents of alloys are listed; hence the remaining percent being magnesium. Table II sets forth available forms of magnesium alloys for the alloys listed in table I and other available alloys by designation numbers.

TABLE I.—CHEMICAL COMPOSITIONS OF MAGNESIUM ALLOYS

[Alloy content, weight percent]

Alloy	Al	Zn	Mn	Zr	Th	Li	Si [1]	Cu [1]	Ni [1]	Ca	Fe [1]
AZ31B	2.5–3.5	0.7–1.3	0.2				0.05	0.05	0.005	[1] 0.04	0.005
HK31A				0.5–1.0	2.5–4.0						
HM21A			0.35–0.8								
					1.5–2.5						
MIA			[2] 1.2				0.05	0.05	0.01	0.04–0.14	
AZ91B	8.3–9.7	0.4–1.0	0.13				0.05	0.30	0.01		
AZ92A	8.3–9.7	1.6–2.4	0.10				0.30	0.10	0.01		

[1] Max. [2] Min.

TABLE II.—AVAILABLE FORMS OF MAGNESIUM ALLOYS

Alloys	Castings	Sheet and plate	Extrusions	Forgings	Welding rod
AZ10A			X		
AZ31B		X	X	X	
AZ61A			X	X	X
AZ63A	X				X
AZ80A			X	X	
AZ81A	X				
AZ91A, B, & C	X				
AZ92A	X				X
AM100A	X				
EK30A	X				
EK31XA	X			X	
EK41A	X				
EZ33A	X				X
HK31A	X	X			
HM21A		X		X	X
HM31A			X		X
HZ32A	X				
LZ141XA		X			
MIA			X	X	X
QE22A	X				
ZE10A		X			
ZE41A	X				
ZH62A	X				
ZK21A			X		
ZK51A	X				
ZK60A			X	X	
(P)ZK60B			X		
ZK61A	X				

All forms of magnesium alloys may be employed in the process of this invention; however, those of high lithium content do not coat as well as alloys having little or no lithium. Over 30 magnesium alloys are available as castings and/or wrought products including sheet, plate, extrusions, and forgings. Alloys which have been processed with various hardening and annealing characteristics are available. An example of an alloy designation might be AZ31B–H24, indicating an alloy containing 3 percent aluminum, 1 percent zinc which has been strain hardened, and partially annealed. For additional information on magnesium alloys, refer to Defense Metals Information Center, Report 206, dated Aug. 26, 1964.

The representative composition of the aqueous bath for the coating process is as follows:

Ammonium bifluoride in range of 32 oz. to 52 oz. per gallon; 42 oz./gallon being preferred;

Ammonium meta-vanadate in range of 8 oz. to 14 oz. per gallon; 11 oz./gallon being preferred;

Water-soluble organic, permanganate, or nitrate ions—2.5—30 oz./gallon.

The water-soluble organic compounds may be selected from polar organic compounds such as ethanol, sodium potassium tartrate, citric acid, ethylene glycol, dimethylsulfoxide, N,N-dimethylformamide, dimethylenetriamine, ethanolamine, allyl alcohol, and piperidine. Potassium or sodium permanganate works well for the source of the permanganate ion. Also, potassium or sodium nitrate is suitable for a source of the nitrate ion.

The solution for the coating process may be comprise of only the bifluoride and the meta-vanadate; however, the coating will form only slowly and is not as protective as coatings containing one of the third constituents (e.g., water-soluble polar compounds, organic, permanganate ions or nitrate ions).

The impressed potential of approximately 135–175 DC volts or 140–190 AC volts required in the process of this invention is preferably increased from zero gradually to the desired value in order to allow time for the high dielectric coating to form which has a tendency to depress the current flow. A rheostat is used to regulate the current flow and to maintain current density. A current density of 24 a./sq. ft. of the anode surface emersed in the solution works well for the process of this invention. A wide range of current densities, however, may be used. Higher current densities will coat faster, but heating may become excessive. Maintaining ambient temperatures for the solution is desirable, although some heating is not harmful. The temperature of the solution must not, however, be allowed to approach boiling as some decomposition will take place. The metal is subjected to the anodic reaction, and the treatment is carried out until the current flow drops to or near zero value at the given potential. When employing a current density of 24 a./sq. ft. and cooling the solution, coatings are accomplished in approximately 15 to 20 minutes.

