Patented Oct. 7, 1947

2,428,749

UNITED STATES PATENT OFFICE

2,428,749

SURFACE TREATMENT OF MAGNESIUM ALLOYS

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No Drawing. Application August 19, 1944, Serial No. 550,314

8 Claims. (Cl. 148—6.20)

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This invention relates to an improved method of producing a protective coating on the surface of aluminum-containing magnesium-base alloys.

Articles of magnesium-base alloys are conventionally protected against corrosion during shipment, storage, and machining, and provided with a paint base by applying to the surface thereof some type of chemical finish, of which the so-called "chrome-pickle," produced by immersing the article in an aqueous solution of chromic acid or a soluble chromate and a strong mineral acid, usually nitric acid, is by far the most common. It has been observed, however, that when the "chrome-pickle" treatment is applied to certain aluminum-containing magnesium-base alloys, there is sometimes obtained, instead of the expected uniform iridescent brass-colored finish ordinarily produced, a coating consisting in part of a loose deposit of a heavy dark gray powder. This powder, which has been identified as an intermetallic compound of magnesium and aluminum (probably Mg_3Al_2 or Mg_4Al_3), not only seriously detracts from the appearance of the treated article but also constitutes a distinct fire hazard, since, in addition to being easily ignited, it produces sparks on the application of slight frictional forces. Unless precautions are taken, simple wire-brushing or grinding of powder-coated parts may cause minor fires in accumulated dust, and even the striking together of two coated articles results in serious sparking. The occasional occurrence of this powder, then, is a serious practical disadvantage in the application of the "chrome-pickle" treatment to magnesium-base alloys of all types.

Extended investigation of the "chrome-pickle" procedure has shown that the dark gray powdery deposit of magnesium-aluminum compound is obtained principally in the treatment of articles formed of magnesium-base alloys containing at least 85 per cent by weight of magnesium and from 4 to 12 per cent of aluminum, especially when these alloys are in a metallurgical state such that a magnesium-aluminum intermetallic compound is present as a discrete phase in the solid metal, as is the usual case with articles which have been pressure die-cast or have been heat-treated and aged. In coating such articles, the "chrome-pickle" solution appears to etch or react with a thin surface layer of the magnesium-base alloy phase constituting the major part of the metal forming the article without appreciably dissolving or otherwise affecting the separate magnesium-aluminum intermetallic compound phase. This undissolved compound remains on the surface of the treated article and gives rise to the non-uniform appearance and sparking hazard mentioned.

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In an effort to eliminate formation of the powdery deposit, the prior art has suggested solution heat-treating the articles before "chrome-pickling" so as to dissolve the discrete intermetallic compound into the body of the magnesium-base alloy matrix. This process, while effective, is inapplicable in many instances since the heat-treating operation alters the physical properties of the metal. In addition, even where such alteration may be tolerated, the metal frequently tends to blister at the high temperatures involved, and must often be refinished before the chemical coating is applied. In so far as is known, no satisfactory solution of the powder formation problem has heretofore been available.

An object of the invention, therefore, is to provide a coating method for magnesium-base alloys which retains the advantages of the "chrome-pickle" process and at the same time eliminates formation of the powdery gray deposit without altering the physical characteristics of the articles treated.

This object is realized in the process of the invention, which consists essentially in subjecting the article to be treated to the action of a solution of the "chrome-pickle" type to which has been added a small proportion of a fluoride. The presence of this latter ingredient insures dissolution of any magnesium-aluminum intermetallic compound present in the metal being treated without otherwise appreciably altering the course of the treatment. The uniform pleasing iridescent brassy finish characteristic of the "chrome-pickle" is invariably obtained, and no formation of dark gray powdery deposit is observed.

