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COLORING OF MAGNESIUM AND ALLOYS THEREOF

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This invention relates to an improved method of coloring magnesium and magnesium-base alloy articles and more particularly to the coloring of magnesium and magnesium-base alloy articles which have been subjected first to electrochemical treatment.

Magnesium and magnesium-base alloys must be given protective coatings to permit their widespread use. These coatings must afford protection against corrosion, abrasion and fire. As is known in the art a protective coating can be applied to magnesium and magnesium-base alloys by electrochemical processes wherein the articles made of such metals are anodically treated in an electrolytic cell containing a suitable electrolyte and with the articles serving as the anode.

It is an object of this invention to treat such protective coatings for decorative effect.

Another object of this invention is to provide a method of coloring magnesium and magnesium-base alloy articles which effects a uniformity of coverage of the articles treated and in which the coating produced is particularized by its high resistance to fading and by its sealing effects.

A further object of the invention is to provide an improved method of coloring electrolytically treated magnesium utilizing a mordant bath which effects permanent retention and adherence of the dye.

A still further object of the invention is to provide an improved method of coloring magnesium or magnesium-base alloy articles wherein after the article has been subjected to electrolytic treatment it is dipped in an improved type of mordant bath before being dipped in the dye bath.

Other objects and features of this invention will be readily apparent to those skilled in the art from the following specification.

In carrying out the present invention the articles formed of magnesium or magnesium-base alloys which are to be colored are subject to anodic treatment in an electrolytic cell, using as an electrolyte a solution of a silicate and a caustic to which may be added a quantity of an organic compound such as phenol. The articles to be coated serve as the anode. Alternating current preferably of 60 cycles and of a density of 20 to 30 amperes per sq. ft., or direct current of a density of 10 to 20 amperes, is passed through the electrolyte for a period of 10 to 30 minutes. This treatment effects a hydrated oxide protective coating which it has been found is highly resistant to corrosion and abrasion and further is highly compatible with paint.

After the protective coating has been formed on the magnesium or magnesium-base alloy surface the coated metal is treated according to the present invention to produce a desired color thereon. After removal from the electrolytic cell the articles being processed are immersed in a mordant bath containing an aqueous solution of two water-soluble salts of acetic acid of which one is ammonium acetate and the other a metallic salt. The salts of acetic acid which are best adapted for use in the present invention with the salt, ammonium acetate, are the metallic salts, aluminum acetate, lithium acetate, zirconium acetate, strontium acetate and barium acetate. In general, a satisfactory mordant bath will comprise a concentration of from about .1% to about .4% of the ammonium acetate and from about .1% to about .6% of one of the metallic acetic acid salts named immediately above.

The ammonium acetate acts as a stabilizing agent and serves to hold the metallic acetic acid salt used with it in solution by providing a common ion-acetate to discourage decomposition of the salt and precipitation of the metal as an oxide in the mordant bath. The ammonium acetate has a neutral action on the anodic protective coating provided on the metal surface and will not injure it, and it further acts as a buffer or stabilizer to stabilize the pH of the mordant bath.

After the article has been dipped in the mordant solution and removed therefrom the surface thereof will retain a film of the metallic acetate. The acetate ion thereof then reacts with the hydrated magnesium oxide finish freeing the metallic ion and allowing it to hydrolyze into a hydrated metallic oxide on the surface of the anodized magnesium article. The hydrated metallic oxide deposited is in the form of a gel and will be retained by the pores in the anodized coating. This provision of a highly hydrolyzed metallic oxide on the anodized article has a sealing effect though it probably does not fully seal the anodized surface but does to a sufficient degree as to be beneficial. The mordant bath is held at a temperature of from 180° F. to 190° F. and the magnesium article is held immersed for about one minute. Maintaining the temperature of the bath at the relatively high temperatures named is primarily for the purpose of reducing the length of time that it is necessary to keep the article being processed immersed and further to preheat the article whereby when it is removed from the mordant bath there will be sufficient heat absorbed by the article to effect a quick evaporation of most of the water film and a neutralization of the acetate ions, thus leaving the metal of the acetic salt as a hydrolyzed oxide on the surface of the article where it serves as a mordant. It has been found that the time of immersion in the mordant bath should not exceed much more than one minute or a stripping action will occur which may break through the anodized coating at sharp edges.

