Aug. 30, 1949. G. E. COATES 2,480,448

PROTECTIVE SURFACE TREATMENT OF MAGNESIUM BASE ALLOYS

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Fig. 1.

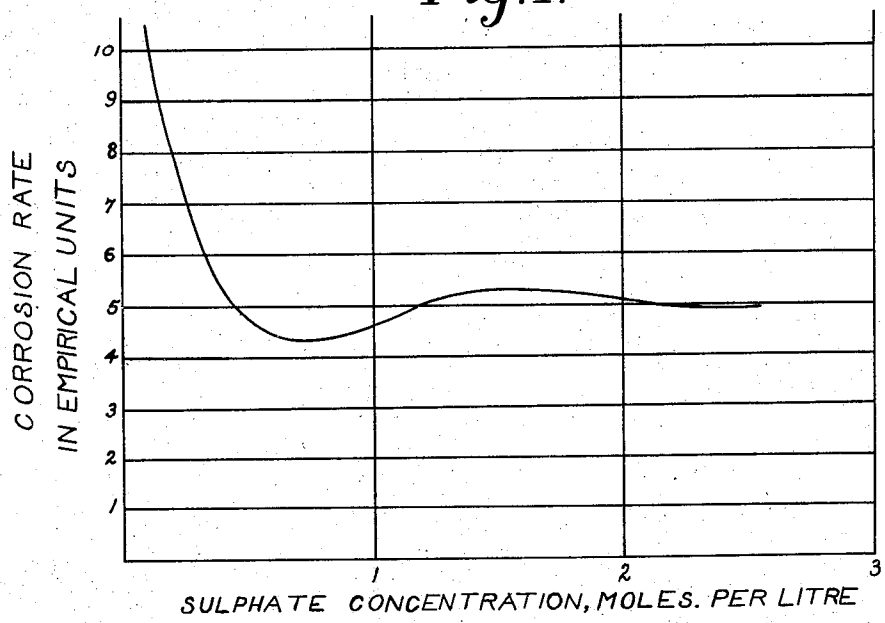
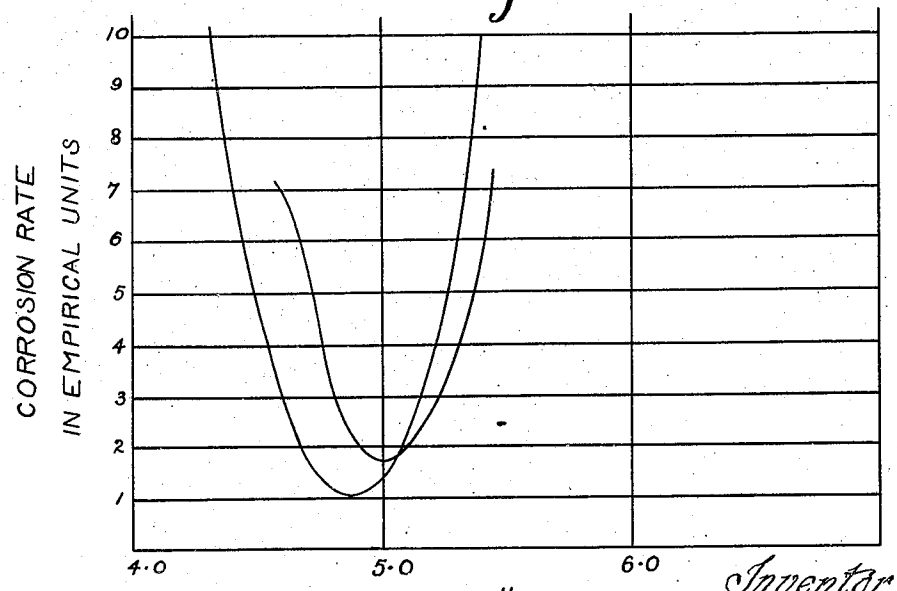


Fig. 2.



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Fig. 3.

