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METHOD OF TREATING MAGNESIUM

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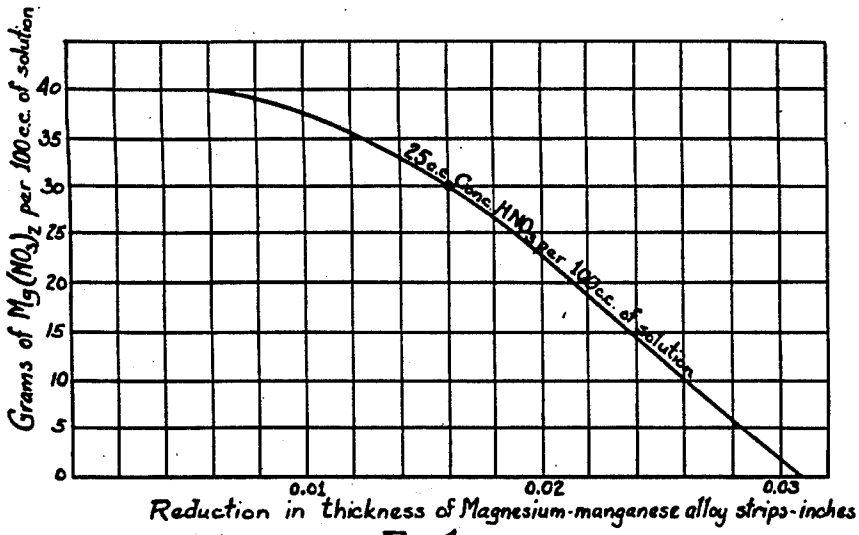


Fig. 1

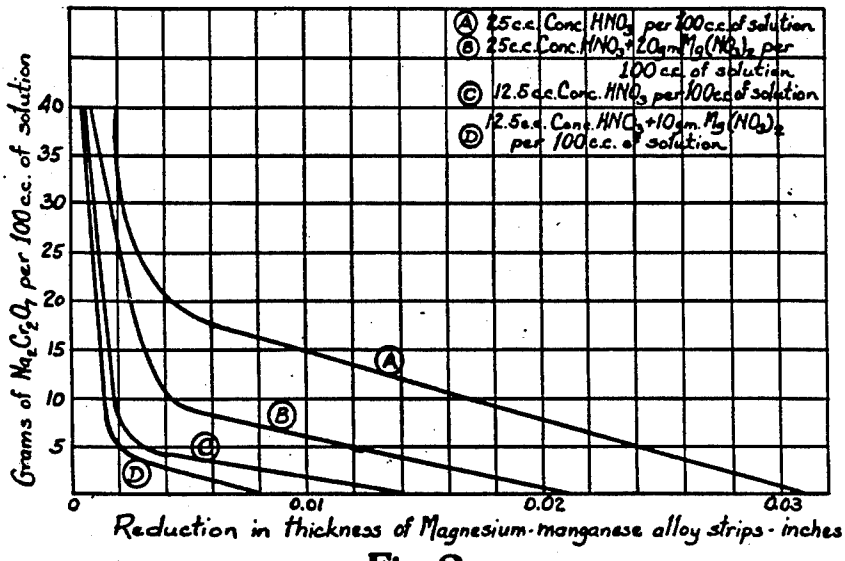


Fig. 2

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METHOD OF TREATING MAGNESIUM

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3 Claims. (Cl. 148—8)

The present invention relates to a method and composition for treating or cleaning the surface 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 removing 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 Patent No. 287,450) to improve the corrosion resistance of magnesium articles by treating with an aqueous solution of nitric acid and potassium bichromate. We have found that while this solution can be satisfactorily used for certain purposes, still a rather high concentration of bichromate is necessary to reduce the attack of the acid on the metal and even then the attack is pronounced whereby useful metal is removed and reagent consumed. We have now found that by using a substantial amount of a magnesium salt such as magnesium nitrate or sulphate with the aqueous solution of nitric acid and bichromate salt, the attack of the acid on the metal can be reduced to a marked extent. The use of magnesium nitrate or magnesium sulphate in the nitric acid solution without the use of a bichromate, we have found has a satisfactory effect in reducing the attack of the acid on the metal and in any case the cost of the magnesium salt per unit weight is but a small fraction of the cost of sodium or potassium bichromate a fact which, of itself aids in reducing the cost of the process and makes it commercially feasible. While we have found that the addition of a substantial amount of a magnesium salt to the nitric acid or nitric acid+bichromate solution has a decided beneficial effect in reducing the attack of the nitric acid on the magnesium article treated therewith, we have also found that the cleaning action of the solution remains very good.