The treating solution used in the process is an aqueous solution containing as the effective ingredients chromic acid or a water-soluble salt thereof, a strong mineral acid, and hydrofluoric acid or a water-soluble salt thereof. The chromate constituent is ordinarily added in the form of chromic anhydride (CrO_3) or an alkali metal or ammonium chromate or bichromate, sodium bichromate being convenient. Concentrations of chromic acid or soluble chromate of at least 2 per cent by weight of the solution are ordinarily required, with 5 to 20 per cent being most satisfactory. The strong mineral acid, which is usually nitric, hydrochloric, or sulfuric acid, is added in a proportion sufficient to maintain the pH value of the solution below about 2.0, pref-

erably about 0.3 to 1.0. Nitric acid is most satisfactory in producing a coating useful as an adherent paint base. The fluoride ingredient is conveniently aqueous hydrofluoric acid or a solid alkali metal or ammonium fluoride or bifluoride, such as sodium fluoride or ammonium bifluoride (NH_4HF_2), although other simple fluorides are operable. Complex fluo-acids and their salts are not effective. The hydrofluoric acid or fluoride should be added in a proportion corresponding to between about 0.06 and about 1.7 per cent by weight of combined fluorine in the solution, values of 0.23 to 0.67 per cent being most advantageous. If concentrations below about 0.06 per cent are used the effectiveness of the solution is impaired, whereas at fluoride concentrations much above 1.3 to 1.7 per cent the solution no longer produces chromate-type coatings but tends to form non-adherent deposits of mottled appearance.

In practicing the invention, the magnesium-base alloy article to be coated is first cleaned by conventional methods such as solvent degreasing or alkaline cleaning. The article is then immersed in the coating bath as described above for a time sufficient to produce a satisfactory finish, usually for 0.2 minute or more, usually about one minute, after which it is withdrawn from the bath, allowed to drain free of solution, washed, and dried. The temperature of the coating bath is not critical, room temperature being customary.

The coatings produced in the manner described are of a uniform color, usually brass-like, are extremely adherent to the base metal, and afford protection against corrosion at least equal to that of the standard "chrome-pickle." They provide an excellent base for subsequent siccative coatings, such as paints or enamels.

The process of the invention, while effective in producing chromate-type finishes on magnesium-base alloys of all types, is particularly advantageous in treating alloys containing at least 85 per cent magnesium and from 4 to 12 per cent of aluminum, with or without lesser proportions of other minor alloying elements such as manganese, zinc, silver, and silicon, since these alloys are the ones which, in certain states of heat treatment, ordinarily contain a magnesium-aluminum intermetallic compound. With such compound-containing alloys, the new method is essential in securing a useful coating. Even in treating articles of alloys of this range of compositions in which an intermetallic compound has not been intentionally precipitated in the metal or is not known to be present, it is advantageous, as a practical measure, to use the process of the invention at all times in place of the conventional "chrome-pickle," since the possibility of gray powder formation due to the unexpected presence of intermetallic compounds is eliminated.

The invention may be further understood by reference to the following examples, which, it will be appreciated, are illustrative rather than limitative.

Example 1

A sand-cast workpiece of Dowmetal C (a magnesium-base alloy containing 9.0 per cent aluminum, 2.0 per cent zinc, and 0.1 per cent manganese, the balance being magnesium), which had been solution heat treated and aged in conventional manner to improve the strength and hardness, and which therefore contained a magnesium-aluminum intermetallic compound as a discrete phase in the metal, was coated according to the invention. The article was first cleaned of dirt and oily matter by alkaline cleaning, and was then immersed for one minute at room temperature in a solution having the following composition:

Sodium bichromate ($Na_2Cr_2O_7.2H_2O$)	pounds	1.5
Nitric acid (sp. gr. 1.42)	pints	1.5
Ammonium bifluoride (NH_4HF_2)	ounces	1⅓
Water, to make 1.0 gallon.		

After immersion the article was drained to remove solution and then washed in water. The protective coating obtained was a uniform iridescent brassy color, and was free of any gray powdery material. No sparking was observed when the workpiece was subjected to wire brushing and grinding operations.

