

(January 26, 1925)

DRY ETCHING OF GLASS

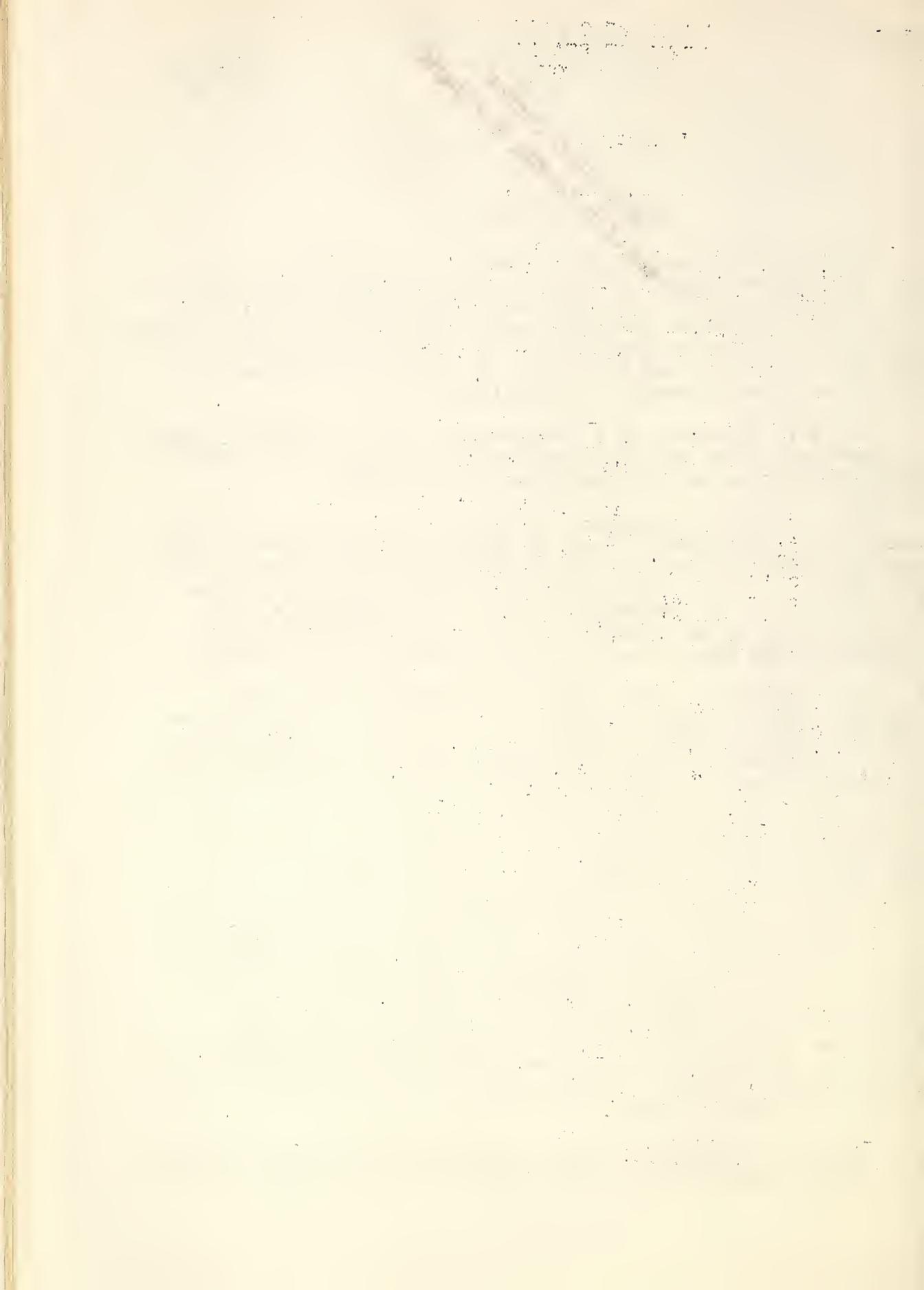
The greater part of the glassware, received for test in the Volumetric Section of this Bureau, is stamped by means of the so-called dry-etching process. The method used is not only more rapid than the usual wax process, but has the added advantage of eliminating the use of strong etching acids and the finished stamp has a frosted effect which requires no filler to make it readily discernible.