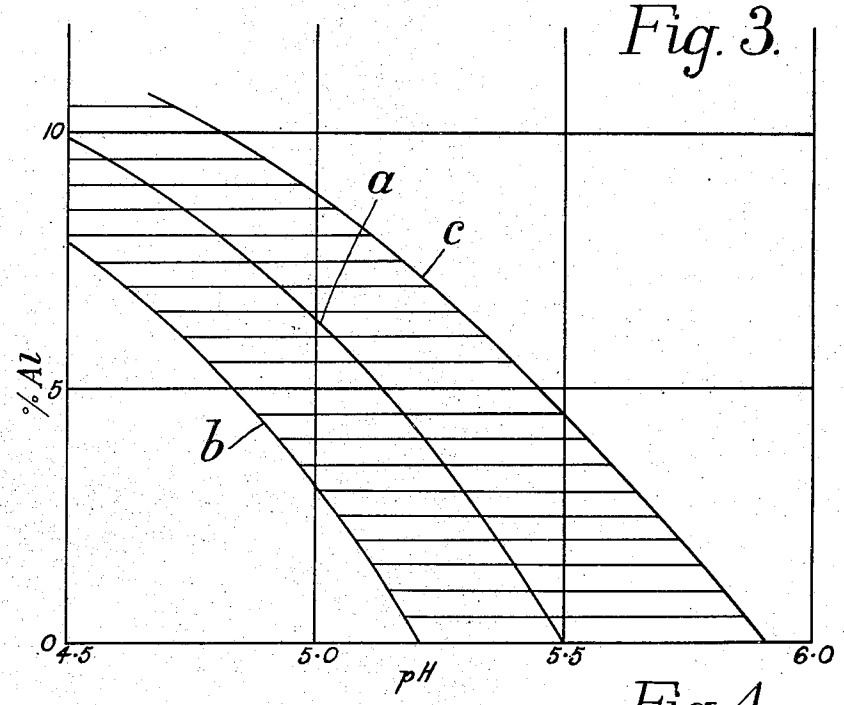
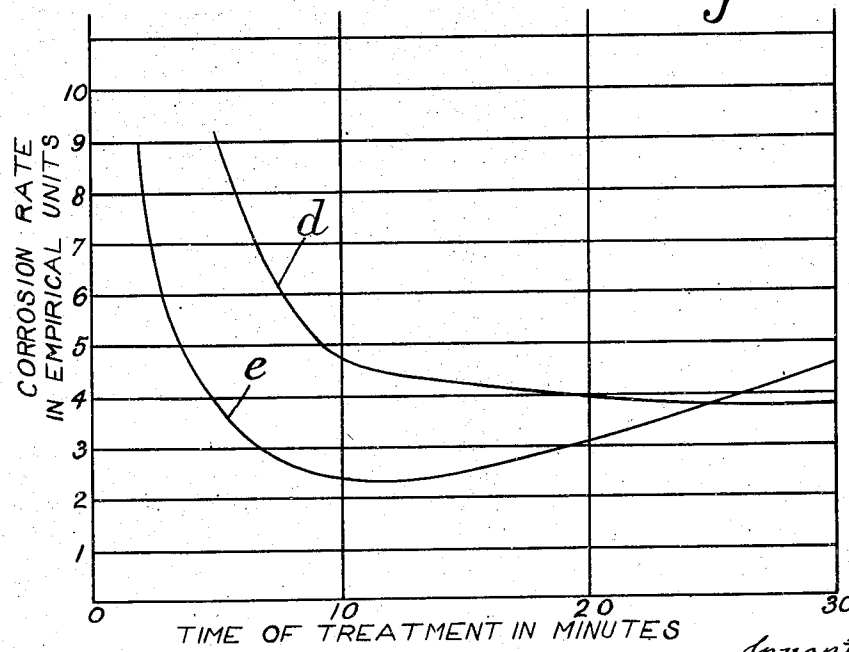


Fig. 4.



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UNITED STATES PATENT OFFICE

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PROTECTIVE SURFACE TREATMENT OF MAGNESIUM BASE ALLOYS

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Application February 21, 1944, Serial No. 523,295
In Great Britain April 28, 1943

1 Claim. (Cl. 148—6.21)

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This application, which is a continuation in part of pending United States application Serial No. 469,444, of Geoffrey Edward Coates, filed December 18, 1942, now abandoned, for Treatment of magnesium base alloys, is for an invention which relates to the protective surface treatment of magnesium base alloys, especially but not exclusively those alloys prepared according to specifications of the British Air Ministry Department of Technical Development hereinafter referred to as D. T. D. specifications.

The protection afforded by dichromate solutions is due to the formation of a protective film of reaction products on the surface of the metal, but simple dichromate solutions are of little practical value because both the rate and total extent of film formation are severely limited.

