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COMPOSITION AND PROCESS FOR ETCHING MAGNESIUM

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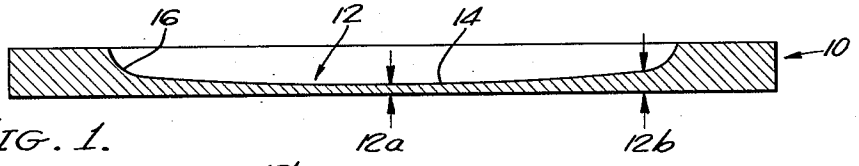


FIG. 1.

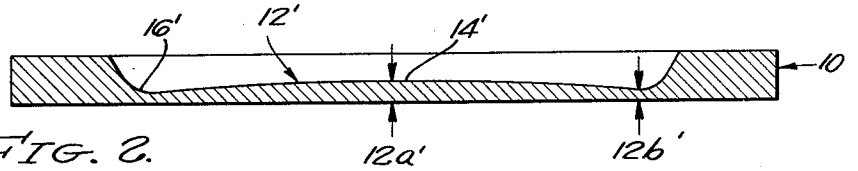


FIG. 2.

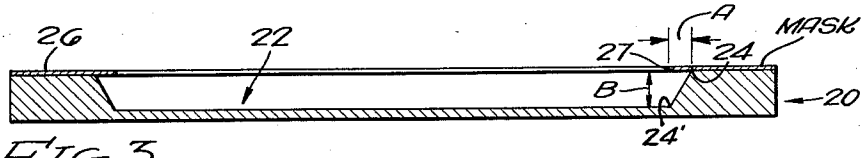


FIG. 3.

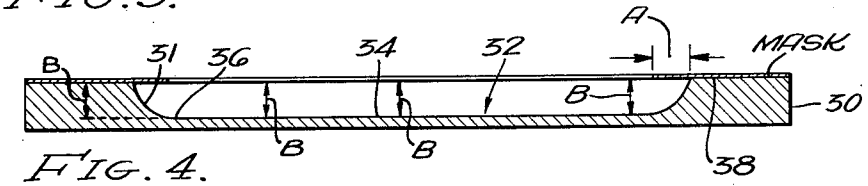


FIG. 4.

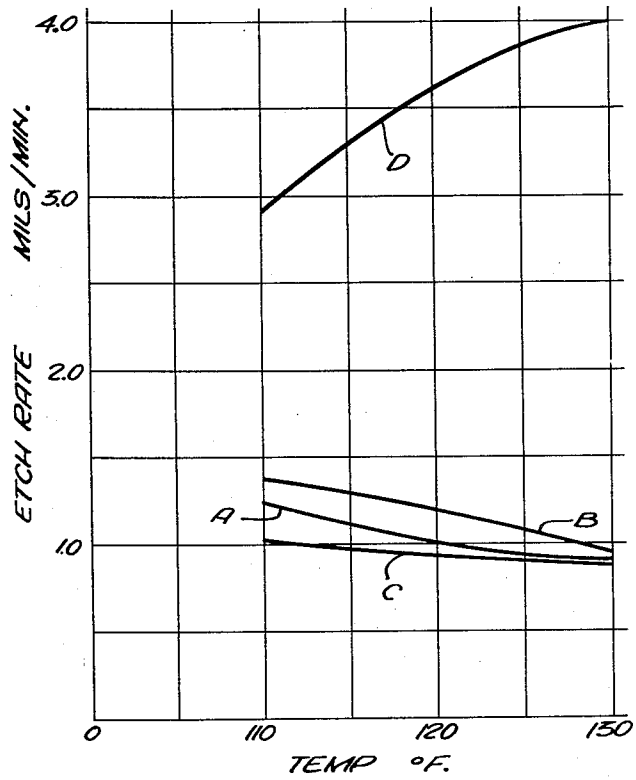


FIG. 5.

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3,053,719
COMPOSITION AND PROCESS FOR ETCHING MAGNESIUM

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This invention relates to the chemical etching or chemical milling of magnesium and its alloys, and is more particularly concerned with the provision of a novel composition and process for the chemical etching of magnesium and its alloys, and the etched article produced by such process.

The term "magnesium" employed throughout the specification and claims is intended to denote magnesium in its pure or commercially available form containing impurities, or magnesium alloys in which magnesium is the basic or dominant metal.

The invention will be described below taken in connection with the accompanying drawing wherein:

FIGS. 1–3 illustrate the disadvantages of prior art magnesium etching techniques;

FIG. 4 illustrates the improved etch obtained employing the etchants and etching procedures of the invention; and

FIG. 5 is a graph particularly illustrating the effect of increasing temperature on the magnesium etching rate employing the principles of the invention as compared to prior art technique.

