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## BRIGHTENING AND CLEANING COMPOSITION AND TREATMENT FOR MAGNESIUM AND MAGNESIUM-BASE ALLOYS

Lawrence Whitby, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Filed Nov. 3, 1958, Ser. No. 771,680  
6 Claims. (Cl. 156-20)

The invention is related both to surface finishing of magnesium and magnesium-base alloy articles and to the removal of scored-in layers resulting from the lubricant used in hot-forming shapes of magnesium metal and its alloys. Magnesium alloys are considered herein to be magnesium-base alloys containing at least 85 weight per-

cent of magnesium. Magnesium and magnesium-base articles, e.g., shapes produced by extruding, drawing, stamping, rolling, die-casting, sand-casting, and permanent mold casting, and articles fabricated therefrom have a dull appearance due largely to tarnishing and scoring of the surface during the shaping operation, and/or attack of the metal surface by ambient gases. Such articles and shapes are customarily given a bright finish treatment to impart greater protection and attractiveness thereto. Such bright finishes are usually obtained by contacting the metal article with an acid solution, e.g., nitric acid or mixtures of aqueous chromic acid and sodium nitrate. The article may be immersed in the acid solution or the solution may be sprayed or brushed on the article. Known compositions and methods of providing a bright finish on magnesium and magnesium alloy articles have a number of drawbacks which include (1) excessive metal removal, (2) rapid depletion of the bath made from such compositions, (3) inefficacy of the composition on certain die-cast alloys, e.g., those designated AZ91 by the American Society for Testing Materials, and (4) staining and discoloration of articles which contain small cracks when treated with chromic acid-containing solutions as a result of which the colored liquid migrates into the cracks from which it later bleeds out over a prolonged period of time following the treatment.

Graphite is commonly employed as one of the ingredients in lubricants used in hot-forming operations. A serious problem has accompanied the employment of such lubricants for shaping magnesium and its alloys. The graphite lubricant is burned in or scored into the contacting surface thereof to produce layers which are extremely difficult to remove. Such layers or even residual traces thereof on the metal surface may interfere with the metal finishing, particularly electroplating, and stimulate wet corrosion on the magnesium or alloy by the electrolytic action between the graphite serving as the cathode and the magnesium serving as the anode.

Heretofore, the most widely used method of removing burnt and scored-in graphite lubricant surface imperfections has been a two-stage treatment consisting first of a 10 to 20 minute soaking period in a near-boiling caustic soda solution and then an immersion in an acid pickle bath consisting essentially of an aqueous mixture of chromic acid and sodium nitrate whereby at least 0.5 mil of metal from the surface was removed. The disadvantages of the known methods of removing this scored-in material include those set out hereinabove, particularly a prolonged treatment time, an undesirably high metal removal, a lack of effectiveness of the known solutions to loosen and dislodge the deeply scored-in graphite, and the cost of such known methods due to the necessity of frequent replacement of active ingredients in the exhausted solution.

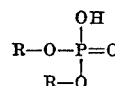
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The problems above-mentioned which are associated with the brightening of magnesium and magnesium alloy articles and to the necessity of removal of scored-in graphite lubricant and the accompanying imperfections on the surface of shaped magnesium and magnesium-base alloy parts have created a long-existing desideratum in the art for an improved composition and method of use thereof for removing such graphitic lubricant residues and for brightening magnesium shapes and fabricated articles generally.

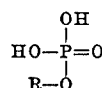
It is, therefore, the principal object of the invention to satisfy this desideratum by providing an improved composition and method of use thereof for the removal of graphitic lubricant from hot-formed magnesium and magnesium alloy shapes and to brighten such shapes and fabricated articles made of such shapes by employing a composition of an alkyl hydrogen ortho-phosphate and nitric acid.

