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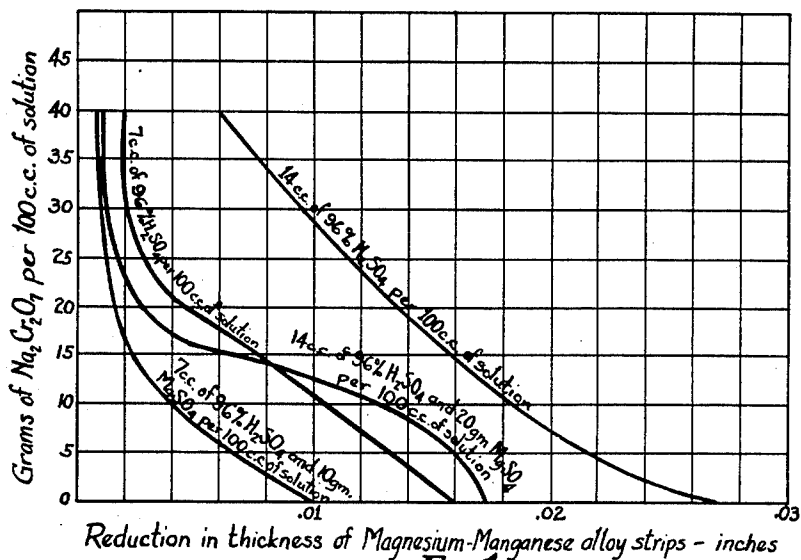
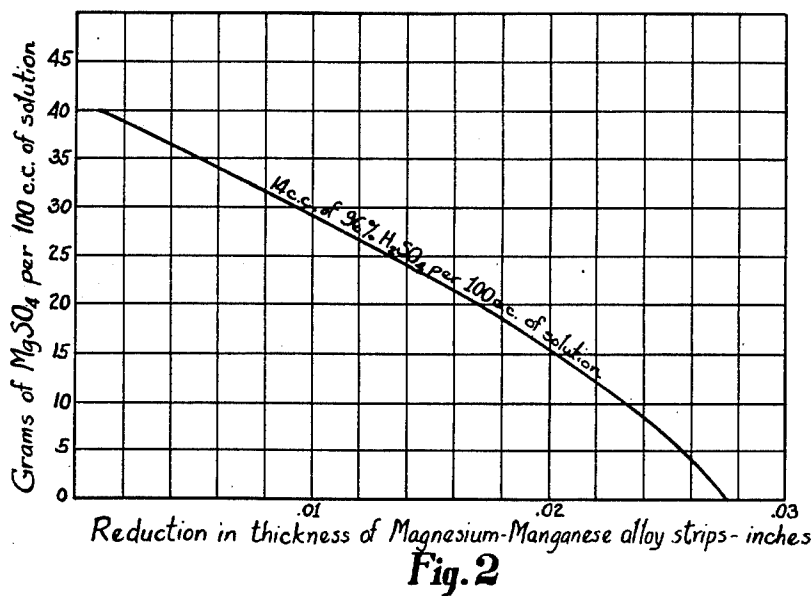
Feb. 26, 1935.

J. A. GANN ET AL

1,992,205

METHOD FOR TREATING MAGNESIUM ARTICLES

Filed Dec. 23, 1931



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Patented Feb. 26, 1935

1,992,205

UNITED STATES PATENT OFFICE

1,992,205

METHOD FOR TREATING MAGNESIUM ARTICLES

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Application December 23, 1931, Serial No. 582,786

5 Claims. (Cl. 148—8)

The present invention relates to a method and composition for treating or cleaning the surfaces of magnesium and magnesium alloy articles to remove surface contaminations and impurities without undue attack on the metal. While the invention deals broadly with the cleaning of magnesium and magnesium alloy articles, it is especially well adapted for cleaning foreign matter from portions thereof that have been welded by means of a gas flame or an electric arc.

It has been heretofore proposed (British Pat. 287,450) to improve the corrosion resistance of magnesium articles by treating with an aqueous solution of nitric acid and potassium bichromate, the use of sulphuric acid + bichromate, or hydrochloric acid + bichromate solutions for this purpose being expressly avoided. We are also aware that an aqueous solution containing 10 to 30 per cent of sulphuric acid has been proposed in U. S. Patent 1,795,473 for use in cleaning magnesium and magnesium alloy articles. The use of sulphuric acid in this manner, we have found, is satisfactory for certain purposes where the loss of metal, due to the attack of the acid, is not objectionable. For many purposes, however, such as the cleaning of magnesium and magnesium alloy sheets, welds, and the like, we have found that the action of 10 to 30 per cent aqueous sulphuric acid alone, is, in general, too drastic. In this connection we have found that the addition of a substantial amount of a magnesium salt to an aqueous sulphuric acid solution has a decided beneficial effect in reducing the attack of the sulphuric acid on the magnesium article treated therein while the cleaning action of the solution is very good.