Amongst what may be described as the dichromate type of treatments for the corrosion protection of Mg base alloys, recourse has been made to a variety of methods in endeavors to overcome the above difficulties but no hitherto published process combines all the desired attributes of a commercial protective treatment which may be summarized as the combination of the following features or requirements:

(*a*) The treatment should cause the minimum dimensional change so that machined articles may be treated without disturbance to machining tolerances, for instance, less than can be reasonably measured with a thousandths of an inch micrometer.

(*b*) The raw materials for compounding the solution should be cheap and of innoxious character, e. g., strongly acid or alkaline solutions should be avoided and the rate of consumption of the ingredients in operation should be low.

(*c*) Time of treatment should be as short as possible, i. e., preferably not more than a few minutes and less than half an hour.

(*d*) The process should be capable of operation at room temperature.

(*e*) The process should be characterized by ease and economy in operation and maintenance and the solutions should be stable.

The present invention provides good commercial protection in a short time at room temperatures where such protection can be secured even in 1 to 3 minutes in certain circumstances. On the other hand, when a higher temperature is used for speeding up the process, for instance to fit in with conjoined processes, the bath still remains stable. Heavy metal salts are avoided because they form heavy metal deposits in the coating, or precipitated or colloidal matter, or

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cause spontaneous change of pH with time or form double salts with some of the solution constituents of insufficient solubility to permit attainment of optimum sulphate concentration. Such salts are therefore excluded from the present application, which is limited to those compounds of which the cations remain in stable solution in the concentration and pH ranges set out below.

The object of the present invention is to provide an improved process for the protection of Mg base alloys by the dichromate method, characterized by, namely, short-time treatment, capacity for treatment at substantially room temperature, avoidance of strongly acid solutions which, in addition to being unpleasant to use, are likely to cause undue dimensional loss and employment of economical stable solutions.

The characteristics of the solutions of this invention are that, in the pH range specified, the cations are stable in aqueous solution, undergo no spontaneous change, are stable in the presence of dichromate ions, do not react with other constituents of the bath to prevent attainment and maintenance of the sulfate and dichromate ion concentrations specified, and do not react with magnesium or form other metal or undesirable deposits on the magnesium surface.

The new combination consists of the following essential requirements (*a*) to (*e*), namely:

(*a*) *Dichromate ions* in concentration not less than 0.05 molar and preferably between 0.2 and 0.5 molar, which region is the optimum when the other factors are at their optima. The most convenient sources of dichromate ions to ensure that the cation simultaneously introduced shall satisfy the above requirements, are the dichromates singly or mixed of H, Li, Na, Mg, K or NH_4.

(*b*) *Sulphate ions.*—In concentration not less than 0.2 molar and preferably between 0.6 and 1 molar which region is the optimum when the other factors are at their optima. The most convenient sources of sulphate ions to ensure that the cation simultaneously introduced shall satisfy the above requirements, are the sulphates of H, Li, Na, Mg, K or NH_4 or mixtures or combinations of any of these. The following cations are also useful in the dichromate constituents, singly or mixed, of my solutions: tetramethyl ammonium, tetraethyl ammonium, and N-methyl-pyridinium ions. Some of these sulphates have never previously been specified as constituents of dichromate solutions for Mg protection. Sulphates such as Al sulphate, alums, nickel sulphate, chromium sulphate or nickel ammonium

sulphate which have been specified for known processes are not suitable for the present process because they would all contribute cations undesirable in respect of the requirements listed above and are excluded. It is believed that the advantages of the sulfate addition in the present process may be explained as follows: The salts employed previously as "activator salts" contain cations injurious in my process due to formation of precipitated or colloidal matter, and the "activator salts" which contain anions other than sulfate do not produce the desired results. This is because sulfate ions have the proper charge and are of the proper size to diffuse through the thin, first-formed film and enable production of a satisfactorily thick film, without causing pitting, reducing the dichromate, or forming insoluble reaction products.

I have found that not only is the choice of the sulphate of essential importance but likewise its concentration. Figure 1 is a graph showing the relationship between sulphate concentration in moles per litre and corrosion rate in empirical units employing uniform treatment times. There is an optimum concentration in the region of 0.6–1 molar. Whereas there is little loss in protection with higher concentrations, concentrations below this region become critical and the protection rapidly falls off so that at less than about 0.2 M the solutions are of no practical value.

(*c*) *Ammonium ions.*—The presence of ammonium ions improves the protective value of the film for any given time of treatment. The concentration is sufficient if the ammonium salt is used for at least one of the other ingredients (*a*) or (*b*) above.