Magnesium etchant systems now in use have a variety of disadvantages. One of the major difficulties which is inherent in these prior art etchants is the dishing of the etched magnesium part. Dishing is caused when the center of the etched portion etches faster than the perimeter areas, which results in more magnesium metal being removed in the center of the part than toward the periphery. Such dishing is illustrated in FIG. 1 of the accompanying drawing wherein the numeral **10** designates a part having a central etched portion **12**. It will be noted that center **14** of the etched portion is deeper than the peripheral portion **16**, so that at the center the metal is considerably thinner as indicated at **12***a* than at the peripheral portion **12***b*. Thus, for example, the center portion of the etch may have a thickness of only 75 mils, whereas the peripheral portion may have a thickness of as much as 125 mils. The aforementioned dishing problem is caused by a differential rate of attack on the magnesium metal surface, resulting from a temperature gradient in the part. Dishing therefore is a function of the etch rate. In order to avoid this dishing problem, it is necessary to have a minimum change of etch rate as a function of temperature.

Another problem encountered in the prior art etching of magnesium is reverse dishing. In this situation, the center area of the etched portion etches slower than the peripheral areas, thus producing a raised area in the center of the etched portion. Thus, for example, viewing FIG. 2 of the drawing, it is noted that the central portion **12′** of the etched article **10** has a raised portion **14′** as compared to the peripheral portion **16′**. In this situation, the thickness of the raised central area indicated at **12***a′* may be, for example, 125 mils, whereas the thickness at the peripheral portions indicated at **12***b′* may be only 75 mils. The major disadvantage resulting from reverse dishing is that stress areas are set up in the fillet portions at **16′**, producing weakened sections at these points.

Another major problem encountered in the prior art etching of magnesium is the control of surface smoothness. Magnesium etchants heretofore have produced surfaces that, while acceptable for certain purposes, are generally of a rough texture not acceptable for certain applications. Thus, magnesium etchants heretofore employed have produced rough surfaces having a profilometer reading of 80 R.M.S. and above. The profilometer is an instrument which is employed to measure roughness of surface in micro-inches. The profilometer is described in the article "How Smooth is Smooth" by B. C. Brosheer in "American Machinist," September 9 and 23, 1948. A standard profilometer is the profilometer Type QA Amplimeter manufactured by the Micrometrical Manufacturing Company, Ann Arbor, Michigan. "R.M.S." is an abbreviation for micro-inches root mean square. A rough surface is undesirable because the greater surface area of metal which is exposed is more susceptible to exidation The hills and valleys of a rough surface also contribute to low fatigue life of a magnesium part compared to a smooth surface. It is desirable to form smooth etched surfaces on a magnesium part; said surfaces having a surface smoothness of 40 to 50 R.M.S.

Another major fault in the prior art etching of magnesium is that these prior art techniques produce an etched part having an etch factor of less than 1. The term "etch factor" is the distance or the amount of undercutting between the edge of the mask and the wall of the etched portion of the part, divided by the vertical depth of the etch. Thus, for example, viewing FIG. 3 of the drawing where numeral **20** represents a part that has undergone etching and **22** is the etched portion thereof, the numeral **24** indicates the extent of lateral etching at the walls of the part adjacent the mask **26**, and the etch factor is the distance A between the edge **27** of the mask and the lateral extent **24** of the etched wall, and the value B is the depth of the etch. For example, the etch factor for a magnesium part etched according to present prior art practice may be on the order of about 0.5. Such an undercut part or a part with an etch factor of substantially less than 1, that is where

$$\frac{A}{B}$$

is substantially less than 1, produces an area of stress weakness at the base of the fillet **24′**.

It is desirable to obtain an etch on magnesium where the etch factor is approximately 1. This is accomplished where the rate of lateral etching is about the same as the rate of vertical etching, so that the amount of undercutting at the mask and the depth of etch are approximately equal. The processes and compositions of our invention are capable of producing a controlled etch factor of any desired value which may be higher than 0.5 and also higher than 1, the process being preferably controlled to obtain an etch factor of about 1.

