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PROCESS FOR APPLYING A PROTECTIVE COATING TO A MAGNESIUM SURFACE

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CONDITIONS	OPERATIONS	MATERIALS
Mg surface is immersed for 15 seconds and then water rinsed.	(A) Cleansing	2 % Acetic Acid solution
The Mg surface is rinsed in a preheated 100°C bath for 5 minutes. The PH of the solution is controlled so as not to diminish appreciably.	(B) Coating	50-95 parts by weight of Sodium Pyrophosphate. 1-5 parts by weight of Sodium Fluoride. 4-40 parts by weight of Nickel Sulfate.
30 seconds	(C) Rinsing	Cold Water
	(D) Air Drying	
The Mg surface is immersed in an aqueous solution for 10 minutes at 70° C.	(E) Coating	5-40% by weight of an aqueous solution of Iron Phosphate.
30 seconds	(F) Rinsing	Cold water

INVENTOR.
William H. Kapfer
Max Kronstein
BY
Arthur W. Collins
ATTORNEY

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PROCESS FOR APPLYING A PROTECTIVE COATING TO A MAGNESIUM SURFACE

William H. Kapfer, Hastings on Hudson, and Max Kronstein, New York, N.Y., assignors, by mesne assignments, to the United States of America as represented by the Secretary of the Navy

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The present invention relates to the art of coating magnesium and more particularly to novel and improved techniques for applying protective coatings to magnesium and the alloys thereof to render the metal surface passive to oxidation and corrosion.

The protection of magnesium from corrosion is a well known problem in the arts due to the tendency of magnesium surfaces to rapidly form coatings of magnesium oxides and hydroxides on contact with moist air or on exposure to salt fog. The formation of these corrosion products often progresses within a short time to a complete loss of metal substance at localized areas, and it has been found that deterioration of the metal surface cannot be prevented by a mere simple application of a suitable organic paint or the like.

In the past various chemical pretreatments of the magnesium surface have also been suggested and introduced into the art to retard corrosion. Typical pretreatments, known heretofore, consist of an extensive chemical surface cleaning and acid pickling operation followed in some cases by a subsequent surface sealing procedure based on the use of a suitable chromate or dichromate immersion or the like. These pretreating and sealing procedures which are preferably carried out at controlled temperature and pH conditions to produce a uniform film on the magnesium surface, provide a surface condition on the magnesium that takes on characteristics of a partly soluble gel which provides a more reliable base for the organic paint or coating than an untreated magnesium surface. Nevertheless, irregularities in coatings thus applied have been found to occur frequently thereby contributing to local and general premature corrosion failures.

It is a principal object of the present invention to provide novel and improved techniques for the surface protection of magnesium and its alloys by interacting the magnesium surface with solutions of other metal ions and compounds to produce a protective metallic coating on the original magnesium surface.

It is a further object of the present invention to provide upon a magnesium or a magnesium alloy surface a novel and improved inorganic coating or film which is a derivative of another metal substance without the application of an external electric current.

It is a further object of the present invention to provide upon a magnesium or magnesium alloy surface a novel and improved base composed of one or more other metal substances for the application of a suitable paint or organic coating.

It is a further object of the present invention to apply a novel and improved metallic deposit or coating upon a magnesium or magnesium alloy surface directly or to apply the same after a chemical cleaning or pickling or chemical treating operation to increase the surface reactivity of the magnesium.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description:

In the drawing, the single figure illustrates diagrammatically the series of steps employed in the invention.

In the practice of the present invention, it is ordinarily desirable first to properly prepare the metal surface prior to the application of the protective coating. In this way a more uniform reactive surface may be obtained for ultimate exposure to the protective immersion fluid. Thus, old corrosion areas, earlier protective coatings, grease, and other contaminations of the surface should be removed to avoid local differences in contact with the immersion fluids.

It is to be understood that it would be possible to use the immersion fluids themselves in some instances for the desired surface preconditioning of the metal surface. This practice, however, would cause some degree of contamination of the treating fluid, decrease the uniformity of the ultimate deposit, and shorten the useful life period of the fluid as a coating solution. Thus, it is preferable to preclean the metal surface using another suitable precleaning process and to apply the new metal surface coating thereafter.

Among the types of surface preparations which were found suitable for the purpose of precleaning are the following: liquid or vapor solvent cleaners, alkali cleaners, and other conventional industrial cleaners known in the art for the removal of grease contaminations; a suitable pickling operation such as immersion for 15 seconds in a 2 percent aqueous acetic acid solution followed by a water rinse; or immersion for 60 seconds in a solution containing 110 grams of aluminum chloride dissolved in a liter of water followed by a water rinse; or the application of successive pickles as for instance the above acetic acid pickle and a subsequent aluminum chloride pickle, each followed by a water rinse. It has been found that the metal surfaces prepared in this manner are more uniform and better suited to the subsequent metallic deposit.