(*d*) *Hydrogen ion concentration.*—It has long been known that if the acidity of dichromate solutions is increased, the rate of protective film formation is also increased. Unfortunately the rate of dissolution of metal from the workpiece surface also increases and the permissible increase in acidity is therefore limited by dimensional tolerances. The protective value is also affected if the acidity falls outside certain limiting ranges for each type of solution. For the solutions according to the present invention the effect of pH variation on the protection afforded by the film in the case of two particular alloys is shown in Figure 2. There are marked indications of an optimum pH value for each alloy. Generally speaking, the optimum depends on the Al content of the alloy as shown in Figure 3 which shows the relationship between the hydrogen ion concentration and percentage of Al in alloys treated according to certain solutions of the present invention. The degree of protection falls off rapidly on either side of the optimum values for each alloy but all values fall within the extreme pH range 4–6.

The pH values quoted were determined by the glass electrode method. Other methods of pH measurement may be used but allowance must be made for variations from the glass electrode values.

(*e*) *Buffer agents.*—Maintenance of the pH value at the optimum or within the permissible range for a given alloy is complicated by the fact that the pH rises as the Mg dissolves during the treatment. In practical operation it is highly desirable for reasons of economy, to be able to treat a number of workpieces in the same batch of solution. This necessitates frequent controlled additions of acid but the frequency of such additions is greatly reduced by incorporating in the solution a weak acid and one of its salts capable of buffering the solution within the desired pH range. Acetic acid is about the best and cheapest organic acid for the buffer mixture together with its sodium or ammonium salt, although any of the other bases listed under (*b*) above may be used. Other weak acids of suitable dissociation constant and salts thereof, both of sufficient solubility, may be used in place of or in addition to the acetic acid and acetate. The buffer acid must not however form an insoluble salt with Mg and must not be oxidized by the dichromate solution. The buffer capacity or resistance of the solution to change of pH is roughly proportional to the concentration of the weak acid and its salt. Occasional major adjustments in pH may be appropriately effected by additions of sulphuric, chromic or nitric acids, ammonia, caustic soda or other suitable bases selected from the list in (*b*) above. The acids and their salts which I prefer for cold solutions are single or mixed acids and single or mixed salts of the acids and preferably of the same acids within the following group, namely, acetic, propionic, butyric, valeric, malonic, succinic, glutaric, adipic, pimelic, phthalic, the cations of the salt being those of lithium, sodium, magnesium, potassium or ammonium. The acids and their salts which I prefer for hot solutions are single or mixed acids and single or mixed salts of these acids and preferably of the same acid, the acids being chosen so that the buffer agent is sufficiently soluble at the temperature of use, from the following group, namely, caproic, oenanthic, malonic, succinic, glutaric, adipic, suberic, pimelic, benzoic and phthalic, and the cations of the salts being those of lithium, sodium, magnesium, potassium or ammonium. In cases where it is desired to secure the maximum possible protection, the sulphate ion concentration should not exceed the optimum region indicated under (*b*) above, and in such cases the major pH adjustment should be made by chromic or nitric acid additions.

The salts used for introducing the dichromate and sulfate ions, the salt of the buffer acid and the base for pH adjustments must be chosen to meet the requirements hereinabove set forth, and suitable cations have been listed above. Any species of cation can be tested by compounding a solution as described, containing it, and determining whether the solution filters without leaving appreciable residue on the filter paper, and whether it shows a change of pH on standing.

To sum up the aforesaid items (*a*) to (*e*), the invention consists in a process for the protective surface treatment of magnesium base alloys in solutions characterized by a dichromate concentration not less than 0.05 mole per litre, a sulphate concentration not less than 0.2 mole per litre, and a hydrogen ion concentration controlled by a buffer agent or addition within the pH range 4–6; the constituent salts being so selected that within this pH range their cations remain in stable solution and the upper limits for the dichromate and sulphate concentrations corresponding to saturation point in the particular solutions used and temperature of use.

Time of treatment to secure the best results for any particular alloy depends on the composition of the alloy. Generally speaking time of treatment must be increased with increasing Al content. In some cases there is an optimum re-

gion from the point of view of time of treatment as shown by the shape of curve *e* in Figure 4. Curve *e* applies to an alloy of composition 7.5% Al, 0.4% Zn, 0.2% Mn. Curve *d* applies to an alloy comprising 6% Al, 1% Zn, 0.2% Mn. The region of maximum curvature of curve *d* is about the point corresponding to, say, 9 minutes. That in curve *e* is about the point corresponding to, say, 7 minutes, although with the alloy of curve *d* an increased time of treatment up to 30 minutes is not detrimental, curve *e* shows that with the alloy of that curve an increased time of treatment—other things being equal—reduces the protection, that is to say increases the corrosion rate in respect of the effect obtained by treatment at a lower time corresponding to the knee of the curve.

