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ETCHING OF DESIGNS AND LETTERING ON METALS

The etching of designs on metals is the subject of frequent inquiries. As an aid in replying to such inquiries, this letter circular has been prepared from the information available in the literature. Most of the formulas and methods described in this circular have been tested here and found to yield satisfactory results, although no extensive experience is involved.

For uniformity the formulas of solutions prepared by dissolving a dry salt in a liquid have been expressed in terms of grams per liter (g/l) and of avoirdupois ounces per gallon (oz/gal) of the resultant solution, while the formulas of solutions prepared from a mixture of liquids have been expressed in terms of milliliters (often called cubic centimeters) per liter (ml/l) and of fluid ounces (1/16 pint) per gal (fl oz/gal). Unless otherwise stated aqueous solutions are referred to, that is, the substances are dissolved in sufficient water to produce the specified final volume. Owing to incomplete data on the densities of the solutions, the conversions from the published formulas may not be strictly accurate. It is believed, however, that they represent closely the desired compositions, which in all cases are subject to modification to meet particular conditions.

The etching of designs on metals is usually accomplished in three steps, namely, (a) application of a protective coating, (b) cutting the design through the coating, (c) etching the design. In the first step, the metal is coated with a thin layer of a substance known as a "resist", so called because it is resistant to the action of the etching solution. It should also have the property of adhering firmly to the metal so as to confine the etching action to the desired areas or lines, and should respond to the cutting tool readily without being disturbed adjacent to the cut.

The second step in the process is the cutting of the design. This may be done either mechanically or chemically, provided the resist is completely removed from the areas which it is desired to etch.

The final step is the etching with a solution that will dissolve the metal. Usually acids are used, although acid salts, neutral salts of a more noble metal than that being etched, or even alkaline solutions, may be used for certain metals or alloys.

The particular process to be used for a specific purpose depends on a number of factors, such as the nature of the metal to be etched, the number of pieces to be etched with the same design, the complexity of the design, and the desired sharpness of the etched lines.

Preliminary steps in the etching process

The surface to be etched should be smooth and free from scratches. It should also be clean so as not to interfere with the uniform etching of the materials. Alkali cleaners or organic solvents are generally used to remove grease from the metal pieces.

Application of resist and cutting the design

Since the application of the resist and the cutting of the design are to a large extent interdependent, they will be discussed together.

Waxes such as paraffin, ceresin, beeswax and ozokerite, are often used as resists (1)*. They may be used either singly, or blended together in mixtures. For example, a mixture of 3 parts of paraffin and 1 part of beeswax has been found very suitable. The melted wax is applied to the surface to be etched, by dipping, brushing or flowing. When the wax is solidified, the design may be cut through it with a sharp tool by hand or by means of a pantograph. (2, 16) Some pantograph devices are constructed so that a number of tools can be operated simultaneously, with considerable saving in time.

* The numbers refer to references in the bibliography, page 3.

In another method (4, 5), the metal surface is coated with a solution of gum guaiacum in alcohol. After the coating has dried, the pattern to be etched is stamped on the surface by means of a rubber stamp wet with a concentrated solution of sodium hydroxide (for example, 300 g/l or 40 oz/gal). The alkali causes the gum to become soluble in water so that when the surface is washed the bare metal is exposed. This washing should be done quickly with a large quantity of water, so that the alkali will not spread over the surface and dissolve the resist from areas it is desired to protect.

A third pretreatment (6, 7) consists in rolling a thin film of ink on the surface to be etched. The type of ink is designated in German publications as "Umdruckfarbe" ("transfer ink", free translation). Investigation of various ink compositions has not been made here. The following mixture(21), however, gave satisfactory results in our tests.

Printer's ink,	10	parts by weight
India ink,	10	" " "
Castile soap,	4	" " "
beeswax,	4	" " "
Animal fat,	2	" " "
Rosin,	1	" " "

The components of this mixture are blended by heating and rubbing to produce a smooth paste.

The ink film, after being applied to the surface, is dusted with finely powdered asphalt, and the two are blended together by gentle heating. If

powdered asphalt is not available, powdered rosin, although less satisfactory, may be substituted for it. If distortion of the metal article by heating is feared, the blending may be done by suspending the treated article for a few seconds in the vapor of alcohol or trichloroethylene.

The cutting of the design is readily carried out in the following manner:- The assembled letters or characters in the form of steel stencils are clamped in a suitable holder. A sheet of tissue paper or fine sandpaper, such as 00, is placed on top of the resist coating and the design is impressed therein with light pressure, such as can be obtained with a small press. On releasing the pressure, the resist adheres to the paper and the desired design is exposed as bare metal.

