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CHEMICAL MILLING OF MAGNESIUM ARTICLES

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This application is a continuation-in-part of my copending application, Serial No. 714,475, filed February 11, 1958, and now abandoned, for Chemical Milling of Magnesium Articles.

This invention relates to the chemical milling of magnesium articles. More particularly, it relates to compositions and methods for the chemical milling of such articles.

Etching by chemical means has been practiced for many generations as a tool of the artisan to produce decorative and useful designs in metals. In ancient times, works of art were etched on medieval armor and, more recently, precise applications of this method have brought modern lithography and engraving to a high state of perfection. In such applications, however, the depth of etch never exceeds about 0.06 inch.

On the other hand, within the past few years the art has commenced to focus its attention on applications involving deeper etches. This attention has been, and is being, motivated by the growing demand for stronger and lighter airframes for aircraft. Heretofore, the structural designs of airframes have been restricted by limitations imposed by conventional machine milling methods which are rather expensive and which do not lend themselves in this area to mass production techniques. Chemical methods of milling, however, do not have such limitations. Moreover, such methods hold promise of opening the door to inexpensive techniques, to mass production methods, to a reduction in the number of individual parts in an airframe and thus to the elimination of a number of riveting, welding and brazing operations.

In attempting to apply chemistry to the milling of metals, however, a number of problems have been encountered. This is especially true in the case of magnesium and magnesium alloys, which are being used more and more in airframe construction because of their lightness and strength properties.

Before mentioning the problems found in the case of magnesium and magnesium alloys, a general description of the steps involved in chemical milling should be given in order to understand the environment of this invention.

As generally developed today, the general procedure of chemical milling comprises the steps of (1) cleaning the article to be etched, (2) masking the surfaces of the article with a chemically resistant coating, (3) scribing the coating to provide the desired design and stripping the undesired maskant from the surface to be etched, (4) etching exposed surface to the desired depth and (5) finishing.

The cleaning procedure involves removal of residual oils and shop soils by an alkaline cleaner. Where heavy greases and other such soils are present, vapor degreasing with a solvent, such as trichlorethylene, prior to alkaline cleaning is performed. Included in the cleaning procedure may be deoxidizing or pre-etching steps to improve surface uniformity and maskant adhesion, since lack of adequate

maskant adhesion has been found to be a cause of abnormal etching.

The maskant functions as a barrier to the etchant media. It is applied to the article by dipping, brushing or spraying. After suitable curing, a template of the design to be milled is placed over the article and the design is scribed through the maskant. In those areas of the surface of the metallic article to be etched, the maskant is then peeled away.

The etching operation is usually performed by placing the masked article into a chemical bath of suitable composition, which bath is mechanically or preferably air agitated to facilitate temperature control, to carry away reaction by-products, and to avoid depletion of the bath at the exposed metal surface. When the desired depth of etch has been reached, as determined by periodic visual examination or by electronic means, the article is manually or automatically removed from the bath.

The finishing operation prepares the article for final inspection and use. When the etched surface comprises by-products of the reaction of certain alloys in the article with the etchant, this operation may involve the use of a chemical deoxidizer which solubilizes the by-products without altering the dimensional tolerances already established. In any event, after rinsing, the etched article is stripped of maskant either manually or by immersion in a solvent solution to destroy the maskant adhesion, the solvent type stripper being preferably used where manual stripping of fragile parts could cause distortion.

Reverting to the etching operation part of the procedure, the function of the chemical bath or etchant is to remove uniformly the exposed metal to precise dimensional tolerances. The etch rate is a function of composition of the etchant and temperature, and should generally be approximately 1.0 mil (0.001 inch) of metal per minute in order to permit holding the depth of etch to close tolerances. Excessively high etch rates produce tapering of articles on immersion and withdrawal from the bath. Where this does occur, the usual practice is to withdraw the article midway in the etch cycle, vertically rotate it 180° and then return it to the bath. Heat exchange equipment may also be used to remove heat released in the chemical reaction and thus help avoid an excessively high etch rate.

An etchant should produce a surface finish consistent with requirements for maximum fatigue strength. Superficial surface appearance is of little structural importance whereas quality of the surface texture is of primary concern. Surface texture (usually expressed as the root mean square (R.M.S.) of the surface profile, which value, usually expressed in microinches, can be determined by instruments, such as a Profileometer) is affected by the grain size and elemental composition of the metal alloy. The etchant should therefore be properly composed and controlled to compensate for the adverse effects which can result from electrochemical interaction between the etchant solution and the various components of the alloy.

Lateral etching under the maskant edge usually proceeds at approximately the same rate as the vertical etch. Thus a slot in a metallic surface cannot be chemically etched to a depth greater than the width. However, the lateral etch rate and the vertical etch rate are usually not the same, wherefore this variance must be taken into account in scribing designs on the maskant. This involves the use

of the etch factor which is defined as the ratio of lateral to vertical etch, which ideally should be 1. Etch factors must be determined for a specific etchant and operating procedure. Once these etch factors are known, however, proper steps can be taken to obtain the design to fine tolerances.