The method of the invention consists essentially of contacting the magnesium or magnesium-base alloy article requiring brightening, or the removal of graphite lubricant therefrom, with the composition of the invention by immersing the article therein, or otherwise applying the solution to the magnesium article, for a period of time of between 0.5 and 15 minutes, removing the article from contact with the solution, and rinsing adhering solution therefrom with water. A high degree of brightening occurs but only a small amount of metal is lost because any appreciable loss is prevented by the formation of an inhibiting film on the surface thereof while being subjected to the action of the solution according to the invention.

The alkyl hydrogen ortho-phosphate employed according to the invention is either the mono-hydrogen or the di-hydrogen ester or mixtures thereof of an alkyl alcohol of five carbon atoms or less. The esters are those formed by reacting phosphoric acid and a lower alkyl alcohol. The monohydrogen ester may be expressed generically as:



the dihydrogen ester as:



where R is an alkyl group of 1 to 5 carbon atoms.

The ratio of the ortho-phosphate ester to nitric acid to use in preparing the composition of the invention is between 10 and 100 volumes of a 52 to 95 percent by weight aqueous solution of  $\text{HNO}_3$  to 100 volumes of the ester. Lower concentrations add more water than is desirable which both increases the dissolution activity of the mixtures for magnesium alloys and decreases the luster obtainable when more concentrated nitric acid is used.

A preferable concentration of nitric acid for admixture with the alkyl hydrogen ortho-phosphate ester is between a 60 and 90 percent by weight aqueous solution of  $\text{HNO}_3$  and the recommended concentration of nitric acid to use is between a 65 and 75 percent by weight aqueous solution.

A proportion of less than 10 volumes of aqueous nitric acid to 100 volumes of the ester will brighten oxide-free magnesium and magnesium alloys but will dissolve oxides only very sluggishly and thence prolong the treatment unduly if metal having an oxidic tarnish is to be treated without prior cleaning. There is also a larger loss due to drag-out, i.e., adhering treating solution when the article being treated is removed from the solution, if the

proportion of nitric acid in the aqueous acid-ester mixture is too low, e.g., under 10 percent by volume, due to the increased viscosity.

The temperature of the bath when applied should be not over 30° C. and preferably should be between 15° C. and 22° C. At a temperature higher than 30° C., the rate of dissolution of the metal tends to rise to undesirable amounts and much of the luster of the finish obtained at the lower temperatures is lost.

A recommended ratio by volume of phosphoric acid ester to nitric acid for use with magnesium-base alloys may be broadly stated to be 100 of the phosphoric acid ester to about 20 of the nitric acid, but for alloys containing 6 percent or more of aluminum which includes a large number of cast alloys, a preferred volume ratio of the ester to the acid is 100 of the ester to between 50 and 80 of the acid. By increasing the proportion of nitric acid, the rate of dissolution of such alloys in the mixture is decreased and the resulting luster is concurrently increased. The increased proportion of nitric acid also lessens the cost of the treating composition. The length of time usually used for immersing an article composed substantially of magnesium or of a low aluminum magnesium-base alloy, i.e., one containing less than about 6 percent Al, into the composition of the invention, or otherwise applying the composition to the magnesium article as by spraying, is between 0.5 and 2 minutes dependent upon the amount of scale to be removed. Usually between 0.5 and 1 minute is ample time for providing a bright finish upon such a low aluminum, magnesium-base alloy article. However, a period up to 15 minutes is sometimes employed to brighten high aluminum magnesium-base alloys and to remove the graphite lubricant which is scored into the sides of drawn or extruded articles of such alloy.

Magnesium or magnesium-base articles thickly coated with graphitic lubricant often appear little affected by the composition of the invention for up to an initial period of as long as two minutes or occasionally a little longer but after such initial period, the graphitic layer abruptly loosens and falls away.

The practice of the invention will be better understood by an examination of the following examples which are illustrative of the invention.