Example 2

A pressure die-casting of Dowmetal K (a magnesium-base alloy containing 10.0 per cent aluminum, 0.5 per cent silicon, and 0.1 per cent manganese, the balance being magnesium), which in the as-cast state contained a magnesium-aluminum intermetallic compound as a discrete phase in the metal, was treated according to the invention. After alkaline cleaning, the die-casting was coated by immersing it for one minute at room temperature in a bath having the following composition:

Chromic anhydride (CrO_3)	pounds	1.0
Nitric acid (sp. gr. 1.42)	pints	0.9
Ammonium bifluoride (NH_4HF_2)	ounces	1⅓
Water, to make 1.0 gallon.		

After immersion, the die casting was drained, rinsed in water, and dried. It exhibited a protective coating similar to that described in Example 1, and free of any gray powdery inclusions.

This application is a continuation-in-part of my copending application Serial No. 429,132, filed January 31, 1942.

I claim:

1. In a method of providing a protective coating on the surface of articles formed of magnesium-base alloys, the step of subjecting the article to the action of an aqueous solution, the dissolved constituents of which consist of a substance selected from the class consisting of chromic acid and water-soluble salts thereof, a strong mineral acid in a proportion sufficient to maintain the pH value of the solution below about 2.0, and a substance selected from the class consisting of hydrofluoric acid and water-soluble salts thereof, in a concentration corresponding to between about 0.06 and about 1.7 per cent by weight of combined fluorine in the solution, for a time sufficient to form a coating on the article.

2. A method according to claim 1 wherein the strong mineral acid is nitric acid.

3. In a method of providing a protective coating on the surface of articles formed of a magnesium-base alloy containing at least 85 per cent by weight of magnesium and from 4 to 12 per cent of aluminum, wherein a magnesium-aluminum intermetallic compound is present as a discrete phase in the metal, the step of immersing the article in an aqueous solution, the dissolved constituents of which consist of at least 2 per cent by weight of a coating substance selected from the class consisting of chromic acid and water-soluble salts thereof, a strong mineral acid in a proportion sufficient to maintain the pH value

of the solution below about 2.0, and a substance selected from the class consisting of hydrofluoric acid and water-soluble salts thereof in a concentration corresponding to between about 0.23 and about 0.67 per cent by weight of combined fluorine in the solution, for a time to form a coating on the article.

4. A method according to claim 3 wherein the strong mineral acid is nitric acid.

5. A method according to claim 3 wherein the coating substance is sodium bichromate and the strong mineral acid is nitric acid.

6. A method according to claim 3 wherein the coating substance is chromic acid and the strong mineral acid is nitric acid.

7. In a process of providing a protective coating on the surface of articles formed of aluminum-containing magnesium-base alloys in which a magnesium-aluminum intermetallic compound is present as a discrete phase in the metal, wherein the article is subjected to the action of an aqueous solution, the dissolved constituents of which consist of chromic acid or a water-soluble salt thereof and a strong mineral acid in a proportion sufficient to maintain the pH value of the solution below about 2.0, the method of insuring dissolution of the aforesaid intermetallic compound during treatment which comprises maintaining dissolved in the treating solution a substance selected from the class consisting of hydrofluoric acid and water-soluble salts thereof in a concentration corresponding to

between about 0.06 and about 1.7 per cent by weight of combined fluorine in the solution.

8. An aqueous solution for producing protective coatings on the surface of magnesium-base alloys, the dissolved constituents of which consists of at least 2 per cent by weight of a substance selected from the class consisting of chromic acid and water-soluble salts thereof, nitric acid in a proportion sufficient to maintain the pH value of the solution below about 2.0, and a substance selected from the class consisting of hydrofluoric acid and water-soluble salts thereof in a concentration corresponding to between about 0.06 and about 1.7 per cent by weight of combined fluorine in the solution.

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