Another difficulty of prior art etchant systems is that in such systems there is produced a high etch rate, for example, at temperatures of about 110° F. the etch ratio of prior art etchants is many times greater than the etchants of our invention, and the etch rates of such prior art etchants increases rapidly as the temperature increases, particularly at temperatures above 110° F. This high etch rate increase contributes to severe dishing and to production of a rough surface, both undesirable features as noted above. For example, in a magnesium etchant composed essentially of sulfuric acid, an etch rate in excess of 7 mils per minute is obtained with the resultant panel having a rough surface, uncontrolled etch line boundaries, and severe dishing. The best prior art etchants known to us will, under like conditions, give etch rates of 3 to 4 mils per minute in the region of about 110° F. Further, as the etching temperature increases, etch rate increases

to an uncontrollable value. In order to produce smooth surfaces without dishing, it has been found necessary to maintain an etch rate (the number of mils (.001 inch) of magnesium metal removed over a period of one minute), of about 2 mils per minute or less, and preferably on the order of about 1 mil per minute, and it is highly desirable to maintain such etch rate over a varying temperature range as etching proceeds.

It is accordingly an object of the present invention to provide a composition and process for production of an etched magnesium part which has substantially no dishing and which is uniform over the entire surface.

A further object is to provide a composition and process for etching magnesium to produce a surface smoothness over the entire etched area which is unobtainable by prior art techniques.

Still another object is to afford a composition and process for etching magnesium in which the etch rate across the whole surface, that is, the depth of etch across the whole surface, is maintained uniform.

Yet another object is the provision of a composition and process for etching magnesium wherein the lateral etch rate is substantially equal to the vertical etch rate.

It is another object of the invention to provide a composition and process for etching magnesium, so as to produce an etched surface having an etch factor as close as possible to 1.

It is still another object to afford a composition and process for etching magnesium wherein the rate of etching at high temperature is not increased by increases in temperature, and wherein the etch rate is sufficiently slow and controllable even at high temperatures so as to obtain smooth, uniform surfaces.

It is a still further object to provide a process for rejuvenating etching baths of the type particularly employed in the invention as these baths become loaded with magnesium sulfate during the process of etching, so as to maintain proper acid concentration, magnesium sulfate concentration and rate of etch to obtain the aforementioned advantages.

Yet another object is the production of an article of manufacture in the form of a chemically etched magnesium product in which the depth of etch across the entire etched surface is uniform, wherein the etch factor is approximately 1, and which is neither dished nor reverse dished, and which has a smooth surface over the entire etched portion.

Other objects and advantages will be apparent from the following description of the invention.

We have found that by etching a magnesium part with an aqueous sulfuric acid solution of a sulfate, preferably sodium sulfate or sodium bisulfate, and containing sodium xylene sulfonate, and preferably, although not necessarily, including a small amount of an hydroxy carboxylic acid such as citric acid, the etch rate is materially reduced to a value such that the etched surface of the part is smooth over the entire bottom area of the etched portion and also along the sidewalls. When it is particularly desirable to form smooth etched surfaces on a magnesium part, the process and compositions of our invention are capable of producing a smoothness of 40 to 50 R.M.S. and as low as 20 to 25 R.M.S., or any variations thereof as may be desired. Also, by practice of the invention the depth of etch can be controlled so that it is substantially the same at the center and periphery of the etched surface due to the uniform etch rate. Thus, regardless of the shape of the original exterior surface, e.g. whether curved, flat or irregular, the bottom of the etched depression formed in such exterior surface will have a depth from said surface which depth is substantially uniform at all portions of the depression bounded by the peripheral sides thereof. Further, by practice of the invention, dishing or reverse dishing of the etch can be prevented, both of which occur in the prior art processes. Moreover, the uniform etch rate in both the lateral and vertical directions obtained by the invention can result in a fillet bordering the etched portion, said fillet having an etch factor of about 1.

Of particular significance, it has been found that by employing the etchant composition and process of the invention at temperatures of etching of about 110° F. and above, as the temperature is raised the rate of etching actually is reduced. This is a surprising phenomenon inasmuch as conventional magnesium etchants produce excessive etch rates at these elevated temperatures, and these etch rates increase with increase in temperature. The reduced rate of etching according to the invention process at these high temperatures results in controlled etching and aids production of uniform, smooth surfaces with an etch factor approximately 1, and the minimum fluctuation of etch rate with temperature according to the invention also aids in preventing the aforementioned dishing.

It has been found necessary for proper functioning of the invention composition to employ a substantial amount of either sodium sulfate or sodium bisulfate in the highly acid aqueous sulfuric acid solution. Since sodium sulfate in sulfuric acid is known to be converted to sodium bisulfate, this latter material can be initially employed in place of the sodium sulfate. In any event, it has been found essential that a substanital proportion of the sulfate ion be present furnished by the sulfuric acid and the sodium sulfate or sodium bisulfate, in conjunction with the xylene sodium sulfonate. In this respect it has been found that alkali metal sulfates or bisulfates other than the sodium salt are not suitable. Thus, for example, where potassium sulfate is employed in place of sodium sulfate, a rough, unsatisfactory surface is obtained.

