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2,869,266

METHOD FOR REMOVING METAL FROM THE SURFACE OF A METAL OBJECT

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Fig. 1.

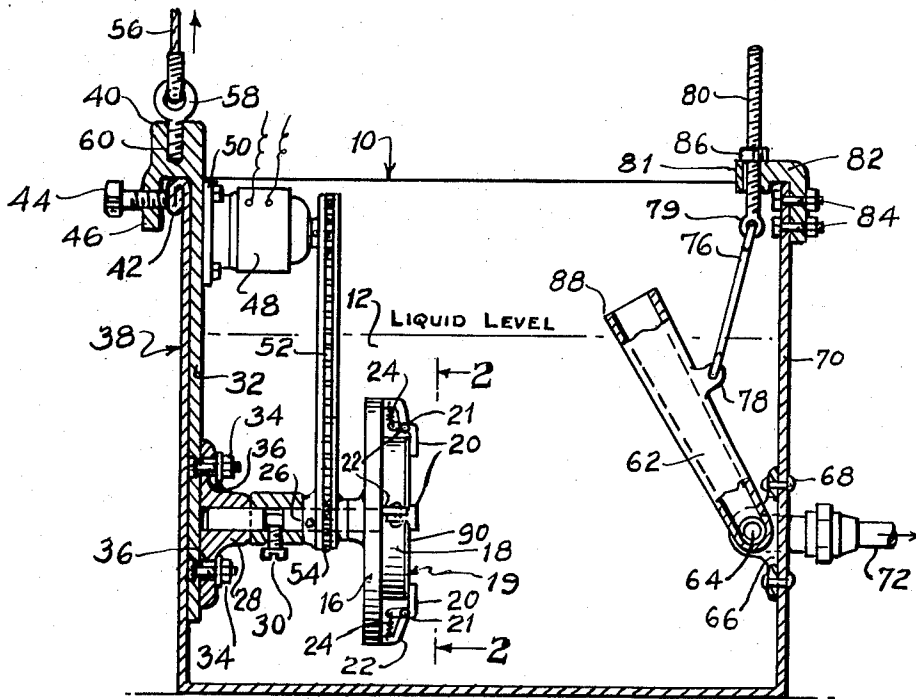


Fig. 2.

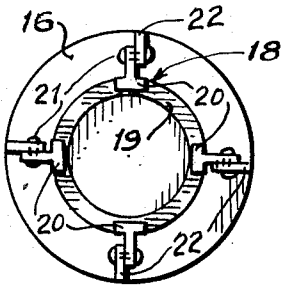


Fig. 5.

Fig. 3.

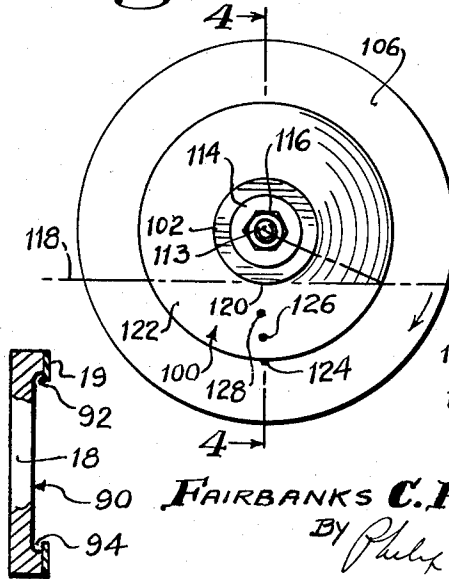
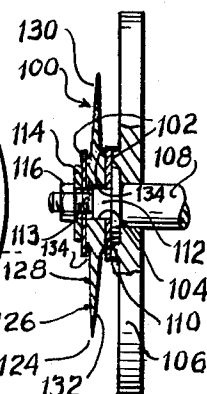


Fig. 4.



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3 Claims. (Cl. 41—42)

This invention relates to the etching or the removal of metal from the surface of a metal object, e. g., one composed of iron, nickel, magnesium, zinc, titanium, aluminum or their alloys. More particularly, the invention is concerned with novel apparatus and procedure for this purpose, especially for the treatment of aluminum and its alloys.