Uniformity of etch is principally the responsibility of the etchant, although outside influences, such as the heat transfer properties of the metal, occasionally exert an effect. Moreover, it has been established that the etchant should produce at the boundary between masked and unmasked areas, in cross-sectional view, two mutually perpendicular sides joined by a smooth fillet of uniform radius.

It has been found that in most cases the etchant bath should be rejuvenated regularly to maintain solution balance and to avoid excessive by-product accumulation. As a result several rejuvenation procedures have been developed, such as, for example, decanting and make-up, filtering and addition of fresh etchant, precipitation and decanting followed by make-up, and the like. In any event the bath as rejuvenated should not adversely change in its etching properties.

Further background on the art of chemical milling can be obtained from U.S. Pat. No. 2,739,047—Sanz.

It is well known in the art that strong acids, such as sulfuric acid and nitric acid, will etch the surface of magnesium metal. The chemical reaction involved is represented by the following reaction equation:

$$Mg+2H^{+}\rightarrow Mg^{++}+H_2\uparrow+heat$$

In applying this knowledge to the chemical milling of articles of magnesium and magnesium alloys (hereinafter sometimes referred to simply as magnesium) it was found to be practically impossible to remove uniformly exposed metal to precise dimensional tolerances at depths of 0.015 inch or more. A surface finish consistent with the requirements for maximum fatigue strength was difficult to obtain. Gas flow erosion patterns appeared on etched surfaces vertically positioned in the acid bath. Localized heat effects were observed, particularly along the boundary between the masked and unmasked areas of the metallic surface, whereat, because excessive heating occurred in the immediate vicinity of the boundary and thereby accelerated the reaction at that point, a relatively deep ditch resulted. Etch rate was difficult to regulate and control. Tapering of vertically disposed articles during the period of immersion in the bath occurred, which indicates that the evolving gas, flowing adjacent and parallel to the surface being etched, forms a dense, adhering, ascending gas blanket which tends to retard the rate of etch. Moreover, an obnoxious overspray occurred which made unsafe working conditions for operating personnel.

As a result of my investigations into the causes of these adverse effects I have reached certain conclusions. First, the bubbles of hydrogen gas formed by the chemical reaction at the exposed, vertical surfaces of the magnesium article in the etchant bath must be evolved slowly and perpendicularly to that surface. Secondly, after evolving from that surface, the bubbles should coalesce into large bubbles before reaching the top of the etchant bath. Thirdly, the increase in etch rate should be disproportionately small for a large increase in the etchant bath temperature.

It is therefore a general object of this invention to provide the art with a magnesium etchant for the chemical milling of magnesium articles, which avoids the adverse effects just mentioned.

More particularly, it is an object of this invention to develop a chemical composition which can dimensionally etch magnesium articles to depths greater than about 0.06 inch at the rate of at least about 1.0 mil of metal per minute while achieving a tolerance of at least ± 0.002 inch. (Machine milling tolerances are 0.010 inch.)

A particularly important object of this invention is to

provide the art with a chemical milling composition for magnesium, which has a substantially constant etch rate over a wide temperature range.

An important object of this invention is to develop a composition for the dimensional etching of magnesium, which, in aqueous solution, avoids the formation of gas flow erosion patterns on etched surfaces.

An important object of this invention is to develop a magnesium etchant bath which avoids a dense ascending and adhering blanket of finely divided gas bubbles along vertically disposed surfaces and the consequent tapering of those surfaces during the period of immersion.

Another important object is to develop an etchant bath which avoids ditching along the fillet radii adjacent to maskant boundaries.

Still another important object is the avoidance of obnoxious overspray from the etchant baths.

A specific object of this invention is to develop an acid etchant for magnesium, which causes hydrogen gas bubbles to be slowly evolved perpendicularly to exposed, vertically positioned, surfaces of magnesium articles.

Still another specific object is to provide an acid etchant for magnesium in which evolved gas bubbles coalesce into large bubbles before reaching the top surface of the etchant bath.

These and other objects which may appear as this specification proceeds are achieved by my invention.

In summary, my invention comprises an acid bath for the chemical milling of magnesium, which consists essentially of an aqueous, acid solution of about 1 to about 3 mols per liter of sulfuric acid and an auxiliary composition consisting essentially of (1) an alkali metal sulfate present in at least a critical, minimum mol concentration and (2) about 0.02 to about 0.2 mol per liter of an arylsulfonic acid conforming to the general formula $R—SO_3—M$, wherein R is a member of the group consisting of an unsubstituted aryl radical and an aryl radical substituted by one or more alkyl side chains with alkyl having up to 3 carbon atoms, and wherein M is a cation and preferably a member of the group consisting of the hydrogen, metal, ammonium and amine radicals. As examples of metal radicals there may be mentioned alkali metal radicals which are radicals of any element of the first group of the periodic system, such as lithium, sodium, potassium, rubidium and cesium, and alkali earth metal radicals which are radicals of any element of the second group of the periodic system, such as magnesium, calcium, strontium and barium.