We have further found that the addition of a suitable chromium compound in substantial amount to the aqueous sulphuric acid + magnesium salt solution, or even to aqueous sulphuric acid alone aids materially in reducing the attack on the magnesium article and produces a solution that has very good cleaning action. The present invention, accordingly, so far as sulphuric acid is concerned, can be considered as an improvement over the procedure described in the aforementioned U. S. Patent 1,795,473.

Accordingly, among the objects of the present invention is the provision of a method and composition for use in cleaning magnesium and magnesium alloy articles without undue attack on the metal itself. Other objects and advantages will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the methods, steps, and compositions hereinafter fully described and particularly pointed out in the claims, the annexed drawing and the following description setting forth in detail several forms of composition and modes of carrying out

the invention, such disclosed forms and modes illustrating, however, but several of the various ways in which the principle of the invention may be used.

In said annexed drawing:—

Fig. 1 is a series of curves illustrating in typical manner the reduction in attack of sulphuric acid on magnesium articles when our improved agents are used; Fig. 2 is a curve showing the reduction in attack of sulphuric acid on magnesium articles when increasing amounts of magnesium sulphate are added to the solution.

Magnesium and magnesium alloy articles, such as ingots, castings, wrought shapes, sheet metal, welded sections and the like, before thorough cleaning, may have surface contaminations and impurities which act in exposure to air and moisture to cause the article to corrode, and where the impurities are present in substantial amount, such as welding flux and oxides on and around a weld, the action is much more severe. The attack caused by such surface contaminations and impurities, we have found, can be eliminated without undue attack on the metal article being cleaned, by treating same in an aqueous bath of sulphuric acid containing a suitable magnesium salt with or without the addition of a suitable chromium compound. Magnesium sulphate, magnesium nitrate, magnesium chloride, and magnesium phosphate, which are salts of strong acids and are soluble in the solution under consideration, are typical examples of suitable magnesium salts; and chromic acid, or salts thereof including chromates or bichromates of magnesium, calcium, ammonium, and alkali metals, are typical examples of suitable chromium compounds. In its broadest phase, the present invention contemplates the use of suitable magnesium and chromium compounds for the purposes at hand not only in sulphuric acid solutions, but in other strong acid solutions, such as hydrochloric, phosphoric, etc., all of which can be satisfactorily used with the same range of concentration (5 to 25 c. c. concentrated acid) as the sulphuric acid with the exception that hydrochloric acid can be used at concentrations up to 40 c. c. of concentrated acid per 100 c. c. of solution.

While we have described our invention in terms of using concentrated acid (96% H_2SO_4 , 36% HCl , 85% H_3PO_4), it is not limited to such use since obviously the acid could be diluted with an amount of water equal to that required to produce a solution of the desired strength per 100 c. c. without departing from the principle of the invention and accordingly the claims are to be construed in that light. Our work in connection with agents to be added to the acid solution indicates that while any suitable magnesium salt can be used, the one having a negative radicle

corresponding to the negative radicle of the acid used, is preferable. In other words, where sulphuric acid is used, we prefer to use magnesium sulphate as the added magnesium compound.

- 5 For simplicity, our present invention will be described in terms of treating strips of rolled sheet, formed from a magnesium alloy consisting of approximately 98.5 per cent magnesium and 1.5 per cent manganese. It is to be understood, however, that the invention is generally applicable to the treatment of magnesium and its alloys, and that it is in no sense limited to that specific alloy or article. The aforementioned strips, before use, were measured for thickness with a
10 micrometer and after treatment were measured again to determine how much the treating solution had reduced the thickness of the strips. As specific examples showing the acid treatment and effect of our agents in reducing the attack of the acid on a magnesium alloy article according to the present invention wherein satisfactory cleaning action was obtained, the following are to be noted:

Example 1

- 25 Several magnesium alloy strips, as described above, were measured for thickness and then immersed for one minute in an aqueous solution containing 7 c. c. of concentrated sulphuric acid (96%) per 100 c. c. of solution. The strips were quickly removed from the solution, immediately washed, and dried to prevent further attack. Upon measuring the thickness of these strips, it was found that the average reduction in thickness per strip was 0.016 of an inch.

Example 2

- In similar manner to Example 1, fresh strips were immersed for one minute in an aqueous solution containing 7 c. c. of concentrated sulphuric acid and 10 grams of magnesium sulphate per 100 c. c. of solution. The reduction in thickness per strip was only 0.010 of an inch in one minute as compared with the reduction in thickness of 0.016 of an inch where the magnesium sulphate was not used.