It is known to etch acid soluble metals such as magnesium, zinc, titanium, and their alloys with an acid solution such as aqueous nitric acid. It is also known to etch alkali soluble metals such as aluminum and its alloys with a solution having a solvent action on the aluminum or alloy surface, such as a hot aqueous alkali solution, e. g. one containing sodium hydroxide. One method of carrying out the etching process employing acids is to immerse the metal part to be etched in the etching bath, while another is to splash the solution contained in a bath against the work, the surface of which is to be etched or dissolved away. The prior art method for etching alkali soluble metals such as aluminum or its alloys is by immersion. However, the use of the conventional immersion or splash methods for etching metal parts often produces non-uniform etching, is difficult to control, and is time consuming. One of the drawbacks of such conventional procedures is the tendency of the metal dissolving or etching liquid to substantially and non-uniformly undercut the surface of the metal adjacent and beneath the edges of the mask or resist which is applied to the metal work piece in order to produce a specific etch pattern.

During the etching of aluminum or its alloys, the sodium hydroxide and certain other ingredients of the etching bath react with aluminum and aluminum alloys, forming hydrogen gas, sodium aluminate, aluminum oxide, and aluminum hydroxide. Since the hydrogen gas is much lighter than air, and considerably lighter than the etching solution, it rapidly rises to the surface of the solution. Since there is undercutting of the mask by the etching solution, there is a tendency for entrapment of some of the hydrogen gas behind the mask. This causes what is known as "gas masking."

For instance, if a part with a round doughnut-shaped mask on it were placed in the solution so that a circular hole could be etched in a piece of aluminum, there would be a tendency, if the part were placed in the vertical position, for the gas to be entrapped under the upper part of the mask whereas it would easily escape from the lower part of the mask. In this way a somewhat egg-shaped hole would be eaten into the part. If the part were placed horizontally rather than vertically, there would be a tendency for some of the gas to form all the way around with the result that the edge effect might be rough rather than smooth.

One object of this invention is to devise novel apparatus and procedure for readily dissolving or removing metal in a controllable manner from the surface of a metal object, e. g., iron, nickel, aluminum, magnesium, zinc, titanium, and the like, or their alloys.

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Another object is to provide apparatus and procedure for the controlled etching of a metal part.

Another object is to design novel apparatus and procedure particularly adapted for the uniform, controlled etching or removal of metal from the surface of a work piece composed of aluminum or its alloys.

A still further object of the invention is the provision of novel apparatus and procedure for the efficient etching or removal of metal from the surface of a metal work piece with substantially even undercutting, if any, of the surface of the metal below the edges of the mask which may be placed over the surface of the metal work piece to produce a desired etch pattern.

Yet another object is to provide novel apparatus and procedure for the efficient etching or removal of metal from the surface of an aluminum alloy work piece, by movement of an alkali solution over the work piece under conditions to prevent substantial and uneven undercutting of the metal of the work piece below and adjacent the edges of a mask placed thereon.

A still further object is the provision of apparatus and procedure for the efficient removal of metal from the surface of a metal work piece such as aluminum or an aluminum alloy using a suitable solvent solution, while maintaining any undercutting of the metal of the work piece below the edges of the mask uniform and at a minimum.

Still another object is to provide apparatus to produce a graduated amount of etching of the surface of a work piece, e. g. to form a tapered part wherein one portion of the etched part has a deeper etch than an adjacent portion.

A still further object is the provision of etching apparatus and procedure for the removal of reaction gas and precipitated solids from the surface of the work piece, especially adjacent and beneath the edges of a mask placed thereon.

