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TREATMENT OF MAGNESIUM AND MAGNESIUM BASE ALLOYS TO INCREASE THEIR RESISTANCE TO CORROSION

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The invention relates to the treatment of metal articles to increase their resistance to corrosion. It has special application to the treatment of magnesium and its alloys to form a corrosion resistant coating for such metals, but is useful also in the treatment of other metals and alloys.

It is an object of my invention to provide an improved method of treating metals and metal articles to increase their resistance to corrosion.

In my copending application Serial No. 608,841, filed August 3, 1945, now U. S. Patent No. 2,465,443, I have disclosed that improved resistance to corrosion of metals, for example, magnesium, aluminum and iron, and alloys in which these metals form the principal ingredient, can be obtained by treating in a boiling solution comprising about 1 to 6% of potassium permanganate and about 0.1 to 1% of a salt of a metal which is lower in the electromotive series than the metal to be protected; and further that the protective value of the coating thereby produced can be further enhanced or the stability of the coating increased by a subsequent treatment which consists in dipping the articles in fuming oil. In my copending application aforesaid I have disclosed further that an especially effective coating can be produced by treating successively in two boiling solutions, each of which comprises about 1 to 6% of potassium permanganate, the first solution containing also a sulphate, such as a sulphate of aluminum, manganese or zinc, and the second containing in addition to the permanganate a salt of a metal which is lower in the electromotive series than the metal which is being treated.

I have discovered that a substantial additional improvement in corrosion resistance of metals, for example, magnesium, aluminum and iron, and alloys in which these metals form the principal ingredient, can be obtained by treating them, before immersion in the boiling potassium permanganate solution, in a solution comprising about 0.1 to 1% of a salt of a metal which is lower in the electromotive series than the metal to be protected. This preliminary treatment may be performed at room temperature, but I prefer that it be performed at the boiling temperature.

Thus my present improved treatment in its preferred form comprises two principal steps; first, a treatment in a solution comprising 0.1 to 1% of a salt of the class described (without the use of potassium permanganate), and second, a treatment in a solution at approximately boiling temperature comprising about 1 to 6% of potassium permanganate. In the second step there may be added to the permanganate solution about 0.1 to 1% of the same salt that was used in the first solution, or at least one salt of a metal which is lower in the electromotive series than the metal which is being treated.

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I have discovered in addition that the preliminary treatment which I have described makes it possible to employ in the second step highly oxidizing salts other than the potassium permanganate such as, for example, sodium or potassium dichromate. However, I have found that superior results are obtained with potassium permanganate so this is representative of my preferred treatment.

I have discovered further that particularly effective results can be obtained when a salt of the group comprising zirconium, thorium, titanium and cerium, is used for the preliminary treatment or is added to the potassium permanganate in the second step of the process. In the case of treatments of magnesium and aluminum, excellent results are obtained also with the use of manganese sulphate for the preliminary treatment with the addition of aluminum sulphate to the potassium permanganate or the sodium or potassium dichromate in the boiling treatment.

The percentages of the components of the boiling solutions are of importance in achieving optimum results.

My improved treatment preferably is preceded by cleaning the surface of the metal article to be protected. This may be accomplished mechanically, chemically, or electrochemically according to well known methods which form no part of the present invention. However, by way of example, removal of the oxides on the surface of magnesium and its alloys can be carried out by immersion in a 5 per cent chromic acid solution.

In some cases it is beneficial to follow the cleaning step just described with an electrolytic degreasing step in which the work is made cathode in a suitable solution. Such treatments are well known in the art, and these known treatments may be practiced as desired, or may be omitted.

In the principal treating steps of my method I immerse the metal or metal articles to be treated in a solution, preferably at boiling temperature, which, as I have stated, comprises about 0.1 to 1% of a salt or salts of a metal which is lower in the electromotive series than the metal being treated. Thereafter I immerse the articles in a solution, at approximately boiling temperature, comprising, for example, potassium permanganate within the limits stated and a salt or salts of a metal lower in the electromotive series than the metal being treated, also within the limits stated. It may be preferable to use in the first solution a salt of a metal which is just slightly lower in the electromotive series than the metal to be protected and to use in the second solution a salt of a metal which is lower in the electromotive series than the metal of the salt used in the first solution. For example, assuming that the metal to be protected is magnesium, the first

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solution may contain aluminum sulphate and the second, a water-soluble zinc salt. However a salt such as $\text{Zr}(\text{SO}_4)_2 \cdot \text{ZrOSO}_3 \cdot 2\text{H}_2\text{O}$ is effective for use in both the first and second solutions. It is essential in all cases that the metal be treated in at least one solution comprising a salt of a metal lower in the electromotive series (the preliminary solution) and that it be subsequently treated in a boiling potassium permanganate solution (or solution of other highly oxidizing alkali metal salt) alone or in combination with a salt or salts of a metal lower in the series.

