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METHOD OF AND BATH FOR COATING
MAGNESIUM

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5 Claims. (Cl. 204—56)

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amended April 30, 1928; 370 O. G. 757)

This invention relates to a method of and baths for applying corrosion resisting coatings on magnesium or magnesium alloys in which magnesium predominates, and has among its numerous objects to provide aqueous alkaline solutions in which magnesium or the alloys thereof may be electrolytically treated to form on such articles a coating that will protect the articles against corrosion.

I am aware that heretofore there have been numerous attempts to devise baths in which magnesium or the alloys thereof may be electrolytically treated to form thereon films that will protect the metal, but so far as I am aware, after a careful study of the literature, no one else has succeeded in producing such films by a process that is commercially practicable. Numerous careful tests show that the baths forming the basis of this application are satisfactory for the purposes set forth.

The invention disclosed and claimed herein is a continuation-in-part of my co-pending application, Serial No. 93,123, filed July 28, 1936.

Generally speaking, the bath must be alkaline and contain an oxidizing ion and/or an ion that will react with the magnesium under conditions of electrolysis to form a film that is a compound of magnesium with the reacting ion. There is evidence that the coating formed by the present method results from both electrolytic oxidation and also deposition. The article to be coated functions as an electrode in the baths hereinafter set forth and either alternating or direct current may be employed, but when the direct current is used the article to be coated should be the anode.

The aqueous solution of the bath may contain either the oxidizing ion or the reacting ion or both. The substances used in making up the bath may be present in quantities from $\frac{1}{2}$ of one percent up to the limit of solubility of each substance in the bath. Good results are obtained at either high or low current densities, that is, from $\frac{1}{2}$ ampere per square foot to 100 amperes per square foot of surface to be coated, and at either high or low temperatures, however, it is preferable to work at a temperature from room temperature to 90° C. The time of treatment depends upon the temperature, the strength of the solution, the current density, and the thickness of coating desired.

The bath must be alkaline, thus, I prefer to use a hydroxide and/or a carbonate or an alkaline compound produced by a reaction of either one of these substances with other salts or oxides such as, tri-sodium phosphate, sodium arsenate, etc., which salts give an alkaline pH. However, as

stated these salts are examples of compounds produced by reaction of salts or oxide with hydroxide, to produce a pH over 7 and the salts used may be sodium, potassium or ammonium. In addition to the alkaline solution, the bath must contain an ion capable of forming a compound with magnesium under conditions of electrolysis, thus, as an oxidizing ion and/or reacting ion one or more water soluble substances selected from the group comprising chromates, dichromates, permanganates, borates, silicates, sulphates, fluorides, phosphates and molybdates must be added to the solution.

The method of practicing my invention is as follows:

The article to be coated is thoroughly cleaned, a clean surface being essential to the formation of good films. Electrolytic cleaning is satisfactory although other known methods of accomplishing this result may be used instead. After cleaning and washing, the article is made the electrode in a bath having the constituents above mentioned in concentrations from $\frac{1}{2}$ of one percent up to the limit of solubility of the respective salts in the bath. The pH of the solution is adjusted on the alkaline side by either sodium, potassium or ammonium hydroxide and/or sodium, potassium or ammonium carbonate. The temperature of the bath is maintained at a range varying from room temperature to 90° C. and the applied current ranges from $\frac{1}{2}$ ampere to 100 amperes per square foot. The time of treatment, as previously stated, depends upon the strength of the solution, the current density, temperature, and type of film desired. As a specific example, when the current density is from 5 to 10 amperes per square foot and the temperature of the bath is 50° C. a satisfactory film is formed in from 20 to 45 minutes.

The following are some percentages of substances used in the bath with very good results:

- (a) 10 percent chromate
2 percent ammonium (or sodium or potassium) sulphate adjusted to pH 7.1 or higher by hydroxide or carbonate
- (b) Same as (a) plus 1 to 5 percent borate and adjusted preferably to a pH 9
- (c) 10 percent chromate
 $\frac{1}{2}$ percent to saturation point of magnesium sulphate adjusted to pH 7.0 or higher by hydroxide or carbonate
- (d) 10 percent chromate
10 percent magnesium sulphate
1 percent sodium (or ammonium or potassium) fluoride adjusted to an alkaline pH by hydroxide or carbonate