The auxiliary composition is quite critical and represents the crux of this invention. I have found that within the critical limits of concentration specified it causes hydrogen gas bubbles to slowly evolve perpendicularly to exposed vertical surfaces of magnesium articles and then coalesce into large bubbles before reaching the top of the bath. Moreover, I have found that this auxiliary composition depresses to a substantial degree an increase in the rate of etch with an increase in bath temperature. Indeed, I have found that the auxiliary compositions of this invention exert a self-regulating effect on the etch rate in that (1) within the range of bath temperatures currently used, an increase in bath temperature causes a reduction in etch rate and (2) ditching no longer appears.

In combination with the aqueous solution of sulfuric acid, the only effects of either the alkali metal sulfate per se or the arylsulfonic acid per se appear to be a reduction in the etch rate of the bath and a reduction in the size of the evolved gas bubbles. Neither the alkali metal sulfate nor the arylsulfonic acid, in the absence of each other, appear to produce any other significant influence on the milling properties of the bath on magnesium. However, together and within critical limits of proportionate concentration, the combination of the alkali metal sulfate and the arylsulfonic acid significantly and

drastically influences the etch rate and gas evolution properties of the acid bath.

The sulfuric acid component of the bath may be furnished as such and/or may be obtained by hydrolysis in water of an alkali metal bisulfate, such as, for example, sodium bisulfate.

The range of concentration of the sulfuric acid component of the bath is based mostly on practical considerations. Below about 1 mol of sulfuric acid per liter the etch rate of the bath containing the components of this invention is too low to be commercially acceptable while above about 3 mols per liter the etch rate of the bath containing the components of this invention becomes excessive, thus giving rise to the aforementioned difficulties. Without the auxiliary composition of this invention, the etch rate of the bath with the sulfuric acid concentration in the range of 1 to 3 mols per liter is too high to be commercially practicable and the gas evolution is rapid and copious. While merely decreasing the concentration of sulfuric acid in the bath to a value less than about 1 mol per liter will decrease the etch rate to a practical level, the resultant gas evolution pattern is a dense blanket of fine gas bubbles.

The alkali metal sulfate component of the auxiliary composition may be furnished as such and/or may be obtained by hydrolysis in water of an alkali metal bisulfate. Representative of the alkali metal sulfate component are sodium sulfate (Na_2SO_4) and potassium sulfate (K_2SO_4) while representative of the alkali metal bisulfate component are sodium bisulfate ($NaHSO_4$) and potassium bisulfate ($KHSO_4$).

The minimum concentration of the alkali metal sulfate component of the bath is critical in this invention. Below a significant, threshold value, the gas released in the chemical reaction behaves as before described with solutions of sulfuric acid only. However, in the presence of the arylsulfonic acid, as soon as said significant minimum mol value is reached, there is a sharp change in the gas flow pattern and the etch rate is at a minimum. From a number of observations, I have determined that for a bath at 25°±5° C. and consisting of from about 1 to about 3 mols per liter of sulfuric acid and from about 0.02 to about 0.2 mol per liter of said arylsulfonic acid, this critical minimum value can be determined by application of the empirical equation

$$\log_e Y = 1.66 - 0.51 \log_e \left(\frac{10X}{Y}\right)$$

wherein Y is the number of mols per liter of solution of sulfuric acid and X is the number of mols per liter of solution of sodium sulfate. For baths at substantially higher temperatures and/or comprising moderate to large concentrations of other components such as citric acid and the like, the critical, minimum mol concentration of sodium sulfate may vary somewhat from the value arrived at by applying the empirical equation. However, the value derived from the equation will be sufficiently close to the true value that the equation can be used under most circumstances to determine substantially the critical minimum value for any given bath. The only upper limit on the mol concentration of sodium sulfate is one of practicality, namely, the point at which the solution becomes saturated with sodium sulfate. From the critical minimum mol value of sodium sulfate to the point of saturation the etch rate is within an acceptable range and the gas flow pattern is that desired. Beyond the point of sodium sulfate saturation there is no significant change in either etch rate or gas flow pattern. However, there is no advantage to be gained by going beyond the saturation point; indeed, it presents a disadvantage from an economic point of view.

The arylsulfonic acid component of the auxiliary composition may comprise one or more arylsulfonic acids. There are several well known types commercially available. Representative of the defined arylsulfonic acids are benzene sulfonic acid, toluene sulfonic acid, xylene sulfonic acid, p-cymene sulfonic acid and the alkali metal salts thereof, such as, for example, sodium xylene sulfonate.