In this process, an ink-impression of the original stamp is transferred to the glass and is then covered with etching salt and exposed to the action of water vapor.

The materials necessary are the etching salt, printing medium or ink, gelatine pads, a roller, and the stamps which are preferably of metal. The salt and printing medium were formerly imported, though they may now be obtained in the United States, we understand. All of the materials, with the exception of the stamps, can be prepared very readily, and but little apparatus will be required for the purpose.

The Bureau has been using a good grade of ammonium fluoride for the etching salt and it has proven very satisfactory. One kilogram of this will last for a considerable time. In order to obtain good results, the salt must be dry and rather fine. As purchased, it is likely to be very coarse with a considerable moisture content. In this case it is melted over a low flame, in a thin, shallow iron dish, and is kept hot for about five minutes, or longer if necessary; some fumes will be given off, but the temperature must not become high enough to cause decomposition. When cool, the fused mass is removed from the dish, by a blow on the bottom, and is then ground to a powder and sifted through metal gauze of not less than No. 30 mesh. About seventy-five grams of salt will be a sufficient working quantity, unless a large number of pieces are to be stamped. This is placed in a calcium chloride desiccator when not in use. The stock supply is kept in a wax or gutta percha bottle, tightly sealed to prevent the etching of any glassware in its immediate vicinity, though usually some time is required for such action to become apparent.

To keep the salt dry while in use, an inexpensive heater may be constructed by mounting two or three electric lights in



a heat-insulated box. The latter can be made of "transite", a hard asbestos board which is worked in much the same manner as wood, but has the advantage of being fire-proof. The top of the box is hinged or simply laid on, and has a hole in the center over which is placed the shallow metal pan containing the salt. The lamps are connected in parallel and the temperature can be regulated sufficiently well by turning them in or out of the sockets. The salt should be warm but must not become hot enough to vaporize.

The stamping medium has been made according to the following formulae with very good results:

1. Take about 70% rosin oil, 25% castor oil, 4.95% vaseline, and 0.05% of dye which is soluble in oil. Mix the ingredients and heat gently 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 from twenty to thirty hours, but the process need not be continuous. If the ink is too thin, add solid rosin, and if stringy, increase the vaseline. Keep it in a tightly covered jar and let stand twenty-four hours before using. It is inclined to become stringy with age or when the temperature is low, but this may be remedied by remelting and adding a few drops of turpentine, or, if available, a little blown castor oil is preferable. When used in warm weather, it should be a little thicker than is generally necessary. The coloring matter assists in determining whether the proper amount of ink has adhered to the glass.

2. 45% rosin, 27% rosin oil, 18% castor oil, 10% vaseline, and a little oil soluble dye.

3. 200 ml castor oil, 95 g rosin, 22 ml vaseline, 10 ml turpentine, and dye.

4. 200 ml castor oil, 80 g rosin, 15 ml vaseline, 10 ml turpentine, and dye.

5. 200 ml castor oil, 155 g rosin, 5 ml cocoa butter, and dye. The cocoa butter is added after the completion of the heating process, and when the mixture is at about 100°C, or less. Ink made according to this formula has a tendency to spread upon standing, and the ink impressions should be transferred to the glass and salted within a few minutes' time. It is of quite uniform consistency.

For all of the above, the heating and blowing process is carried on as in formula 1. The proportions are approximate. The rosin used should be of good quality, but when rosin oil is obtainable it would probably be better to use it in place of

the solid form, at least in part, since a large amount of the latter gives an ink of less uniform composition

The ink probably has no active part in the reaction, but serves to hold the salt and seems to bring it more intimately in contact with the glass.