#### Example 1

A bath of the composition of the invention was made up by placing 100 volumes of technical grade ethyl hydrogen ortho-phosphate, consisting of approximately equal parts by volume of the mono- and di-hydrogen phosphoric acid esters, in a stainless steel container. The container was provided with an exhaust system to remove any offensive gases, an agitator for maintaining substantially uniform temperature and composition, and a cooling system for temperature control. 55 volumes of concentrated nitric acid, having a specific gravity of 1.40 and consisting of a 67 percent by weight aqueous solution of HNO<sub>3</sub>, were added with stirring into the phosphoric acid ester. The mixture was yellowish-brown in color and evolved small quantities of nitrogen dioxide, but, upon aging for several days, the mixture became almost colorless and could be heated to at least 80° C. without noticeable reaction. A die casting of a magnesium alloy consisting essentially of 9 percent Al, 1 percent Zn, about 0.2 percent Mn, and the balance Mg, having a tarnished exterior, was immersed in the bath of the invention at 24° C., and agitated therein for 30 seconds. It was thereafter removed, drained from 15 to 30 seconds and thoroughly rinsed with water. After drying, the magnesium casting showed a highly bright finish. The weight loss showed that such finish was obtained with less than 0.1 mil of metal removal on each surface.

#### Example 2

A bath of the invention was prepared by admixing 100 volumes of technical ethyl hydrogen ortho-phosphate and 25 volumes of the 67 percent by weight aqueous solution of HNO<sub>3</sub> (specific gravity of 1.40) in a stainless steel container similarly as in Example 1. The bath then stood for 24 hours after which a graphite-coated deep-drawn, hot-formed magnesium alloy shape, consisting essentially of 3 percent Al, 1 percent Zn, about 0.2 percent Mn, and the balance Mg was immersed in the bath at 22° C. and retained therein for 1.5 minutes. At the end of that time, the graphite contaminant adhering to the surface peeled away suddenly leaving only the most deeply scored imperfections. After an immersion of an additional 3 minutes, the surface of the metal was completely free of any graphite blemishes; the shape was then removed from the bath, drained for 15 seconds, and rinsed in running water at room temperature. The graphite contaminant removed by the above means resulted in a bright clean metal surface of a high luster. The total metal removed from the magnesium piece was only 0.1 mil per side or a total reduction in size of the article between parallel faces of 0.2 mil.

#### Example 3

A bright finish bath in accordance with the invention was prepared as in the above examples except that 80 volumes of the 67 percent by weight aqueous solution of HNO<sub>3</sub> were admixed with 100 volumes of technical grade ethyl hydrogen ortho-phosphate. A metal casting consisting of substantially 9 percent Al, 1 percent Zn, about 0.2 percent Mn, and the balance Mg was immersed in the bath thus prepared and allowed to remain therein for 2 minutes at a temperature of 21° C. and thereafter removed and rinsed in running water at tap water temperature. A high luster was thus obtained with a metal removal of less than 0.1 mil per side.

#### Example 4

For chemically brightening magnesium alloys containing little or no aluminum, such as M alloys, ZK60 and HK31 alloys, a bath consisting of 100 volumes of isopropyl dihydrogen ortho-phosphate and 15 volumes of the 67 percent by weight aqueous solution of HNO<sub>3</sub> was prepared. The magnesium alloy articles, having dull tarnished surfaces, set out in the table below were immersed for the periods of time shown in the table. A highly lustrous finish was produced on the article without undue loss of the metal.

| Alloy      | Composition in percent     | Time of immersion in minutes | Loss of metal in mils/side | Appearance     |
|------------|----------------------------|------------------------------|----------------------------|----------------|
| 55 M alloy | 1.2 Mn, balance Mg         | 1                            | <0.1                       | Bright luster. |
| HK31       | 3.0 Th, 6 Zr, balance Mg   | 1                            | <0.1                       | Do.            |
| ZK60       | 6.0 Zn, 0.5 Zr, balance Mg | 1                            | <0.1                       | Do.            |

The phosphoric acid esters most commonly employed in preparing composition of the invention are the di- and mono-hydrogen ortho-phosphates of methyl, ethyl, and isopropyl. Phosphoric acid esters of other alcohols, e.g., propyl, butyl, and amyl, may be used, but articles treated in such compositions are more difficult to rinse.