The concentration of the arylsulfonic acid component should be in a range of about 0.02 to about 0.2 mol per liter. Below the minimum concentration the etch rate is too high for commercial acceptance and the surface finish of the chemically milled surface becomes too rough for commercial acceptance. Above the maximum concentration the etch rate becomes too low for commercial acceptance and, since the solubility of the specified arylsulfonic acids is quite low, too great an increase over the maximum concentration limit would increase the solids concentration of the bath to an intolerable point after being in use for awhile.

The bath of this invention may optionally comprise other compositions of benefit, without adversely affecting the synergistic properties of the auxiliary composition. Thus, the presence in small proportion (preferably in a range of about 0.003 to about 0.08 mol per liter of solution) of a hydroxycarboxylic acid, such as, for example, citric acid and tartaric acid, helps prevent smut formation on the milled surfaces of articles of magnesium alloy. Hence, the term "consisting essentially of" as used in this specification and in the claims is intended to exclude the presence of other compositions in such proportions as to interfere substantially with the properties and characteristics possessed by the compositions of this invention while to permit the presence of other compositions in such amounts as not substantially to affect said properties and characteristics adversely.

An example of the composition of an etchant bath of this invention is as follows.

COMPOSITION A

Components:	Weight percent
Sulfuric acid	15.0
Sodium sulfate	26.5
Sodium xylenesulfonate	1.5
Citric acid	0.5
Water	56.5

A bath of this composition can be used to chemically mill magnesium until the magnesium ion concentration reaches a value of about 1.4 mols per liter or, to state it another way, until the magnesium concentration reaches a value of about 0.28 pound per gallon. At this level of concentration the magnesium sulfate precipitate in the etchant tank interferes with the etching of the metal in that the etched surface of the article becomes specked with nodules. The bath can be rejuvenated, however, by removing half of the bath and replacing by a solution of the above composition.

This invention has a feature of advantage in that the chemical milling bath can be prepared merely by mixing together water and a dry composition consisting essentially of an alkali metal bisulfate and an arylsulfonic acid in solid form which usually will be chemically as a salt. Upon dissolving in water the alkali metal bisulfate hydrolyzes and forms sulfuric acid and alkali metal sulfate. A preferred range of concentrations of such a dry mixture is 99 to 90 weight percent of alkali metal bisulfate and 1 to 10 weight percent of the arylsulfonic acid. The concentration limits of the alkali metal bisulfate are dependent on the concentration limits of the arylsulfonic acid. The quantity of such a mixture added to water should be such as to give a bath having a sulfuric acid concentration in the range of about 1 to about 3 mols per liter of solution. This quantity, using at least technical grade components, is

generally in a range of about 2 to about 8 pounds per gallon of water. For mixtures comprising 99% by weight of alkali metal bisulfate, the range is about 2.2 to about 7 while for mixtures comprising 90% by weight of alkali metal bisulfate the range is about 2.4 to about 7.8.

An example of such a dry composition is as follows.

COMPOSITION B

Components:	Weight percent
Sodium bisulfate	95.5
Sodium xylenesulfonate	4.5

To make up a chemical milling bath from this composition, dissolve the composition in water in a proportion of 6 pounds of composition per gallon of water.

Other components may be included in the dry composition. An example of such a mixture is the following formulation, the components thereof being technical grade.

COMPOSITION C

Components:	Weight percent
Sodium bisulfate	95.2
Citric acid	1.6
Sodium xylenesulfonate	3.2

To make up a magnesium milling bath add 6 pounds of the composition to each gallon of water in the bath.

Another example of such a dry mixture formulation is as follows, the components thereof being technical grade, to wit—

COMPOSITION D

Components:	Weight Percent
Sodium bisulfate	94.3
Citric acid	1.0
Sodium xylenesulfonate	4.5
Ethylene glycol	0.2

The ethylene glycol in the composition is included as a dust laying agent. To make up a bath add 4.8 pounds of the composition per gallon of water.

Where it is feasible or desirable to use sulfuric acid, the bath can be prepared by mixing together the acid and water and then adding to it a dry mixture which supplies the auxiliary composition. An example of a formulation of such a dry mixture is as follows, the components being technical grade.

COMPOSITION E

Components:	Weight percent
Niter cake ($NaHSO_4$)	91.8
Sodium xylenesulfonate	4.7
Citric acid	3.3
Ethylene glycol	0.2

To make up a chemical milling bath with this composition, add to water at a rate of 3.3 pounds and 0.97 pound of 98% sulfuric acid per gallon of solution. For optimum conditions, adjust the acidity of the bath so formed by the addition of sulfuric acid or caustic soda until 26.0 milliliters of 1 N sodium hydroxide per 5.0 milliliters of the bath are required to titrate a sample of the bath to a bromthymol blue end point.