A number of particular metal deposit solutions which are next applied in accordance with the present invention were found to provide improved protective coatings for the magnesium metal surface. Some such solutions which were found to provide successful deposits were based on solutions of cadmium salts, zinc salts, chromium salts, nickle salts, aluminum salts, a combination of cadmium and chromium salts, and combinations of other metal salts. Many of these salt solutions exhibited their own peculiar characteristics, which made them more suitable for certain uses. Thus, some of them were found to provide coatings which were more suitable than others for use as a base for paints or other organic films (such as waxes or the like). Others, particularly those based on the cadmium and chromium salts, were found to provide better results than others in use without the subsequent chemical surface modification or sealer operation which are disclosed more fully hereinafter. Deposits obtained from solutions based on zinc salts were found very sensitive to variations in the pH of the solution and generally less suitable as a paint base prior to a chemical modification or seal.

The form of the metals preferably used in the preparation of the solution is any form which allows enough metal ions to enter the solution; that is, any of the salts or compounds of the metal having sufficient water solubility in the final treating solution. The most desirable metal salts used were in the form of sulfates or nitrates, but others such as cyanides, fluorides, etc. were also successfully used.

The solutions were compounded using varying concentrations of the metal salts together with varying amounts of pyrophosphate in distilled water. Small amounts of

sodium fluoride and other suitable fluorides were also found to be beneficial.

To cite some specific examples, the following solutions have been sucessfully used in applying suitable protective metal deposits upon the magnesium surface in accordance with the present invention.

	(1)	(2)	(3)	(4)	(5)
	Grams	*Grams*	*Grams*	*Grams*	*Grams*
(a) Cadmium sulfate	18.5	27.4	27.4	36.6	36.5
Sodium pyrophosphate	394.0	200.0	394.0	200.0	394.0
Sodium fluoride	10.0	10.0	10.0	10.0	10.0
(Distilled water to make 2,000 ml. in all cases.)					
(b) Copper sulfate	19.5	39.0	78.0		
Sodium pyrophosphate	200.0	200.0	200.0		
Sodium flouride	10.0	10.0	10.0		
(Distilled water to make 2,000 ml. in all cases.)					
(c) Cadmium cyanide	80.0				
Sodium pyrophosphate	120.0				
Sodium fluoride	40.0				
(Distilled water to make 2,000 ml. in all cases.)					
(d) Chromium sulfate	72.2	72.2	90.0	103.0	
Sodium pyrophosphate	200.0	394.0	200.0	200.0	
Sodium fluoride	10.0	10.0	10.0	10.0	
(Distilled water to make 2,000 ml. in all cases.)					
(e) Chromic nitrate	60.0	60.0			
Sodium pyrophosphate	200.0	400.0			
Sodium fluoride	10.0	10.0			
(Distilled water to make 2,000 ml. in all cases.)					
(f) Nickel sulfate ($NiSO_4$)	90.0	70.0			
Sodium pyrophosphate	200.0	200.0			
Sodium fluoride	10.0	10.0			
(Water to make 2,000 ml.)					
(g) Aluminum nitrate	94.0	125.0			
Sodium fluoride	10.0	10.0			
Sodium pyrophosphate	196.0	195.0			
Water	1,700.0	1,670.0			
(h) Chromium nitrate	60.0	60.0			
Cadmium sulfate	80.0	62.0			
Sodium fluoride	10.0	200.0			
Sodium pyrophosphate	200.0	10.0			
(Water to make 2,000 ml.)					

Each of the above solutions has been used sucessfully in accordance with the present invention with and without the prior pickling or cleaning operation, described above, to provide a uniform effective protective metallic coating on the surface of magnesium and magnesium alloy metals. The process of the application of the metallic deposit from each of the above solutions was characterized by the fact that no external electrical energy is needed to provide the desired coating. The process is also characterized by the fact that no additional metal matter is needed to induce the inter-reaction between the magnesium or magnesium alloy surface and the fluid, although the presence of such metals was not found to destroy the utility of the process.

As a more specific working example of the application of a particularly successful protective metallic deposit on a group of magnesium panels, the panels were first precleaned and pickled for 15 seconds in a 2 percent aqueous acetic acid solution and water rinsed. The panels were then immersed for five minutes in a preheated 100° C. bath containing 18.5 g. of cadmium sulfate, 394 g. of sodium pyrophosphate and 10 g. of sodium fluoride in 2000 ml. of distilled water. During the immersion operation the pH of the solution was controlled so as not to diminish appreciably. After the immersion treatment the panels were rinsed in water for 30 seconds and air dried.