Example 3

- 50 An aqueous solution containing 29 c. c. of concentrated hydrochloric acid (36%) per 100 c. c. of solution, on the average reduced the thickness of the magnesium alloy strips 0.044 of an inch in one minute while the same strength solution containing 10 grams of magnesium chloride reduced the thickness of the strips on the average of only 0.029 of an inch.

Example 4

- 60 An aqueous solution containing 9 c. c. of phosphoric acid (85%) per 100 c. c. of solution, on the average reduced the thickness of the magnesium alloy strips 0.011 of an inch, while the same strength solution containing 10 grams of magnesium phosphate reduced the thickness of the strips on the average only 0.004 of an inch.

- Referring more particularly to the drawing, the curves are based on the reduction in thickness of strips of magnesium alloy sheet containing 1.5 per cent of manganese, as described in connection with the examples above. These curves are based on the average of a number of tests and accordingly they can be considered as a close approximation of the results obtainable in the carrying out of the present process. In Fig. 2, the curve represents the reduction in thickness of

magnesium alloy strips in inches where an aqueous solution containing 14 c. c. of concentrated sulphuric acid per 100 c. c. of solution was used, and to which increasing amounts of magnesium sulphate up to 40 grams per 100 c. c. of solution were added, the sulphuric acid concentration remaining constant. The strips, in each case, were immersed in the solution for a period of one minute, following which they were promptly washed, dried, and then measured to determine the reduction in thickness. Referring particularly to the curve, it is to be noted that an aqueous solution containing 14 c. c. of concentrated sulphuric acid per 100 c. c. of solution reduced the thickness of the magnesium-manganese alloy strips approximately 0.027 of an inch in one minute. The use of 20 grams of magnesium sulphate with 14 c. c. of concentrated sulphuric acid in 100 c. c. of aqueous solution decreased the attack so that at the end of one minute the reduction in thickness of the strips being treated was approximately 0.017 of an inch. In like manner, the use of 40 grams of magnesium sulphate and 14 c. c. of concentrated sulphuric acid in 100 c. c. of aqueous solution cut down the attack so that the reduction in thickness of the pieces being treated was approximately 0.001 of an inch. In this connection it is to be noted that even with this high percentage of magnesium sulphate present in the sulphuric acid solution, the solution still acted in efficient manner to clean the surface of the metal.

The curves shown on Fig. 1, in similar manner to Fig. 2, are based upon the treatment of magnesium-manganese alloy strips for one minute in an aqueous sulphuric acid or aqueous sulphuric acid + magnesium sulphate solutions to which increasing amounts of sodium bichromate were added. The use of 40 grams of sodium bichromate with 14 c. c. of concentrated sulphuric acid in 100 c. c. of solution, cuts down the average reduction in thickness of the strips to approximately 0.006 of an inch as contrasted with the use of an aqueous solution containing 40 grams of magnesium sulphate and 14 c. c. of concentrated sulphuric acid per 100 c. c. of solution, wherein the reduction of thickness is only approximately 0.001 of an inch. Obviously at the higher concentrations, for instance, 30 to 40 grams of chromium compound or magnesium salt per 100 c. c. of acid solution, the use of magnesium sulphate is less costly and much more efficient than sodium bichromate in reducing the attack of the acid on the metal. The use of 20 grams of magnesium sulphate with 14 c. c. of concentrated sulphuric acid in 100 c. c. of aqueous solution has the effect of cutting down the reduction in thickness of the strips (one minute treatment) from approximately 0.027 of an inch as noted, to approximately 0.017 of an inch. The use of sodium bichromate with this sulphuric acid + magnesium sulphate solution acts to lessen the reduction in thickness incurred during the treatment up to a point where about 25 grams of sodium bichromate are used in 100 c. c. of solution, above which the effect of further additions of sodium bichromate is small and almost unnoticeable. The use of 7 c. c. of concentrated sulphuric acid per 100 c. c. of solution with or without 10 grams of magnesium sulphate therein acts in somewhat parallel manner to the like solutions containing 14 c. c. of concentrated acid with the exception that curves are pushed to the left to a marked extent, relative to the 14 c. c. sulphuric acid curves, due primarily to

the lower concentration of the acid. Looking at the curves and results as a whole, it is to be noted that the addition of magnesium sulphate to the aqueous sulphuric acid solution, not only had a marked effect, but the addition of sodium bichromate to the sulphuric acid-magnesium sulphate solution acts to still further accentuate the protective effect of the magnesium sulphate in the solution. It is thus obvious that the addition of a suitable magnesium salt, such as magnesium sulphate, to an aqueous strong-acid solution marks a distinct advantage in cutting down the attack of the acid on the metal and moreover, the addition of suitable chromium compounds, such as sodium bichromate, to the strong-acid + magnesium salt solution, presents still further advantages for the purpose at hand.