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

According to the invention, gas formed by the etching reaction during etching of a metal such as magnesium, titanium, iron, nickel, or zinc, or its alloys, aluminum or its alloys, is constantly removed from the metal work piece or part undergoing treatment, so that there will be no gas masking or entrapment of gas below and behind the edges of a mask which may be placed on the work piece. To bring about such gas removal, the metal part or work piece is placed in position in the tank and suspended or immersed in the etch bath in such a manner as to permit rotation of the work piece preferably about an axis disposed at an angle to the vertical axis of the tank. Most desirably, the work piece is positioned vertically in the tank and rotated about substantially the horizontal axis of the tank. In this way, all portions of the part being etched will, at one time or another, be at the top, sides, and bottom as the part rotates around this axis. When any particular portion of the part being etched is down low so that the etch cavity is above it, the hydrogen gas will readily escape. As such portion is rotated around the axis to the higher position so that the etch cavity is below it in the tank, the gas will tend to be trapped behind the upper edge of the mask, but will be released shortly thereafter when the part is rotated to bring such upper edge of the mask to a low position, as previously indicated.

Thus, the gas normally tending to become trapped will be continuously released from the work piece by the above described rotation thereof according to the invention. This rotation need not be at any particular speed but should be fast enough so that the gas will be removed at very regular intervals. For instance, in my invention, a rotational speed of twenty or thirty revolutions per

minute should be sufficient to prevent the build-up of any material quantity of hydrogen gas behind the mask. However, the speed of rotation could be slower or faster than that above indicated, depending on the size of the part being etched, the nature of the etch pattern, etc.

By rotation of the part being etched in the manner noted above, while a certain amount of etching may take place under the edges of the mask on the surface of the work piece, there is thus prevented the highly undesirable non-uniform deep etching beneath the edges of the mask adjacent a particular portion of the work piece.

Another advantage of such rotation is that it permits the continuous circulation of solution by virtue of the movement of the part so that fresh solution will constantly reach the portions of the part adjacent the mask where used, as well as the more exposed portions of the cavity. In this way there will be produced a uniform etch across the entire surface being etched rather than deep etching in the center of such surface with a decreased amount of etching in the outer portions of the exposed surface. This circulation also minimizes or prevents the accumulation of precipitates, if such are formed in the reaction, and aids in the removal of gas bubbles from the surface or adjacent thereto over the entire etched surface as well as beneath the undercut portions thereof.

Continuous movement of the etching liquid over the surface of the metal work piece thus facilitates attack thereof by the solution in the selected, e. g. unmasked areas, of the work piece, and also has a scouring effect on such surface. Such scouring action assists in removing so-called smut, often formed on the surface of a metal work piece during etching. This is noted particularly where the work piece being processed is aluminum or an alloy thereof, in which case such scouring action also aids in the removal of any aluminum compounds such as the oxide or hydroxide which may adhere to the surface of the work piece. Smut appears on surfaces of aluminum alloys, particularly when aluminum is alloyed with elements, such as, for example, copper, iron and silicon, etc. Such aluminum alloys when etched with caustic soda, produce a film which is black and highly adherent to the surface. If desired or found necessary, a further brightening step may be employed where the residual smut not removed by the scouring action makes such procedure desirable. These smuts are soluble in HNO_3 , mixtures of HNO_3 and H_2SO_4 , and in mixtures of chromic and sulfuric acids.

The solvent solution, after making contact with the rotating work pieces, is conducted away, carrying with it the aforementioned solids and gaseous foam. By rotation of the work piece according to the invention, there will be substantially no accumulation of solids adjacent the mask, since there will be no dead air spaces behind the mask. This also promotes uniform etching and the adherence of the etch to the design requirements.

The invention will be more clearly understood by reference to the following description of a preferred embodiment taken in connection with the accompanying drawing wherein:

Fig. 1 is a cross section of the device, shown partly in full for clarity;

Fig. 2 is a view taken on line 2—2 of Fig. 1;

Fig. 3 shows a front elevation of a modification of the device of Fig. 1;

Fig. 4 is a section taken on line 4—4 of Fig. 3; and

Fig. 5 shows a section through the work piece of Fig. 1 illustrating, in an exaggerated way for purposes of clarity, even undercutting beneath the edges of the mask on the work piece.

Referring to the drawing, numeral 10 represents a tank containing a body of metal dissolving liquid 12, such as acids or alkali solutions, e. g., hot alkaline solution containing sodium hydroxide. Mounted vertically in the lower portion of the tank for rotation substantially about a horizontal axis is a turntable 16. A work piece 18 hav-

ing a mask 19 thereon, e. g., in the form of a resist, is clamped in vertical position against the turntable 16 by means of hooked clamps 20, each pivoted as at 21 on a curved arm 22 connected at one end of the turntable 16 near the outer periphery thereof. Each clamp 20 is urged into operative position, as seen in Fig. 1, by means of a tension spring 24 fastened at one end to the clamp and at the other end to the arm 22.

The turntable is mounted on a horizontal shaft 26 journaled in a bracket 28 and fixed against axial movement by means of set screw 30. Bracket 28 is mounted for vertically adjustable movement on a plate 32 by means of bolt and nut assemblies 34, the bolts passing through vertical slots 36 in the bracket 28. Plate 32 is a flat elongated member which is positioned in contact with the inner surface of a wall 38 of tank 10, and is supported thereagainst by an upper flange 40 resting on the upper lip 42 of the tank, the plate 32 being held firmly in position by means of a bolt 44 passing through a downwardly extending member 46 integrally connected to flange 40, the end of the bolt 44 frictionally engaging the outer surface of lip 42.

A motor 48 positioned on a bracket 50 suitably connected to the upper end of plate 32, drives shaft 26 for rotation of turntable 16, by means of a chain 52 meshing with a sprocket 54 on the shaft 26. Plate 32 and the entire assembly connected thereto, including the turntable 16 and motor 48, may be withdrawn from the tank 10 by a cable 56 passing through a ring 58, in turn connected through a screw 60 to flange 40, the cable being attached at its other end to a crane or other hoisting mechanism (not shown).

To adjust the level of liquid 12 in tank 10, a nozzle 62 is provided, the nozzle being pivotally supported on a hollow trunnion 64 mounted on a bracket 66 which is connected by rivets 68 to wall 70 of the tank. Hollow trunnion 64 communicating with the interior of the nozzle 62 is connected to a pipe 72 for removal of liquid from the nozzle. Nozzle 62 is supported by an arm 76 pivotally connected at one end to a bracket 78 on the outer wall of the nozzle, the other end of arm 76 being pivotally retained in a ring 79 of a vertically adjustable screw 80 received in an inwardly overhanging end 81 of a flange 82 connected to the top of the tank by means of bolts 84. A nut 86 on screw 80 can be adjusted so as to impart to nozzle 62 the desired degree of inclination thereof in order to place the outer end 88 of the nozzle at a selected position relative to the level of liquid 12 in tank 10. Contact of the nut 86 with the upper surface of flange 82 maintains the nozzle 62 in a fixed position.

In operation according to the embodiment of Fig. 1, the work piece 18 is noted to be completely immersed in the body of etching liquid 12. As the work piece is rotated on the turntable 16, all portions of the work piece will be continuously moved from a lower to a higher position in the body of etching liquid. In this manner, hydrogen gas formed in the etching reaction and which may be trapped adjacent the edge of the mask 19 and the cavity 90 being etched in the work piece when such edge of the mask is at a high position, will be discharged upwardly through the liquid as the work piece rotates sufficiently to place the aforementioned edge of the mask at a lower position. This rotating movement of the work piece also aids in removing sludge or solids formed in the reaction from crevices or places closely adjacent the edges of the mask and etched cavity 90, in that as the work piece rotates to place a portion of the mask in a high position, sludge trapped adjacent the edges of such mask portion tends to drop out of its previously lodged position into the solution. This effect is of advantage in those etching procedures employing etchants which produce by the etching reaction precipitates which deposit on the metal, and particularly in the undercut portions behind the mask, and which may thus result in uneven or

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undesirable etch patterns, as for example where alkaline agents are used to etch aluminum.

In the foregoing manner, as the work piece rotates on the turntable, a small amount of even uniform undercutting, indicated at 92 and 94 in Fig. 5, takes place beneath the inner edge of the mask.

Although the invention thus far has been described above chiefly in connection with the etching of metal plates, it is to be understood that metal parts of other shapes, including square, oblong or irregular shapes, can be etched by means of the metal part rotating concept of the invention. Thus, for example, say it is desired to reduce all the dimensions of a square or cubical part uniformly. The part, without any coating mask thereon, can be rotated in the body of etching solution 12 on a central axis parallel to the side edges of the part. In this manner all surfaces of the part will be equally etched because as the result of such rotation, fresh solution of uniform etching power will be continuously presented to all of these surfaces. Hence, there will be no chance of the building up of precipitate on the top surface of the part and of the trapping of gas adjacent the bottom surface of the part, which generally take place in conventional operation when the part is not rotated in the solution. In this respect the upward evolution of hydrogen gas formed in the reaction, and the removal of precipitate from the surfaces of the part are facilitated by my rotation procedure.

The invention principles can be utilized also to form a graduated or tapered etch, i. e., one of gradually varying thickness. According to this modification, a work piece 100 has a centrally positioned mask 102 disposed on both sides of the work piece, there being a centrally located aperture 104 through the work piece and masks 102. The work piece 100 is vertically positioned on a vertically disposed turntable 106 located in an etching tank (not shown). Turntable 106 is drivingly rotated by a centrally positioned shaft 108 having a collar 110. A reduced portion 112 at the end of the shaft 108 has a screw 113 connected thereto, and portion 112 and such screw are received in aperture 104 of the work piece, which is secured to the turntable by a clamp 114 held in position by a nut 116 threadably engaging screw 113.

The turntable 106 and work piece 100 thereon are positioned in the etch tank so that the liquid etchant level 118 is below shaft 108 and is approximately tangent to the lower-most peripheral edge 120 of the masks 102, as seen in Figs. 3 and 4. It is thus seen that as the work piece 100 rotates, only the lower portion 122 thereof is at any time immersed in the etchant fluid. Further, it is noted that a point 124 on the outer periphery of such portion 122 remains in the body of solution longer than any other point, e. g. 126, on the surface of the lower portion 122, since point 124 travels through an arc of greater radius than any other such point. Also, for the same reason, point 126, which is closer to the outer periphery of the work piece 100 than point 128 on the surface of lower portion 122, remains in the body of etchant solution longer than point 128.

Hence, as work piece 100 rotates, the solution etches the surface of the work piece unevenly, the depth of etch on the opposite surfaces of such metal part graduating from a maximum at the outer periphery of the part to a minimum about the inner periphery of the work piece adjacent the outer edges of the masks 102, as clearly indicated in Fig. 4. Thus, for example, when the work piece is etched on both sides, the cross section of the etched portion of the work piece will be wedge shaped, as seen in Fig. 4, and tapering in the direction of the outer periphery of the part. The work piece 100 will also be shortened radially due to the etching action of the solution along the outer peripheral edges of the work piece. The etched surfaces 130 and 132 thus obtained on opposite sides of work piece 100 are of uniform taper, and a minimum amount of even undercut-

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ting 134 is produced in the metal part adjacent the outer edges of masks 102 and the etched surfaces 130 and 132. It is noted in this embodiment that any hydrogen gas trapped adjacent the edges of the masks 102, will be removed on rotation of the immersed portion 122 of the work piece to its uppermost position out of the solution, and that sludge tending to lodge adjacent the masks will be removed during rotation of the work piece.

The above procedure for producing tapered plates may be applied to circular, square, rectangular, etc., parts as long as they are symmetrical with the axis of rotation. For example, a square billet could be turned on its longitudinal axis to round off the sharp edges as well as to produce other effects with or without masking. During rotation of the part, the exposed portion thereof, i. e., above the surface of the bath, may be sprayed with water, so that the residual chemical thereon will not continue to etch that portion of the part which is at any time disposed above the solution level.

If desired, the masks 102 may be omitted, since the surfaces of the work piece 100 covered thereby are above the liquid level 118 and hence are free from contact with the main body of etching solution. However, the masks protect the surfaces of the plate 100 which are not to be etched from any etching liquid which may be splashed thereagainst during rotation of the plate in the bath, or as result of turbulence of the liquid surface.

If desired, the work piece first may be etched for a period to produce an etch pattern of varying thickness employing the principles of Figs. 3 and 4, and thereafter the work piece may be completely immersed with uniform etching then carried out according to the technique illustrated in Fig. 1. Also, if desired, this combination of etching procedures may be reversed, with the work piece first subjected to etching according to the principles of Fig. 1, and thereafter treated to produce an etch pattern of graduated depth according to the technique of Figs. 3 and 4.

While in the preferred embodiments, the work piece is shown as mounted vertically in the tank and rotated on a horizontal axis, the work piece may be inclined at an angle to the vertical and rotated on an axis inclined to the horizontal, so long as successive portions of the work piece move continuously from a lower to a higher position in the body of etching solution according to the invention principles. Thus, for example, if desired, work pieces 18 and 100 can be mounted at a 30° angle to the vertical, and rotated on an axis of about 30° to the horizontal, while still realizing the benefits of the invention as regards obtaining even etching, with removal of gas and, especially where employing aluminum or its alloys as the work piece, any solids formed in the reaction from adjacent and beneath the mask or masks on the work piece. Further, even where the work piece is mounted substantially horizontally in the tank and is rotated on an essentially vertical axis, movement of the work piece with respect to the etchant bath, will tend more or less to dislodge gas and sludge trapped adjacent the edges of the mask, and where no undercutting beneath a mask is involved, centrifugal force resulting from such rotary movement will tend to remove gas and sludge from the work piece, and the benefits of the invention will be realized to some degree. However, the latter modification is not as efficient and does not produce as good results as in the preferred embodiments wherein the work piece is mounted either vertically or at an acute angle to the horizontal in the etched tank.

Where the work piece is aluminum or an alloy thereof and the tanks are heated by coils, the precipitate of aluminum hydroxide and/or aluminum oxides in the solvent or etching bath resulting from the etching reaction forms deposits on such coils and also on the surface of the etching tank. In order to prevent or reduce the formation of hard adherent scale, there may be added to the

alkaline etching solution agents which keep the precipitate flocculent.

If it is desired to remove precipitated solids continuously from the etch tank 10 without resorting to periodic shutdowns for removal of such sludge, the procedure and equipment disclosed in applications Serial No. 449,994 of Emmette R. Holman, filed August 16, 1954, may be employed.

According to the preferred embodiment of the invention for etching or removing metal from an aluminum or aluminum alloy material, which is alkali soluble, a hot aqueous solution is generally employed containing an alkali such as sodium or potassium hydroxide, trisodium phosphate, soda ash or the like, or mixtures thereof. Preferably a sodium hydroxide solution is used. Temperature is generally maintained in a range say from 100° F. to about boiling during treatment, although lower temperatures may be used. Generally, the alkali concentration employed in such solutions range from 0.1 to 10 normal.

While the invention has been described particularly in connection with the etching of aluminum or an alloy thereof by means of alkali solution, it is of course understood that acid soluble metals such as magnesium, iron, nickel, titanium and zinc can also be effectively etched by the apparatus and procedure described herein, employing acid etchants such as aqueous nitric acid, aqueous hydrofluoric acid, or mixtures thereof depending on the nature of the metal. Further, it is noted that aluminum may also be etched by means of an acid etching solution such as hydrochloric acid or by means of solutions of salts such as ferric sulfate.

Of course it will be understood that the apparatus described herein should be constructed of materials which are substantially inert to attack by the etchant solutions employed, and those skilled in this art will know how to select such materials.

While I have described a particular embodiment of my invention for the purposes 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.

I claim:

1. A process of etching a surface of a metal work piece with a metal dissolving solution, comprising masking a portion of said surface with a resist substantially less soluble in said solution than said metal, and dissolving metal from the unmasked portion of said surface and substantially uniformly undercutting the periphery of said resist, by completely immersing said surface in said solution and continuously rotating said surface immersed in said solution in a plane at a substantial angle to the horizontal and on an axis transverse to said surface, to prevent the entrapment under the resist of gases liberated by the action of said solution on the metal work piece surface.

2. A process as set forth in claim 1, wherein said plane is substantially vertical.

3. A process as set forth in claim 2, wherein said axis is substantially horizontal.

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