A number of outstanding advantages stem from the practice of the invention. A high luster is obtained on cast, drawn, extruded or otherwise shaped articles of magnesium and magnesium-base alloys which is superior to that obtained heretofore by any known bright pickle or finish composition or method of providing a finish on such articles. The invention is particularly adapted for the efficient removal of scored surface layers due to graphite from the lubricant employed in the shaping thereof. The degree of etch and amount of metal lost are

extremely low. Usually the scored surface layer drops away from the magnesium article in the form of a thin peel within a short time after the immersion of the scored piece in the composition in accordance with the practice of the invention. The advantages of the invention have far-reaching economic significance. The long and tedious method of brightening the surface of magnesium articles resulting in substantial metal loss according to known practice may now be replaced by the fast acting and more efficient method of the invention, which employs relatively low-cost and readily available ingredients, to produce a brighter finish with a relatively low metal loss. In addition, the composition of the invention is an excellent solvent and/or degrading agent for oils and greases and the invention may, therefore, be used on metal surfaces having oily or greasy coatings thereover without prior degreasing treatment.

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. The composition for cleaning and brightening the surfaces of articles of magnesium and magnesium-base alloys which consists by volume of 100 parts of an alkyl hydrogen ortho-phosphate having up to 5 carbon atoms in the alkyl group and between 10 and 100 parts of an aqueous solution of nitric acid containing between 52 and 95 percent by weight of  $\text{HNO}_3$ .

2. The composition for cleaning and brightening the surfaces of articles of magnesium and magnesium-base alloys which consists by volume of 100 parts of a mixture of alkyl mono-hydrogen ortho-phosphates and alkyl dihydrogen orthophosphates having up to 5 carbon atoms in the alkyl group and between 20 and 80 parts of an aqueous solution of nitric acid containing between 60 and 90 percent by weight of  $\text{HNO}_3$ .

3. A composition for cleaning and brightening the surfaces of articles of a magnesium-base alloy which consists by volume of 100 parts of an alkyl hydrogen ortho-phosphate ester selected from the class consisting of the mono-hydrogen and the dihydrogen esters of methyl, ethyl, isopropyl, and butyl phosphoric acid esters and mixtures thereof, and between 50 and 80 parts of an aqueous solution of nitric acid containing between 65 and 75 percent by weight of  $\text{HNO}_3$ .

4. The method of cleaning and brightening the surfaces of a metal article composed of at least 85 percent magnesium consisting of admixing by volume 100 parts of an alkyl hydrogen ortho-phosphate with between 10

and 100 parts of an aqueous solution of nitric acid containing between 52 and 95 percent by weight of  $\text{HNO}_3$  and contacting the surfaces of said article with the solution so made, at a temperature of between  $15^\circ$  and  $30^\circ$  C. for between 0.5 and 15 minutes.

5. The method of cleaning and brightening the surfaces of a metal article containing at least 85 percent magnesium consisting of admixing 100 parts by volume of a mixture of alkyl mono-hydrogen ortho-phosphates and alkyl dihydrogen ortho-phosphates having up to 5 carbon atoms in the alkyl group and between 20 and 80 parts of an aqueous solution of nitric acid containing between 60 and 90 percent by weight of  $\text{HNO}_3$ , contacting the surfaces of said article with the solution so made, at a temperature of between  $15^\circ$  and  $22^\circ$  C. for between 0.5 and 15 minutes, removing the article from contact therewith, and rinsing with water.

6. The method of removing graphite lubricant adhering to the surfaces of a magnesium-base alloy article containing at least 85 percent Mg and at least 6 percent Al, consisting of admixing by volume 100 parts of a mixture of esters consisting of ethyl mono-hydrogen and ethyl dihydrogen ortho-phosphates and between 50 and 80 parts of an aqueous solution of nitric acid containing between 65 and 75 percent by weight of  $\text{HNO}_3$ , immersing said article in the solution so made, at a temperature of between  $15^\circ$  and  $22^\circ$  C. for between 0.5 and 15 minutes, removing the article therefrom, and rinsing with water.

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