Still another example of such a dry formulation is, the components listed being technical grade:

COMPOSITION F

Components:	Weight percent
Sodium sulfate	87.5
Sodium xylenesulfonate	7.2
Citric acid	5.1
Ethylene glycol	0.2

To prepare a chemical milling bath, add to water 2.15 pounds of the composition and 2.10 pounds of 98% sulfuric acid per gallon of solution. For optimum conditions of chemical milling adjust the acidity of the bath by the addition of sulfuric acid or caustic soda so that 26.0 milliliters of 1 N sodium hydroxide per 5.0 milliliters of the bath are required to titrate a sample of the bath to a bromthymol blue end point.

Compositions E and F when used as indicated at an operating temperature of the bath in a range of 85° to 100° F., give an etch rate from 1.1 to 1.5 mils/minute, an average etch factor of 1.45, an R.M.S. surface finish of 45 to 75, depending on the alloy, and have been used to chemically mill all common wrought magnesium alloys, including FS–1, HK–31A and HM–21.

In working with the compositions of this invention I have observed that they exert a leveling effect on rough surface finishes. In other words, rough finishes can be smoothed out by immersion in the etchant. Thus, in actual production use of Composition E, all surface finishes, regardless of their original condition, tend to approach a final finish of 45 microinches. This final finish may be approached from the rougher side or the smoother side as the case may be. This leveling effect is a feature of advantage in this invention because it enables consistent finishes to be obtained regardless of the depth of etch and also because it makes possible the dimensional reduction of magnesium castings with an improvement in surface finish.

This latter point is significant because it has not been possible heretofore to chemically mill magnesium castings at practical etch rates without deterioration of the surface profile. High etch rates (5 to 10 mils per minute) in mineral acids improve the surface profile but render maintenance of tolerances and definition of patterns almost impossible to achieve. At these high etch rates, the heat exchange problem is also extreme. Consequently, chemical milling of magnesium castings has heretofore been impractical on a production scale.

On the other hand, the etchant bath of Composition E is suitable for design milling of AZ–91 and HK–31A sand castings in addition to wrought alloys. Retention or modest reduction of the R.M.S. of the original castings is obtained. Actual finishes obtained with 50% dimensional reduction have been on the order of 175 R.M.S. where the initial was 350 R.M.S. Moreover, it has been observed that the longer the article is in the bath the smoother the finish becomes up to approximately 20 mils removal at which point the RMS value gradually levels off.

Where a more substantial improvement of the surface finish of castings is desired, an etchant bath consisting of 2.9 pounds of Composition F and 2.3 pounds of 66° Baumé sulfuric acid per gallon of solution is useful. For optimum conditions, adjust the acidity of the bath so that a 5.0 milliliter sample of etchant solution will titrate to 28.5 milliliters of 1 N sodium hydroxide solution at the bromthymol blue end point.

This bath reduces surface finish to approximately 90 to 110 R.M.S. within 20 minutes when the original R.M.S. is in the 300 to 400 range. However, it is suitable for the over-all dimensional reduction of castings and wrought alloys. Design milling of sand castings and of wrought alloys in this bath is not practical.

To illustrate the critical concentrations and the synergistic effect of this invention, the following examples are presented.

Example 1

A 1-liter aqueous solution was prepared which comprised 200 grams (2 mols per liter) of sulfuric acid. No arylsulfonic acid was present. The solution was at room temperature (25° C.).

A magnesium panel was then partially immersed in the solution for a specific period of time, removed, rinsed and

the thickness of the etched portion measured. The difference in thickness between etched and unetched portions of the panel was then determined and this difference, divided by the time of immersion and also by 2 since both sides of the panel were exposed to the bath, gave the etch rate. Weighed amounts of sodium sulfate were then dissolved in the solution and the procedure repeated after each addition. The following table sets forth the etch rate and gas flow pattern observations made.

TABLE I

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
0	0	22.7	Very Fast, Large Gas Bubbles.
50	0.4	12.5	Do.
100	0.7	6.5	Medium Large Gas Bubbles.
150	1.0	5.5	Medium Gas Bubbles.
200	1.4	4.25	Do.
250	1.8	3.62	Smaller Gas Bubbles.
300	2.1	2.00	Fine Gas Bubbles.
350	2.5	1.00	Slow, Fine Gas Bubbles.
400	2.8	2.60	Do.
450	3.2	0.5	Do.
500 (sat. sol'n.)	3.5	0.35	Do.

It will be observed that one effect of the addition of sodium sulfate to the sulfuric acid bath is to decrease the etch rate of the solution. Another effect is to decrease the size of the evolved gas bubbles. In the region of practical etch rates, from the 250 grams per liter concentration of Na_2SO_4 on up to saturation, the gas evolution is in the form of a dense gas blanket while in the region of desired gas pattern, from the 250 grams per liter concentration down to zero concentration, the etch rates are too large to be commercially practical.

Example 2

A 1-liter aqueous solution corresponding to that of Example 1 in that it comprised 200 grams (2 mols per liter) of sulfuric acid but containing 20 grams (0.1 mol per liter) of sodium xylene sulfonate was prepared. The solution was at room temperature (75° F.). The same procedure set forth in Example 1 was followed and the following tabulated data and observations were obtained.