As also disclosed in my copending application aforesaid, other constituents can be added to the treating solution as may be desired for special purposes, for example, to impart a particular color or texture to the protective coating or otherwise to vary its appearance or character in respects which do not substantially alter its corrosion resistant properties. For example, small amounts of selenic acid may be employed in the treatment of magnesium by either the single solution method or the two solution method I have described. I have found that selenic acid, when added in small amounts up to about 0.05 per cent, imparts a dark reddish or mahogany color and gives a very smooth surface. In the two solution method, the selenic acid would be added to the second of the two solutions described.

The salt of the metal which is lower in the electromotive series than the metal to be protected preferably is a sulphate, although acetates may also be used.

Treatment in the first solution may be continued for a period of 5 to 20 minutes or longer. Treatment in the second solution may be on the order of 30 minutes or longer. However as the solutions used do not cause any appreciable dimensional change, the time of treatment can be extended as desired. The metal may be washed between successive immersions but that is not necessary. At the conclusion of the treatment, the articles are washed in hot water and allowed to dry. If desired, they are then dipped in fuming oil, for example, in refined corn oil, for a period of a few seconds to one minute. During this treatment some evolution of gas will be observed, and at such time at this evolution ceases, the treatment can be terminated.

Finally, the articles are washed in hot soapy water and allowed to dry, or de-oiling can be performed by immersing in a boiling aqueous solution containing 2% potassium permanganate and 0.1% of a sulphate such as aluminum or zinc sulphates. In the case of magnesium alloys, the coating varies in color from black to gray or maroon, according to the particular alloy treated. The coating grows blacker as the percentage of aluminum in the alloy increases. Thus a magnesium alloy which does not contain aluminum takes a maroon color while a magnesium alloy containing 9% of aluminum takes a dark gray to black color.

The coatings produced by the treatments I have described are very adherent and can be brushed heavily with a hard bristle brush without any apparent harm to the coatings.

Example 1

By way of specific example of the practice of my invention, whereby its nature and advantages may be more fully understood, I shall now describe the treatment of a specimen of rolled sheet of a magnesium alloy containing about 6.5% aluminum, 0.2% manganese and 0.7% zinc,

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balance substantially magnesium plus usual impurities. The sheet was cleaned and degreased and then immersed for a period of 10 minutes in an aqueous solution, at boiling temperature, containing 1% manganese sulphate. After removal from this solution, the specimen was then immersed for a period of 30 minutes in a boiling aqueous solution containing 6% potassium permanganate. Upon removal from the second solution the specimen was dipped in fuming refined corn oil and then washed. The specimen, when dried, had a brownish-black color.

Example 2

A specimen of rolled sheet of a magnesium alloy of the same composition given in Example 1 was treated as follows: Cleaned and then immersed for a period of 10 minutes in an aqueous solution, at room temperature, comprising 0.1% titanium sulphate. After removal from this solution, the sheet was then immersed for a period of 30 minutes in a boiling aqueous solution containing 2% potassium permanganate and 0.1% titanium sulphate. Upon removal from the second solution the specimen was dipped in fuming oil and then cleaned. A tough adherent coating of black color was produced.

Example 3

A specimen of rolled sheet of magnesium alloy of the same composition given in Example 1 was treated as follows: It was cleaned and then immersed for a period of 15 minutes in an aqueous solution, at boiling temperature, comprising 0.1% zirconium sulphate. After removal from this solution, the sheet was then immersed for a period of 40 minutes in a boiling aqueous solution containing 6% potassium dichromate and 0.6% zirconium sulphate. Upon removal from the second solution the specimen was washed and allowed to dry. The coating was very smooth and of an even satin black color.

Example 4

A specimen of rolled sheet of an aluminum alloy containing about 7.0% silicon, 0.3% magnesium, balance substantially aluminum plus usual impurities, was treated as follows: Immersed for a period of 15 minutes in a 1% boiling aqueous solution of $\text{Zr}(\text{SO}_4)_2 \cdot \text{ZrOSO}_3 \cdot 2\text{H}_2\text{O}$ at room temperature. Thereafter it was immersed for a period of 45 minutes in a boiling solution containing 6% potassium permanganate and 0.6% $\text{Zr}(\text{SO}_4)_2 \cdot \text{ZrOSO}_3 \cdot 2\text{H}_2\text{O}$. These treatments were followed by dipping the specimen in fuming vegetable oil for 5 minutes, after which the specimen was washed in hot water to remove the oil film. The coating obtained was black. The treated sheet was tested by immersion in a 20% sodium chloride solution for 300 hours, after which no sign of corrosion was to be observed.

Example 5

A specimen of sheet steel containing about 0.28 to 0.33% carbon, 0.40 to 0.60 manganese and 0.80 to 1.1% chromium, balance substantially iron plus usual impurities, was cleaned and immersed for a period of 10 minutes in a boiling aqueous solution, comprising 0.1% cerium sulphate. After removal from this solution the sheet was then immersed for a period of 30 minutes in a boiling aqueous solution containing 6% potassium permanganate and 0.6% cerium sulphate. Upon removal from the second solution, the specimen was dipped in fuming oil and then cleaned. The coating produced was tough and adherent. The

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color would be described as black or brownish black.