Another procedure (6, 7) for applying the resist is as follows:- The desired design is first printed on the surface with an ink which contains a considerable amount of fats. The inked surface is then coated with a rapidly drying spirit varnish, which dries readily over the bare metal but not over the greasy ink. The resist is then removed from the inked areas by a solvent that does not affect the dried varnish film. Petroleum oil has been recommended for this purpose. Before etching, the surface must finally be degreased by light rubbing with some material such as tripoli powder or by a suitable solvent. This method, though time-consuming, is specially useful on a curved surface or in locations where it is difficult to use the steel stencils described in the previous method.

Still another process (8, 9, 10, 11) in the preparation of the surface for etching consists in first printing the background, or that part of the surface to be protected from the etching, with heavy printing ink, which is then dusted with powdered "dragon's blood"[1] or with a mixture of powdered asphalt and rosin. After the powder has been brushed or blown off from the dry, bare metal, the ink and acid-resisting powder are fused together by baking, if heating does not affect the metal, or by the cold fusion process with alcohol vapor described previously. The contrivance for printing the design on the surface may be a simple rubber or linoleum stamp prepared with the design depressed instead of being in relief as in the ordinary rubber stamp. By another rather rough method, the design may be printed in reverse on tissue paper with heavy printer's ink. While the ink is still tacky, the tissue is applied to the metal surface and allowed to dry. The tissue is then removed after moistening it with water, leaving the ink film as the resist on the metal.

For quantity production, the printing of the design on the surface is most easily accomplished by first making a master plate in the manner used in photoengraving. A large drawing in black and white is made of the desired design, which then is photographed and reduced to the desired size. The design is transferred to a sensitized zinc plate[2] by clamping

[1] Dragon's blood is a dark red resinous substance exuded by certain trees. It is used extensively in the photoengraving process as a resist.

[2] The zinc plate may be sensitized by coating it with a film of gelatin and potassium bichromate. Directions and formulas are given in Bulletins No. 80, No. 175 and No. 173 of the American Newspaper Publishers Association Mechanical Bulletins.

the photographic negative over the zinc plate and exposing to the rays from an arc light. Light renders the exposed areas insoluble in the etching reagent, whereas unexposed areas (portions covered by the opaque film) are dissolved when the zinc plate is etched with dilute nitric acid. The resulting master plate with the exposed areas or background of the design raised in relief is used for transferring the design onto the article to be etched, which is often done in a flat-bed printing press. The master plate, after being inked with an asphalt-base ink, is rolled with a clean printer's roller which picks up the ink and transfers it to the article to be etched. This is followed by dusting with asphalt powder, as has already been described. Sometimes the etching of the master plate is omitted, since the areas of the sensitized zinc plate exposed to the light acquire the property of being wetted by and holding the ink, whereas ink will not stick to the unexposed areas.

Etching

It should be remembered that the solutions used in etching are corrosive to the skin and clothing and should be handled with care. If any of the acids should get on the skin, wash immediately with a large amount of water and neutralize any remaining acid with baking soda.

After a satisfactory resist has been applied to the metal surface and the design cut into it, the surface is ready for the etching. It is important that the etching action should take place uniformly over the entire exposed area and not be localized at certain points. It should also progress down into the metal and not undercut the areas covered by the resist and thereby spread over the surface.

The choice of the etching reagent is dependent on the nature of the metal being etched. It is often advisable to perform a few preliminary tests to determine the type and concentration of etching solution which gives the most satisfactory results. The formulas suggested here will serve as a starting point for experiments to enable one to decide upon the best reagent.

Reagents for iron and steel

The usual etching solution for iron and plain carbon steel is dilute nitric acid. One part of concentrated nitric acid diluted with three parts of water has been found to give satisfactory results in most cases. The following variation of the nitric acid solution has certain advantages, although it cannot be used where alcohol would dissolve the resist, as is the case with gum guaiacum, or with resists produced on the metal by photographic processes.

	ml/l	fl oz/gal
Nitric acid (sp. g. 1.42)	220	28
Hydrochloric acid (sp. g. 1.18)	20.5	3
Ethyl alcohol 95 percent	110	14
Water, balance		

A concentrated aqueous solution of ferric chloride is often used to etch steel.

