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COLORING PROTECTIVE COATING ON MAGNESIUM AND ITS ALLOYS

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This invention relates to an improved method of coloring hydrated oxide protective coatings upon the surface of articles of magnesium and magnesium-base alloys.

Articles of magnesium and magnesium-base alloys are commonly provided with some form of chemical finish to prevent attack of the metal by corrosive agents to which it may be exposed. One of the known finishes, the one to which the present invention is directed, consists essentially of an adherent coating of hydrated oxide formed on the surface of the magnesium article by interaction of the base metal with water, usually in the presence of alkalies. Such coatings may be produced as thick relatively soft layers by subjecting the article to the action of hot water at elevated pressures, (as described in U. S. Patent Reissue 16,340) or by immersing it in a boiling alkaline solution of an oxidizing agent, (as disclosed in U. S. Patent 1,642,309). More desirably, the oxide coatings may be prepared in hard, dense, thin form, either by subjecting the magnesium article to the action of a 2 to 20 per cent water solution of alkali metal hydroxide under pressure at temperatures of 150° to 250° C., (as set forth in the publication "Dowmetal Bulletin DM3a," and in my co-pending applications, Serial No. 224,510, filed August 12, 1938, now U. S. Patent No. 2,250,472, and Serial No. 348,681, filed July 31, 1940), or by anodizing the article in an aqueous polyhydric alcohol solution of an alkali at temperatures of 50° to 150° C. (as explained in detail in my co-pending application Serial No. 369,628, filed December 11, 1940).

As is known, hydrated oxide protective coatings upon magnesium articles, such as those described, may be colored to produce decorative effects either by incorporating a soluble dye in the solution used in forming the coating, or, in some instances, by dipping the coated article in a water solution of the dye. Unfortunately the former method is disadvantageous in that, although satisfactory colorings are obtained, the dye is gradually decomposed at the operating temperatures and must be replaced. The latter method does not always give uniform colorings, is limited in the number of colors which can be thus applied, and is not applicable to the hard, dense type of oxide coating.

It is therefore an object of the invention to provide a simple method of coloring hydrated magnesium oxide protective films which is not subject to the disadvantages mentioned.

According to the present invention, hydrated oxide coatings upon articles of magnesium and magnesium-base alloys are colored by immersing the coated article in an aqueous solution of a water soluble dye and a water soluble salt of an unsubstituted organic carboxylic acid. In this way uniform colorings of any desired shade may easily be prepared.

Among the salts which may be employed in the dyeing solution, the alkali metal, ammonium, and aluminum salts of oxalic acid and such carboxylic acids as the saturated aliphatic acids, e. g. formic, acetic, and propionic acids, alicyclic acids, e. g. cyclohexane carboxylic acid, aromatic acids, e. g. benzoic, and aralkyl carboxylic acids, e. g. phenyl acetic acid, are most suitable. Salts of acetic acid, especially ammonium acetate, aluminum acetate, and the alkali metal acetates, are greatly to be preferred, since the colorings obtained with these agents are unusually deep and true, and the process is very easily controlled. In general, the salt should be present in a concentration between about 0.1 and about 10 grams per liter of solution, preferably 0.2 to 2 grams, although other concentrations are operable. Salts of substituted carboxylic acids, such as the hydroxy-aliphatic acids, e. g., citric and tartaric acid, are not satisfactory.

A variety of soluble dyes may be used in the invention. However, it has been found that the Neolan dyes, i. e. chromium-containing mordant azo dyes, particularly organo-chromium complex mordant ortho-hydroxy azo dyes (as described in Melliand's Textilber. 6, 674–6 (1925), or in J. Soc. Dyers and Colourists 50, 282 (1934)), are especially suitable. Typical dyes which have been used include:

Neolan Green B
Neolan Green BL (conc.)
Neolan Bordeaux R (red)
Neolan Orange G
Neolan Yellow G
Neolan Black 2R
Alizarin Sapphire Blue (Colour Index No. 1054)
Naphthol Yellow S (Colour Index No. 10)

The dye is ordinarily employed in a concentration between about 0.1 and about 10 grams per liter, suitably 0.2 to 1.0 gram, although other proportions may sometimes be used.

The dyeing solution of the invention is preferably substantially neutral, e. g., at a pH value of 6.0 to 7.0. It may be used at any temperature from room temperature up to the boiling point, temperatures of 50° to 100° C. being preferred. At these temperatures, only 5 to 30 minutes are

required to produce an excellent coloring. The dyeing treatment has no appreciable effect on the corrosion resistance of the hydrated oxide coatings.