The sodium xylene sulfonate of the invention composition aids in producing a desirably slow etch rate on the order of about 1 mil per minute, which, in turn, is of major importance in obtaining the smoothly etched magnesium surfaces of the invention. Further, it has been found that apparently the sodium xylene sulfonate is responsible for the decreasing etch rate as a function of increasing temperature especially at etchant temperatures of the order of 110° F. and above.

Although not a necessary ingredient of the invention composition for etching magnesium, the inclusion of a simple hydroxy carboxylic acid improves the etching action of the composition. Thus, for example, the addition of a small amount of citric acid appears to improve fillet formation and also to improve surface smoothness. In place of citric acid, other hydroxy carboxylic acids such as tartaric, malic, or glycollic acid may be employed. The polyhydroxy carboxylic acids are preferred.

It was observed that as the etching of magnesium parts proceeds in the aforementioned etchant composition, the etched surface smooths considerably. We found that the increasing content of magnesium sulfate produced in the bath during the etching period contributed to this improved functioning of the bath. We have accordingly observed that when magnesium sulfate is added to the initial composition, the foregoing result can be accomplished more quickly to produce panels having good fillets, excellent line definition, no dishing, and a surface, for example, of 40–40 R.M.S., meaning a smoothness of 40 R.M.S. with the grain of the metal and a smoothness of 40 R.M.S. across the grain of the metal. However, it will be understood that since, as pointed out above, magnesium sulfate is formed in the bath as etching proceeds, it is not necessary that the magnesium sulfate be present in the initial bath, although the initial presence of this material is preferred. Thus, the initial bath need not contain magesium sulfate, but in preferred practice magnesium sulfate may be included in the original bath, e.g. by adding this material directly thereto, or by adding a portion of a solution which was previously used in etching magnesium and thus contains magnesium sulfate.

In order to obtain the improved results of the invention, it has been found that the above ingredients should be present in the solution or etching bath preferably in

such proportions that an etch rate of about 0.8 to about 1.5 mils per minute is maintained. To obtain such results, the following overall approximate ranges of proportions of the ingredients should be employed in the solution:

TABLE I

Material:	Overall range, percent by weight
$MgSO_4.7H_2O$	0 to 12
Na_2SO_4 or $NaHSO_4$ (anhydrous basis)	10 to 20
Citric acid or equivalent acid	0 to 1
Sodium xylene sulfonate	1.5 to 6
Sulfuric acid—66° Baumé	16 to 23
Water, remainder.	

However, for obtaining best results, the following preferred proportions are employed:

TABLE II

Material:	Preferred range, percent by weight
$MgSO_4.7H_2O$	4 to 8
$NaSO_4$ or $NaHSO_4$ (anhydrous basis)	12 to 16
Citric acid or equivalent acid	0.4 to 0.6
Sodium xylene sulfonate	3 to 5
Sulfuric acid—66° Baumé	18.4 to 22.4
Water, remainder.	

As aforementioned, the magnesium sulfate can be present initially in the solution, but if not, it will form as etching proceeds. The presence of citric acid or equivalent acid noted above is preferred, but is not necessary.

If proportions of ingredients greater or less than those set forth in Table I are employed, the results of the invention including uniform, low etch rate, smoothly etched surfaces and walls, and good fillets, are generally not obtainable. When employing the proportions within the preferred ranges of Table II, generally the best results are produced as regards smoothly etched surfaces having a 40 to 50 R.M.S. or less profilometer reading with and across the grain, uniform depth of etch over the etched surface, good fillet formation, and etch factor of about 1.

The various components of the solution can be added separately to water to form the working solution, or those components which are generally obtainable in dry form can be mixed and packaged, and the resulting composition added to an aqueous sulfuric acid solution to produce the invention composition. Thus, for example, sodium sulfate and xylene sodium sulfonate, with or without citric or equivalent acid, and with or without magnesium sulfate, can be mixed in certain proportions, and the resulting mixture added to aqueous sulfuric acid to produce the aforementioned working etching solutions. Such mixtures excluding magnesium sulfate can also be used as make-up for a spent solution, as described hereinafter.

