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3,134,702

CHEMICAL MILLING OF MAGNESIUM METAL AND MAGNESIUM ALLOYS

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The invention provides a novel aqueous acidic solution and method employing such solution for the controlled removal of metal from a surface of a magnesium metal or magnesium-base alloy article. Both magnesium metal and magnesium-base alloys wherein the magnesium content is at least about 75 percent by weight will hereinafter be referred to as magnesium.

In the production of extruded, rolled, molded, cast, or fabricated magnesium articles, it is often desirable to reduce the dimensions of the magnesium articles and particularly to reduce the cross-sectional area of members comprising the articles.

A method of uniformly reducing the dimensions of magnesium articles and more particularly reducing the cross-sectional area of members thereof by submerging the articles in a bath of specified composition accompanied by movement of either the submerged article or of the bath relative to each other is described in our co-pending application S.N. 596,390, filed July 9, 1956, now U.S. Patent No. 3,039,909. Such process is often referred to broadly as chemical milling. In that application, a highly efficient and economical method of producing uniformly dimensioned magnesium articles without undesirable concomitant formation of pits, ridges, striations, raised areas, rounded corners, and the like, associated to a more-or-less extent with theretofore known dimensioning methods is described. The method therein described consists essentially of submerging the magnesium article in an aqueous acidic bath comprising from about 0.70 to 25.0 percent by weight of nitric acid and from about 3 percent by weight to the saturation point in said bath of a nitrate selected from the nitrates of ammonium, alkali metals, and alkaline earth metals, and the balance water. The method of dimensioning magnesium articles according to S.N. 596,390 was a definite advancement in the art.

However, we have now discovered a novel aqueous composition and method employing such composition, for chemically milling or uniformly dimensioning magnesium articles which removes metal from the surfaces of the magnesium article at an even more uniform rate which is more easily controlled and which results in a smoother finished article than is attainable by the practice of the invention set out in S.N. 596,390.

The present invention, accordingly, is an improved method of dimensioning or chemically milling magnesium articles. It employs a novel aqueous composition consisting essentially of phosphoric acid, a nitrate salt selected from the class consisting of nitrates of ammonium, alkali metals, alkaline earth metals such as magnesium, and mixtures thereof, an aliphatic polyhydric alcohol, and the balance substantially water.

The proportional parts of the ingredients of the novel composition of the invention may vary over a rather wide range. They may be employed as follows:

Between 5 and 85 parts by volume of aqueous phosphoric acid, containing at least 85 percent H_3PO_4 in water, or equivalent amount of such acid and water;

Between 5 and 25 parts by volume of the polyhydric alcohol, but not in excess of a total of 100 parts of the acid and alcohol;

Additional water, if necessary, to make 100 parts of the composition by volume; and

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Between 1 and 45 percent, by weight of the aqueous composition so made, of the nitrate salt.

The preferred proportional parts of the ingredients of the composition of the bath are as follows:

Between 20 and 30 parts by volume of aqueous phosphoric acid, calculated as 100 percent H_3PO_4 ;

Between 10 and 17 parts by volume of the polyhydric alcohol;

Sufficient water to make 100 parts by volume; and

Between 3 and 5 percent, by weight of the aqueous composition so made, of the nitrate salt.

The preferred temperature range of the treating composition employed in the practice of the invention is between 70° and 90° F. When the ingredients of the bath are employed within the preferred range, as set forth above and within the preferred temperature range, a metal removal rate is obtained of between 0.0005 and 0.002 inch per exposed surface per minute.

The invention is carried out by admixing the ingredients of the composition in any order of addition in a suitable vessel or vat and continuing agitation for a time sufficient to render the aqueous composition substantially uniform and thereafter immersing the magnesium article to be chemically dimensioned or milled therein for a period of time sufficient to remove the thickness of metal desired. It is preferred that the article be moved relative to the bath during at least a part of the period of immersion.

One mode of carrying out the invention is to fill a suitable vat or vessel provided with a stirring means with a measured volume of water, admix therewith the desired volume of the polyhydric alcohol which is commonly either a glycol containing from 2 to 5 carbon atoms or glycerine, then admix phosphoric acid, usually having a concentration of at least 85 percent by weight, to provide the desired concentration of the acid in the aqueous composition, and then admix sufficient soluble nitrate salt to provide the desired concentration of the NO_3 radical.

The magnesium article to be milled is usually first degreased, if necessary, as by immersing it in an aqueous alkaline solution, e.g. one containing about 3 weight ounces of sodium carbonate and about 2 ounces of sodium hydroxide per gallon of water, at a temperature of between 190° and 212° F. for between 3 and 10 minutes, removing it therefrom and rinsing it with water. The thus cleaned magnesium article is then immersed in the aqueous treating composition of the invention for sufficient time to remove the desired amount of metal therefrom at a temperature of between 60° and 180° F. It is then removed therefrom and rinsed with water. Either the article being treated or the treating composition should be maintained in a state of motion for at least a part of the period of immersion in the composition, relative to the other for satisfactory results.

