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CHROMATE-COATING MAGNESIUM AND ITS ALLOYS

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This invention pertains to an improved chromate coating for articles of magnesium and the magnesium-base alloys, to a method of producing such a coating, and to the articles thus coated. It pertains especially to the formation on magnesium articles of such coating which is highly resistant to corrosion and adapted to be used as an improved basis coating or undercoating for thermoplastic film or sheet adhered thereto.

The term magnesium, as used herein, refers to magnesium metal or a magnesium-base alloy which contains about 85 percent or more of magnesium. A chromate coating, as used herein, refers to a coating which is formed by subjecting magnesium articles to the action of a solution containing a chromium compound in an acidic aqueous solution and which is thought to contain a chromate as a constituent. Such a coating is known to impart corrosion-resistant properties to magnesium.

Among the known methods of chromate-coating magnesium articles by subjecting the magnesium article to the action of such an aqueous solution containing a chromium compound, as by protracted immersion therein, are: immersion in a solution containing a fluoride followed by another one containing an alkali salt of an oxyacid of chromium; immersion in one containing chromic sulfate and an alkali metal chromate; immersion in one containing a water-soluble fluoride and a strong mineral acid; immersion in one containing a water-soluble chromate and a small percent of an inorganic water-soluble fluoride; immersion in one containing chromic acid or its soluble salts, hydrofluoric acid or its water-soluble salts, and a strong mineral acid such as aqueous nitric acid.

Conventional coating solutions and coatings formed on magnesium by immersion in or brush-application of aqueous solutions containing chromium compounds have been unsatisfactory in a number of particulars. Variations in the color of the coated article, lack of uniformity of thickness of the coating, formation of powdery material on the coating during the coating process, failure to build up a coating of desired thickness, and high metal loss are some of the particulars in which these known coating solutions and coatings have been unsatisfactory. Furthermore, in the process of forming chromate coatings by use of solutions of chromium compounds now known, the accumulation of altered chromium and magnesium compounds in the bath during usage has necessitated discarding the bath and replacing it by a fresh bath at uneconomically frequent intervals.

An object of the present invention is to provide an improved chromate coating for magnesium. Another object is to provide a method of forming such coating which is thicker and offers greater protection to the magnesium than do heretofore known coatings. Another object is to provide a chromate coating which when applied to magnesium produces a superior undercoating or basis for the application of thermoplastic film or sheet such as one of polyvinyl chloride. A further object

is to provide a chromate coating solution which is economical of active ingredients and has a long service life. A still further object is to provide a chromate coating solution which undergoes very little build-up of undesirable compounds and which may be revived by mere addition of active ingredients to the solution which therefore need not be discarded after relatively short periods of usage as heretofore has been found necessary. An additional object is to provide magnesium articles, e. g., extrudes, plates, sheets, bars, rods, channels, angles and the like, comprising a base magnesium metal and a thermoplastic outer film or sheeting adhered thereto by a superior bond involving the novel chromate undercoating of the invention. Means of realizing these and related objects will be made clear in the following description of the invention.

The invention is predicated upon the discovery that by preparing a dilute aqueous solution of chromic acid in the presence of an effective amount of ammonium, hydrogen, alkali, or water-soluble alkaline earth sulfate, there is produced a chromate coating on magnesium articles having a desirable uniformity of color and thickness and high resistance to corrosion. The corrosion resistance of the coating has been found to be further enhanced by the presence of an arsenate or acid arsenate of ammonium, or an alkali or alkaline earth. The bath has a long useful life and can be reactivated by mere additions of active ingredients. The coating obtained provides a desirable bond for adhesively securing a thermoplastic film to the metal. The invention then consists of the improved coating composition, coating method, and coated article so produced herein described and particularly pointed out in the claims, the following description setting forth various modes of practicing the invention.

In practicing the invention, the magnesium article is degreased, if considered necessary, by a conventional degreasing method. The degreasing step, which is for the purpose of removing any film of an oily or greasy nature formed on the surface of the magnesium article to be coated consists of immersing in, or rubbing with, an aqueous alkaline solution, e. g., a water solution of sodium carbonate and sodium hydroxide. The degreased magnesium is thereafter rinsed free of residual alkali with water and dried.