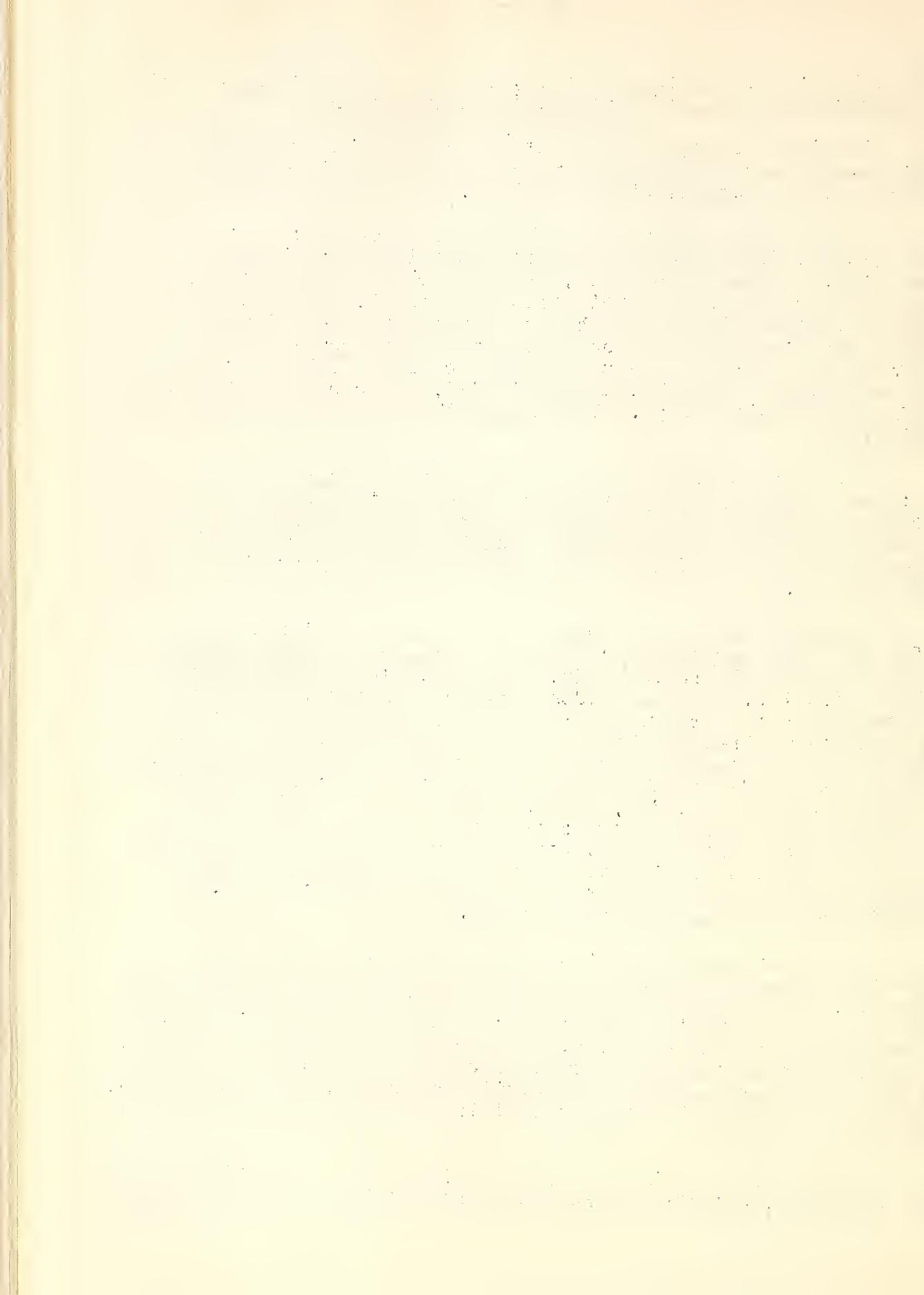
The gelatin pads are made by heating together over a water-bath, 400 grams of photographic gelatin and 1200 ml of water. When melted, skim, and add 840 ml of glycerine, poured in carefully to avoid formation of air bubbles, and 100 ml of hot molasses which has previously been skimmed. This quantity will make four gelatin sheets about 10 x 10 x 3/16 in. Heat the mixture until free from bubbles, skimming occasionally. When thoroughly blended, let cool slightly and pour into shallow trays. In summer, the molasses may be omitted.

A fairly durable tray of convenient size has for the bottom a ground-glass plate 10 x 10 in., with sides made of heavy cardboard held securely in place with gummed paper tape. The ground face of the glass, which is for the purpose of producing a mat surface on the gelatin sheet, is on the inside of the tray.

After greasing the sides with a little vaseline, clean off the glass carefully, and set the tray on a level surface and when the gelatin is ready, pour it in to a thickness of about 3/16 in., and let harden. If the gelatin is left undisturbed in the tray until required for use and is kept in a moderately air-tight box, it will not deteriorate seriously and the mat or working surface will remain in good condition. The gelatin pads, which are strips about 8 x 2 in., are cut from the sheet as needed, and only the amount required for immediate use should be separated from contact with the glass. The pads should not be used for a day or two after pouring, and if sticky, they will be improved by brushing off with alcohol on the mat side; dry, by brushing off with a blunt edged scraper of bone or hard rubber.