Resists such as the spirit-varnish film in the fourth resist described above will not withstand the action of strong acids. For such purposes a less corrosive reagent, for instance, a copper chloride solution slightly acidified with nitric acid, or one prepared according to the following formula (8) will be useful.

	g/l	avoir oz/gal
Copper sulphate, $CuSO_4.5H_2O$	200	27
Zinc sulphate, $ZnSO_4.7H_2O$	8	1
Sodium chloride, NaCl	165	22

Stainless steel is etched with much more difficulty than ordinary low-carbon steel. Ferric chloride (sometimes called iron perchloride), usually with the addition of hydrochloric acid, is the most widely used reagent for this type of steel. The time required for the etching to be completed is much longer (about 30 minutes) than that for the plain carbon steel. After the etching has been completed and the resist removed, it is advisable to repassivate the surface by immersion in concentrated nitric acid, if practicable. This treatment restores the original property of corrosion resistance to the stainless steel.

Reagents for nonferrous metals and alloys

Copper and its alloys may be conveniently etched with ferric chloride solutions. A formula (10) which has been recommended for etching brass is

	g/l	avoir oz/gal
Ferric chloride, $Fe_2Cl_6.1\frac{1}{2}H_2O$	45	6
Hydrochloric acid, HCl (sp.g. 1.18)	55 (47 ml)	7.3 (6 fl oz)

Some other formulas (7) for etching copper and brass are:

	g/l	avoir oz/gal
(a) Potassium chlorate, $KClO_3$	27	3.6
Ferric chloride, $Fe_2Cl_6.1\frac{1}{2}H_2O$	60	8
Nitric acid, HNO_3 (sp.g. 1.42)	46 (31 ml)	6.1 (4.1 fl oz)
(b) Ferric chloride, $Fe_2Cl_6.12H_2O$	390	52
Hydrochloric acid, HCl (sp.g. 1.18)	84 (70 ml)	11 (9 fl oz)
Alcohol 95 percent - balance		
(c) Potassium chlorate, $KClO_3$	20	2.7
Hydrochloric acid, HCl (sp.g. 1.18)	80 (68 ml)	10.7 (8.7 fl oz)

Zinc may be etched with dilute nitric acid. A solution containing sulphuric acid and sodium dichromate has also been used for this purpose, as well as a solution of the following composition.

	ml/l	fl oz/gal
Glacial acetic acid, $HC_2H_3O_2$ (sp.g. 1.05)	400	51.2
Nitric acid, HNO_3 (sp.g. 1.42)	100	12.8
Alcohol, 95 percent - balance		

Aluminum may be etched with dilute hydrochloric or hydrofluoric acid. (If the latter acid is used, more than usual precautions must be taken to keep from breathing the fumes or getting any in contact with the skin.) A 5 percent solution of sodium hydroxide may also be used for etching aluminum, provided the resist is unaffected by this solution.

Nitric acid is the common etching reagent for silver, and may be used as a 20 percent solution in water.

Etching procedure

After the design has been cut in the resist on the article and a suitable etching reagent has been selected, the next step is the actual etching. In working with small articles, the back and sides are first usually given an acid-resisting coating, such as asphalt varnish, which is allowed to dry. They are then completely immersed in the etching solution. Best results are obtained if the bubbles formed in the action are removed from the surface which is being etched. This can be accomplished by gently swabbing the surface. After a sufficient depth of cut has been obtained, the articles are removed from the etching bath, washed with water, and any acid remaining on the pieces is neutralized with a weak sodium carbonate solution. They are again washed, dried, freed from the resist coating with a suitable solvent and finally coated with a thin film of oil, varnish, or lacquer to prevent corrosion. In the etching of small designs on large surfaces, immersion of the whole article in the bath is not feasible. Here, the etching solution may be swabbed on the design with a rag held on the end of a stick, or a dam may be built around the design and the solution poured into the enclosed area. A rubber ring with a cross-section of about 1/2 inch square has been found suitable for a dam. A coating of petrolatum on the lower side of the ring prevents leakage of the solution between the ring and the resist. Dams may also be built up out of such materials as clay, plaster, molding wax or asphalt.

After the etching has been completed, the solution may be poured off if convenient, or most of it may be pipetted off by suction into a suitable container and the last traces removed with a damp sponge.

Contrast coloring of the metal after etching

The etch produced with acids is often not readily visible under all lighting conditions. Coloring of the design or of the unetched areas is often resorted to in order to produce a pleasing appearance and to attract attention to the design, trade mark or lettering. An almost unlimited

field is available to the etcher for producing various effects in color. A coloring process may be substituted for the etching process by using a solution which colors as well as etches, or the etching may be completed first and followed by the coloring. Sometimes the colors are produced by spraying colored enamels on the etched design. After the enamel has dried, a solvent is used which dissolves the resist but does not affect the enamel, which therefore remains in the etched lines and areas. Two-color effects may be produced by the use of masks or stencils to block off parts of the design.