The degreasing step may be followed by an activation step or it may be immersed without further preparation in the novel coating solution of the invention. Activation consists of activating the surface of the magnesium, i. e., making it a more receptive site upon which to form the chromate coating. The activation is carried out for the purpose of removing any bits of metal or metal compounds that may have been acquired through handling or that may have been formed as a result of exposure to contaminating influences. Among the metal compounds removed by activation are the oxides and carbonates of magnesium and other metals. The activation may be carried out by one of several ways. One effective way is to prepare a 0.5 percent by volume aqueous solution of 30 weight percent aqueous hydrofluosilicic acid or a 0.5 percent by volume aqueous solution of 50 weight percent hydrofluoric acid and immersing the magnesium article in the solution at about room temperature or a little above, say 70° to 90° F. The duration of immersion in the hydrofluosilicic acid solution should be about 0.5 minute and that of immersion in the hydrofluoric acid preferably about one minute but which may be from 0.5 to 2 minutes.

If desired, the degreasing and activating steps may be combined in a single step. Either of the two solutions, A and B set out below, will serve as a bath in which

the magnesium may be immersed in a combined step. The bath temperature should be about 175° to 185° F. and the duration of the immersion between 1 and 5 minutes, but preferably about 2 minutes.

Solution A.—50 grams of tetrasodium pyrophosphate ($Na_4P_2O_7$), 20 grams of sodium metaborate

($NaBO_2 \cdot 2H_2O$)

dissolved in sufficient water to make 1 liter of solution at room temperature.

Solution B.—50 grams of sodium tetraborate or borax ($Na_2B_4O_7 \cdot 10H_2O$), 20 grams of tetrasodium pyrophosphate ($Na_4P_2O_7$) dissolved in sufficient water to make 1 liter of solution at room temperature.

Routine analytical tests of the activating baths during their usage and the addition of the constituents shown to be depleted by the operation are recommended. Addition of hydrofluosilicic or hydrofluoric acid to the activating baths and of tetrasodium pyrophosphate to the degreasing-activating baths will be found necessary. The borate component depletes rather slowly and will be found seldom to require replenishment.

The activating step is completed by rinsing the magnesium article well with water.

After the degreasing step, if performed, or degreasing and activating steps, the magnesium piece or article is treated as by immersing for about 1 to 6 minutes at room temperature but preferably between room temperature and 150° F. in the aqueous solution prepared in accordance with the invention containing chromium trioxide, which forms chromic acid when added to the solution, and ammonium, hydrogen, alkali, or water-soluble alkaline earth sulfate. The ammonium, alkali, or alkaline earth sulfate serves as a promoter. As an alkaline earth metal sulfate, calcium sulfate is particularly suitable because its solubility of 0.6% in water at room temperature in the presence of dilute chromic acid allows it to dissolve to a desirable extent and yet permit an excess of the sulfate to be present on the floor of the bath container as a reserve. Such reserve is readily available for replenishing the bath as rapidly as it is used up in the process. Accordingly, the invention contemplates the use of an excess of calcium sulfate in the aqueous solution in which it serves as a promoter for the chromate treatment. There may also be advantageously present an ammonium, alkali, or alkaline earth arsenate or acid arsenate as a further protection against corrosion.

The components of the chromate coating solution may vary within rather broad limits. The chromic oxide may be between about 0.25 and 3.0%, but preferably is between about 0.5 and 1.5 percent by weight of the aqueous solution. The sulfate compound must be present in an amount sufficient to yield at least 0.075 percent and not more than 2.2 percent of the sulfate fraction (SO_4) based upon the weight of the chromate solution. The preferred average percent of the sulfate fraction is between 0.18 and 0.75. For example, when the sulfate is added as ammonium sulfate, the ammonium sulfate may be between 0.1 and 3.0 weight percent and is preferred to be between 0.25 and 1.0 percent. If an arsenate or acid arsenate is desired it may conveniently be added as crystalline disodium acid arsenate, having the formula $Na_2HAsO_4 \cdot 7H_2O$. It may be added in an amount between 0.1 and 1.0 weight percent but preferably between 0.3 and 0.5 weight percent based on the chromate solution. Equivalent amounts of the arsenate (AsO_4) or acid arsenate ($HAsO_4$) may be added as ammonium, alkaline earth or other alkali arsenates or acid arsenates. The pH value of the solution must be between 0.9 and 1.8 but best results are obtained when the pH value is between 1.2 to 1.6.

The chromate-coating solution of the invention may be used over a long period of service by additions at intervals of the active ingredients therein.

After immersion in the chromate-coating solution the magnesium article may now be water-rinsed. The coating is thereafter dried by placing the coated magnesium in an oven, or by exposing it to fairly dry atmospheric conditions. The temperature of the oven is not critical so long as it remains below the softening temperature of the coated piece; it is preferably not over 450° F.