It is essential that the pads, especially those used for the impressions, should be elastic and have a uniform mat surface. To preserve them in good condition and prevent drying out, they are kept in a tightly covered box when not in use. The impression pad must first be cleaned with benzol and dried, then laid face down on a ground-glass plate; over it is put a strip of rubber packing, or a similar material, and the ink-pad, which is protected by its layer of ink, may be placed right side up on this.

A pad which has become even partially hard and shiny should be discarded, but when a new one is not available, the old way



be improved if dipped in hot water until softened, then laid face down on a ground-glass plate, being careful to press out the air bubbles, and left to stand over night. If required for use immediately, the pad is renovated by immersing in cold water a few minutes, to soften the surface without permitting it to become sticky, then it is brushed off at once with alcohol, to prevent "blistering", and is ready for use.

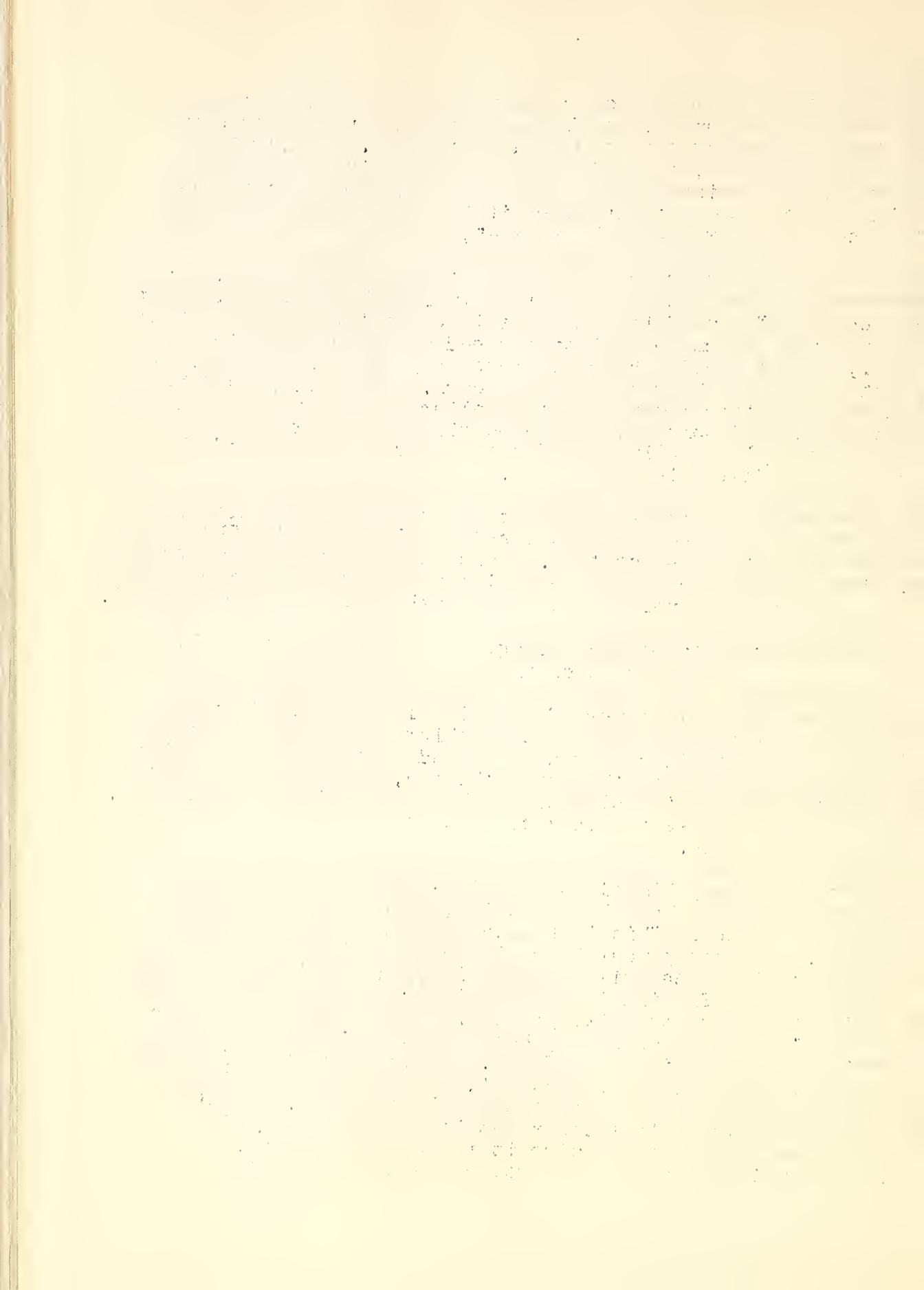
The roller proper is made of gelatin, like the pads, and is cast on a core of wood or 6 mm brass tubing which is left in it permanently. The mold is made of thin brass tubing, about 2 cm in diameter and 7 cm long, into one end of which is fitted a stopper, the core being held in place by pushing one end of it through a hole in the center of the cork. The mold should be oiled to facilitate removal of the roller, when set. The gelatin mixture is cooled somewhat before pouring and after it has hardened the mold is slipped off the roller. The ends of the core or shaft fasten into a handle.