For example, an overall and preferred range of proportions of such solid compositions are as follows:

TABLE III

Material	Overall Range	Parts by Weight	
		Preferred Range (without $MgSO_4$)	Preferred Range (with $MgSO_4$)
Na_2SO_4 or $NaHSO_4$ (anhydrous basis)	45 to 84	71 to 81	48 to 62
Citric acid or equivalent acid	0 to 4	2 to 3	0.5 to 2
Sodium xylene sulfonate	10 to 25	16 to 24	12 to 20
$MgSO_4.7H_2O$	0 to 35	0	20 to 35

Compositions within the ranges specified in Table III can be added to the proper proportions of sulfuric acid and water to form working solutions substantially as given above in Tables I and II. It will be understood that the relative proportions of each of the ingredients of the compositions in the dry form and the concentration of

the dry mixture employed in the solution should be chosen so that when the dry mixture is added to sulfuric acid and water, the percentage of the respective ingredients in solution will be preferably within the ranges specified in Tables I and II.

The operational temperature of the etchant baths formed from the etchant compositions of the invention is preferably in the range of about 105 to 115° F., most desirably about 110° F. However, as pointed out above, as the temperature of the etchant is increased above 110° F. during the etching operation, the etch rate will decrease rather than increase and, hence, no danger of an inordinate rate of etching is present, with the attendant disadvantages noted above, including formation of a rough etched surface.

This phenomenon is brought out in Example 1 below, illustrating the principles of the invention, and described in connection with FIG. 5 of the drawings, showing a graph with etch rate in mils per minute against temperature.

Example 1

The following compositions A, B, C and D were prepared and AZ–31B magnesium alloy parts of the same size and shape were respectively etched in each of solutions A, B, C and D for the same time, the etching solutions each varying in temperature from 110° F. to 130° F.

	Parts by Weight—Compositions			
	A	B	C	D
Magnesium Sulfate $7H_2O$	456.0	456.0	456.0	456.0
Sodium Sulfate	897.2	897.2	897.2	897.2
Citric Acid	24.4	24.4	24.4	24.4
Sodium Xylene Sulfonate	154.5	107.2	215.0	00.0
Sulfuric Acid, 66° Baumé	1,061.4	1,061.4	1,061.4	1,061.4
Water	2,612.0	2,664.0	2,504.0	2,782.0

It will be noted from FIG. 5 that each of the invention compositions containing sodium xylene sulfonate produced a curve showing an etch rate less than 1½ mils per minute at etching temperature of 110° F., and a decrease in etch rate as etch bath temperature increased from 110 to 130° F., whereas the composition D, similar to compositions A, B, and C, but not containing sodium xylene sulfonate, commenced etching at a high etch rate of almost 3 mils per minute and the etch rate increased relatively rapidly with increase in temperature to an etch rate of 4 mils per minute at 130° F.

It will be seen also that as the amount of sodium xylene sulfonate is increased from 2% in composition B to 3% in composition A, and 4% in composition C, the corresponding curve is lowered to an etch rate approaching the most desirable rate of about 1 mil per minute. See the curve for composition C containing the largest amount (4%) of sodium xylene sulfonate. That is, while at 110° to 120° F. the etch rate for compositions A to C is above 1 mil per minute, between 120° F. and 130° F. the etch rate either closely approaches or drops slightly below 1 mil per minute. Etch rates slightly below 1 mil per minute, e.g. about 0.8 mil per minute, are suitable for producing the invention results. The use of larger amounts of sodium xylene sulfonate than that employed in composition C is impractical from the economic standpoint, since the cost of such larger amounts of sodium xylene sulfonate in the bath becomes prohibitive, and the results obtained are not significantly better than those obtained using composition C.

Further, it will be observed from FIG. 5 that as the amount of sodium xylene sulfonate is increased the effect of increase of temperature from 110° to 130° F. is lessened; that is, the curve tends to flatten out so that only a relatively small decrease in etch rate occurs as temperature increases from 110° to 130° F., and the etch rate remains close to 1 during this increase in temperature. Compare, for example, the relatively flat curve for

composition C as compared to the curve for composition A or B, containing much smaller amounts of sodium xylene sulfonate.

The etched magnesium surfaces produced by compositions A, B and C were smooth with profilometer readings varying from about 40 to about 50 R.M.S. both with and across the grain, whereas the etched surface produced in etchant D not containing sodium xylene sulfonate had a rough surface of about 80 R.M.S. both with and across the grain. Further, the etched surfaces employing compositions A to C were not dished (see FIG. 4), whereas etching with composition D produced a dished surface. See FIGS. 1 and 2.