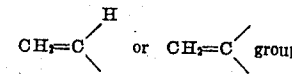
The coating obtained by treating magnesium according to the invention is tough and relatively impervious to attack by materials which ordinarily come in contact with magnesium in use. The coating can be varied somewhat in color dependent upon the formulation used. For example CrO_3 and $CaSO_4$ give a dark brown to black coating whereas in the presence of disodium acid arsenate they give a tan to brown coating. The thickness of the coating is increased by a longer period of immersion.

Although the chromate coating of the invention provides valuable protection for magnesium articles against corrosion and abrasion as well as being decorative, a desirable embodiment of the invention is the production of thermoplastic film covered magnesium articles having a chromate coating on the magnesium upon which a suitable adhesive hereinafter described is applied, said chromate coating serving as an undercoating for the thermoplastic film and providing an improved bonding surface for the plastic film.

The chromate coating of the invention protects the magnesium prior to application of the thermoplastic film outer-coating and provides a clean smooth surface free of magnesium oxide, magnesium carbonate or other foreign materials. It insures an excellent bond between the magnesium and rubber resin adhesive, as described hereafter; the bond formed is of such tenacity that, after cure, the thermoplastic cannot be peeled therefrom without rupturing the thermoplastic film adhering to the magnesium. During the service of the article comprising thermoplastic sheet or film adhered to magnesium, the resistant undercoating of the invention protects the article against corrosive substances which find their way through cracks or small irregularities which may develop in the film during use or may attack the metal at the interface of the thermoplastic and magnesium and would otherwise result in oxidation and other deteriorating chemical action at the surface.

Heretofore, bonding of the thermoplastic outer film covering to the magnesium has been unsatisfactory due to failure of the bond between the adhesive and the magnesium unless uneconomical processes and coating compositions were employed. Chromate-coating the magnesium according to the invention before application of the adhesive has provided a bonding surface which permits the formation of a bond of high tenacity.

Among the thermoplastic outer film coverings for which the chromate coating herein described is adapted to be used as an undercoating are homopolymers and copolymers of a polymerizable monomeric mix containing at least one unsaturated organic compound having in its molecule at least one methylene group attached to a carbon atom by an olefinic double bond, i. e., at least one



Examples of such monomeric compounds are vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, methyl acrylate, ethyl acrylate, styrene, methyl methacrylate, methyl ethacrylate, acrylonitrile, vinyl valerate, vinyl caproate, and allyl esters of monocarboxylic acids such as allyl butyrate, allyl esters of polycarboxylic acids such as diallyl adipate, allyl esters of inorganic acids such as allyl chloride, and allyl esters of unsaturated acids such as allyl acrylate.

One method of producing plastic film-covered magnesium articles according to the invention comprises cleaning and chromate-coating magnesium panels or sheets as above described; spraying the chromate-coated sheets with a synthetic rubber-resin adhesive dissolved in an organic solvent, e. g., Kotal 330, procurable from the Naugatuck Chemical Company, Naugatuck, Connecticut, and spreading the adhesive evenly on one side thereof as by a squeeze-roller; heating the adhesive-coated magnesium to about 300° F.; advancing it so that the adhesive-coated surface comes into parallel contact with the surface of a thermoplastic sheet, e. g., polyvinyl chloride, at about room temperature and under tension; and thereafter subjecting the contacting surfaces of the thermoplastic sheets and chromate-coated magnesium sheet to a pressure to press the magnesium sheet and thermoplastic sheet firmly against each other to cause them to adhere firmly to each other and passing the thus adhering sheets through heating zones maintained at a suitable curing temperature which cure the adhesive, e. g., a temperature between 200° and 300° F.

The magnesium sheets which were thus coated first with the protective chromate coating of the invention and subsequently had bonded thereto an abrasion resistant and pleasing appearing thermoplastic film may be fabricated into a number of objects.

This embodiment of the invention is especially applicable in producing such objects as thermoplastic film-covered magnesium articles as jewelry boxes, luggage, shipping and storage containers, instrument cases, and panels to be used in the construction of cabinets, counters, and tables.

The invention may be practiced by any of a wide number of modes. But a few of these modes are set out below by way of illustration in Examples 1 to 14.

