

UNITED STATES PATENT OFFICE

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ANODIC COATING OF MAGNESIUM

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This invention relates to an improved method of producing abrasion- and corrosion-resistant coatings upon the surface of articles of magnesium and magnesium-base alloys.

It is known that coatings can be formed on articles of magnesium and magnesium-base alloys by anodic treatment in aqueous alkaline solutions. However, such coatings are very soft and porous, and afford little protection to the base metal. By the addition of certain compounds to the alkaline bath it is possible to improve somewhat the corrosion resistance of the coatings formed, but in no case is any significant change effected in the resistance of the coatings to mechanical abrasion.

It is, therefore, an object of the present invention to provide an anodic treatment for magnesium and its alloys which produces a coating which, in addition to being satisfactorily resistant to corrosion by aqueous media, is also exceptionally resistant to abrasion.

This object is attained in the invention according to a process in which the magnesium or magnesium-base alloy article to be protected is immersed in a solution consisting essentially of a strong base dissolved in a mixture of water and at least one water-soluble alcohol or alcohol-ether, the solution being maintained at a temperature between about 50° and about 150° C., and is then subjected to anodic oxidation while so immersed. As a result of this treatment, there is formed on the metal surface a dense thin coating or film, usually gray in color, which has a high resistance to scratching and rubbing, and is also resistant to corrosive action. This coating provides exceptionally effective protection for the base metal against factors tending to attack it under ordinary usage.

In so far as is known, any strong base may be employed in the treating solution according to the invention, although the alkali metal hydroxides, such as sodium, potassium, and lithium hydroxides are distinctly better than other bases. Optimum hardness and uniformity of the coating appear to result when lithium hydroxide is used. In general, the base should be present in a concentration from at least 30 grams per liter of solution up to its solubility limit, concentrations of 90 to 120 grams per liter being especially advantageous.

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The water-soluble alcohol component of the solution may be a monohydric alcohol, such as methanol or ethanol, a polyhydric alcohol such as ethylene glycol, propylene glycol, glycerol, or mannitol, an alcohol-ether such as 2-ethoxy ethanol or diethylene glycol, or mixtures of two or more of these substances. Those alcohols and alcohol-ethers containing at least two hydroxyl groups are preferred because of their lower volatility, which minimizes loss by evaporation. The alcohol or alcohol-ethers are customarily added to the treating solution in a concentration between about 50 and about 500 milliliters per liter of solution, values of 100 to 200 milliliters being particularly suitable.

In practicing the invention, the magnesium or magnesium-base alloy article to be treated is first cleaned thoroughly, as by machining, buffing, sanding, or pickling for a few seconds in a dilute aqueous mixture of nitric and sulfuric acid. With heavily oxide-coated articles, boiling dilute aqueous chromic acid may be necessary to effect complete cleaning. Grease films, if any, on the metal may be removed by solvent degreasing or cathodic alkaline cleaning.

After cleaning, the article is immersed in an aqueous alcoholic alkali solution according to the invention, and is subjected to electrolysis which produces an anodic oxidation. Sufficient electric potential, either alternating or direct, is applied between the article and another electrode, such as iron or magnesium, in contact with the treating solution to produce a current density at the article between 1 and 100 amperes per square foot, most desirably 10 to 20 amperes per square foot. A low potential, usually 3 to 10 volts is preferred, since at increased potentials, say 20 to 80 volts, the coatings formed are somewhat softer than at the lower voltages. During the electrolysis treatment the solution is maintained at a temperature between about 50° and about 150° C. and usually below the boiling point at atmospheric pressure. Temperatures between 60° and 100° C. are preferred, with 70° to 80° C. being most advantageous. In general, the electrolytic treatment requires from 1 to 60 minutes to produce a satisfactory coating, depending on the temperature, current density, and whether D. C. or A. C. is used, the latter requiring about twice the time of the former. At 70° to 80° C. and 10 to 20

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amperes per square foot, times of 15 to 30 minutes give optimum results.