In any given case, the optimum value for any of the variables may be determined by means of accelerated corrosion tests representative of the particular service conditions the article is required to withstand. A saline immersion or spray test applied in well-known manner is generally regarded as representative of marine atmospheric exposure and it is on this basis that my ranges and the results in the figures have been established.

Variation in the ionic concentrations do not cause sudden changes in the effectiveness of the solution, and working limits must therefore be selected having regard to the degree of protection required.

Drag-out loss is minimized by using the lower concentrations in any given range, by treating in the cold, and by suspending the workpiece above the bath for a few seconds after treatment. The dichromate concentration tends to fall with use and further additions must be made as indicated by simple analysis. The sulphate concentration on the other hand rises when sulphuric acid instead of chromic or nitric acid is used for the occasional major adjustments in pH.

One additional advantage arising from the fact that good protection is secured by a few minutes' treatment in the cold is that it may be applied as a simple swabbing process to finished parts in situ, e. g. cut edges of sheet, welds, repairs or even as a maintenance treatment. If, nevertheless, the solutions are heated, the time of treatment may be even further reduced and for certain applications this may more than offset the disadvantages incurred by the heating. Examples are where the treatment is a step in a continuous production line and tank capacity is limited by considerations of floor space or where output must be temporarily or permanently increased in an existing treatment plant. The solutions are stable on heating but if the evaporation loss of acetic acid becomes serious, the acetic acid and acetate should be substituted in whole or in part by single or mixed acids and single or mixed salts of these acids and preferably of the same acid, as disclosed above for hot solutions.

For best results, whether the solution is used cold or hot, it is desirable to submit the workpieces to a cleaning pre-treatment. Solvent degreasing should be adopted if necessary followed by any of the standard published methods for Mg with the exception of sand or shot blasting or the use of hydrofluoric acid dips which reduce the protective value of the treatment. A quick pickle in cold dilute acid (HNO_3 or H_2SO_4 or a mixture of these acids) is a good method, but where dimensional loss is to be minimized, chromic acid or alkaline cleaning should be used. In the latter case it may be desirable in some cases to extend slightly the protective treatment time. Alternatively, anodic polishing in accordance with the methods disclosed in British patent specifications Nos. 550,175 and 550,176 may be employed as the pre-treatment.

The following table gives a number of specific examples in accordance with which the invention may be carired into effect:

Table I

For magnesium alloys substantially Al free and containing up to 2.5% manganese in accordance with specifications D. T. D. 118, 140A and 142, a high degree of protection is secured by cleaning by one of the methods described above and immersing for three minutes at room temperature in a solution made up as follows:

	Parts by weight
Ammonium, sodium or potassium dichromate, singly or mixed	50–100
Ammonium sulphate (or, if desired, the equivalent amount of sodium sulphate if the ammonium salt is used for one of the other constituents)	80–120
Acetic acid	10
Hydrated sodium acetate (or the equivalent amount of ammonium acetate particularly if the ammonium salt is not used for the other constituents)	25
Water to make up to	1,000

The pH of this solution must be adjusted, e. g. with ammonium hydroxide, to between 5.2 and 5.9 but preferably to 5.5. After washing the material is found to be coated with an adherent greenish or gold brown protective film which also provides an excellent basis for the usual type of paint coating applied to magnesium alloys.

In cases where a good, but not necessarily the highest, degree of protection is required, the treatment time may be reduced to one minute. Alternatively, the above concentrations may be reduced by as much as 50% and the treatment time kept at 3 minutes.