Some of the above panels were then successfully tested and used as finished products, others were used as a base for paint and lacquer applications, and still others were chemically modified or sealed in a manner more fully described hereinafter prior to ultimate test as a finished product.

This new magnesium surface system was found to be superior in corrosion resistance to untreated magnesium surfaces. A further increase in the life of the new system, especially its paint bonding life, was observed when the new surface system was further modified chemically to increase its uniformity, reduce its degree of porosity, and decrease the amounts of soluble matter not desirable in the final state. Treatments of this kind which were used successfully included the following examples:

Example I

Some of the magnesium panels which were treated as described above in column 3 chemically modified by immersion in a water solution of 170 grams per gallon of industrial iron phosphate for appoximately 40 minutes at 85° C. Other of said panels were modified by immersion in an aqueous mixture of a sodium phosphate compound for a similar time duration at a similar controlled temperature. Metal salt additives of vanadium and molybdenum were also used with the iron phosphate and sodium phosphate mixtures and acted as modifiers and accelerators of the same.

Example II

Another form of surface modification was carried out upon the panels described in column 3 by surface pickling the same with a metal salt solution of 40 grams of ammonium vanadite in 100 ml. of water. In this particular application the panels were immersed in the solution at room temperature and the temperature was then increased to 70° C. and held for 10 minutes. Immediately following this imersion, a 30 second cold water rinse using running water was applied.

Example III

Another surface modification of the panels in column 3 was obtained by immersing the panels for 4 minutes at room temperature with a surface modifying solution of a phosphate or fluoride compound followed by a rinse for 30 seconds in cold water.

Example IV

Another very successful method of modifying or sealing the new system consisted of immersing the panels described in column 3 in a dichromate sealer of 570 grams of sodium dichromate and 8.6 grams of calcium fluoride dissolved in one gallon of water to which 1 ml. of a wetting agent, "Tergitol O8" (a 40% aqueous solution of the sodium sulfate derivative of 2-ethyl hexanol) is added. The panels were immersed at approximately 98° C. for about 30 minutes, rinsed in cold water for 30 seconds, and allowed to dry.

The magnesium surfaces prepared by the above described applications of new metal deposits with or without the subsequent application of the surface modification have been found to differ from magnesium surfaces used in the past in that the manner in which the processes can be adapted to obtain the desirable high degree of uniformity and water resistance is less critical. Similarly, the new coating systems have also been found to exhibit a longer useful life even when exposed to a corrosive environment such as salt spray fog or water.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for applying a protective coating to a magnesium surface said process comprising the steps of cleansing said surface; contacting the surface with an aqueous solution having an elevated temperature and consisting essentially of 50–95 parts by weight of sodium pyrophosphate, 1–5 parts by weight of sodium fluoride, and 4–40 parts by weight of a metallic salt selected from the group consisting of cadmium sulfate, copper sulfate, chromium sulfate, nickel sulfate, cadmium cyanide, chromic nitrate, and aluminum nitrate; rinsing the surface; drying the said surface in the air; immersing the said surface in a 5–40% by weight aqueous solution having an elevated temperature of one from the group consisting of iron phosphate, ammonium vanadite, and sodium

dichromate; and rinsing the surface so that the coated surface exhibits a high degree of uniformity and stability.

2. A process for applying a protective coating to a magnesium surface said process comprising the steps of cleansing said surface; contacting the surface with an aqueous solution having an elevated temperature and consisting essentially of 50–95 parts by weight of sodium pyrophosphate, 1–5 parts by weight of sodium fluoride, and 4–40 parts by weight of cadmium cyanide whereby the cadmium is plated upon the magnesium surface; rinsing the cadmium coated magnesium surface; drying the said surface in the air; immersing the said surface in a 40% by weight aqueous solution having an elevated temperature of ammonium vanadite; and rinsing the said surface so that the cadmium coated magnesium surface exhibits a high degree of uniformity and stability.

3. A process for applying a protective coating to a magnesium surface said process comprising the steps of cleansing said surface; contacting the surface with an aqueous solution having an elevated temperature and consisting essentially of 50–95 parts by weight of sodium pyrophosphate, 1–5 parts by weight of sodium fluoride, and 4–40 parts by weight of nickel sulfate whereby the nickel is plated upon the magnesium surface; rinsing the nickel plated magnesium surface; drying the said surface in the air; immersing the said surface in a 5% by weight aqueous solution having an elevated temperature of iron phosphate; and rinsing the said surface so that the nickel coated magnesium surface exhibits a high degree of uniformity and stability.

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