TABLE II

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
0	0	10	Very Fast, Large Gas Bubbles.
50	0.4	7	Do.
100	0.7	3.2	Fast, Small Gas Bubbles.
150	1.0	1.2	Slower, Small Gas Bubbles.
200	1.4	0.4	Do.
250	1.8	0.7	Slow, Large Gas Bubbles.
300	2.1	0.85	Do.
350	2.5	1.02	Faster, Large Gas Bubbles.

From the table it will be observed again that the effect of adding sodium sulfate is to decrease the etch rate. From a comparison of Tables I and II it will be observed that one effect of the sodium xylene sulfonate is also to decrease the etch rate. This effect appears to be cumulative. However, a comparison also shows that at a mol per liter concentration of sodium sulfate of 1.4 the etch rate reached a minimum which held within the desirable range on further additions of sodium sulfate and that thereafter a gas flow pattern change occurred. The minimum concentration of sodium sulfate derived by applying the empirical equation is about 1.3 mols per liter.

Example 3

A 1-liter aqueous solution, at about 80° F., similar to that of Example 2 except that it contained only 100 grams (1 mol per liter) of sulfuric acid, was prepared and the same procedure was followed as indicated in both Examples 1 and 2. The following tabulated data and observations were obtained.

TABLE III

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
50	0.4	3.62	Fast, Small Gas Bubbles.
100	0.7	2.75	Do.
150	1.0	0.83	Slow, Small Gas Bubbles.
200	1.4	0.50	Do.
250	1.8	0.37	Do.
300	2.1	0.15	Very Slow, Small Gas Bubbles.
350	2.5	0.08	Do.
400	2.8	0.30	Slow, Clinging Gas Bubbles.
450	3.2	0.25	Do.
500 (sat. sol'n.)	3.5	0.15	Very Slow, Clinging Gas Bubbles.

The gas flow pattern inflection was not too discernible under the conditions of measurement because of the low acidity of the solution. However the etch rate change was definitely observed. The mol per liter concentration of sodium sulfate at the minimum etch rate change appears to be 2.4. By applying the empirical equation, the mol per liter concentration is about 2.6.

Example 4

A 1-liter aqueous solution at room temperature and consisting of water, 150 grams (1.5 mols per liter) of sulfuric acid and 20 grams (0.1 mol per liter) of sodium xylene sulfonate was prepared and the same procedure as involved in Examples 1–3 was followed. The following tabulated data and observations were obtained.

TABLE IV

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
50	0.4	5.12	Medium Size and Small Bubbles.
100	0.7	3.0	Small Bubbles.
150	1.0	0.25	Slow, Small Bubbles.
200	1.4	0.32	Do.
250	1.8	0.32	Slow, Clinging, Med. Size Bubbles.
300	2.1	0.45	Very Slow, Clinging, Large Bubbles.
350	2.5	0.77	Do.
400	2.8	0.38	Do.
450 (sat. sol'n)	3.2	0.20	Slower, Large Bubbles.

It will be observed that at the point of gas flow pattern inflection the mols per liter concentration of sodium sulfate is 1.8. The minimum mols per liter concentration as determined by the empirical equation is about 1.8.

Example 5

A 1-liter aqueous solution at room temperature and consisting of water, 250 grams (2.5 mols per liter) of sulfuric acid and 20 grams (0.1 mol per liter) of sodium xylene sulfonate was prepared and the same procedure as mentioned in Examples 1–4 was followed. The following tabulated data and observations were obtained.

TABLE V

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
25	0.2	4.37	Fast, Large and Small Bubbles.
50	0.4	3.50	Fast, Larger and Small Bubbles.
75	0.5	3.01	Do.
100	0.7	2.30	Slower, Fewer Large Bubbles, More Small Bubbles.
125	0.9	1.95	Slower, Fewer Smaller Bubbles, More Large Bubbles.
150	1.0	1.02	Slow, Nearly All Large Bubbles.
175	1.2	1.30	Faster, Large Gas Bubbles.
200	1.4	1.52	Do.
225	1.6	1.65	Large Foamy Bubbles.
250	1.8	1.77	Do.
275	1.9	1.81	Do.
300	2.1	1.97	Do.
325	2.3	1.75	Slower, Large Foamy Bubbles.
350	2.5	1.55	Do.
375	2.6	1.30	Do.
400	2.8	1.10	Do.

From the table, it will be observed that at the point of minimum etch rate, which apparently coincides with the point of gas flow pattern inflection, the mols per liter concentration of sodium sulfate is 1.0. According to the empirical equation the minimum mol per liter concentration of sodium sulfate is about 1.0.

Example 6

A 1-liter aqueous solution at room temperature and comprising 300 grams (3 mols per liter) of sulfuric acid and 20 grams (0.1 mol per liter) of sodium xylene sulfonate was prepared and the same procedure as mentioned in Examples 1–5 was followed. The following tabulated data and observations were obtained.

