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DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS  
WASHINGTON 25, D. C.

Letter  
Circular  
LC892

(March 16, 1948)

(Supersedes  
LC150)

DRY ETCHING OF GLASS

Much of the glassware received for test in the Volumetric Laboratory of this Bureau is stamped by means of the dry-etching process, which is more rapid than the usual method and avoids the use of strong etching acids.

In this method, an ink impression of the original seal is transferred to the glass, covered with etching salt, and exposed to the action of steam or water-vapor. The decomposing salt mat-etches the glass with which it comes in contact, reproducing the design on the seal. The materials required consist of the etching salt, printing medium or "ink", gelatin pads, roller, and seals, all of which, with the exception of the last, can be prepared by the user.

Purified ammonium bifluoride is used as the etching salt. The stock supply of salt is kept in a bottle composed of gutta-percha or other resistant material, tightly sealed over with melted wax to prevent leakage of fumes. Prepare about 100 grams of this for the working supply, which is kept in a metal dish and stored in a desiccator.

The salt, which must be dry and fine for satisfactory results, is first prepared by setting it inside the heater (described later) to dry for several days, after which it is ground in a mortar and stored for the working supply. To prepare the salt for use, 15 grams of the dried salt are warmed, finely ground and sifted (through a 60 mesh sieve) into a flat metal dish 4 inches in diameter. The sifted salt may be used as long as it remains in good condition, but it requires grinding and sifting at the beginning of the day's run. When it becomes charged with ink, as shown by a slight tinge of color and flaky texture, it will not adhere properly to the ink impression, and is discarded. The salt, being very hygroscopic, must be kept warm while exposed to air, and all utensils coming in contact with it are warmed before using and well rinsed afterward.

While in use, the salt is kept dry by means of a 100 to 120-watt heater composed of electric light bulbs mounted in a box 10 inches long, 8 inches wide, and 8 inches deep. The walls and bottom of the box are made of transite (a hard



asbestos board) fastened together with angle bars and bolts, the vertical angle bars extending 1 1/2 inches below the box to form the legs. The light bulbs screw into porcelain sockets connected in parallel. A sheet-metal cover resting 1 1/2 inches below the top of the box is provided with a 3 7/8-inch opening, over which the dish containing the sifted salt is placed. The salt dries better when spread in a thin layer over the bottom of the dish. The temperature inside the box is about 70° to 80°C depending upon the wattage, and the heat radiated by the metal cover serves to dry the surrounding air to some extent. Avoid inhaling the salt.

A transparent shield mounted on the 8-inch front of the box protects the operator during the salting process. Two 5/8-inch strips of aluminum about 36 inches long are bolted to the vertical angle bars, extending 18 inches upward, then bending over the box. The strips, braced together with connecting pieces, form a somewhat flexible framework, to which is attached a sheet of transparent, noninflammable, plastic material. To allow ready access to the work, the width of the plastic is kept to 11 inches for a distance of 6 inches above the box, increasing to 18 inches beyond that point.

Two 1/2- to 3/4-inch camel's-hair brushes are used for the salting process, one to apply the salt, the other to remove the excess. To keep them dry without injuring the texture by overheating, they rest on a small table of metal gauze beside the salt dish. The brushes may be cleaned by rinsing in hot water at the end of the day.

The printing ink may be made according to any of the following methods with good results.

1. Take about 70% rosin oil, 25% castor oil, 5% vasoline, and a little oil-soluble dye. Mix the ingredients and heat over a sand-bath at 150°C, blowing compressed air through the mixture until it reaches the maximum thickness obtainable. This usually requires a total time of twenty to thirty hours, but the process need not be continuous. If this ink is too thin, add solid rosin, and if stringy, increase the vasoline. Keep in a covered jar and let stand at least twenty-four hours before using. It improves with aging but may become stringy at low temperatures, in which case it should be remelted and a few drops of turpentine or castor oil added. The coloring matter is used to assist in determining whether the proper amount of ink is adhering to the glass being stamped.

2. Use 45% rosin, 27% rosin oil, 18% castor oil, 10% vasoline, and oil-soluble dye.



3. Use 90 grams rosin, 200 ml castor oil, 25 ml vaseline, 10 ml turpentine, and dye.

In the last two formulae, blow compressed air through the oils at 150°C for about twenty hours, cool to 120°C, add the rosin and blow until blended, then add the vaseline and continue blowing until thoroughly mixed; cool to 100°C, add turpentine and dye, and mix well. The ingredients must be of good quality, but the proportions are approximate. Lump rosin is preferable to the powdered variety, being less subject to adulteration, but it should be pulverized before adding it to the mixture. The castor oil can be obtained already blown, so that by using blown oil of medium viscosity in formula No. 3, the blowing process could probably be avoided.

The consistency of the ink is important, for while it should be stiff in order to retain sufficient salt, the stamps will be ragged if it is stringy. A slightly stiffer ink may be desirable in summer, since thin ink smears and does not hold enough salt.