EXAMPLE 1

A panel of magnesium alloy composed of 96% magnesium, 3% aluminum, and 1% zinc, having the dimensions of 3" x 6" x 0.04", was degreased by immersing for 2 minutes at room temperature in an alkaline solution prepared by dissolving 3 weight oz. of sodium carbonate and 2 weight oz. of sodium hydroxide in sufficient water to make a gallon of solution. The so treated panel was removed from the solution, rinsed with water, and dried at about 150° F. The rinsed panel was thereafter immersed for 2 minutes at room temperature in the novel aqueous chromate coating solution of the invention, having a pH value of 1.21, containing the following active constituents or ingredients by weight of solution: 1.0% of CrO_3, 0.75% of $CaSO_4 \cdot 2H_2O$. This was more

$$CaSO_4 \cdot 2H_2O$$

than necessary to saturate the solution and therefore some of it settled to the bottom of the solution.

The so treated panel was removed from the solution, rinsed well with water, and dried at about 150° F. Examination of the so treated panel showed that an etched surface was obtained which was coated with a protective dark brown to black chromate coating having a uniform thickness of at least 0.1 mil. The improved corrosion resistance of the coating is set out in tabulated form following Example 2.

Additional runs were made in which panels of similar composition and dimensions were immersed in coating solutions having 0.75% $CaSO_4 \cdot 2H_2O$ but in which the percentage of CrO_3 was varied including 0.25%, 0.5%, 3.0% and 5.0%. The coating formed from the coating solution containing 0.5% CrO_3 compared favorably with that containing 1.0% CrO_3 but was thinner for the same period of immersion. A coating was formed from the 0.25% CrO_3 solution but it formed very slowly. After immersion of a panel for 20 minutes, only a thin coating of less than 0.1 mil was formed. A panel was immersed in the 3.0% CrO_3 solution for 15 seconds. After that

relatively short period, a thin coating formed but appeared to redissolve thereafter. The 5.0% CrO_3 solution was too concentrated and a satisfactory coating was not obtained on the panel.

EXAMPLE 2

Another panel of the same dimensions and of the same alloy as that used in Example 1 was degreased, rinsed and dried in the same manner as in Example 1, and then immersed for 3 minutes in an aqueous chromate coating solution containing the following effective constituents by weight of solution:

1.0% of CrO_3
0.75% of $CaSO_4 \cdot 2H_2O$
0.4% of $Na_2HAsO_4 \cdot 7H_2O$

The so treated panel was rinsed and dried as in Example 1. Examination of the panel showed that an etched surface was obtained which was coated with a tan to brown chromate film, having a uniform thickness of about 0.2 mil. The improvement in corrosion resistance is set out in the table below.

Examples were run in which times of immersion and the percentage of acid arsenate present were varied. The effect upon corrosion resistance, as determined by ASTM–B–119–49T, is set out as Examples 3 to 6 of the table.

Other examples were run in which time of immersion and the sulfate used were varied. The effect of such variations are shown in the table as Examples 7 to 14. The same magnesium alloy panels were used in Examples 1 to 14 and were subjected to the same preparatory treatment.

Example 15 consisted of subjecting an untreated magnesium alloy panel of the same composition as those used in Examples 1 to 14 to the salt spray test. The greater attack on the metal is shown in the table.

Table

[Examples 1 to 14 contained 1.0% by weight of CrO_3]

Example	Percent Sulfate by weight	pH	Time Immersed in Minutes	ASTM-B-119-49T Salt Spray Test—Percent Attack in 16 Hours
1	0.75 $CaSO_4$	1.21	2	40
2	0.75 $CaSO_4$ + .40 $Na_2HAsO_4 \cdot 7H_2O$	1.23	3	30
3	0.75 $CaSO_4$ + 0.10 $Na_2HAsO_4 \cdot 7H_2O$	1.23	3	30
4	0.75 $CaSO_4$ + 0.10 $Na_2HAsO_4 \cdot 7H_2O$	1.23	6	25
5	0.75 $CaSO_4$ + 0.20 $Na_2HAsO_4 \cdot 7H_2O$	1.20	3	25
6	0.75 $CaSO_4$ + 0.50 $Na_2HAsO_4 \cdot 7H_2O$	1.35	6	30
7	0.30 $CaSO_4$	1.25	2	20
8	0.25 Na_2SO_4	1.21	2	40
9	0.50 Na_2SO_4	1.27	2	40
10	0.50 K_2SO_4	1.18	3	50
11	0.25 $(NH_4)_2SO_4$	1.20	2	30
12	0.50 $(NH_4)_2SO_4$	1.26	2	30
13	0.50 $SrSO_4$	1.14	3	50
14	3.00% $MgSO_4 \cdot 7H_2O$	1.43	3	30
15	No treatment	----	----	85

