

UNITED STATES PATENT OFFICE

2,288,995

SURFACE TREATMENT OF MAGNESIUM
AND ITS ALLOYSHerbert K. De Long, Midland, Mich., assignor to
The Dow Chemical Company, Midland, Mich.,
a corporation of MichiganNo Drawing. Application April 13, 1940,
Serial No. 329,533

6 Claims. (Cl. 148—6)

This invention relates to the surface treatment of magnesium and magnesium-base alloys.

An object of the invention is to devise a simple and inexpensive method of treating the surface of articles of magnesium or magnesium-base alloys to form thereon a decorative and protective finish. Another object is to provide a surface finish for such articles to which coatings such as paint films adhere with great tenacity, even after prolonged exposure to the atmosphere, and which cooperates with such coatings to render the coated article highly corrosion-resistant.

Briefly, the process of the invention contemplates forming a surface finish on articles of magnesium and magnesium-base alloys by subjecting the article to the action of an aqueous solution essentially comprising a water-soluble fluoride and an acid reactive with metallic magnesium. This treatment tends to etch or roughen the metal slightly, forming a surface to which siccative coatings, such as films of paint, varnish, lacquer, or enamel, adhere strongly without blistering. At the same time, the treatment also forms a protective chemical finish on the metal which is somewhat corrosion-resistant itself, and has the further property of cooperating with siccative coatings applied thereto to provide a highly corrosion-resistant film on the metal article.

In so far as I am aware, the treating bath according to the invention may contain any water-soluble fluoride. Hydrofluoric acid, simple fluorides such as sodium fluoride, acid fluorides such as potassium bifluoride, and complex compounds such as fluosilicic acid, fluoboric acid, and their salts, are all suitable. The bath also may comprise any acid chemically reactive with metallic magnesium. The common strong mineral acids, e. g., hydrochloric, nitric, and sulfuric acids, are ordinarily employed, but other acids, both inorganic and organic, e. g., phosphoric, acetic, chloroacetic, and citric acids, and the like, may also be used. Chromic acid and similar acids which do not react appreciably with magnesium are not operable.

Although the fluoride and the acid, which constitute the effective ingredients of the bath may be employed in any proportions, relatively dilute aqueous solutions of these materials are by far the most satisfactory in the process. The fluoride is preferably used in a concentration corresponding to between about 0.2 and about 6 per cent by weight of fluorine in the solution. If hydrochloric acid is employed as the acid, a con-

centration of 0.2 to 7 per cent by weight of hydrogen chloride in the bath is desirable. In the case of nitric acid, the preferred range is between about 4 and about 20 per cent by weight. Other acids should be used in corresponding dilutions. Concentrations of the fluoride and the acid lower than those stated are less effective in the treatment according to the invention, and concentrations higher than the preferred ranges given tend to increase the attack on the magnesium surface and to produce a much less desirable surface finish.

In carrying the invention into practice, the article of magnesium or magnesium-base alloy is first freed of surface contamination, grease, etc., by wire-brushing, sanding, or chemical cleaning. It is then subjected to the action of an aqueous fluoride-acid solution of the type described by spraying or washing the solution on the metal, or by immersing the article in the solution. The temperature of the treating solution is not critical, ordinary room temperature being convenient. Immersion times of 0.5 to 2 minutes are customary, although somewhat longer times are not detrimental. After treatment the article is rinsed in water or in dilute aqueous alkali to remove the acid solution, and is then usually allowed to dry.

The fluoride-acid bath imparts a pleasing surface appearance and a protective coating to the article, which for many purposes may be then used without further treatment. However, the surface finish resulting from the process is especially suited to serve as a base for additional protective coatings, such as chemical and anodic coatings, electrodeposited metal films, and particularly siccative or resinous films, such as paints and enamels. In applying these latter films, the surface treated article is given a primer coat and then several finish coats of the paint. The resulting finished surface is highly corrosion-resistant, much more than that of similar painted articles which have not been previously treated according to the invention, principally because of the improved adherence of the paint film.

The following examples will illustrate the invention, but are not to be construed as limiting its scope:

Example 1

50 Rolled sheets of a magnesium-base alloy containing 4.0 per cent aluminum and 0.3 per cent manganese, the balance being substantially magnesium, were carefully cleaned to remove grease and dirt. They were then immersed at room temperature for one minute in a water solution,

containing 1.2 per cent by weight of hydrogen fluoride (HF) and 0.63 per cent of hydrogen chloride (HCl), after which they were rinsed in water and dried.

Example 2

The process described in Example 1 was repeated, except that the treating bath was a water solution containing 3.6 per cent by weight of hydrogen fluoride (HF) and 11.6 per cent by weight of nitric acid (HNO₃).

Example 3

Sheets prepared as in Examples 1 and 2, and similar sheets which had been cleaned but had not been subjected to the fluoride-acid bath, were painted by applying one coat of a zinc chromate primer (such as N. A. F.-P27) and two coats of an ordinary enamel. All the sheets were then exposed to outdoor atmosphere for one and one-half years. In the case of the chemically treated sheets, there was, at the end of the exposure, little observable corrosion, and the paint films adhered firmly to the metal, even when it was bent double. The untreated sheets, in contrast, showed a much poorer corrosion resistance, and the paint films were far less adherent.

It will be appreciated that the invention provides an unusually advantageous method of finishing and protecting the surface of articles of magnesium and its alloys. Unlike most prior processes, only a single treatment is required; the chemicals used are inexpensive and in low concentration. No electrolytic apparatus is needed. The process is extremely simple, rapid, and effective.

It is to be understood that the foregoing description is illustrative rather than strictly limitative, and that the invention is co-extensive in scope with the following claims.

I claim:

1. The method of treating the surface of articles of magnesium and magnesium-base alloys which comprises subjecting the article to the action of a solution consisting essentially of water, a water soluble fluoride, and a strong mineral acid.
2. In a method of treating the surface of articles of magnesium and magnesium-base alloys, the step which comprises subjecting the article to the action of a solution consisting of water, an acid reactive with metallic magnesium and a water soluble fluoride, the latter being employed in a concentration corresponding to between about 0.2 and about 6 per cent by weight of fluorine in the solution.
3. A process according to claim 2 wherein the acid employed is nitric acid, the same being present in a concentration between about 4 and about 20 per cent by weight of the solution.
4. A process according to claim 2 wherein the acid employed is hydrochloric acid, the same being present in a concentration of between about 0.2 and about 7 per cent by weight of hydrogen chloride in the solution.
5. An article formed of magnesium or a magnesium-base alloy the surface of which is covered with a protective coating prepared according to the process of claim 1.
6. The method of treating the surface of articles of magnesium and magnesium-base alloys which comprises: subjecting the article to the action of a solution consisting of water, a water soluble fluoride, and a strong mineral acid; rinsing the article to remove the treating solution; drying; and covering the dried article with a silicate coating.

HERBERT K. DE LONG.