Coloring of the metal by chemical solutions is very often done. (13,15) If the highlights are to be colored or plated, the appropriate treatment is applied to the whole article before the resist is applied. The design is later etched through the colored or plated coating in the usual manner. If it is desired to color the design, this is done before the resist is removed. A large number of solutions have been developed for obtaining various colors on metals. The following are typical:-

Black coloring of iron (Hess)

The objects are first copper-plated by immersing for about 10 seconds in a solution made by mixing solutions A and B and diluting to 1 liter (or 1 gallon) with water.

Solution A - 10 g (1.4 avoir oz) copper sulphate, $CuSO_4.5H_2O$ in 250 ml (8.1 fl oz) water

Solution B - 15 g (2 avoir oz) stannous chloride, $SnCl_2.2H_2O$ in 17 ml (2.3 fl oz) hydrochloric acid (sp. g. 1.18) and 100 ml (13 fl oz) water.

After the plating is completed, the objects are rinsed and blackened by immersion for two or three minutes in a solution prepared as follows:-

Dissolve by heating 1.5 kg (12.5 lbs) of sodium thiosulphate in 1 liter (or 1 gallon) of water. Allow to cool and add 65 ml (8.7 fl oz) of concentrated hydrochloric acid. Small amounts of hydrochloric acid are necessary from time to time to reactivate this solution.

Black coloring of brass

Immerse for about 30 minutes in the following solution:-

	g/l	avoir oz/gal
Basic copper carbonate, $CuCO_3.Cu(OH)_2$	35	4.6
Aqua ammonia (sp. g. 0.90)	105 (115 ml)	13.8 (14.7 fl.oz)

Black nickel plating is often used to color zinc, aluminum and other metals.

Miscellaneous methods

If it is desired simply to mark a steel specimen with some sort of an identification symbol or to write on the surface in large bold letters in which blurring of the edges is of no consequence, it is possible to apply the etching solution directly to the steel surface without the aid of a resist. The solution is best applied by a pen which is resistant to the acid, such as a wooden stylus or quill pen. A stainless steel pen is also satisfactory for this purpose. A rubber stamp with a pad of blotting paper or asbestos is sometimes used. The following "ink" has been used for work of this kind:-

	g/l	avoir oz/gal
Nitric acid, HNO_3 (sp. g. 1.42)	760 (530 ml)	100 (68 fl oz)
Silver nitrate, $AgNO_3$	25	3.3

Electrical etching devices (16) and tools are available with which lines can be drawn on metal by a rapidly vibrating point connected to a source of low voltage current. A small arc is formed by the make and break circuit between the vibrating point and the piece being etched, thereby leaving a permanent cut in the metal. This machine may be constructed as a multiple pantograph so that a large number of pieces may be marked at one time from a single master plate.

Electrolytic etching

Etching of nearly all metals may be accomplished by making them anodic in a suitable solution. (This is just the opposite of electroplating.) In general a solution of a salt of the same metal as that which is being etched may be used, or a neutral salt of sodium or potassium. For example, copper may be etched anodically in a solution containing 200 g/l or 27 oz/gal of copper sulphate (blue vitriol). Steel may be etched by making it the anode in a solution containing 60 g/l or 8 oz/gal of sodium chloride (table salt). The cathode should be of carbon or of any metal that is not attacked by the solution. A direct current is used with a low voltage, usually from 2 to 4 volts. The voltage should be regulated so as to produce a current that dissolves the metal, but does not evolve much oxygen, which may lift off the resist. One advantage of electrolytic etching is that the metal is not attacked except when the current is passing, and hence the depth of the lines can be readily controlled.

A design may also be produced on metal sheet by mechanical means. (17) The areas which are to remain bright and shiny are covered with masking tape or a stencil. The article may then be sand-blasted to dull the surface and produce a pleasing contrast.

The descriptions of some of these methods have of necessity been brief, and the reader is referred to the bibliography at the end for more complete details.

Sources of supply for various chemicals

The chemicals and other materials called for in this letter circular may be obtained in small amounts from a drug store. In larger amounts they may be ordered through a wholesale drug firm or a chemical supply house.

The materials which may possibly not be obtainable from the above sources are.

Material	May be obtained from
Dragon's blood	Dealer in photoengraving supplies
Printer's ink	Printing establishment or dealer in printing supplies
Powdered asphalt (a hard brittle asphalt is required to permit powdering)	Manufacturer or distributor of asphalt materials, such as: Barber Asphalt Corporation, Barber, N. J., or Allied Asphalt and Mineral Corporation, New York, N. Y.

The magazine "Chemical Industries" (1) issues an annual directory of sources of supply for practically all of the ordinary chemicals. This magazine may be consulted in most public libraries.

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