The roller consists of a metal or wooden cylinder, 1 1/2 inches long and 5/8 inch in diameter, mounted in a handle.

The seal is made of brass or steel, the design being positive with sharp lines in high relief, and the face of the seal must be even. When the seal is applied to the impression pad, a reversed impression results, which on being transferred to the glass is again reversed, becoming positive like the original. Rubber seals will not withstand the solvent action of the ink.

The metal seal is attached to a short wooden handle. When the design is completely enclosed, as for example by a circle, an air vent is provided by drilling a small hole through the base of the seal inside this enclosure, leaving an open space in the wooden block just above it. This is especially desirable for small seals.

To prepare the gelatin for the pads, heat 1200 ml of water and 400 grams of photographic gelatin over a water-bath. When melted, skim and add 100 ml of molasses and 640 ml of glycerine, pouring carefully to avoid formation of bubbles. Heat the mixture until free from bubbles, skimming occasionally, and when thoroughly blended, let cool slightly and pour into trays. This quantity makes four gelatin sheets about 10 x 10 x 3/16 inches in size. The molasses may be omitted in summer.

Four trays are provided for holding and storing the gelatin. Each tray consists of a 10 x 10 inch ground-glass base and shallow sides of heavy cardboard, held securely together by gurned



paper tape. The upper surface of the glass must be ground in order to produce a mat surface on the gelatin sheet.

After greasing the sides of the tray with a little vaseline, clean the glass bottom carefully, set the tray on a level surface, and when the gelatin is ready, pour it to a thickness of about 3/16 inch and allow it to "set." It should not be used for a couple of days. To preserve the mat or working surface, the gelatin is left in the tray undisturbed. The gelatin pads, 8 x 2 inches in size, are cut as needed, with care to avoid detaching more material than necessary from contact with the glass. The trays are stored in a tightly closed case to keep the gelatin from drying out and losing its resiliency. Hardened pads should be discarded.

Sticky pads are brushed off lightly with alcohol on the mat side, then wiped lightly across with a blunt-edged scraper to dry them. A slightly hardened pad may be improved by holding it under a water tap for a minute to soften the surface without allowing it to become sticky, then brushing off at once with alcohol to prevent "blistering."

Two pads are required, one for the ink, the other for transferring the ink impression to the glass. The resiliency of the gelatin pad is greatly improved by mounting it with rubber cement on a sponge-rubber foundation pad, which is in turn, cemented to a stiff strip of metal or wood to preserve the even surface of the gelatin. Pads are kept in condition by placing them face upward in a tightly closed box. Nothing is allowed to rest on the mat surface.

Impression pads are cleaned by brushing off very lightly with a typewriter brush dipped in benzol, drawing the straight edge of the brush over the surface to hasten drying. The benzol, being inflammable, must be kept far away from flame or heat. A 4-ounce cone graduate mounted on a broad, heavy base, makes a convenient receptacle which may be used with reasonable safety; the graduate should not be over half full. Alcohol may be used for cleaning, but it dries the pads, destroying the elasticity. Used impressions should not be allowed to remain on the pad indefinitely.

A small amount of ink is spread evenly over the ink pad by means of the roller, which must be run over the pad occasionally while in use, adding ink as necessary, to maintain a thin, uniform coating. The ink pad and roller are kept in a covered compartment and may not require cleaning for several days unless the ink becomes thickened. Whenever cleaning is indicated, a stiff card pushed over the surface of the pad will remove most of the ink, and the rest may be washed off with benzol.

The glassware to be stamped must be clean and dry, and the





seal, impression pad, and other implements must also be clean.

Touch the seal lightly on the ink pad, then place it on a clean pad to obtain the ink impression which is to be transferred to the glass, pressing very lightly to insure good contact with the pad without spreading the ink. This impression should have a slightly rounded surface with a "glossy" appearance. The seal must be re-inked each time, otherwise the impression on the glass will be too thin and sufficient salt will not adhere. The ink impression is transferred from the pad by rolling the glass over it lightly. The impression on the glass must be even in color and just heavy enough to retain the salt well. If it is unsatisfactory, check to see that the metal seal makes good contact with both the ink pad and the impression pad, that the pads are in good condition, and that the ink pad has a uniform coating of proper thickness.

Apply the etching salt to the ink impression on the glass by means of a camel's-hair brush, patting it in very gently, then lightly brushing off any salt not retained by the ink. It is especially important to remove scattered particles from soft glass. In damp weather, warm the glass a few moments to dry it before applying the salt.

The salted impression should be of uniform color and fine-grained texture, with the design completely covered. Defects become more apparent after steaming, and if an unsatisfactory result is anticipated, the salted impression should be wiped off at once and the technique checked to locate the source of the trouble. Generally the ink impression is at fault, but the salt may be too coarse or overcharged with ink.