The frequency of the alternations when A. C. is used does not appear to be critical, as a wide range of frequencies may be used, e. g. 25 to 300 cycles per second, 60 cycles per second being preferred.

The following example will illustrate the invention:

Example

Carefully cleaned articles of Dowmetal X-alloy (a magnesium-base alloy containing 3.0 per cent aluminum, 0.2 per cent manganese, and 3.0 per cent zinc, the balance being magnesium) were immersed in a water solution containing 100 grams of lithium hydroxide per liter and 200 milliliters of ethylene glycol per liter, the solution being maintained at a temperature of 70° C. A direct current potential of 5 to 8 volts was then applied to the articles using an iron cathode, causing current to flow at a density of 15 amperes per square foot. Anodization in this manner was carried out for 30 minutes, after which the articles were removed from the bath, washed, and dried. They were covered with a thin dense corrosion-resistant gray film which had an abrasion resistance of 88 grams, as measured with a Hauelsen abrasiometer (see H. G. Arlt, Proc. Am. Soc. Testing Materials, 40, 967 (1940)), using Aloxite powder and an air pressure of 12 ounces per square inch.

Anodic coatings prepared in similar manner with the exception that no ethylene glycol or other alcohol was present in the treating solution had an abrasion resistance of only one-third to one-fourth that obtained in the present of glycol.

While magnesium articles provided with anodic coatings according to the invention have, in addition to high abrasion resistance, a corrosion resistance entirely adequate for most uses, the corrosion resistance may be further improved by sealing the anodic coating by suitable chemical treatment. Dipping the coated article in a hot dilute non-acidic solution of a water-soluble chromate for a few minutes is especially effective. Treatment with hot water or hot alkali metal hydroxide solutions also serves to seal the anodic coating.

The coatings of the invention may be dyed any desired color simply by immersing the coated article in an aqueous solution of a water-soluble dye of the proper color. The dye diffuses throughout the coating, and is retained permanently. However, care must be taken to immerse the article in the dye solution immediately after the anodic coating is formed, since articles which

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have been exposed to the air for more than a few minutes absorb the dye only superficially.

If desired, for special uses, the anodic coatings according to the invention may be impregnated with oils, waxes, or resins. The coatings also serve as effective paint bases.

This application is a continuation-in-part of my copending application Serial No. 469,628, filed December 11, 1940, now abandoned.

10 I claim:

1. A method of producing a dense, thin abrasion- and corrosion-resistant coating upon articles of magnesium and magnesium-base alloys which comprises immersing the article in a solution consisting of water, an alkali metal hydroxide in a concentration of at least 30 grams per liter of solution, and a water-soluble aliphatic hydroxyl compound selected from the group consisting of methanol, ethanol, ethylene glycol, propylene glycol, glycerol, mannitol, 2-ethoxyethanol, and diethylene glycol in a concentration between 50 and 500 milliliters per liter of solution, said solution being maintained at a temperature between 60° and 100° C., and subjecting the article while so immersed to anodic electrolysis at a current density between 1 and 100 amperes per square foot and at a potential not exceeding about 10 volts.

2. A method according to claim 1 wherein the alkali metal hydroxide employed is lithium hydroxide.

3. A method according to claim 1 wherein the water-soluble aliphatic hydroxyl compound is diethylene glycol.

4. A method according to claim 1 wherein the water-soluble aliphatic hydroxyl compound is ethylene glycol.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,923,502	Prier	Aug. 22, 1933
2,229,252	Michel et al.	Jan. 21, 1941

FOREIGN PATENTS

Number	Country	Date
294,237	Great Britain	Sept. 12, 1929
387,437	Great Britain	Feb. 9, 1933
429,344	Great Britain	May 24, 1935
483,798	Great Britain	Apr. 26, 1938
513,837	Great Britain	Jan. 17, 1938
594,062	Germany	Mar. 9, 1934