When it is desired that certain portions of the metal article retain their original dimensions, such portions may be masked off or stopped off by a suitable masking material. Such masking material may be any material which is substantially impervious to the chemical milling solution, e.g. it may be any one of a number of acid-resistant resin, such as polyvinylchloride as suggested in column 2, line 68, of U.S. Patent 3,039,909, or fibrous materials. Any of such materials prevents access of the aqueous acid solution to the thus masked portions which thereby retain their original size while the unmasked portions are appropriately reduced in size by the action of the treating composition.

A series of test runs was made, some for the purpose of illustrating the invention and others for the purpose

of comparison. The test runs made for comparison were in accordance with existing practices considered to be among those producing best results by methods known prior to the present invention. Those runs which are illustrative of the invention are designated examples and those not illustrative of the invention and for comparison are designated comparative runs.

In all test runs, the same general procedure was followed. The order of addition of each of the components, when employed, was as follows: The water was placed in a suitable container. The acid was first added followed by the polyhydroxy alcohol, to make 100 parts by volume. The nitrate salt, calculated in percent by weight of the aqueous solution, was then admixed therewith.

Samples of the magnesium alloy set out in the table, having a size of 1" x 3" x 1", were prepared, degreased in an alkaline solution, water-rinsed, and then immersed in accordance with the invention in one of the aqueous solutions set out in the table below, while continuing to agitate the solution mildly by means of a blade-type agitator or air injection, at the temperature and for the time shown in the table. The rate of metal removal, the uniformity of the metal layer removed, and the appearance of the thus chemically milled surfaces are also set out in the table. In the table, the percent of all ingredients in the treating composition is by volume except the acid salt (when employed) and the nitrate salt which are in percent by weight of the aqueous composition. The maximum and minimum thicknesses of metal removed per minute in the test runs, as set out in the table, from each sample panel was ascertained. The average value of the maximum and minimum thicknesses was then calculated by dividing the sum of the maximum and minimum thicknesses by 2.

known practices were in some instances rough and lack-luster (satiny).

An examination of Examples 1, 2, 3 shows more specifically the greater uniformity of metal removed in accordance with the practice of the invention than in accordance with known practice. In each of the examples of the invention the average difference between the maximum and minimum thicknesses of metal removed (calculated by adding the maximum and minimum values together and dividing the sums obtained by 2) was 0.0005". In contrast thereto, the average difference between the maximum and minimum thicknesses of metal removed in experimental runs A-F, which are illustrative of prevailing conventional practice (similarly calculated as in the examples of the invention), were 0.003, 0.003, 0.0035, 0.003, 0.003 and 0.004 inch, respectively. The average of these values is 0.00325. To show the extent to which uniformity is attained by the practice of the invention in contrast to that attained by the runs illustrating prior practice, $0.00325/0.0005=6.5$, i.e. the uniformity attained by the practice of the invention may be said to be 6.5 times that attained by the employment of the best known practices.

The practice of the invention offers a number of advantages for chemically milling, etching, or dimensioning of magnesium articles. Among such advantages are:

- Better controlled rate of etching;
- A smoother and brighter etched surface;
- Sharper relief, i.e. substantial absence of rounded corners;
- Greater uniformity of thickness of metal removed;
- Insignificant undercutting unless an unusually thick layer of metal is sought to be removed, and then such undercutting as occurs is substantially uniform.

Test No.	Alloy	Chemical Milling Solution ¹	Time (Min.)	Temp., ° F.	Rate of Metal Removal, in./min.	Metal Removed Per Surface, in.		Uniformity of Chemical Milling ⁴ , in.	Appearance of Dried Treated Surface
						Maximum	Minimum		
A.....	AZ31 ²	12% nitric acid (70% strength); 88% water, by volume 45% Mg(NO ₃) ₂ ·6H ₂ O, by weight. ¹	20	81-89	0.001	0.0235	0.0175	±0.003	Bright and smooth.
B.....	AZ31	14% nitric acid (70% strength); 86% water, by volume 40% NaNO ₃ , by weight. ¹	20	82-92	0.001	0.023	0.017	±0.003	Do.
C.....	AZ31	18% NaHSO ₄ ; 5% citric acid; 3% monochloroacetic acid; 74% water, by volume; 10% NaNO ₃ , by weight. ¹	10	85-90	0.003	0.032	0.025	±0.0035	Bright but had a satin appearance.
1.....	AZ31	30% phosphoric acid (100% strength); 16% ethylene glycol; 54% water, by volume; 5% NaNO ₃ , by weight. ¹	16	80-82	0.00065	0.011	0.010	±0.0005	Bright and smooth.
2.....	AZ31	30% phosphoric acid (100% strength); 17% glycerine; 53% water, by volume; 5% NaNO ₃ , by weight. ¹	24	80-86	0.0008	0.0195	0.0185	±0.0005	Do.
D.....	HK31 ³	12% nitric acid; (70% strength); 88% water, by volume; 45% Mg(NO ₃) ₂ ·6H ₂ O, by weight. ¹	20	81-95	0.001	0.0235	0.0175	±0.003	Bright but core area rough.
E.....	HK31	14% nitric acid (70% strength); 86% water, by volume; 40% NaNO ₃ , by weight. ¹	20	82-92	0.001	0.023	0.017	±0.003	Do.
F.....	HK31	5% citric acid, 3% monochloroacetic acid; 92% water, by volume; 18% NaHSO ₄ , by weight, ¹ 10% NaNO ₃ , by weight. ¹	8	80-85	0.003	0.028	0.020	±0.004	Satin bright.
3.....	HK31	30% phosphoric acid (100% strength); 17% glycerine; 53% water, by volume; 5% NaNO ₃ , by weight. ¹	40	80-82	0.0005	0.0205	0.0195	±0.0005	Bright and smooth.