From the mordant bath the article is taken to a dye bath. It is to be noted that the article is moved after a brief pause to allow partial drying of the mordant treated surface, directly to the dye bath from the mordant bath, there is no water rinse for to so treat the article would wash away metallic ions before they had an opportunity to hydrolyze. The dye bath used in the present invention employs water-soluble organic dyes which should preferably be either an acid or a chrome type dye, such as azo dyes or azo dyes containing chromium. The following are examples of dyes that may be used:

Calco Yellow AN
Calco Orange AN
Calco Red SCN
Calco Green AN
Calco Blue AN
Alizarine Yellow R
Alizarine Cyanine Green G Extra New
Alizarine Blue SAE
Alizarine Blue Black (BA Extra 1 gr/1 Chrome Yellow Extra Conc.)
Neolan Orange G
Neolan Bordeaux R
Neolan Blue 2G (Conc.)
Neolan Black WA Ex. High Conc.
Tartrazine
Diamond Red BHA Extr. Conc.
Anthraquinone Blue BN

The pH value of the dye bath, usually ranging from 5.0 to 8.5 depending on the dye used, will be stabilized by contaminations carried over from the mordant bath. The concentration of the dyes in the aqueous bath is from about 1 gram to about 5 grams per liter, and in general about 2 grams per liter is most suitable. Bath temperatures of from about 65° C. to 80° C. are satisfactory. The parts are immersed from one to two minutes if pastel shades are desired and from three to ten minutes for the darker shades, depending on the dye used. On immersion of the mordant treated anodized article into the dye bath a reaction occurs between the hydrated metallic oxide and the dye to form insoluble color lakes. These color lakes fixed upon the processed article impart to it a permanent color.

Imparting a color to magnesium or magnesium-base alloys in the manner above described effects a greater depth of color than by other methods known. The final coating is uniform and very highly resistant to fading in sunlight, and furthermore at least a partial sealing of the anodic coating is effected.

The following example illustrates the method of coloring of articles made of magnesium or magnesium-base alloys according to the present invention.

Example

Panels made of magnesium and magnesium-base alloys were first subjected to an anodic oxidation treatment. For this an electrolyte was used consisting of an aqueous solution of a caustic base and a soluble silicate to which was added an organic compound. The composition of this bath may vary as follows:

	By weight
Sodium hydroxide	23 to 25%
Phenol	.2 to .3%
Sodium silicates (water glass)	2.5 to 3.5%

The temperature of the electrolyte was maintained at 180° F. With the magnesium articles serving as the anode, direct current of a density of 15 amperes per sq. ft. was passed through the electrolyte for a period of 20 minutes.

The anodic coating formed on articles subjected to treatment as above is corrosion and abrasion resistant and comprised a hard, dense coating of hydrated magnesium oxide.

The anodized panels were then transferred to the mordant bath, an aqueous solution having therein:

	Grams per liter
.5% of aluminum acetate	5
.3% of ammonium acetate	3

This mordant bath was held at a temperature of between 180° to 190° F. After immersion for about one minute the panels were removed and after a brief pause to allow for drainage and partial drying, they were directly transferred to the dye bath.

The dye bath was comprised of an aqueous solution of 2% anthraquinone Blue BN. The temperature of the bath was 75° C. and the panels were held in this dye bath for about 3 minutes. This resulted in the articles being dyed a royal blue.

The foregoing example has been by way of illustration only and it is understood that it is not to be construed as limiting the invention.

Utilizing the method above described coatings having practically any desired shade of color are obtainable. The coatings provided are homogenous and uniform and afford a very high degree of protection against mechanical abrasion and corrosion.