It will be appreciated from the preceding description and examples that my improved treatment is extremely simple in character and can be practiced without the use of special equipment. Moreover, it requires only a short time to produce an effective coating of smooth and pleasing appearance, the color of which can be varied. Another advantage of my treatment is that it is carried out without the use of acids or other substances which are dangerous to handle. The treatment is applicable to sheet, castings or articles made of dissimilar metals.

The terms and expressions which I have employed are used in a descriptive and not a limiting sense, and I have no intention of excluding such equivalents of the invention described, or of portions thereof, as fall within the purview of the claims.

I claim:

1. The method of treating magnesium and magnesium base alloy articles, which comprises immersing the articles in an aqueous solution in which the solute consists of about 0.1 to 1% of a sulphate of a metal which is below magnesium in the electromotive series, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature comprising about 0.1 to 1% of a salt of a metal which is below magnesium in the electromotive series and about 1 to 6% of potassium permanganate, said solutions being adapted to increase the resistance of said articles to corrosion.

2. The method of treating magnesium and magnesium base alloy articles, which comprises immersing the articles in an aqueous solution in which the solute consists of about 0.1 to 1% of a salt of a metal which is below magnesium in the electromotive series, and thereafter immersing the articles in a boiling aqueous solution comprising about 0.1 to 1% of a salt of a metal which is below magnesium in the electromotive series and about 1 to 6% of potassium permanganate, said solutions being adapted to increase the resistance of said articles to corrosion.

3. The method of treating magnesium and magnesium base alloy articles, which comprises immersing the articles in an aqueous solution at approximately room temperature consisting of about 0.1 to 1% of manganese sulphate, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature comprising about 1 to 6% of potassium permanganate, said solutions being adapted to increase the resistance of said articles to corrosion.

4. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature consisting of about 0.1 to 1% of manganese sulphate, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature comprising about 0.1 to 1% of a salt of a metal which is lower in the electromotive series than the metal to be protected and about 1 to 6% of potassium permanganate and which is effective to increase resistance to corrosion.

5. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution in which the solute consists of about 0.1 to 1% of a salt of a metal which is below magnesium in the

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electromotive series, and thereafter immersing the articles in a boiling aqueous solution in which the solute comprises primarily about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

6. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature consisting of about 0.1 to 1% of at least one salt selected from the group consisting of zirconium, thorium, titanium and cerium, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute comprises primarily about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

7. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution consisting of about 0.1 to 1% of at least one salt selected from the group consisting of zirconium, thorium, titanium and cerium, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute consists of about 0.1 to 1% of a salt of a metal selected from a group comprising zirconium, thorium, titanium and cerium and about 1 to 6% of potassium permanganate, said solution being effective to increase the resistance of said articles to corrosion.

8. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature in which the solute consists of about 0.1 to 1% of a zirconium salt, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute comprises primarily about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

9. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature in which the solute consists of about 0.1 to 1% of a zirconium salt, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute comprises primarily about 0.1 to 1% of a zirconium salt and about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

10. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature in which the solute consists of about 0.1 to 1% of



and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute comprises primarily about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

11. The method of treating magnesium and magnesium base alloy articles to increase their

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resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature in which the solute consists of about 0.1 to 1% of



and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute consists of about 0.1 to 1% of $\text{Zr}(\text{SO}_4)_2 \cdot \text{ZrOSO}_3 \cdot 2\text{H}_2\text{O}$ and about 1 to 6% of potassium permanganate.

12. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in an aqueous solution at approximately room temperature in which the solute consists of about 0.1 to 1% of manganese sulphate, and thereafter immersing the articles in an aqueous solution at approximately boiling temperature in which the solute comprises primarily about 0.1 to 1% aluminum sulphate and about 1 to 6% of potassium permanganate, said solutions being effective to increase the resistance of said articles to corrosion.

13. The method of treating magnesium and magnesium base alloy articles to increase their resistance to corrosion, which comprises immersing the articles in a boiling aqueous solution

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in which the solute consists of about 0.1 to 1% of a salt of a metal which is below magnesium in the electromotive series, and thereafter immersing the articles in a boiling aqueous solution in which the solute comprises primarily about 0.1 to 1% of a salt of a metal which is below magnesium in the electromotive series, and about 1 to 6% of a highly oxidizing alkali metal salt selected from the group consisting of water soluble permanganates and dichromates, said solutions being effective to increase the resistance of said articles to corrosion.

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The following references are of record in the file of this patent:

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Number	Country	Date
510,353	Great Britain	July 24, 1939

Certificate of Correction

June 20, 1950

Patent No. 2,512,493

RENE GIDE

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 32, for the word "solution" read *solutions*;
and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.
Signed and sealed this 26th day of September, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.