- (e) 10 percent chromate
2 percent ammonium sulphate
2 percent sodium (or potassium or ammonium) molybdate adjusted to an alkaline pH by hydroxide or carbonate
- (f) Same as (e) plus 1 to 5 percent borate
- (g) 10 percent chromate
1/2 percent to 2 percent magnesium sulphate
1 percent to 5 percent ammonium sulphate
1/2 percent to 2 percent fluoride adjusted to alkaline pH by hydroxide or carbonate
- (h) 1 percent to 20 percent chromate
1 percent to 10 percent borate adjusted to alkaline pH by hydroxide or carbonate
- (i) 10 percent chromate
1/2 percent to 5 percent chrome sulphate
1 percent to 5 percent ammonium sulphate
- (j) 10 percent chromate
2 percent ammonium sulphate
1 percent to 5 percent aluminum sulphate
- (k) 10 percent chromate adjusted to a pH 9.0 with ammonium hydroxide
- (l) 10 percent chromate adjusted to pH 12 to 13 by sodium hydroxide
- (m) 1 percent to 20 percent chromate
1 percent to 10 percent phosphate adjusted within a range of pH 7.0 to pH 12.0
- (n) Varying amounts of water soluble chromates from 1/2 percent to limit of solubility of chromate in the solution which is adjusted to an alkaline pH by a water soluble hydroxide
- (o) 1 percent to 10 percent phosphate adjusted within a pH range of pH 7.0 to pH 12.0
- (p) 1/2 of one percent to limit of solubility water soluble sulphate adjusted to an alkaline pH by one or more water soluble substances selected from group of hydroxides, carbonates and compounds produced by these substances
- (q) 1 percent to 10 percent borate adjusted to an alkaline pH by hydroxide
- (r) 0.25 percent to 5 percent fluoride adjusted to alkaline pH by hydroxide
- (s) 10 percent chromate
2 percent to 5 percent tri-sodium phosphate

In the specification and appended claims, where the salts are not specifically designated, I desire it to be understood that any water soluble salt that is not detrimental to the metal being treated may be used, that is, the sodium, potassium, and ammonium salts as well as the water soluble aluminum and magnesium salts.

As further examples of substances used with success, the following are cited:

- (1) Sodium hydroxide and potassium permanganate; (2) sodium carbonate and potassium permanganate; (3) sodium bichromate and sodium silico-fluoride adjusted to pH 10 with sodium hydroxide; (4) a mixture of sodium carbonate, sodium fluoride, sodium silicate and sodium chromate; (5) strongly alkaline solutions

of sodium chromate either by itself or in combination with silicates and/or sulphates; (6) an alkaline solution of chromate and permanganate.

- 5 The alkaline solution of a chromate referred to in the specification and claims may be formed from a water soluble chromate or dichromate, a mixture of these salts or chromic acid or a mixture of chromic acid with a water soluble chromate or dichromate, rendered alkaline, if necessary, by addition of an alkali. In some instances, the solution contains a concentration of the metal and/or alloy of the metal being treated. These ions tend to produce a more favorable condition for coating by electrolysis. It is essential that the bath composition be regulated so as to hold these ions in solution.

The above mentioned substances used in the magnesium treating baths are mentioned by way of illustration and not of limitation, since the invention comprehends baths of the character broadly indicated above and is not to be limited except by the appended claims.

The invention disclosed herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

What I claim is:

- 30 1. A method of forming protective coatings on magnesium and alloys thereof in which magnesium predominates, which comprises passing an electric current through the metal while it is functioning as electrode in an aqueous alkaline solution of a water soluble chromate, such solution containing at least 0.5 per cent of a water soluble salt selected from the group consisting of the sulphates, borates, phosphates and silicofluorides, at a current density of from 0.5 to 100 amperes per square foot.
- 35 2. A method according to claim 1, in which the electrolytic bath consists of an alkaline solution of a water soluble chromate containing at least 0.5 per cent of a water soluble sulphate.
- 45 3. A method according to claim 1, in which the electrolytic bath consists of an alkaline solution of a water soluble chromate containing at least 0.5 per cent of a water soluble silicofluoride.
- 50 4. A method according to claim 1, in which the electrolytic bath consists of an alkaline solution of a water soluble chromate containing at least 0.5 per cent of a water soluble phosphate.
- 55 5. A method of forming protective coatings on magnesium and alloys thereof in which magnesium predominates, which comprises passing an electric current through the metal at a current density of from 0.5 to 100 amperes per square foot, while the metal is functioning as electrode in an aqueous alkaline solution of a water soluble chromate in which the sole effective coating agent is the chromate.
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