For magnesium alloys containing Al to specifications D. T. D. 59A, 88B, 136A, 120A, 281, 285, 289, 325, 348 and 350, a very high degree of protection is secured by cleaning by one of the methods described above and immersing for 8–12 minutes in the same solution but of pH adjusted to suit the Al content as indicated in Figure 3. In this figure the central curve *a* represents the pH values for maximum protection. A tolerance is provided at each side of this curve as shown by the curves *b* and *c*. The shaded area between the curves *b* and *c* gives the working range for good protection. Thus, for an alloy containing 6% Al, 1% Zn and 0.2% manganese the pH range should be 4.8–5.3, but preferably 5.0–5.1. For an alloy containing 7.5% Al, 0.4% Zn and 0.2% Mn the pH should be adjusted to between 4.6 and 5.2 but preferably between 4.8 and 4.9. After washing, the materials are found to be coated with an adherent black protective film which also provides an excellent basis for the usual type of paint coating applied to Mg alloys.

In cases where a good, that is commercially satisfactory but not necessarily the highest degree of protection is required, the treatment time may be reduced to 5–8 minutes. Alternatively, the above concentrations may be reduced by as much as 50% and the treatment time kept at 8–12 minutes.

In the following Tables II to VI the pH values may be adjusted as described above.

Table II

This table may be taken to comprise the recommended range of ingredients.

Dichromate (Cr_2O_7)—Over 0.05 molar (up to saturation point).

Sulphate (SO_4)—Over 0.2 molar. (In cases where the dichromate concentration is increased, the sulphate concentration should preferably follow suit up to saturation point.)

Buffer mixture, e. g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, over 0.1 molar CH_3COO—. When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4–6 depending on alloy composition and time of treatment.

Time of treatment—This depends on the composition of the alloy, the solution composition and its pH and varies between ½–30 minutes.

Table III

This table may be taken to comprise the range where the degree of protection is that corresponding to temporary protection of parts during fabrication, storage or transit, or the like.

Dichromate (Cr_2O_7)—Over 0.1 molar (up to saturation point).

Sulphate (SO_4)—Over 0.3 molar. (In cases where the dichromate concentration is increased, the sulphate concentration should preferably follow suit up to saturation point.)

Buffer mixture, e. g. acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, over 0.1 molar CH_3COO—. When other weak acids and their salts are used as buffer mixture, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4–6 depending on alloy composition and time of treatment.

Time of treatment—As in Table II.

Table IV

This table comprises the ranges for parts requiring a good average degree of protection.

Dichromate (Cr_2O_7)—0.1 to 0.6 molar.

Sulphate (SO_4)—0.4 to 2.0 molar.

Buffer mixture, e. g. acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, from 0.2 molar CH_3COO— to 1.0 molar CH_3COO—. When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4–6 depending on the alloy composition and time of treatment.

Time of treatment—As in Table II.

Table V

This table gives the optimum composition for the protective values of the highest order.

Dichromate (Cr_2O_7)—0.2 to 0.5 molar.

Sulphate (SO_4)—0.6 to 1 molar.

Buffer mixture, e g. acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, 0.2 to 1.0 molar CH_3COO—. When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

Ammonium ions (NH_4)—0.4 to 3 molar.

pH 4.6–5.9 depending on the alloy composition and time of treatment.

Time of treatment—1–30 minutes depending on the alloy composition.

Major pH adjustments in this case should preferably be made by nitric not sulphuric acid, to maintain the sulphate ion concentration at the optimum.

Table VI

This represents the effect of increased temperature.

A magnesium alloy containing 7.5% Al, 0.4% Zn and 0.2% Mn is given a cleaning pre-treatment as described above and treated for ten minutes in the optimum solution of Table V containing adipic acid and sodium adipate and of pH 4.35 (measured in the cold by glass electrode) heated to 60–80° C. After washing, the specimen is found to be coated with a black adherent film. When tested by a saline test in known manner, the protective value of this film is found to be of the order of twice that obtained by treatment at room temperature under the optimum conditions; instead of taking the benefit of the heat by increased protection for the same time of treatment, it may be taken by similar protection for a shorter time of treatment.

I claim:

A process for the portective surface treatment of magnesium base alloy which comprises treating the alloy with a solution consisting of water, 0.2 to 0.5 mol per liter of dichromate ion of at least one compound of the group consisting of the dichromates of lithium, potassium, sodium, magnesium, and ammonium, 0.6 to 1.0 mole per liter of sulfate ion of at least one compound chosen from the group consisting of the sulfates of lithium, potassium, sodium, magnesium, and ammonium, a buffer mixture comprising acetic acid and sodium acetate and containing 0.2 to 1.0 mole per liter of acetate ion and adapted to maintain the pH of the solution at from 4.6 to 5.9, the said dichromate and sulfate compounds being so chosen as to yield an ammonium ion concentration of 0.4 to 3 moles per liter.

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