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 certain forms of composition and modes for 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 shows a curve illustrating the reduction in attack of nitric acid on magnesium-manganese alloy strips when magnesium nitrate is added in varying amounts to the solution. Fig. 2 is a series of curves illustrating in typical manner the reduction in attack of nitric acid on magnesium articles when certain of our improved agents are used.

Magnesium and magnesium alloy articles such as ingots, castings, wrought shapes, sheet metal, welded sections, and the like may have, surface contamination and impurities before thorough cleaning, 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 nitric acid containing a suitable magnesium salt with or without the addition of a suitable chromium compound. Magnesium nitrate and magnesium sulphate which are salts of strong acids and are soluble in the solution under consideration are typical examples of suitable magnesium salts; 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 purpose at hand in aqueous nitric acid solutions. In this connection, our work indicates that magnesium nitrate is the preferable magnesium salt to use and magnesium chromate is the preferable chromium compound to use from a protection standpoint, although for most purposes sodium or potassium bichromates will be used due to their lower cost. For simplicity, the nitric acid will be referred to as c. c. of concentrated acid (70 per cent), while the other ingredients will be referred to in terms of grams per 100 c. c. of solution in order to standardize and put all of the examples and tests on a comparable basis. For the same reason the 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 micrometer and after treatment were measured again to determine how much the treating solution had reduced the thickness of the strips. We give the following specific examples of the nitric acid treatment showing the effect of our agents in reducing the attack of the nitric acid on a magnesium alloy article according to the present invention wherein satisfactory cleaning action was obtained.

Example 1

Several magnesium alloy strips, as described above, were measured for thickness and then immersed for one minute in an aqueous solution containing 25 c. c. of concentrated nitric acid 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 approximately 0.031 of an inch.

Example 2

In similar manner to Example 1, fresh strips were immersed for one minute in an aqueous solution containing 25 c. c. of concentrated nitric acid and 30 grams of magnesium nitrate per 100 c. c. of solution. The average reduction in thickness per strip was only 0.016 of an inch as compared with the reduction in thickness of 0.031 of an inch where the magnesium nitrate was not used.

Example 3

In similar manner to Example 1, fresh strips were immersed for one minute in an aqueous solution containing 15 c. c. of concentrated nitric acid and 30 grams of magnesium nitrate per 100 c. c. of solution. The average reduction in thickness per strip was only 0.008 of an inch.

Example 4

In similar manner to Examples 1 and 2, fresh strips were immersed for one minute in an aqueous solution containing 25 c. c. of concentrated nitric acid and 10 grams of sodium bichromate 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 0.017 of an inch.

Example 5

In similar manner to Example 4, fresh strips were immersed for one minute in an aqueous solution containing 25 c. c. of concentrated nitric acid, 10 grams of sodium bichromate, and 20 grams of magnesium nitrate per 100 c. c. of solution. The average reduction in thickness per strip for this treatment was only 0.004 of an inch which was approximately one-fourth the corresponding reduction in thickness when the magnesium nitrate was omitted. Reducing the nitric acid from 25 c. c. to 20 c. c. in this example further reduced the reduction in thickness of the fresh strips treated to approximately 0.003 of an inch.

Referring more particularly to the drawing, the curves are based on the reduction in thickness of strips of magnesium-manganese alloy sheet containing 1½ 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 carrying out the present process. In Fig. 1 the curve represents the reduction in thickness of magnesium alloy strips in inches where an aqueous solution containing 25 c. c. of concentrated nitric acid per 100 c. c. of solution was used and to which increasing amounts of magnesium nitrate up to 40 grams per 100 c. c. of solution were added, the nitric acid concentration remaining constant. The strips in each case were immersed in the solution for a period of one minute at approximately room temperature, following which they were promptly washed, dried and then measured to determine the reduction in thickness. Referring particularly to the curve, it will be seen that the aqueous solution containing 25 c. c. concentrated nitric acid per 100 c. c. of solution reduced the thickness of the magnesium-manganese alloy strips approximately 0.031 of an inch in one minute. The use of 20 grams of magnesium nitrate with 25 c. c. of concentrated nitric acid per 100 c. c. of solution decreased the attack so that at the end of one minute the reduction in thickness of the strips being treated was approximately 0.021 of an inch. In like manner, the use of 40 grams of magnesium nitrate and 25 c. c. of concentrated nitric acid per 100 c. c. of an aqueous solution thereof cut down the attack so that the reduction in thickness of the pieces being treated was approximately 0.006 of an inch. In this connection, it is to be noted, that even with this high percentage of magnesium nitrate present in the nitric acid solution, the solution still acted in efficient manner to clean the surface of the metal.