It will be appreciated that the invention provides an inexpensive coating composition of low concentration for protecting articles of magnesium and magnesium-base articles, an economical and convenient method of protecting such articles, and articles of manufacture comprising the so coated magnesium article, an adhesive applied thereon and an outer covering of abrasion-resistant thermoplastic film bonded thereto.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. In a method of producing a coating on an article composed of at least 85 percent magnesium, the step which consists of subjecting the article, for a period of between 1 and 5 minutes, to the action of an aqueous solu-

tion at a pH between 0.9 and 1.8 containing as effective constituents based upon the weight of the solution between about 0.25 and 3.0 percent of chromium trioxide and a sulfate selected from the class consisting of ammonium, hydrogen and alkali metal and alkaline earth metal sulfates in an amount sufficient to provide the chemical equivalent SO_4 group corresponding to the sulfate fraction contained in 0.1 to 3.0 percent ammonium sulfate.

2. The method of claim 1 wherein the sulfate is ammonium sulfate.

3. The method of claim 1 wherein the sulfate is calcium sulfate.

4. The method of claim 1 wherein the sulfate is hydrogen sulfate.

5. The method of claim 1 wherein the sulfate is magnesium sulfate.

6. The method of claim 1 wherein the sulfate is sodium sulfate.

7. In a method of producing a coating on an article composed of at least 85 percent magnesium, the step which consists of subjecting the article to the action of an aqueous solution at a pH between 0.9 and 1.8 containing as effective constituents based upon the weight of the solution between about 0.25 and 3.0 percent of chromium trioxide, a sulfate selected from the class consisting of ammonium, hydrogen, and alkali metal and alkaline earth metal sulfates in an amount sufficient to provide the chemical equivalent corresponding to the sulfate fraction contained in 0.1 to 3.0 percent ammonium sulfate, and a corrosion inhibitor selected from the class consisting of the arsenates and acid arsenates of ammonium and alkali and alkaline earth acid arsenates and arsenates in an amount sufficient to provide the chemical equivalent corresponding to the arsenate fraction contained in 0.3 to 0.5 percent of $Na_2HAsO_4 \cdot 7H_2O$.

8. The method of claim 7 wherein the acid arsenate is sodium acid arsenate.

9. A composition for forming a protective surface coating on articles of magnesium and magnesium alloys consisting essentially of an aqueous solution containing as effective constituents based upon the weight of the solution between about 0.25 and 3.0 percent chromium trioxide and a sulfate selected from the class consisting of ammonium, hydrogen, and alkali metal and alkaline earth metal sulfates in an amount sufficient to provide the chemical equivalent SO_4 group corresponding to the sulfate fraction contained in 0.1 to 3.0 percent ammonium sulfate.

10. A composition for forming a protective surface coating on articles of magnesium and its alloys consisting essentially of an aqueous solution containing as effective constituents based upon the weight of the solution between about 0.25 and 3.0 percent chromium trioxide, a sulfate selected from the class consisting of ammonium, hydrogen, and alkali metal and alkaline earth metal sulfates in an amount sufficient to provide the chemical equivalent corresponding to the sulfate fraction contained in 0.1 to 3.0 percent ammonium sulfate, and a corrosion inhibitor selected from the class consisting of arsenates and acid arsenates of ammonium and alkali and alkaline earth acid arsenates and arsenates in an amount sufficient to provide the chemical equivalent corresponding to the arsenate fraction contained in 0.3 to 0.5 percent of $Na_2HAsO_4 \cdot 7H_2O$.

11. An article of manufacture consisting essentially of a base metal of at least 85 percent magnesium, having a protective surface coating on said base metal composed of the composition formed by treatment with the composition of claim 9, a rubber adhesive on said surface coating, and a thermoplastic outer film covering adhered thereto comprising a polymer from a polymerizable monomeric mix containing a monomer having an olefinic double bond therein, which outer film covering is integrally bonded by said adhesive binder to said surface coating.

12. The article of claim 11 wherein said polymer is polyvinyl chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,035,380	Wilhelm	Mar. 24, 1936
2,454,799	Hart et al.	Nov. 30, 1948
2,471,909	Spruance	May 31, 1949
2,502,476	Ott et al.	Apr. 4, 1950
2,662,034	Mason et al.	Dec. 8, 1953