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COATING MAGNESIUM AND MAGNESIUM ALLOYS

Herman W. Hemker, Euclid, and Donald L. Epink, Cleveland, Ohio, assignors to The Parker Appliance Company, Cleveland, Ohio, a corporation of Ohio

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It is known that magnesium metal, because of its low specific gravity, is highly advantageous for employment where weights should be kept at a minimum. The strength and serviceability of articles have been improved by employing the magnesium in the form of alloys.

Furthermore, many proposals have been made for so treating articles formed of magnesium or magnesium alloys that they are resistant to corrosion, which is known to be highly and quickly damaging by reason of the high reactivity of magnesium metal to oxygen, particularly in the presence of saline solutions. Upon accelerated corrosion tests, however, it has been found that the best of the prior proposals give a maximum life not exceeding 100 to 150 hours and most of the proposed treatments lead to failure in much shorter times.

In accordance with the present invention, an article formed of magnesium or magnesium alloy is given a superficial treatment which produces a condition of high resistance to corrosion, whereby the article remains stable over periods, under accelerated corrosion tests, amounting to many hundred hours.

Fundamentally, the non-corrodability is produced by treating the article superficially with an aqueous solution at high temperature, this solution being highly alkaline and containing dissolved therein a strong oxidizing agent. In addition, it is preferred to introduce additional soluble substances into the treating solution which operate jointly with the other ingredients of the solution to produce a high resistance to corrosion, such additional substances including soluble borates, ferrocyanides, acetates, antimonates, and aluminates.

In preparing the solution, and for the purpose of having a low vapor tension at the operating temperature, it is desirable to have essential saturation of the solvent water by the solutes; and in particular it is preferred to select mixtures of oxidizing agents in order to avoid limitation of effective concentration by the mass action effect and limiting solubility of a single oxidizing agent. It will be understood that the additional solutes introduced have, in addition to chemical and physical protective effects upon the article, also an effect of increasing the boiling point of the aqueous solution and therewith permitting operation in liquid phase at a high temperature.

It has been found that advantageous treating solutions can be prepared at solution densities which represent from 20 to 25 per cent of water, with the remainder in the form of dissolved ma-

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terial. Further, the solution contains such a high concentration of alkali that the pH value is in excess of 13, and preferably is so close to pH 14 that the actual analytic reading is indeterminate. At such high concentrations of soluble alkali, total dissociation of the dissolved material cannot occur and hence there is always present an excess of undissociated alkali.

It has been found that the procedure is effective upon magnesium metal and upon commercially available alloys thereof. Among such alloys are the following, which are identified by arbitrary designations in lieu of trade mark names:

Alloy A: 1.5% manganese, 0.3% silicon, balance essentially magnesium.

Alloy B: 0.15% manganese, 0.4% to 1% zinc, 0.3% silicon, 5.8 to 7.2% aluminum, balance essentially magnesium.

Alloy C: 0.3% manganese, 1.0% zinc, 2.7% aluminum, balance essentially magnesium.

Alloy D: 0.2% manganese, 0.6% zinc, 9.0% aluminum, balance essentially magnesium.

As specific examples of practice under this invention, the following may be given:

Example I

A bath is prepared which comprises a water solution containing 1200 grams of sodium hydroxide, 720 grams of sodium bichromate, 600 grams of sodium nitrate, 240 grams of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), 300 grams of sodium acetate, together with a quantity of water which gives a boiling temperature in excess of 120°C ., as for example 1200 milliliters.

This solution has a water content of about 28% by weight. It is brought to the maximum temperature short of ebullition, and the articles formed of alloy B are suspended in the bath and held immersed for 45 minutes. Upon removal, the articles are rinsed in water at 20°C . and are then found to have gained a condition of resistance to accelerated salt spray treatment which prevents objectionable corrosion for as long as 800 hours.

Example II

A similar treatment, at maximum temperature short of ebullition, was given in a treating solution made from 125 grams of water, 125 grams of sodium hydroxide, 48 grams of sodium bichromate and 40 grams of sodium nitrate. The articles of alloy A demonstrated resistance to the accelerated salt spray test for 350 hours; articles of alloy B for 300 hours; and articles of alloy C for 150 hours.

Example III

When 20 grams of borax, or quantities of boric acid or sodium metaborate containing boron equivalent to that of the said quantity of borax, was added to the bath of Example II, articles of alloy A resisted the accelerated test for 350 hours and articles of alloy B for 500 hours.