Steam the salted impression immediately for about 2 seconds and let it stand for about 3 minutes, then resteam slightly in 2 minutes, repeat in 1 minute, and wipe off after another minute has elapsed. It may be necessary to modify the technique since the time required for the salt to act, the amount of steaming needed and other features of the process vary with atmospheric conditions and the quality of the glass. Occasionally in damp weather, no steaming is required. When steaming for the last time, it is sometimes advisable to let the salted impression become rather moist until the salt and ink blend to a paste without spreading; wipe off at once to prevent over-etching. Warming the salted impression before the second steaming is also effective.

The procedure necessary to obtain good results at any time will have to be determined to some extent by experiment, and a few trial stamps should be made each day and with each new lot of glassware before attempting any extensive operations. The time required may vary from 3 to 6 minutes.



When the salted impression is completed, a clear narrow border appears along the edges, with slight cloudiness outside this, though it is not an infallible indication. The salted impression, when finished, should be wiped off immediately with a piece of damp cloth to prevent any further action of the salt, which serves only to produce a ragged appearance. It is best to wash off the glassware with water, but this may be done when convenient, provided it is not too long delayed. A good stamp should be white and sharply defined.

With a little experience as to timing and steaming, from six to eight or more pieces of glassware may be run through together. The ink impressions are applied to the entire lot; then each piece is salted, steamed immediately, and set aside until ready for resteamng. Generally, fewer pieces can be stamped as a group in summer, especially if the relative humidity is high. Under those conditions, less steaming is required and the glass etches faster.

Pyrex and other varieties of resistant glass require somewhat different treatment. With glass of this type, the salted impression is steamed and then held in a Bunsen flame a few moments, heating the entire area until it acquires a "moist" appearance due to the melting of the ink. The glass must be hot to the touch, but the salted impression should retain its moist appearance until the etching is nearly completed. Steam immediately and repeat two or three times at about 7-second intervals. Before steaming for the last time, it may be advisable to reheat the glass a moment. A total time of only 20 to 30 seconds is required to complete the process; then the salted impression is wiped off with a damp cloth. When the glass is thick, the heat disperses rapidly, and it may be necessary to reheat the salted impression several times, steaming each time. The process is completed when the impression remains white, failing to remelt when held in the flame.

A few trial stamps placed on a Pyrex beaker should enable the operator to acquire the proper technique. The glass must be warmed carefully, to avoid overheating, for while the salted impression spreads if warmed slowly, excessive heat decomposes the ingredients too rapidly, as indicated by a dry, dead-white appearance which remains unchanged upon reheating. When the glass has not been heated enough or cools too soon, the impression may also appear rather dry and white, but in this case it responds when reheated and should be treated as previously described. Graduated apparatus must not be heated at any point where a change in the effective volume might occur. Four pieces of Pyrex glass can be handled together conveniently. They are first inked and salted but not steamed; then one or two pieces are heated and steamed as described until the stamps are finished.



When available, hot, "dry" steam gives best results, but the steam from a shallow metal pan of water heated on an electric hot-plate is satisfactory. For protection from drafts, two small metal shields partially encircle the hot-plate and pan on opposite sides; they extend about 5 inches above the pan and are braced together at the bottom; the lower portion is perforated so as to allow circulation of air around the hot-plate to prevent overheating.

Stamps can be removed by buffing with rouge.

#### ETCHING INK FOR GLASS

A very satisfactory diamond ink may be prepared by adding 1 ml of concentrated sulphuric acid to 10 grams of finely pulverized ammonium bifluoride and mixing together in a lead crucible. Apply by means of a steel pen, and let stand about 1 minute. Pyrex glass should be warmed to promote the process. An etching ink may also be prepared by stirring equal parts of hydrofluoric acid and ammonium fluoride together in a 10 ml wax cup, adding sufficient barium sulphate (about three or four times the bulk of the acid) to thicken it to the desired consistency. The ink is barely fluid enough to regain its level surface when the pen is removed from it. This ink requires very little mixing but must be stirred occasionally while in use. It is applied by means of a ball-pointed steel pen, which must be re-dipped frequently and cleaned off from time to time. The etching is completed in about 15 seconds. Warming the glass slightly before and after applying the ink produces a whiter mark and avoids spreading. A larger quantity of the acid and ammonium salt may be mixed together and kept in stock, the barium sulphate being added only as required; or all the ingredients may be mixed together at once and kept for use when needed. The barium sulphate is very heavy, however, and settles to the bottom; hence it must be well stirred before using. These mixtures must be kept in gutta-percha bottles provided with wax-coated stoppers, the tops being sealed with wax after using.

The quality of barium sulphate used is of great importance in making good etching ink. It is best prepared by precipitating barium chloride with an excess of sulphuric acid, washing well by decantation, filtering, and drying at 120°C. By this method a very fine powder is obtained.

Since hydrofluoric acid causes serious burns and even ulcers if left in contact with the skin, great care must be taken both in making and in using the ink not to allow it to spatter or touch the person. The presence of the acid on the skin is not detected immediately, but the burns are exceedingly painful and difficult to alleviate. While using the acid, avoid breathing the fumes, protect the eyes with goggles, and wear rubber gloves. When finished, bathe exposed skin with a solution of sodium carbonate as an added precaution.