While the curves have been set up to show the use of 7 and 14 c. c. of concentrated sulphuric acid per 100 c. c. of solution with or without the addition of other ingredients, the invention is not limited to those specific amounts, since obviously the principle holds over a broad range of acid concentration, as well as additive ingredients. Where sulphuric acid and a magnesium salt, such as magnesium sulphate, are used, we prefer to use them in an aqueous solution, containing per 100 c. c. thereof, sulphuric acid in amount from 5 to 25 c. c. (based on concentrated acid) and magnesium sulphate in amount from 10 to 40 grams. Specifically a mixture of 10 c. c. of concentrated sulphuric acid with 20 grams of magnesium sulphate per 100 c. c. of aqueous solution is well adapted for general use. Where a suitable chromium compound, such as sodium bichromate, is used in the above solution in place of the magnesium sulphate, we prefer to use it in amount from 5 to 40 grams per 100 c. c. of solution. Specifically, 10 c. c. of concentrated sulphuric acid and 20 grams of sodium bichromate per 100 c. c. of solution can be used for most purposes. On the other hand, where sulphuric acid, magnesium sulphate, and sodium bichromate are to be used together in aqueous solution, we prefer to use them in the following ranges per 100 c. c. of solution: 5 to 25 c. c. of concentrated sulphuric acid, 5 to 30 grams of magnesium sulphate, and 5 to 40 grams of sodium bichromate. A specific mixture of these materials per 100 c. c. of aqueous solution that we have found highly advantageous for use, consists of 10 c. c. of concentrated sulphuric acid, 15 grams magnesium sulphate, and 20 grams of sodium bichromate. The time necessary to leave the magnesium or magnesium alloy article subjected to, flooded with, or immersed in the solution depends upon the amount of impurities and surface contaminations to be removed, the temperature involved in the treatment, and the strength of the cleaning solution. The examples and curves set forth above are based upon treatment of the magnesium alloy strips at room temperature or slightly above same, which temperatures we prefer to use although higher temperatures even up to the boiling point of the solution can be used. It is to be noted in this connection that at higher temperatures the cleaning action of the solution is faster and accordingly the time of treatment must be reduced to obtain equivalent cleaning action to that obtained at room temperature, other factors remaining constant. Ordinarily, a few seconds up to a minute is sufficient for treating the articles in the stronger solutions noted above, while several minutes may

be taken where the articles require considerable cleaning, the temperature of the solution is low, or the solution is very weak. While we have specifically mentioned sulphuric acid, magnesium sulphate, and sodium bichromate in the examples above, we do not wish to be limited to those exact materials, since, the invention is applicable to a whole series of equivalent materials as hereinbefore set forth.

For simplicity the term "magnesium" as used heretofore and in the claims is to be understood to cover not only magnesium itself, but alloys thereof wherein the magnesium predominates.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the process and composition herein disclosed, provided the means stated by any of the following claims or the equivalent of such stated means be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. A method of treating a magnesium article which comprises subjecting said article to the action of an aqueous solution the constituents of which are per 100 cc. thereof, from 5 to 25 cc. of concentrated sulphuric acid, from 5 to 30 grams of a magnesium salt selected from the group consisting of magnesium chloride, magnesium sulphate, magnesium phosphate, and from 5 to 30 grams of a chromium compound selected from the group consisting of chromic acid, the chromate and bichromate of ammonia, calcium, magnesium, alkali metals.

2. A method of treating a magnesium article which comprises subjecting said article to the action of an aqueous solution the constituents of which are per 100 cc. thereof, from 5 to 25 cc. of concentrated sulphuric acid, from 5 to 30 grams of a magnesium salt selected from the group consisting of magnesium chloride, magnesium sulphate, magnesium phosphate, and from 5 to 30 grams of sodium bichromate.

3. A method of treating a magnesium article which comprises subjecting said article to the action of an aqueous solution the constituents of which are per 100 cc. thereof, from 5 to 25 cc. of concentrated sulphuric acid, from 5 to 30 grams of magnesium sulphate, and from 5 to 30 grams of sodium bichromate.

4. A method of treating a magnesium article which comprises subjecting said article to the action of an aqueous solution containing per 100 cc. thereof from 10 to 15 cc. of concentrated sulphuric acid, from 10 to 20 grams of magnesium sulphate, and from 15 to 25 grams of sodium bichromate.

5. A method of treating a magnesium article which comprises subjecting said article to the action of an aqueous solution the constituents of which are per hundred cubic centimeters thereof, from 5 to 25 cubic centimeters of an acid selected from the group consisting of phosphoric acid and sulphuric acid, from 5 to 30 grams of a magnesium salt selected from the group consisting of magnesium chloride, magnesium sulphate, and magnesium phosphate, and from 5 to 30 grams of a compound selected from the group consisting of chromic acid, the chromates and bichromates of ammonia, calcium, magnesium, and alkali metals.

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