The stamp is made of brass, steel or other hard metal and the lines should be sharp, clean, and in high relief. The design on the stamp is positive. This, applied to the impression pad, gives a reversed impression which on being transferred to the glass is again reversed, becoming positive, like the original.

The glassware to be stamped must be clean and dry. The implements also must be kept clean.

A moderately thin layer of printing ink is spread on a ground-glass plate, by means of the roller. A uniform coating of ink is spread on the mat side of a pad by running the roller over the inked plate and then over the pad, alternately, until the proper thickness is obtained on the pad. While in use, also, the ink-pad must be kept evenly covered by running the roller over it occasionally.

Touch the stamp 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. This impression should have a "glossy" appearance. The stamp must be re-inked each time, otherwise the impression on the glass will be too light, and sufficient salt will not adhere. The ink impression is transferred from the pad by rolling the glass over it, lightly. A good impression should not have a "patchy" appearance, but must be uniform in color, indicating an even thickness of ink. It is sometimes advisable to steam the impression for a moment, let it stand to allow the moisture to evaporate off, and then apply the salt. A faint impression may give satisfactory results on very soft glass, but the harder varieties require it to be rather heavy. A pale, or nonuniform impression produces a defective stamp.



Sprinkle the etching salt over the impression on the glass, working it in very lightly with a camel's-hair brush (about 1/2 in. size), and brush off any excess which does not adhere to the ink. For soft glass it is especially important to remove superfluous particles of salt.