The following descriptions and examples illustrate the use of this invention and sets forth the preferred embodiments. Changes or modifications within the scope of this invention may be found desirable by those skilled in its application.

EXAMPLE I

A group of AZ–31B magnesium alloy coupons or metal pieces approximately one-half inch by 4 inches by 0.065 inch are vapor degreased in trichloroethylene and then acid etched in a bath constituted of 8 fluid ounces of nitric acid, 2 fluid ounces of sulfuric acid, and 90 fluid ounces of distilled water. After rinsing, one of the coupons is made the anode, and another coupon is made the cathode of a DC power source which is capable of at least 175 volts and 5 amperes output. The coupons are then immersed or contacted with an aqueous bath or a solution of the following composition:

Ammonium bifluoride 42 oz./gal.

Ammonium meta-vanadate 11 oz./gal.

Ethanol 32 fluid ounces/gallon

The potential is gradually increased by the use of the rheostat maintaining a current density of approximately 24 a./sq. ft. until a potential of 15 volts is reached, requiring approximately 10 minutes. At **150** point, the system is allowed to remain for an additional 10 minutes, during which time the current density drops to or near zero. The anode is then removed and rinsed in water. The resultant coating is dark brown, hard, smooth, and not easily damaged.

EXAMPLE II

Magnesium alloy coupons are prepared and cleaned as in example I. The basic solution of ammonium bifluoride 42 ounces/gallon and of ammonium meta-vanadate 11 ounces/gallon is prepared and divided into a number of smaller solutions of 200 milliliters each. Into each 200 milliliters portion is added one of the constituents listed in table III (below) to complete the aqueous bath for use in the experiments of this example. Coupons were treated in the same manner as example I using 135–175 DC volts.

AC potential works quite well, and AC potential may be substituted for DC potential. However, the DC potential appears to give slightly more consistent and uniform coatings.

TABLE III

Amount	Compound	Appearance of Coating
	None	Gray
4 g.	Potassium Permanganate	Khaki Tan
4 g.	Sodium Potassium Tartrate	Dark Brown
4 g.	Citric Acid	Brown
20 ml.	Ethylene Glycol	Dark Brown
20 ml.	Dimethylsulfoxide	Brown
20 ml.	N,N-Dimethylformamide	Dark Brown
10 ml.	Diethylenetriamine	Brown
10 mil.	Ethanolamine	Brown
30 ml.	Allyl Alcohol	Dark Brown-Gray
20 ml.	Piperidine	Brown

The above list of organic compounds does not exhaust the possibilities which may be employed in the solutions of this invention, but is merely representative of some of the preferred compounds. A polar organic compound of the types listed provides sufficient conductivity and catalytic action to allow the coating process to proceed at the desired rate to yield a satisfactory finished product.

In order to evaluate the protective efficiency of the coatings, the coated magnesium alloy coupons were placed in a 5 percent salt spray chamber maintained at 97° F. A diagonal scribe mark through the coating exposing the substrate metal was placed on each coupon. An untreated coupon was included for comparison. After only a few hours the untreated coupon was covered with corrosion spots, whereas the treated coupons were unaffected. After 100 hours exposure, the untreated panel was badly corroded, whereas the treated panels showed only a slight bleaching of color in the coating and no corrosion evidence in the scribe mark. After 200 hours, some of the coupons displayed occasional spots of discoloration, although the scribe marks were still free of corrosion. After 300 hours of exposure, some of the spots of discoloration developed very small white protrusions. Even after 400 and 500 hours of exposure, the increase in corrosion was barely perceptible, much unlike any other protective coated magnesium where, once begun, corrosion runs rampant.

The benefits directly attainable from the invention will be best understood by a review of the characteristics and properties of the coating. The coatings of this invention may be characterized and described by its following properties:

a. Unaffected by temperatures above the melting point of magnesium alloys.

b. A uniform dark brown or gray color with a surface roughness comparable to 20–40 microinches R.M.S. (root mean square).

c. Completely nonchalking, with hardness above that penetrable by fingernail.

d. A high resistance to corrosion coating which extends its inhibiting influence over minor imperfections and voids in the coating. The exact chemical mechanism responsible for this is not clearly understood, but it is apparently caused by the very slow leaching of a slightly soluble inhibiting ion (vanadate) from the coating.

e. Inhibition properties which significantly reduce the velocity of attack when corrosion does begin.