Having particularly described and pointed out my invention, I claim:

1. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises briefly immersing the electrolytically coated article in a heated mordant bath consisting of an aqueous solution of a water-soluble metallic salt of acetic acid, in a proportion between 1 gram and about 6 grams per liter, and a stabilizing agent, in a proportion between 1 gram and about 4 grams per liter for preventing the decomposition of said water-soluble metallic salt of acetic acid, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

2. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for a brief period of time in a heated mordant bath consisting of an aqueous solution of aluminum acetate, in a proportion between 1 gram and about 6 grams per liter, and a stabilizing agent, in a proportion between 1 gram and about 4 grams per liter, for preventing the decomposition of said aluminum acetate, removing the article from the mordant bath, permitting it

to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

3. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated articles for about one minute in a heated mordant bath consisting of an aqueous solution of ammonium acetate, in a proportion between 1 gram and about 4 grams per liter, and a water-soluble metallic salt of acetic acid, in a proportion between 1 gram and about 6 grams per liter, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

4. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in a heated mordant bath consisting of an aqueous solution of ammonium acetate in a proportion between about 1 gram and about 4 grams per liter and aluminum acetate in the proportion between about 1 gram and about 6 grams per liter, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a water-soluble lake-forming dye.

5. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution of ammonium acetate in a proportion between about 1 gram and about 4 grams per liter and aluminum acetate in a proportion of between about 1 gram and about 6 grams per liter, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution of an azo dye containing chromium.

6. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for a brief period of time in a heated mordant bath consisting of an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a water-soluble dye.

7. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution of ammonium acetate, in a proportion between 1 gram and about 4 grams per liter, and a water-soluble metallic salt of acetic acid in a proportion between 1 gram and about 6 grams per liter, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution of a water-soluble dye.

8. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution of an organic acid type dye.

9. A method of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, comprising immersing the electrolytically coated article for about one minute in a mordant bath heated to a temperature of between 180° to 190° F., and consisting of an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate whereby a film is provided upon the surface of the article which reacts with the hydrated oxide coating to deposit hydrated aluminum oxide, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of an organic acid type dye, which dye is adapted to react with the hydrated aluminum oxide to form an insoluble color lake.

10. A method of producing a colored corrosion and abrasion resistant coating upon articles formed of magnesium and magnesium-base alloys, consisting of electrolytically treating the article to be coated in an electrolyte composed of an aqueous solution of sodium hydroxide, 22 to 25% by weight, sodium silicate, 2.5 to 3.5% by weight and phenol .2 to .3% by weight, briefly immersing the electrolytically coated article in a heated mordant bath comprising an aqueous solution of ammonium acetate, in a proportion between 1 gram and about 4 grams per liter, and water-soluble metallic salt of acetic acid, in a proportion between 1 gram and about 6 grams per liter, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a water-soluble dye.

11. A method of producing a colored corrosion and abrasion resistant coating upon articles formed of magnesium and magnesium-base alloys, consisting of electrolytically treating the article to be coated in an electrolyte composed of sodium hydroxide, 22 to 25% by weight, sodium silicate, 2.5 to 3.5% by weight and phenol, .2 to .3% by weight, immersing the electrolytically coated article for about one minute in a mordant bath heated to a temperature of between 130° to 190° F., and compriisng an aqueous solution of ammonium acetate in a proportion between about 1 gram and about 4 grams per liter and water-soluble metallic salt of acetic acid taken from the group consisting of aluminum acetate, lithium acetate, zirconium acetate, strontium acetate and barium acetate, in a proportion between 1 gram and about 6 grams per liter, removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

12. A method of producing a colored corrosion and abrasion resistant coating upon articles formed of magnesium and magnesium-base alloys, consisting of electrolytically treating the article to be coated in an electrolyte composed of an aqueous solution of sodium hydroxide, 22 to 25% by weight, sodium silicate, 2.5 to 3.5% by weight and phenol, .2 to .3% by weight, immersing the electrolytically coated article for about one minute in a heated mordant bath comprising an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5

grams per liter of aluminum acetate, removing the article from the mordant bath, permitting it to partially dry, and next treating the article in an aqueous solution of a water-soluble dye.