Also, it is noted that smoother surfaces were obtained using composition C than compositions B and A. Thus the flatter the curve and the closer it is to the 1 mil per minute etch rate, the most desirable are the results produced.

However, where, for example, the non-dishing advantage of the invention can be sacrificed, and it is desired that the etched magnesium surface be smooth regardless of dishing, the amount of sodium xylene sulfonate employed can be reduced below the 2% by weight of solution of composition B, down to as low as about 1.5%. See Table I. This will result in an etch rate above 1.5 when operating at temperatures between 110° and 130° F., the etch rate increasing with decrease in sodium xylene sulfonate content. While this increased etch rate may produce some dishing, the etched surface is smooth and uniform as contrasted to the rough etched surface produced in the total absence of sodium xylene sulfonate in the etchant, e.g. when employing a composition such as that of composition D.

Example 2

The following solid mixture was prepared:

TABLE IV

Material:	Parts by weight
$NaSO_4$	75.7
Citric acid	2.2
Sodium xylene sulfonate	22.1

This composition was added to water together with magnesium sulfate and 66° Baumé sulfuric acid solution, employing per gallon of solution 2 lbs. of the composition of Table IV, 0.70 lb. $MgSO_4.7H_2O$ and 2.35 lbs. 66 Baumé sulfuric acid, to form 100 gallons of the working solution having the approximate composition shown in Table V below.

TABLE V

	Percent by weight of solution
$MgSO_4.7H_2O$	6.2
Na_2SO_4	13.7
Citric acid	0.4
Sodium xylene sulfonate	4.0
Sulfuric acid—66° Baumé	20.9
Water	54.8

AZ–31B magnesium alloy panels with dimensions of 9" x 19" were etched to a depth of 215 mils in the etching solution of Table V, at operating temperature of 110 to 130° F. in a period of 185 minutes.

The etched panels had a profilometer reading of 40–40, indicating an excellent smooth surface, excellent line definition and well shaped fillets. The etched panels had a uniform depth of etch across the whole etched surface which was neither dished nor reverse dished, and the panels had an etch factor on the order of about 1.05. The etch produced is illustrated in FIG. 4, wherein the panel **30** has a gently rounded wall **31** substantially in the form of a quarter circle with the undercut A substantially equal to the depth of etch B. The bottom **32** of the etched surface is smooth and uniform, and the depth of the etch from the surface **38** to the bottom **32** of the etched depression is substantially uniform at all portions of the bottom **32**, at all angles to the section illustrated in FIG. 4, the metal having the same thickness at the center **34** of the etch and at the peripheral edge **36** thereof.

Similar etching runs were made with the following magnesium alloys: HK–31A, HM–21 and EX–61 (sand cast). Results similar to those obtained using AZ–31B alloy were obtained.

Example 3

The procedure of Example 2 is carried out except that citric acid is omitted from the composition and the amount of water is increased to 55.2%. The results obtainable are similar to those of Example 2 except that the fillets are not quite as well formed as in the etched panels of Example 2.

Example 4

Magnesium sulfate is omtted from the composition of Table V of Example 2, and the amount of water is increased to 61.0%. A procedure similar to Example 2 results in etched parts having the advantages noted in Example 2, except that the etched surfaces and walls are not as smooth as in the runs of Example 2, the profilometer reading being 50–60 R.M.S.

Example 5

When tartaric acid or malic acid is substituted for the citric acid in the composition of Example 2 substantially the same results as in Example 2 are obtainable.

In order that the invention etchants function in the most efficient manner, it is necessary that a maskant be employed which has good adhesion to the metal surface. Otherwise, release of the mask from the metal surface results, causing variable etch factor along the fillet, i.e. at the etch line along the edge of the mask, to produce a non-linear, e.g. curved or bowed line, which is undesirable. Thus, for example, the etching composition of the invention can operate efficiently using the improved maskant composition of the co-pending application Serial No. 579,717, filed April 23, 1956, of Atkins and Edds, comprising chloroprene, polymer, carbon black and a phenolic, e.g. phenol-aldehyde, resin.

As previously noted, during the period of etching, the etchant ionizes magnesium into solution, and magnesium sulfate is formed by the etching reaction. As the etching proceeds, the solution becomes loaded with magnesium sulfate to a point where the etchant is reduced in effectiveness. At this point the etch rate diminishes and the surface becomes rough. In the operation of the invention employing the compositions aforementioned, we have found that by reducing the concentration of the magnesium sulfate, preferably by removal of a portion of the bath, and adding additional composition of the invention not containing magnesium sulfate, the etching bath may thus be rejuvenated and continued to be employed as effectively as at its initial stages of use. Hence, by practicing the rejuvenation procedure, an additional feature of the invention process, the etchant composition of the invention does not reach an overloaded, inoperable condition.