In forming a colored article, the magnesium or magnesium-base alloy article is first subjected to a suitable treatment, such as those already considered, to form a hydrated oxide protective coating. The article is then buffed or brushed, if necessary, to remove any loose material and to produce a high gloss, after which it is immersed in the dye solution to color the coating. The article is then rinsed and dried, after which it may, if desired, be waxed or polished to improve the gloss.

The following example will illustrate the invention:

Example

Articles of extruded Dowmetal J alloy (an alloy containing 6.5 per cent aluminum, 0.2 per cent manganese, and 0.7 per cent zinc, the balance being magnesium), were treated to form a hard, dense, thin hydrated oxide protective coating by immersing them for 5 minutes in a 10 per cent aqueous sodium hydroxide solution maintained at a temperature of 200° C. under a pressure of 225 lbs. per sq. in. The articles were then rinsed and dyed by immersing them for 10 minutes in a boiling aqueous solution of 0.2 per cent ammonium acetate and 1.0 per cent of Neolan Bordeaux R. The articles were dyed a pleasing uniform red color.

It is to be understood that the foregoing description is illustrative rather than strictly limitative of the invention.

I claim:

1. In a method of coloring hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the step which comprises immersing the coated article in an aqueous solution of a water-soluble dye and a water-soluble salt of an unsubstituted organic carboxylic acid.

2. A method as defined in claim 1 wherein the water-soluble salt is a salt of acetic acid.

3. In a method of coloring hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the step which comprises immersing the coated article in a substantially neutral aqueous solution of a water-soluble dye and a water-soluble salt of an unsubstituted organic carboxylic acid.

4. In a method of coloring hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the steps which comprise immersing the coated article in an aqueous solution of a chromium-containing mordant azo dye and a water-soluble salt of an unsubstituted organic carboxylic acid.

5. A method as defined in claim 4 wherein the water-soluble salt is a salt of an acid selected from the class consisting of saturated aliphatic acids, alicyclic acids, aromatic acids, and aralkyl carboxylic acids.

6. A method as defined in claim 4 wherein the water-soluble salt is a salt of an unsubstituted aliphatic carboxylic acid.

7. A method as defined in claim 4 wherein the water-soluble salt is a salt of acetic acid.

8. In a method of coloring hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the step which comprises immersing the coated article in a substantially neutral aqueous solution containing a water-soluble dye in a proportion between about 0.2 and about 10 grams per liter and a water-soluble salt of an unsubstituted organic carboxylic acid in a proportion between about 0.1 and about 10 grams per liter.

9. In a method of coloring hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the step which comprises immersing the coated article in an aqueous solution containing a chromium-containing mordant azo dye in a proportion between about 0.2 and about 10 grams per liter and a water-soluble salt of an unsubstituted aliphatic carboxylic acid in a proportion between about 0.1 and about 10 grams per liter.

10. A method as defined in claim 9 in which the water-soluble salt is a salt of acetic acid.

11. In a method of coloring hard, dense, thin hydrated oxide protective coatings upon surfaces of articles of magnesium and magnesium-base alloys, the step which comprises immersing the coated article for a period between about 5 and about 30 minutes in a solution containing a water-soluble organo-chromium complex mordant ortho-hydroxy azo dye in a proportion between about 0.2 and about 10 grams per liter and a water-soluble salt of acetic acid in a proportion between about 0.1 and about 10 grams per liter, the solution being maintained at a temperature between about 50° C. and about 100° C.

12. A method as defined in claim 11 wherein the acetic acid salt is aluminum acetate.

13. A method as defined in claim 11 wherein the acetic acid salt is ammonium acetate.

14. A method as defined in claim 11 wherein the acetic acid salt is an alkali metal acetate.

15. Articles of magnesium and magnesium-base alloys having on the surface thereof a hydrated oxide protective coating colored according to the method of claim 1.

16. Articles of magnesium and magnesium-base alloys having on the surface thereof a hydrated oxide protective coating colored according to the method of claim 4.

17. Articles of magnesium and magnesium-base alloys having on the surface thereof a hydrated oxide protective coating colored according to the method of claim 9.

18. Articles of magnesium and magnesium-base alloys having on the surface thereof a hydrated oxide protective coating colored according to the method of claim 11.

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