¹ The liquid ingredients are on a 100 percent by volume basis; the nitrate salt is in percent by weight of the liquid ingredients.

² AZ31, composition in percent by weight: about 3 Al, 1 Zn, 0.4 Mn, and balance Mg.

³ HK31, composition in percent by weight: about 3 Th, 0.7 Zr, and balance Mg.

⁴ Obtained by dividing the sum of the maximum and minimum thickness of metal removed, in inches, by 2.

Reference to the table shows that superior results were obtained in both better control of the rate of removal and in uniformity of the thickness of the metal removed when the magnesium test panels were chemically milled in the composition of the invention, in accordance with the improved method employing such composition. The table further shows that when the composition of the invention was employed, the appearance of the finished surface was always bright and smooth whereas panels treated with other compositions selected from the best

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. An aqueous acidic treating bath for chemically dimensioning magnesium articles comprising by volume between 5 and 85 parts of phosphoric acid, having a concentration of at least 85 percent H₃PO₄; between 5 and 25 parts of an aliphatic polyhydric alcohol (the total of the acid and alcohol not exceeding 100 parts); balance water, as needed, to make 100 parts by volume; and between 1 and 45 percent by weight of the composi-

tion so made of a nitrate salt selected from the class consisting of the nitrates of ammonium and alkali and alkaline earth metals.

2. An aqueous acidic treating bath for chemically dimensioning magnesium articles comprising by volume phosphoric acid in amount equivalent to between 20 and 30 parts of 100 percent acid; between 10 and 17 parts of an aliphatic polyhydric alcohol; sufficient water to make 100 parts by volume; and between 3 and 5 percent by weight of the composition so made of a nitrate salt selected from the class consisting of the nitrates of ammonium and alkali and alkaline earth metals.

3. The bath of claim 2 wherein the aliphatic polyhydric alcohol is selected from the class consisting of aliphatic glycols having between 2 and 5 carbon atoms, glycerine, and mixtures thereof.

4. The bath of claim 3 wherein the aliphatic polyhydric alcohol is ethylene glycol.

5. The bath of claim 3 wherein the aliphatic alcohol is glycerine.

6. The bath of claim 2 wherein the nitrate salt is magnesium nitrate.

7. The bath of claim 2 wherein the nitrate salt is sodium nitrate.

8. The method of chemically dimensioning magnesium article consisting of immersing a substantially grease-free magnesium article to be sized in the bath of claim 1 at a temperature of between 60° and 180° F. while maintaining a relative motion between said bath and said article for at least a portion of the time of immersion, allowing the article to remain thus immersed until the dimensions of said article are reduced to the size desired, removing the article from the bath, and rinsing it with water.

9. The method according to claim 8 wherein said bath is maintained at a temperature of between 70° and 90° F.

10. The method of chemically dimensioning a magnesium article consisting of immersing a substantially

grease-free magnesium article to be sized in the bath of claim 2 at a temperature of between 60° and 180° F. while maintaining a relative motion between said bath and said article for at least a portion of the time of immersion, maintaining the article immersed for a time sufficient to reduce the dimensions of the members of said article to the size desired, removing the so treated article from the bath, and rinsing it with water.

11. The method of selectively chemically dimensioning a magnesium article consisting of masking off the portions of said article which are to remain unreduced in size with a coating material which is impervious to aqueous acidic solutions and immersing the thus partially coated article in the bath of claim 1 at between 60° and 180° F. while maintaining a relative motion between said bath and article for at least a portion of the time of immersion until the unmasked portions of said article are reduced to the desired dimensions, removing the so treated article, and rinsing the article with water.

12. The method according to claim 11 wherein the bath is maintained at a temperature of between 70° and 90° F.

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