I claim:

1. Method of providing a surface of magnesium and its alloys with a decorative and protective coating, said method comprising subjecting said surface of magnesium and its alloys to an aqueous bath of ammonium bifluoride and ammonium meta-vanadate, impressing a potential of a predetermined value of volts and a predetermined value of current density for a predetermined period of time for anodic reaction to occur and form on said surface a decorative and protective coating.

2. Method of claim **1** and wherein said surface prior to being subjected to anodic reactions is subjected to vapor degreasing and cleaning; said aqueous bath comprises ammonium bifluoride about 42 ounces/gallon, ammonium meta-vanadate about 11 ounces/gallon, and an additional ingredient selected

from the polar compounds consisting of ethanol, sodium potassium tartrate, citric acid, ethylene glycol, dimethylsulfoxide, N,N-dimethylformamide, dimethylenetriamine, ethanolamine, allyl alcohol, piperidine, potassium permanganate, sodium permanganate, sodium nitrate, and potassium nitrate in an amount from about 2.5 to about 30 ounces/gallon.

3. Method of claim 2 and wherein said surface is vapor degreased in trichloroethylene and said cleaning is done by acid etching in a bath constituted of about 8 fluid ounces of nitric acid, 2 fluid ounces of sulfuric acid, and 90 ounces of distilled water; said impressed potential of a predetermined value of volts is in the range of approximately 135–190 volts; said predetermined value of current density is about 24 a./square foot; said predetermined time is from about 10 to about 20 minutes; and said protective coating formed is corrosion resistant.

4. Method of claim 3 and wherein said impressed potential of a predetermined value of volts is in the range of approximately 140–190 AC volts.

5. Method of claim 4 and wherein said impressed potential of about 150 AC volts is reached in about 10 minutes and said volts are allowed to remain for about an additional 10 minutes during which time said current density drops to about zero value.

6. Method of claim 3 and wherein said impressed potential of about 150 DC volts is reached in about 10 minutes and said volts are allowed to remain for about an additional 10 minutes during which time the said current density drops to about zero value.

7. An article of magnesium and its alloys covered with a decorative and protective coating as set forth in the method of claim 1.

8. An article of magnesium and its alloys covered with a decorative and protective coating as set forth in the method of claim 2 and wherein said additional ingredient is ethanol in an amount of 32 fluid ounces/gallon.

9. An article of magnesium and its alloys covered with a decorative and protective coating as set forth in the method of claim 2 and wherein said additional ingredient is selected from potassium permanganate, sodium potassium tartrate, and citric acid in an amount of about 4 grams per 200 milliliters of said aqueous bath.

10. An article of magnesium and its alloys covered with a decorative and protective coating as set forth in the method of claim 2 and wherein said additional ingredient is selected from ethylene glycol, dimethylsulfoxide, N,N-dimethylformamide, diethylenetriamine ethanolamine, allyl alcohol and piperidine in an amount from about 10 milliliters to about 20 milliliters per 200 milliliters of said aqueous bath.

11. An aqueous solution for anodizing magnesium and its alloys comprising ammonium bifluoride in an amount in the range of 32 oz. to 52 oz. per gallon and ammonium meta-vanadate in an amount in the range of 8 oz. to 14 oz. per gallon.

12. The aqueous solution of claim 11 and wherein said ammonium bifluoride is present in an amount of 42 oz. per gallon, ammonium meta-vanadate is in an amount of 11 oz. per gallon, and an additional ingredient is present in an amount from about 2.5 oz. to about 30 oz./gallon; said additional ingredient being selected from the polar compounds consisting of ethanol, sodium potassium tartrate, citric acid, ethylene glycol, dimethylsulfoxide, N,N-dimethylformamide, dimethylenetriamine, ethanolamine, allyl alcohol, piperidine, potassium permanganate, sodium permanganate, sodium nitrate, and potassium nitrate.

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