Example IV

When 10 grams of potassium ferrocyanide were added to the bath of Example II, articles of alloy A treated therein showed resistance for 260 hours, of alloy B for 310 hours, and of alloy C for 170 hours.

Example V

When 20 grams of borax and 10 grams of antimony trioxide were added to the bath of Example II, articles of alloy A showed resistance for 400 hours and of alloy B for 500 hours.

Example VI

When 10 grams of potassium ferrocyanide and 20 grams of sodium acetate were added to the bath of Example II, articles of alloy A showed resistance for 250 hours, of alloy B for 550 hours, and of alloy C for 150 hours.

Example VII

When 9 grams of borax, 5 grams of trisodium phosphate, 2 grams of potassium ferrocyanide and 5 grams of sodium aluminate were added to the bath of Example II, articles of alloy A showed resistance for 225 hours, of alloy B for 300 hours and of alloy C for 250 hours.

Example VIII

When 10 grams of borax and 20 grams of sodium acetate were added to the bath of Example II, articles of alloy A showed a resistance for 200 hours, of alloy B for 500 hours, and of alloy C for 200 hours. The water content is about 34 per cent.

Example IX

When 9 grams of borax and 5 grams of trisodium phosphate were added to the bath of Example II, articles of alloy B showed resistance for 200 hours.

Example X

Employing the bath of Example II, but with 30 grams of sodium bichromate, and also adding 10 grams of borax, 5 grams of antimony trioxide and 25 grams of sodium acetate, and treating as before, articles of alloy A endured 300 hours before failure of the coating, and articles of alloy B endured 350 hours.

Example XI

When the quantity of sodium bichromate of the bath of Example II was reduced to 28 grams, with other ingredients retained the same, and with the addition of 4 grams of borax, 4 grams of antimony trioxide, 4 grams of sodium acetate, and 7 grams of sodium aluminate, articles of alloy A endured for 500 hours, and articles of alloy B for 200 hours.

The foregoing statements of times of resistance are based upon the salt spray test, but are not necessarily the maximum for the particular alloys.

The accelerated salt spray test, referred to above, is the standard test which comprises spraying the coated piece with a 20% salt solution at a temperature of 90 degrees F., as set forth in Governmental Specification AN-QQ-S-91.

The illustrative baths have the common features of composition and behavior in that they are used at high temperature, exhibit a high alkalinity, and contain a soluble oxidizing agent. In addition, many of the baths also comprise an addition agent or agents selected from the water soluble borates, ferrocyanides, acetates, aluminates, alkaline phosphates and antimonates.

The temperature should be above 100 degrees C. and can be 170 degrees C., which is permitted without ebullition or excess loss of vapor, by reason of the high content of freely soluble solutes in the bath. In particular, it has been found advantageous to operate in the liquid phase at a temperature close to the boiling point of the selected mixture, usually between 135 and 145 degrees C.

The alkali employed in the bath is preferably the hydroxide of an alkali metal element such as sodium, potassium, lithium, etc., in order that a sufficiently high quantity of freely soluble alkali may be contained in the solution. It is preferred to avoid organic alkalies as they have a tendency to break down and be driven off at the higher temperatures of treatment.

The oxidizing agent employed for the bath includes freely soluble nitrates, as salts of alkali metals, for the reason that such salts are highly soluble and do not become ineffective through forming precipitates from reaction with other ingredients of the bath or from reaction with the metals of the magnesium alloy itself. In addition, the oxidizing agent of the bath should include a highly soluble chromate, such as an alkali metal chromate, inclusive of the sodium, potassium and lithium salts. The chromate may be introduced in the form of dichromate as this is converted to chromate in the bath itself.

Among the addition agents which have been found valuable for modifying the feasible operating temperature, and for co-action with the alkaline bath containing the nitrate or other highly oxidizing salt and a chromate, it is preferred to employ a soluble borate by introducing borax, boric acid, or sodium metaborate into the solution. Other feasible additions include other soluble borates, potassium and other soluble ferrocyanides, antimony trioxide (which is amphoteric and forms antimonate in the alkaline bath), sodium and other soluble acetates, sodium and other soluble aluminates, trisodium and other soluble phosphates, together with mixtures of more than one of such ingredients, as pointed out in the examples above.