Also, as etching proceeds, and as magnesium goes into solution, the sulfuric acid is consumed in forming magnesium sulfate. We have found that when the acid number (milliequivalents of sodium hydroxide necessary to neutralize 5.0 cc. of etchant to bromothymol blue endpoint) employed as a measure of acid concentration, is depleted by the chemical milling or etching of the magnesium parts, then depending on the acid number of the resulting bath, a certain proportion of the bath is discarded and a certain amount of etchant, excluding magnesium sulfate, e.g., the composition noted above in Table IV, is added to the remaining bath, together with a certain amount of sulfuric acid, as will be noted in the rejuvenation chart in Table VI below.

Where citric acid is not employed in the composition

of Table IV the percentage of sodium sulfate is increase to 77.9%.

Example 6

In Table VI below is set forth in chart form the acid number, the percentage of the original bath to be disposed of corresponding to said acid number, the amount of etchant composition of Table IV which is to be added corresponding to such acid number, and the pounds of 66° Baumé sulfuric acid to be added per 100 gallons of bath.

TABLE VI

Acid No.	Percent of Bath to be Dumped	Pounds of Etchant from Table IV to be added per 100 Gallons of Bath	Pounds of 66° Be H_2SO_4 to add per 100 Gallons of Bath
26.0	17	34.9	47
25.9	18	36.9	50
25.8	20	41.0	55
25.7	21	43.0	58
25.6	22	45.0	63
25.5	24	49.2	66
25.4	25	51.3	69
25.3	26	53.3	72
25.2	27	54.5	75
25.1	28	57.4	78
25.0	29	59.5	81
24.9	30	61.5	83
24.8	31	63.5	86
24.7	32	65.6	89
24.6	33	67.7	92
24.5	34	69.7	94
24.4	35	71.8	96
24.3	36	73.8	99
24.2	36	73.8	101
24.1	37	75.9	104
24.0	38	77.9	106
23.9	39	80.0	108
23.8	40	82.6	110
23.7	40	82.0	112
23.6	41	84.0	113
23.5	42	86.0	115

Example 7

The 100 gallons of etch bath of Example 1, were continued to be used for etching additional magnesium parts until the acid number of the bath decreased to 26.0. Etching was interrupted and following the chart of Table VI, about 17% by weight of the total bath was discarded, and to the remaining bath was added 38.6 pounds of the etchant composition of Table IV and about 47 pounds of 66° Baumé sulfuric acid. The components of the resulting bath were now within the proportions given in Tables I and II above.

The composition and process of the invention possess, in addition to other aforementioned advantages, the following advantages over conventional etchants and processes for etching magnesium: The invention composition preferably operates in a temperature range of 105–115° F., and tap water at ambient temperatures passed through cooling coils in the etching tank is sufficient for cooling. Between 105 and 115° F. etch rate diminishes, and no dishing at these elevated temperatures occurs even over large surfaces. Conventional magnesium etchants on the other hand, are operated at a lower temperature of 85° F. to 100° F., and this lower operating range requires refrigeration for cooling. At the latter operating temperatures, dishing of the etched part takes place, and at temperatures above 100° F. employing conventional etchants, the etchant produces increased dishing, uncontrolled etch rate and poor surface. With the etching composition of the invention smooth surfaces with profilometer readings of 40 to 50 are obtainable, whereas with conventional magnesium etchants, rough etched surfaces are obtained generally with profilometer readings in excess of 100. When employing the bath rejuvenation procedure of the invention, the magnesium sulfate concentration does not drastically change and the bath can be operated almost indefinitely. In conventional magnesium etching procedures the gradually increasing magnesium sulfate concentration builds up to such an extent that the etchant soon becomes uncontrollable.

While in preferred practice it is desirable to operate according to the invention in a manner to attain all of the aforementioned invention advantages, including smooth uniform surface, absence of dishing, controllable etch rate, etch factor on the order of about 1, good line definition, and well formed fillets, it will be understood that under some conditions of practice of the invention only one or more, but less than all, of the aforementioned advantages may be realized, particularly where it is not necessary that all of the advantages be attained in etching a particular magnesium part. Thus, for example, where it is desirable to produce a smoothly etched part regardless of dishing, that is, where absence of dishing is not important, the invention process employing the invention etchant can be carried out in such a manner, as previously described, that a smooth surface is attained even though the surface may be dished. Likewise, for example, where a uniform undished surface is of major importance and smoothness of surface is relatively immaterial, the principles of the invention may be applied to attain an undished surface and uniform depth of etch, the smoothness of the surface corresponding to a profilometer reading in excess of say 50.