TABLE VI

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
25	0.2	5.05	Large Bubbles.
50	0.4	3.0	Slower, Large and Small Bubbles.
75	0.5	2.08	Slower, More Small, Some Large Bubbles.
100	0.7	1.10	Slow, Large at First, Then All Small Bubbles.
125	0.9	0.57	Do.
150	1.0	0.62	Faster, Clinging, Med. Sized Bubbles.
175	1.2	0.95	Faster, Large, Clinging Bubbles.
200	1.4	1.02	Do.
225	1.6	1.12	Do.
250	1.8	1.87	Med. Size, Clinging Bubbles.
275	1.9	2.40	Faster, Larger Bubbles.
300	2.1	2.70	Do.
325	2.3	2.70	Do.
350	2.5	2.35	Do.
375	2.6	1.98	Do.
400	2.8	1.60	Do.

In the table it will be observed that at the point of minimum etch rate the gas flow pattern is just on the verge of becoming inflected. At this point the mols per liter concentration of the sodium sulfonate is 0.9. By calculation based on the empirical formula the minimum concentration of sodium sulfate is 0.9 mol per liter of solution.

From the data of Examples 2–6, from which the empirical equation was derived, it will be observed that from about the point of minimum etch rate to the saturation point for sodium sulfate, the gas flow pattern is that desired, namely, large gas bubbles evolving slowly and perpendicularly to vertically disposed surfaces of the magnesium panels.

The following example illustrates the effect of adding citric acid to the bath of this invention.

Example 7

A 1-liter aqueous solution was prepared which comprised 200 grams (2 mols per liter) of sulfuric acid, 20 grams (0.1 mol per liter) of sodium xylene sulfonate and

8.7 grams (0.05 mol per liter) of citric acid. The solution was at room temperature (25° C.). The procedure described in Example 1 was likewise followed here and the following tabulated data and observations were made.

TABLE VII

Na_2SO_4 in Soln.		Etch Rate (mils/min.)	Gas Flow Pattern
grams	mols/liter		
0	0	7.0	Dense, Fine Grain Bubbles.
50	0.4	6.5	Do.
100	0.7	4.0	Do.
150	1.0	0.75	Do.
200	1.4	0.50	Do.
250	1.8	0.25	Sharp Change—Large Gas Bubbles.
300	2.1	0.50	Do.
350	2.4	1.00	Do.
400	2.8	1.00	Do.
450	3.2	0.50	Do.

From the table it will be observed that, at the point of minimum etch rate, the gas flow pattern changed and also the mols per liter concentration of sodium sulfate is 1.8. Calculation on the basis of the empirical equation indicates that the minimum concentration of sodium sulfate for this bath should be about 1.3 mols per liter. However, within the limits of experimental error, this is regarded as being sufficiently close for a first approximation.

Example 8

A magnesium milling bath was prepared by mixing together 650 grams of sodium bisulfate, 30 grams of sodium xylenesulfonate, 10 grams of citric acid and 870 grams of water. The temperature of the bath was raised to 100° F. and the etch rate on a magnesium panel was measured as in the preceding examples. The temperature of the bath was then increased and the etch rate on a fresh magnesium panel corresponding to the first panel was measured. This procedure was repeated several times. In each case the surface finish on the etched portion of each panel was measured after removal from the bath. The following table is a compilation of the measurements made.

TABLE VIII

Bath Temperature (° F.)	Etch Rate (mils/min.)	Surface Finish (microinches)
100	1.20	40
110	1.12	40
120	0.75	50
130	0.50	57
140	0.33	50
150	0.33	55
170	0.65	85

The table shows that up to about 150° F. an increase in bath temperature causes a decrease in etch rate. Keeping in mind that heat is released by the chemical reaction involved, and that normally an increase in temperature tends to increase the rate of reaction, this showing indicates that the compositions of this invention possess a self-regulating function. Runaway reactions are therefore avoided and localized heat effects, such as occur at the fillets of the magnesium article to cause ditching, are nullified.

The table also shows that as the bath temperature increases the roughness of the surface finish also increases. This increase, however, up to 150° F., is rather minor and is overshadowed by the self-regulating function of the compositions of this invention.

The maximum bath temperature at which the self-regulating feature is present is dependent on the concentrations of the components of the bath. However, this maximum bath temperature limit is not thought to fall below 120° F. for any of the compositions of this invention and since, under present conditions, it is unlikely that bath temperatures above 120° F. will be used (pres-

ent-day maskants tend to become loose and peel off at about 120° F.), I have established, as a general, practical limitation, a maximum bath temperature of about 120° F. for the compositions of this invention.

Although not shown in the table, I have found that the self-regulating function is also present from 100° F. down to 70° F. Since it is unlikely that bath temperatures below 70° F. will be used with the compositions of this invention (because, in order to establish and maintain bath temperatures below 70° F. under operative conditions, elaborate refrigeration equipment will generally be required, which is not practical), I have established, as a general, practical limitation, a minimum bath temperature of about 70° F.