The curves shown on Fig. 2 are based upon the treatment of magnesium-manganese alloy strips for one minute at approximately room temperature in aqueous nitric acid or aqueous nitric acid + magnesium nitrate solutions to which increasing amounts of sodium bichromate were added. Referring more particularly to the drawings, the curve showing the use of 25 c. c. of concentrated nitric acid, 20 grams of magnesium nitrate and increasing amounts of sodium bichromate per 100 c. c. of solution clearly shows that the use of magnesium nitrate in this solution had a highly beneficial effect in decreasing the reduction in thickness of the magnesium-manganese alloy strips treated therein for one minute as compared with a like treatment with the same strong acid solution not containing the magnesium nitrate. In face the entire curve shows less reduction in thickness for all amounts of sodium bichromate added when compared to the like strong nitric acid curve wherein magnesium nitrate was omitted. In similar manner to the 25 c. c. of concentrated nitric acid solution curves, a pair of 12½ c. c. of nitric acid curves are shown. These curves are pushed to the left to a pronounced extent relative to the 25 c. c. nitric acid curves due primarily to the reduction in acid strength. This pair of curves also set forth in definite manner that the addition of magnesium nitrate to the nitric acid solution acts to decrease the rate of attack of the nitric acid to a pronounced degree. Looking at the curves and results as a whole, it is to be noted, that the addition of magnesium nitrate to the aqueous nitric acid solution not only had a

marked effect, but the addition of sodium bichromate to the nitric acid + magnesium nitrate solution acts to still further accentuate the protective effect of the magnesium nitrate in the solution. It is thus obvious that the addition of a suitable magnesium salt such as magnesium nitrate to the aqueous nitric 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 nitric 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 12.5 and 25 c. c. of concentrated nitric acid per 100 c. c. of aqueous solution with or without the addition of other ingredients, the invention is not limited to those specific amounts since the principle holds over a broad range of acid concentration, as well as additive ingredients. The examples and curves have been described in terms of using concentrated nitric acid (70 per cent) for ease of explanation, but, it is to be understood that the invention is not limited to the use of concentrated acid 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 spirit of the invention, and accordingly the claims are to be construed in that light. Where nitric acid and a magnesium salt such as magnesium nitrate are used, we prefer to use them in an aqueous solution containing per 100 c. c. thereof nitric acid in amount from 10 to 30 c. c. (based on concentrated acid) and magnesium nitrate in amount from 10 to 40 grams. Specifically, a mixture of 15 c. c. of concentrated nitric acid with 30 grams of magnesium nitrate per 100 c. c. of aqueous solution is well adapted for general use. On the other hand, where nitric acid, magnesium nitrate, 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:—10 to 30 c. c. of concentrated nitric acid, 5 to 30 grams of magnesium nitrate, 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 20 c. c. of concentrated nitric acid, 20 grams of magnesium nitrate, and 10 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 the 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 nitric acid, magnesium nitrate, 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 hereinfore 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. In a method of removing surface impurities from a magnesium article, the step which consists in subjecting the article to the action of a solution containing, per hundred cubic centimeters thereof, 10 to 30 cubic centimeters of concentrated nitric acid, 5 to 30 grams of a magnesium salt selected from the group consisting of magnesium nitrate, magnesium sulphate, and from 5 to 40 grams of a chromium compound selected from the group consisting of chromic acid, the chromate and bichromate of ammonia, calcium, magnesium, and alkali metals.

2. In a method of removing surface impurities from a magnesium article, the step which consists in subjecting the article to the action of a solution containing, per hundred cubic centimeters thereof, 10 to 30 cubic centimeters of concentrated nitric acid, 10 to 30 grams of magnesium nitrate, and 5 to 40 grams of sodium bichromate.

3. In a method of removing surface impurities from a magnesium article, the step which consists in subjecting the article to the action of a solution containing, per hundred cubic centimeters thereof, 10 to 30 cubic centimeters of concentrated nitric acid, 5 to 30 grams of magnesium sulphate, and 5 to 40 grams of sodium bichromate.

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