It has often been found advantageous to employ more than one such agent, in order to get an effect greater than that by use of a corresponding total quantity of only one such agent.

By the term "freely soluble" is meant a condition of solubility by which the total content of solutes exceeds the content of water in the bath. Thus, a maximum proportion of water is about 55% by weight, and it is preferred to operate with the water content between 25 and 30 percent by weight, wherewith the bath is saturated at the operating temperature with dissolved compounds which preferably are the freely soluble alkali metal salts, alkaline salts and alkalies. Under these conditions, the coating procedure upon magnesium and the commercial magnesium alloys containing 88% or more of magnesium, for example, may be effected in 45 minutes at a temperature of 135 to 145 degrees C. for an optimum effect, but good results are obtainable by treating for any length of time between 15 and 60

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minutes between 120 and 170 degrees C. when alkali metal hydroxide is employed as alkali. It will be understood that the treatment may likewise be employed with other alloys containing magnesium as an ingredient and having the defect of corrosiveness due to the magnesium content.

Thus, a preferred range of proportions for ingredients of the bath is as follows:

	Preferred	Range
	Grams	Grams
1. Water.....	125	
2. Freely soluble inorganic alkali (alkali metal alkali).....	125	62.5 to 187.5
3. Oxidizing agents:		
(a) Alkali metal nitrate.....	40	20 to 60
(b) Alkali metal chromate or dichromate.....	48	24 to 72
4. Addition agents.....	30	0 to 75

In metallographic investigation of the treated articles, it is found that there is no intergranular corrosion in the samples; but, with articles demonstrating relatively low salt spray resistance, some pitting appears which may be due to thin spots or pin holes in the protective coating.

It is preferred to employ the material at high concentration, under the conditions stated, with the solids present in quantity to effect saturation at the reaction temperature. An excess of the solute mixture is usually present at reaction temperature; and upon cooling to room temperature the bath forms a heterogeneous mass of crystals. The bath can be employed in an open pot, as the boiling point is so high that no ebullition or bubbling occurs; and air contact with the solution has no essential influence upon its life.

A presently used proportion is that of employing three-fourths of a gallon of the bath in Example I in treating up to 10 square feet of several alloys, but even after articles aggregating this superficial area have been passed through the bath there still appears no sign of depletion or exhaustion of the bath from capability of producing the desired result. Upon prolonged use, precipitation of a non-water-soluble substance occurs but this does not impair the efficiency of operation and can be removed if desired.

The precise chemical composition of the coating film is unknown. It is not electrically conductive and has a color range from gray to black, being a light to medium gray in most instances. The coating is so thin that it does not essentially change the dimensions of the article.

It is obvious that the invention can be employed in many ways other than those of the specific examples and within the scope of the appended claims.

We claim:

1. The method of providing a corrosion-resistant coating upon surfaces of magnesium and high-magnesium-content alloys, which comprises

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contacting the surface at a temperature of 120 to 170 degrees C. for substantially 15 to 60 minutes with an aqueous solution prepared by dissolving in water, as the predominant constituents, 62.5 to 187.5 parts of alkali metal hydroxide, substantially 24 to 72 parts of alkali metal bichromate, and substantially 20 to 60 parts of alkali metal nitrate, the proportion of water in the solution being between 20 and 55 per cent, and the solution having a pH value in excess of 13.

2. The method as in claim 1, in which the aqueous solution in addition contains substantially 30 to 75 parts of freely soluble alkali metal salts of weak acids.

3. The method as in claim 1, in which the aqueous solution in addition contains substantially 30 to 75 parts of a mixture of borax and alkali metal acetate, at least one-third of the said mixture being borax and the amount of acetate being at least as great as the amount of borax.

4. The method of providing a corrosion-resistant coating upon surfaces of magnesium and high-magnesium-content alloys, which comprises contacting the surface at substantially maximum temperature short of ebullition for about 45 minutes with an aqueous solution prepared by dissolving in water, 125 parts of alkali metal hydroxide, substantially 48 parts of alkali metal bichromate, and substantially 40 parts of alkali metal nitrate, and substantially 30 parts of a mixture of borax and alkali metal acetate, substantially one-third of the mixture being borax, the proportion of water in the solution being between substantially 25 to 34 per cent, and the solution having a pH value in excess of 13.

HERMAN W. HEMKER.
DONALD L. EPPINK.

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