13. A method of producing a colored corrosion and abrasion resistant coating upon articles formed of magnesium and magnesium-base alloys, consisting successively of electrolytically treating the article to be coated in an electrolyte composed of an aqueous solution of sodium hydroxide, 22 to 25% by weight, sodium silicate, 2.5 to 3.5% by weight and phenol, .2 to .3% by weight, immersing the electrolytically coated article for about one minute in a mordant bath comprising an aqueous solution of about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate, at a temperature between 180° to 190° F., removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution of an organic acid type water-soluble dye.

14. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution of ammonium acetate in a proportion between about 1 gram and about 4 grams per liter and aluminum acetate in a proportion of between about 1 gram and about 6 grams per liter, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution of an azo dye containing chromium, the dye concentration being between about 1 gram and 5 grams per liter.

15. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in a mordant bath consisting of an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate, at a temperature between 180° to 190° F., removing the article from the mordant bath, permitting it to partially dry, and next immersing the article in an aqueous solution containing about 2 grams per liter of a water-soluble dye.

16. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution of ammonium acetate in a proportion between about 1 gram and about 4 grams per liter and aluminum acetate in a proportion of between about 1 gram and about 6 grams per liter, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution containing an organic acid type dye in a proportion between about 1 gram and 5 grams per liter, the solution being maintained at a temperature between about 65° C. and about 80° C.

17. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in an aqueous solution containing about 3 grams per liter of ammonium acetate and about 5 grams per liter of aluminum acetate, at a temperature between 180° to 190° F., removing the article from the aqueous solution, permitting it to partially dry, and next immersing the article in an aqueous solution containing an organic acid type dye in a proportion between about 1 gram and 5 grams per liter, the solution being maintained at a temperature between about 65° C. and about 80° C.

18. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for a short period of time in a heated mordant bath consisting of an aqueous solution of a water-soluble metallic salt of acetic acid taken from a group consisting of aluminum acetate, lithium acetate, zirconium acetate, strontium acetate, and barium acetate, in a proportion of between 1 gram and about 6 grams per liter, and a stabilizing agent for preventing the decomposition of said water soluble metallic salt of acetic acid, in a proportion of between 1 gram and about 4 grams per liter, removing the article from the mordant bath and permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

19. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in a heated mordant bath and consisting of an aqueous solution of a water-soluble metallic salt of acetic acid taken from a group consisting of aluminum acetate, lithium acetate, zirconium acetate, strontium acetate, and barium acetate, in a proportion of between 1 gram and about 6 grams per liter, and ammonium acetate in a proportion of between 1 gram and about 4 grams per liter, removing the article from the mordant bath and permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

20. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about one minute in a mordant bath heated to a temperature of between 180° to 190° F., and consisting of an aqueous solution of about 5 grams per liter of a water-soluble metallic salt of acetic acid taken from a group consisting of aluminum acetate, lithium acetate, zirconium acetate, strontium acetate, and barium acetate, and about 3 grams per liter of ammonium acetate, removing the article from the mordant bath and permitting it to partially dry, and next immersing the article in an aqueous solution of a lake-forming dye.

21. A process of coloring electrolytically produced hydrated oxide coatings on articles of magnesium and magnesium-base alloys, which comprises immersing the electrolytically coated article for about a minute in a mordant bath heated to a temperature of between 180° to 190° F., and consisting of an aqueous solution of about 5 grams per liter of a water soluble metallic salt of acetic acid taken from a group consisting of aluminum acetate, lithium acetate, zirconium acetate, strontium acetate, and barium acetate, and about 3 grams per liter of ammonium acetate, removing the article from the mordant bath and permitting it to partially dry, and next immersing the article in an aqueous solution containing an organic acid type dye in a proportion between about 1 gram and 5 grams per liter, the

solution being maintained at a temperature between about 65° C. and 80° C.

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