Within the range of magnesium milling bath temperatures of about 70° F. to about 120° F. the self-regulating function of the compositions of this invention is present and forms a significant and valuable aspect of this invention.

When the concentration of alkali metal sulfate is near the point of gas flow change and etch rate inflection, it has been noted that other salts such as, for example, magnesium sulfate, ammonium sulfate and ammonium nitrate, when added to the bath, will bring about the desired gas flow change and etch rate inflection. However, not more than about 10% by weight of the critical minimum concentration of sodium sulfate can be replaced by other salts; at least about 90% by weight of the critical minimum concentration of sodium sulfate must be present under the concepts of this invention.

From these and other considerations it should be realized that as this invention may be embodied in several forms without departing from the spirit or essential characteristics thereof, the embodiments described in this specification are illustrative and not restrictive, since the scope of the invention is defined by the appended claims rather than by the description preceding them, and all changes that fall within the metes and bounds of the claims or that form their functional as well as conjointly cooperative equivalents are therefore intended to be embraced by those claims.

What is claimed is:

1. An etchant bath for the chemical milling of magnesium articles, which consists essentially of an aqueous solution of 1 to 3 mols per liter of sulfuric acid; an alkali metal sulfate present in at least a critical, minimum mol concentration which corresponds substantially to the value of X in the empirical equation

$$\log_e Y = 1.66 - 0.51 \log_e \left(\frac{10X}{Y}\right)$$

wherein Y is the number of mols per liter of sulfuric acid in the bath and X is the number of mols per liter of sodium sulfate in the bath; 0.02 to 0.2 mol per liter of an arylsulfonic acid corresponding to the formula $R—SO_3—M$ wherein R is a member of the group consisting of unsubstituted aryl radicals and aryl radicals substituted by one or more alkyl side chains with each alkyl group having up to 3 carbon atoms, and wherein M is selected from the group consisting of hydrogen, metal, ammonium and amine radicals.

2. An etchant bath according to claim 1, wherein said arylsulfonic acid is sodium xylene sulfonate.

3. An etchant bath according to claim 1, wherein the temperature is in a range from about 70° F. to about 120° F.

4. An etchant bath according to claim 1, which comprises a small proportion of a hydroxycarboxylic acid.

5. An etchant bath according to claim 4 wherein said hydroxycarboxylic acid is citric acid.

6. An etchant bath for the chemical milling of magnesium articles consisting essentially of 15 weight percent of sulfuric acid, 26.5 weight percent of sodium sulfate, 1.5 weight percent of sodium xylene sulfonate, 0.5 weight percent of citric acid and 56.5 weight percent of water.

7. A composition of matter for use in aqueous solution for the chemical milling of magnesium articles, which consists essentially of 95.2 weight percent of sodium bisulfate, 3.2 weight percent of sodium xylene sulfonate and 1.6 weight percent of citric acid.

8. A composition of matter for use in aqueous solution for the chemical milling of magnesium articles, which consists of 94.3 weight percent of sodium bisulfate, 4.5 weight percent of sodium xylene sulfonate, 1.0 weight percent of citric acid and 0.2 weight percent of ethylene glycol.

9. A process for the chemical milling of magnesium articles, which comprises immersing the surface to be etched in an aqueous solution consisting essentially of 1 to 3 mols per liter of sulfuric acid; an alkali metal sulfate present in at least a critical, minimum mol concentration corresponding substantially to the value of X in the empirical equation

$$\log_e Y = 1.66 - 0.51 \log_e \left(\frac{10X}{Y}\right)$$

wherein Y is the number of mols per liter of sulfuric acid in the bath and X is the number of mols per liter of sodium sulfate in the bath; 0.02 to 0.2 mol per liter of an arylsulfonic acid conforming to the formula $R—SO_3—M$ wherein R is a member of the group consisting of unsubstituted aryl radicals and aryl radicals substituted by one or more alkyl side chains with each alkyl group having up to 3 carbon atoms, and wherein M is selected from the group consisting of hydrogen, metal, ammonium and amine radicals; and water.

10. A process according to claim 9 wherein said arylsulfonic acid is sodium xylene sulfonate.

11. A process according to claim 9 wherein the temperature of said solution is in a range from about 70° F. to about 120° F.

12. A process according to claim 9 wherein said solution comprises about 0.003 to about 0.08 mol per liter of a hydroxycarboxylic acid.

13. A process according to claim 12 wherein said hydroxycarboxylic acid is citric acid.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,031,276 April 24, 1962

Jacque L. Duvall

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, line 57, for "sulfonate" read -- sulfate --; column 12, TABLE VII, heading to columns 1 and 2 thereof, for "Na_3SO_2" read -- Na_2SO_4 --.

Signed and sealed this 18th day of September 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents