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2,885,273

METHOD OF ETCHING METALLIC MATERIALS

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The present invention relates broadly to the art of chemical milling or etching of metals, and is more particularly concerned with a new and improved process of preparing the metal surfaces for the etching operation.

In the copending patent application of Manuel C. Sanz, Serial No. 389,289, filed October 30, 1953, now identified as Patent No. 2,739,047, issued March 20, 1956, which is assigned to the assignee of the present application, there is disclosed a method of chemical milling or etching a structural shape. As is set forth therein, said method includes the steps of forming the sheet or skin to the desired configuration, masking predetermined areas of the sheet, and chemically milling the unmasked areas of the sheet to a desired depth whereby the masked areas are unaffected by the milling and act as stiffeners or reinforcement sections for the formed sheet.

In the practice of the foregoing method it has been found preferable to employ a caustic etchant in solution at about 190° F., and that the masking be accomplished generally by use of a taping method which includes the steps of masking the areas to be etched with paper backed tape, applying a plurality of coats of modified neoprene paint to the unmasked area, baking the part for about two hours to cure said paint, and removing the paper maskant. After application of a special lead or polyethylene-backed tape to the marginal edges of the part, etching is accomplished in the caustic solution.

While utilization of the caustic or alkaline etch process set forth in the Sanz Patent 2,739,047 has been productive of considerable success in the milling of a wide variety of parts, there has been encountered in some areas a problem in the disposal of the waste material resulting from use of caustic etchant. To explain, in the chemical milling of aluminum and aluminum alloys with sodium hydroxide, there is formed a product believed to be essentially sodium aluminate. And since flushing this material into a city sewerage system is not entirely advisable, and in some areas is statutorily prohibited, the conventional method of disposal is by dumping some distance out in a large body of water, such as an ocean. However, as can be appreciated, such a method of disposal is not entirely feasible at inland localities and its practice is accordingly associated with considerable expense.

Further, since the temperature of the caustic etching solution must of necessity be relatively high, normally not more than five degrees above or below 190° F., it is apparent that the maskant itself must be capable of withstanding such temperatures. As a result, the masking material is somewhat costly, and its method of application time-consuming.

It is accordingly a primary aim of the present invention to substantially overcome the foregoing problems by the provision of a novel masking method particularly well adapted for use with an acid-etching process.

Another object of the invention is to provide a maskant for use on metal surfaces during the chemical milling thereof, said maskant being relatively low in cost, sim-

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ple to apply and remove, and which is productive of improved results.

Another object of this invention lies in the provision of a novel method of reducing the thickness of predetermined areas of metal parts, which includes the steps of cleaning and deoxidizing the part, treating said part with a chromate conversion coating, applying to the part a strippable protective maskant resistant to acid etchant, removing portions of said maskant from the areas to be etched, and exposing the part to an acid etchant to reduce the thickness of the unmasked areas.

Other objects and advantages will become more apparent in the light of the description which follows.

As is stated in the noted patent application of Manuel C. Sanz, chemical milling or etching is employed primarily as a weight saving device by removing certain areas of aircraft wing skins and the like to thereby produce integral stiffening members adjacent the etched areas of relatively lesser mechanical stress. Chemical milling is thus designed to replace in part the relatively expensive and time-consuming machine milling, and in addition, is capable of performing many tasks not feasible or considered possible for normal machine milling.

To explain, chemical etching may be performed after the forming operation, whereas machining is generally limited to slightly contoured parts, and forming after machining is difficult. Further, chemical milling is not limited by machining restrictions with respect to the shape of the part, direction of cut, or limiting radius of cutters. Complex shapes, broad or narrow cuts, and comparatively sharp corners are possible in a single operation. And with chemical etching, metal may be removed on both surfaces of the sheet at the same time, if desired. In addition, etching with chemicals does not require highly skilled operators, may be performed with conventional equipment, and permits a number of parts to be treated at the same time.

And even further advantages are obtainable by practice of the present invention, the steps of which will now be set forth in brief, reference being made hereinafter to the specific details of each step.

The part to be etched, which may be aluminum, aluminum alloys, magnesium, and other like metals, is preferably first degreased, cleaned and deoxidized, after which a suitable chromate conversion coat is applied thereto. A strippable plastic protective coating may then be applied to a predetermined thickness, the areas to be etched are preferably then scribed by means such as a heated stylus, the plastic coating removed from said areas to be etched, the part located in an acid milling bath, and upon completion of the etching operation, the coating then removed from the areas not etched.

With specific reference now to each of the preferred steps in applicants' method, the part to be etched may first be degreased by exposure to vapors of a solvent such as trichlorethylene, perchlorethylene or the like. This may be accomplished in a manner well-known in the art, as for example, by use of a tank containing along its bottom portion a quantity of solvent heated to a temperature sufficient to cause vaporization, the vapors being substantially confined within said tank and caused to pass over the parts therein by use of a coolant circulated in pipes carried by the tank side walls adjacent the upper portion thereof. Normally it is sufficient that the parts remain in the degreasing tank for between two and five minutes, and during said period there is normally adequate condensation of the solvent on said parts to substantially entirely remove any oily films, finger marks, and the like therefrom.

The parts may then be caused to pass through a cleaning and rinsing step, and one cleaning procedure found quite suitable to date includes the use of a mild alkaline

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inhibited cleaner dissolved in water which is preferably heated to a relatively high temperature. A particularly effective cleaner is that identified to the trade as "Miller's Arrow Speed," produced by Miller Chemical Co. of Columbus, Ohio, and understood to comprise sodium hydroxide buffered to a pH of about 12 with sodium carbonates and sodium silicates.

A solution of a cleaner of the foregoing type, adequate to remove from the parts mill markings, dirt and other foreign material, may be prepared by dissolving approximately seven ounces of cleaner in about one gallon of tap water. A predetermined quantity of the solution may be located in the desired cleaning tank, and with the temperature of said solution maintained in the neighborhood of 175° F., the parts to be cleaned may be immersed therein. For the average application, as when cleaning aluminum and aluminum alloys, five to ten minutes immersion of the part in the cleaning solution has been found adequate.

It is desirable that excess alkaline cleaning solution be entirely removed from the part, and accordingly, the part is thereafter rinsed to a water-break free surface. A preferred manner of achieving this result is to dip the part for 2-5 minutes in a tank containing tap water heated to between 110 and 180 degrees F., or in the alternative, by a water spray heated to substantially the same temperature.

Following the rinse step it is advantageous that aluminum oxides on the surfaces of the part be removed, and this may be accomplished by the use of a deoxidizing bath, spray or the like. A bath is preferred by reason of the uniformly accurate results to date, and an effective deoxidizing solution for use therein may be prepared by dissolving 12-14 ounces of a compound identified by the Diversey Corp. of Chicago as "Diversey 514 Etch," and which consists of a mixture of sodium acid sulfate and sodium bichromate salts provided with a slight (2% to 4%) addition of fluosilicate salt, in a gallon of water. This material, by a mild etching action, serves to prepare the surface for the subsequent steps in the present process.

It has been found that eight to twelve minutes immersion time in the deoxidizing solution is normally sufficient, and following said step, the part should again be rinsed to a water-break free surface. This may be accomplished in substantially the same manner as the earlier described rinse, employing if desired a constant overflow-spray of room temperature tap water for a period of two to five minutes.

It is thereafter of considerable importance, in order to assure good adhesion of the strippable coating, that there be applied to the cleaned and deoxidized surface a chemical conversion coating of suitable composition. A number of such protective films are adaptable to the present purposes, and among those which have produced effective results to date is a material marketed by American Chemical Paint Co. of Ambler, Pa., under the label "Alodine 1200," which is essentially comprised of a mixture of salts, and which is productive of phosphate, dichromate, and fluoride ions when put into solution. This conversion coating chemical typically includes the salts of chromium trioxide, sodium (or potassium) phosphate, sodium (or potassium) fluoride, and sodium (or potassium) nitrate.

Such conversion coating chemical has to date provided the more superior coating, and although applicants are not presently aware of its specific chemical composition, it is understood to be of the character disclosed in Patents Nos. 2,438,877, 2,494,910 and 2,516,685, and thus to comprise phosphate, dichromate and fluoride ions, and certain non-ionic wetting agents. When prepared and applied in the manner herein described, a solution of Alodine 1200 provides essentially an amorphous mixed metallic oxide coating which is dense, rather hard, and apparently non-porous. As used in the present process prior to the strippable coating, the Alodine material becomes an integral part of the metal surface and provides a continuous bond between said surface and the strip-

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pable coating which is believed equal to or superior to anodizing.

One explanation for the successful action of the chromate films would appear to be that the aluminum being treated dissolves in the solution and reduces some of the hexavalent chromium to the trivalent state. As this dissolving action takes place, the pH of the solution at the metal-solution interface is raised to the point at which trivalent chromium precipitates in the form of a gel. Apparently combined in the gel are varying amounts of the hexavalent chromium and compounds of aluminum. As would be expected, the exact nature of the precipitate is governed by the pH of the conversion solution, the nature of the catalyst radicals, and the ratio of their concentration to that of the chromium compounds. Since the chromate conversion solutions are not easily wet by water, and they have a non-porous structure, they keep corrosive media from contact with the base metal.

The Alodine compound may be applied in solution form either by spraying, immersion, or brush-on procedure, it being apparent that the concentration of the solution will vary with the particular method employed. Thus, it has been found that approximately three ounces of Alodine 1200 to a gallon of tap water is preferable for the immersion method, while should the brush-on procedure be used, an effective solution is best made from 3 ounces of Alodine 1200 to one gallon of water acidulated with 0.5 ounce (15-20 ml.) of nitric acid. In either case solution temperature is preferably maintained at 85° F., plus or minus 15 degrees. Generally speaking, with either method of application an adequately protective coating is accomplished in from three to five minutes; however, by the brush-on process, it may upon occasion be found that a slightly longer time is required to produce a coating of the desired thickness, which is indicated by a relatively deep tan color.

Following application of either of the noted chromate conversion coatings, it is desirable that the filmed part be rinsed by dipping or spraying for ½ to 1 minute in room temperature tap water. The part is then dried, any suitable means being employed, such as a hot air oven or air blast, the temperature of which is not substantially in excess of 180° F.

Upon completion of the metal pretreatment as above described, there is applied to the entirety of the part to be etched a strippable protective plastic coating. A number of various materials may be found suitable, and in this regard, the coating agent should be desirably characterized by ready strippability without the use of vigorous chemical agents, ability to withstand the heat and concentration of the etchant, relatively low cost, and ease of application. Several compounds are possessive of these properties, and among those to be mentioned are certain of the vinyls, cellulose acetate butyrate, polyethylene and the like. To date the vinyls have been found most effective, and one compound particularly well adapted as a maskant is that identified as "Delco X-1000," produced and marketed by Delco Chemical Products Co. of Los Angeles, California. While variations may of course be practiced in the composition of the strippable material employed, Delco X-1000 is understood to consist essentially of approximately 80% by weight of methyl isobutyl ketone and methyl ethyl ketone, 18.4% polyvinyl chloride polymer, and 1.6% cellulose acetate butyrate.

A strippable coating of a compound characterized as above is preferably formed by spraying and adequate acid resistance can normally be accomplished by applying two homogeneous wet cross coats to opposite surfaces of the part to be etched. This will provide a coating approximately two mils in thickness; however, where additional protection appears necessary, a third coating of the vinyl material may be applied to a thickness of about one mil after the preceding coats have dried, or said preceding coats may be covered with a film of acid resistant black

lacquer or paint of the general type sold by Andrew H. Brown Co. of Laurel, Md.

Subsequent to coating opposite surfaces of the part with the strippable film, there is located upon said part a template of predetermined configuration provided with open areas corresponding to those portions of the part which it is desired to chemically etch. Thus, a typical template may present in plan the appearance of lattice work, the connecting members representing those portions of the part which will be unaffected by the etchant, and the windows or open areas therebetween ultimately being subjected to chemical milling and consequently reduced in cross-sectional thickness. Utilizing a template of this general type, an outline of the areas to be etched is scribed along the inner marginal edges of the longitudinally and/or transversely extending members by means of a sharp tool such as a heated stylus, the latter being preferred because of its effective sealing action along the cut edges of the strippable coating or maskant. Thereafter, the template is removed, and those portions of the coating which lie in superimposed relation to the areas to be etched are removed by a relatively simple manual peeling operation. There is thus exposed the unmasked areas of the part to be etched.

The part is now in condition for the acid etching operation, and this may be accomplished by lowering the prepared part into a suitable tank containing (for aluminum and aluminum alloys) hydrochloric acid at the preferred concentrations and temperatures to be noted. Optimum etching results have been obtained upon known aluminum alloy materials when the etching proceeds at a rate approximately 0.001 inch per minute. Accordingly, the temperature and concentration of the etchant are calculated to produce this rate upon the alloy being milled. Thus, utilizing 2.2 to 2.4 normal HCl at a temperature of $85 \pm 2^\circ$ F. will normally etch 75S aluminum alloy at the desired rate, while substantially the same etch rate may be accomplished on 24S and 61S aluminum alloys with 2.8 to 3.0 N HCl at $115 \pm 2^\circ$ F. However, if desired, the concentrations and/or temperatures can be varied to meet particular conditions. As for example, a 2.8 to 3.0 N HCl solution may be used at about 75° F. to etch 75S alloy. In addition, as will be appreciated, additions of aqueous or anhydrous HCl to the bath will necessarily have to be made to restore the concentration to the desired level, and this may generally be calculated upon the basis of one gallon 20° Baumé HCl for each 0.75 pound of aluminum removed, or approximately four pounds of anhydrous HCl for each pound of aluminum removed.

It can of course be calculated as to the time required to reduce the cross-sectional thickness of a particular metallic material to a certain point, and upon completion of this period, the thickness may be measured by means known to the art. Thereafter, when it is determined that the desired depth of etch has been reached, the part is removed from the acid bath, and subjected to a suitable post treatment to substantially remove the acidic smut which is formed during etching.

The post treatment may comprise first immersing the etched part in a relatively strong alkaline solution, one compound which has been found effective being sodium hydroxide provided with additives of a wetting agent and a sodium gluconate anti-caking agent, also identified as "Etchalume 14" by its manufacturer, Enthone, Inc., of New Haven, Conn. Essentially, this material has a high caustic content, and a suitable solution of this etch cleaner may be formed by dissolving 6 ounces in about a gallon of water. Conversion of the smut formation from an acid to alkaline condition may normally be obtained by immersing said part in the prepared solution for approximately three minutes, with the temperature of said solution maintained around $165 \pm 5^\circ$ F.

Thereafter the part may be suitably rinsed to remove substantially all the Etchalume solution, and a one or

two minute tap water rinse or dip is normally adequate for thorough flushing. Removal of the alkaline smut formation may then be effected by immersing the part in 1:1 nitric acid bath for as long as required. After again thoroughly rinsing the part, the remainder of the plastic film may be removed. If it is desired that the conversion coating be removed, the part is again dipped in the Etchalume bath for about twenty seconds, rinsed, immersed in the nitric acid bath, and finally rinsed.

Final trim and any necessary drilling may then be accomplished.

It may thus be seen from the foregoing that there is provided a process of chemical milling or etching metallic parts which is simple to perform, productive of accurate results, and capable of effecting substantial economies over present processes. Thus, the pretreatment steps may be performed with conventional equipment by workmen of moderate skills, utilizing materials of relatively low cost. And insofar as the etching step itself is concerned, there exists no substantial waste disposal problem since the acid solution may be reclaimed, and the aluminum chloride by-product effectively recovered and made available to a commercial market. Further, the process may be effectively employed to taper or step etch, within the meaning well-known to the art. In addition, regarding the process in its entirety, changes may readily be effected therein to make it adaptable to other metals, such as titanium, stainless steel, and the like.

It will be appreciated that changes may be made in the compositions and procedures herein disclosed without departing from the spirit of the invention as defined in the subjoined claims.

We claim:

1. In a method of acid etching excess material from demasked surface portions of an aluminum part to provide that part with an etched area having a well-defined edge portion, the masking steps of: forming an amorphous, mixed metallic oxide surface coating integral with said aluminum part, forming a mask on said aluminum part by providing a continuous, strippable, acid-resistant organic coating in adhering relation to said oxide coating, and subsequently stripping an edge-defined portion of said mask therefrom, said amorphous, mixed metallic oxide surface coating being formed by time-extended contact between pre-cleaned deoxidized surface portions of said aluminum part and a solution containing dichromate, phosphate, and fluoride ions and combining with said organic coating to establish said well-defined edge portion during acid etching of said part.

2. A method of chemically milling excess material from an aluminum-like part by exposure of masked and unmasked portions thereof to a solution containing an acid etchant to provide that part with an etched area having a sharply-defined edge portion, and which includes the masking procedure of: forming an amorphous, mixed metallic oxide surface coating integral with said aluminum part, forming a mask on said aluminum part by setting a strippable organic film which is chemically impermeable to said acid etchant solution in adhering relation to said oxide coating, and subsequently manually lifting an edge-defined portion of said organic film from adhering relation to said coating, said amorphous, mixed metallic oxide surface coating being formed by time-extended contact between pre-cleaned deoxidized surface portions of said aluminum part and a solution containing dichromate ions and combining with portions of said organic film to establish said sharply-defined edge portion during exposure of masked and unmasked portions of said part to a solution containing said acid etchant.

3. The method defined in claim 2 wherein the organic film is comprised of a vinyl based material.

4. The method defined in claim 3 wherein the vinyl based material is comprised substantially of polyvinyl chloride polymer.

5. The method of etching smooth, sharply-defined edges

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in a surface of a metal part comprised substantially of aluminum by exposing masked and de-masked surface portions thereof to a hydrochloric acid solution and which includes the masking steps of: forming an amorphous, mixed metallic oxide surface coating integral with said metal part, forming a thin, vinyl based mask on said part in adhering relation to said mixed metallic oxide coating, and subsequently manually lifting an edge-defined portion of said vinyl based mask from adhering relation with said mixed metallic oxide surface coating and from abutting relation with other portions of said vinyl based mask, said mixed metallic oxide surface coating being formed by time-extended contact between pre-cleaned deoxidized surface portions of said metal part and a solution containing dichromate, phosphate, and fluoride

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ions and combining an unlifted portion of said vinyl-based mask to provide said smooth, sharply-defined edges in said aluminum part when etched in the hydrochloric acid solution.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,885,273

May 5, 1959

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

Column 6, lines 56, 57 and 65, claim 2, strike out "aluminum", each occurrence.

Signed and sealed this 22nd day of December 1959.

(SEAL)

Attest:

KARL H. AXLINE
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Commissioner of Patents