It will be understood that for different magnesium alloys etched by a given composition and under a given set of operating conditions according to the invention, the results as to smoothness, non-dishing and other advantages obtained by practice of the invention, as noted above, will vary to some extent.

The compositions of representative illustrative magnesium alloys which can be etched according to the invention are as follows, the quantities listed being in percent, the balance of the composition in each case being magnesium: magnesium alloy AZ–31B containing 2.5–3.5 aluminum, .2 manganese, .7–1.3 zinc, .04 calcium, .3 silicon and .05 copper; the alloy HK–31A containing 2.5–4 thorium and .5–1.0 zirconium; the alloy HM–21 containing 1.5–2.5 thorium and .35–.8 manganese; and the alloy EK–41 containing .15 manganese, .30 zinc, .4–1 zirconium and 3.0–5.0 rare earths.

The term "consisting essentially of" as used in the definition of the ingredients present in the compositions claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

While we have described particular embodiments of our invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

We claim:

1. A composition of matter which when added to aqueous sulfuric acid forms an etching solution for magnesium, which consists essentially of about 45 to about 84 parts by weight of a member of the group consisting of sodium sulfate and sodium bisulfate, about 10 to about 25 parts by weight of sodium xylene sulfonate, and a hydroxy carboxylic acid of the group consisting of citric, tartaric, malic and glycollic acids, in an effective amount up to about 4 parts by weight of said composition.

2. A composition of matter which when added to aqueous sulfuric acid forms an etching solution for magnesium, which consists essentially of about 71 to about 81 parts by weight of sodium sulfate, about 16 to about 24 parts by weight of sodium xylene sulfonate, and about 2 to about 3 parts by weight of a hydroxy carboxylic acid of the group consisting of citric, tartaric, malic and glycollic acids.

3. A composition of matter which when added to aqueous sulfuric acid forms an etching solution for magnesium, which consists essentially of about 75.7% by weight

of sodium sulfate, about 2.2% by weight of citric acid and about 22.1% by weight of sodium xylene sulfonate.

4. An aqueous acid etching solution for magnesium, which consists essentially of about 10 to about 20 parts by weight of a member of the group consisting of sodium sulfate and sodium bisulfate, about 1.5 to about 6 parts by weight of sodium xylene sulfonate, and about 16 to about 23 parts by weight of sulfuric acid calculated as 66° Baumé sulfuric acid, based on 100 parts by weight of the solution.

5. A process for etching a magnesium part at an etch rate of about 0.8 to about 1.5 mils per minute to obtain a smooth etched surface, which comprises treating said part in an aqueous acid solution as defined in claim 4.

6. An aqueous acid etching solution as defined in claim 4, wherein said member is sodium sulfate, and including magnesium sulfate in an effective amount up to 12 parts by weight, calculated as $MgSO_4 \cdot 7H_2O$, and citric acid in an effective amount up to about 1 part by weight, based on 100 parts by weight of the solution.

7. A process for etching a magnesium part at an etch rate of about 0.8 to about 1.5 mils per minute to obtain a smooth etched surface having a profilometer reading of about 40 to about 50 R.M.S. with and across the grain of the metal and an etch factor of about one, which comprises treating said part in an aqueous acid solution as defined in claim 6, the temperature of said solution ranging from about 110° F. to about 130° F.

8. A composition of matter which when added to aqueous sulfuric acid forms an etching solution for magnesium, which consists essentially of about 45 to about 84 parts by weight of a member of the group consisting of sodium sulfate and sodium bisulfate, and about 10 to about 25 parts by weight of sodium xylene sulfonate.

9. A composition of matter as defined in claim 8, wherein said member is sodium sulfate.

10. A composition of matter as defined in claim 1, wherein said hydroxy carboxylic acid is citric acid.

11. A composition of matter which when added to aqueous sulfuric acid forms an etching solution for magnesium, which consists essentially of about 45 to about 84 parts by weight of a member of the group consisting of sodium sulfate and sodium bisulfate, about 10 to about 25 parts by weight of sodium xylene sulfonate, a hydroxy carboxylic acid of the group consisting of citric, tartaric, malic and glycollic acids, in an effective amount up to about 4 parts by weight of said composition, and magnesium sulfate in an effective amount up to about 35 parts, calculated as $MgSO_4 \cdot 7H_2O$, by weight of said composition.

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