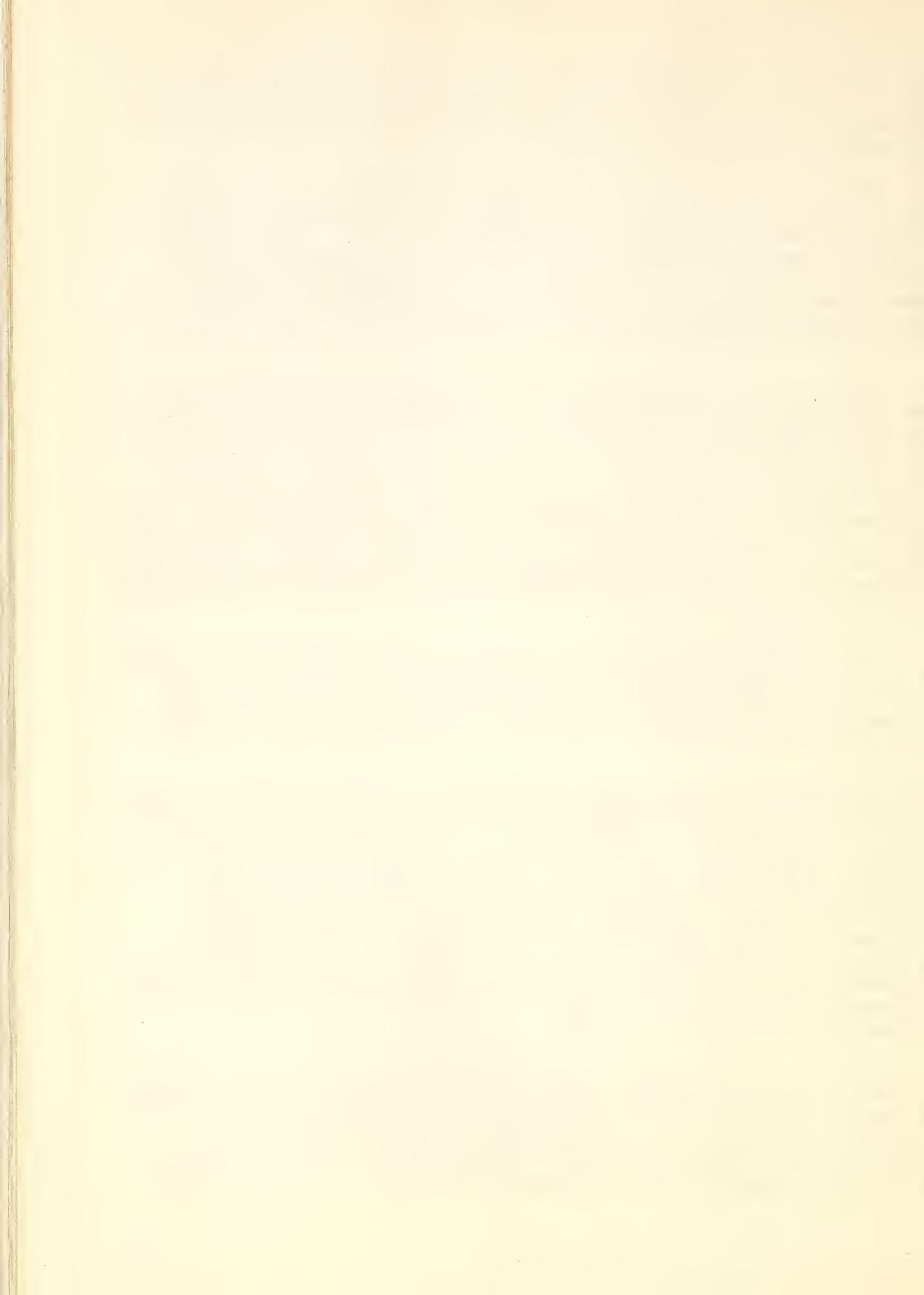
From the appearance of the salted impression, not only before, but especially after, steaming, it is usually possible to judge how successfully the stamp will take. Nonuniform coloring generally indicates a defective impression, but an uneven distribution of the salt is also often due to its coarseness, in which case it requires regrinding and sifting. If an unsatisfactory result is anticipated, the stamp should be wiped off immediately.

Expose the salted stamp to the action of steam for several seconds, then let it stand about a minute or perhaps longer. It may be necessary to repeat this process several times, since the time required for the salt to act, the amount of steaming necessary and other features of the process vary with atmospheric conditions and the quality of glass. It sometimes happens that no steaming is needed. When steaming for the last time it is often advisable to allow the salted stamp to become very moist so that the salt and ink blend to a thick paste; but it should not become moist enough to run, and must be wiped off at once to prevent smearing.

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 to carry out any extensive operations.

When the stamp is completed, a clear narrow border appears along the edges, with slight cloudiness outside of this, though it is not an infallible indication. The stamp, when finished, should be wiped off immediately to prevent any further action of the salt which serves only to produce a ragged appearance. It is best also 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 outlined. If patchy or unevenly etched it is generally either because the impression pad is in poor condition, the ink-pad is not evenly covered or may need to be cleaned and re-inked, or the salt is not sufficiently fine and dry.

Pyrex and other varieties of resistant glass usually require different treatment, and in general, the harder the glass, the more difficult it is to stamp. For such glass, the salted impression is held over a low, almost smoky, Bunsen flame (about 1/2 inch high) for a few seconds until it has a "moist" appearance, caused by the melting of the ink, then it is set



aside for a minute or so, the process being repeated if necessary. The warming must be carefully done to prevent smearing; also, too much heat causes the ink to harden and the salt to decompose before the completion of the process, shown as soon as the salted stamp has a white, dry appearance even when warmed. When cool, the glass is washed off with water. Good results may be obtained also by steaming the salted impression first, then warming as described, then steaming again a few seconds, and allowing it to stand, as before. Repeat if necessary, and wash off. Graduated apparatus must not be heated at any point where possible deformation of the glass will cause a change in the volume contained or delivered by it.

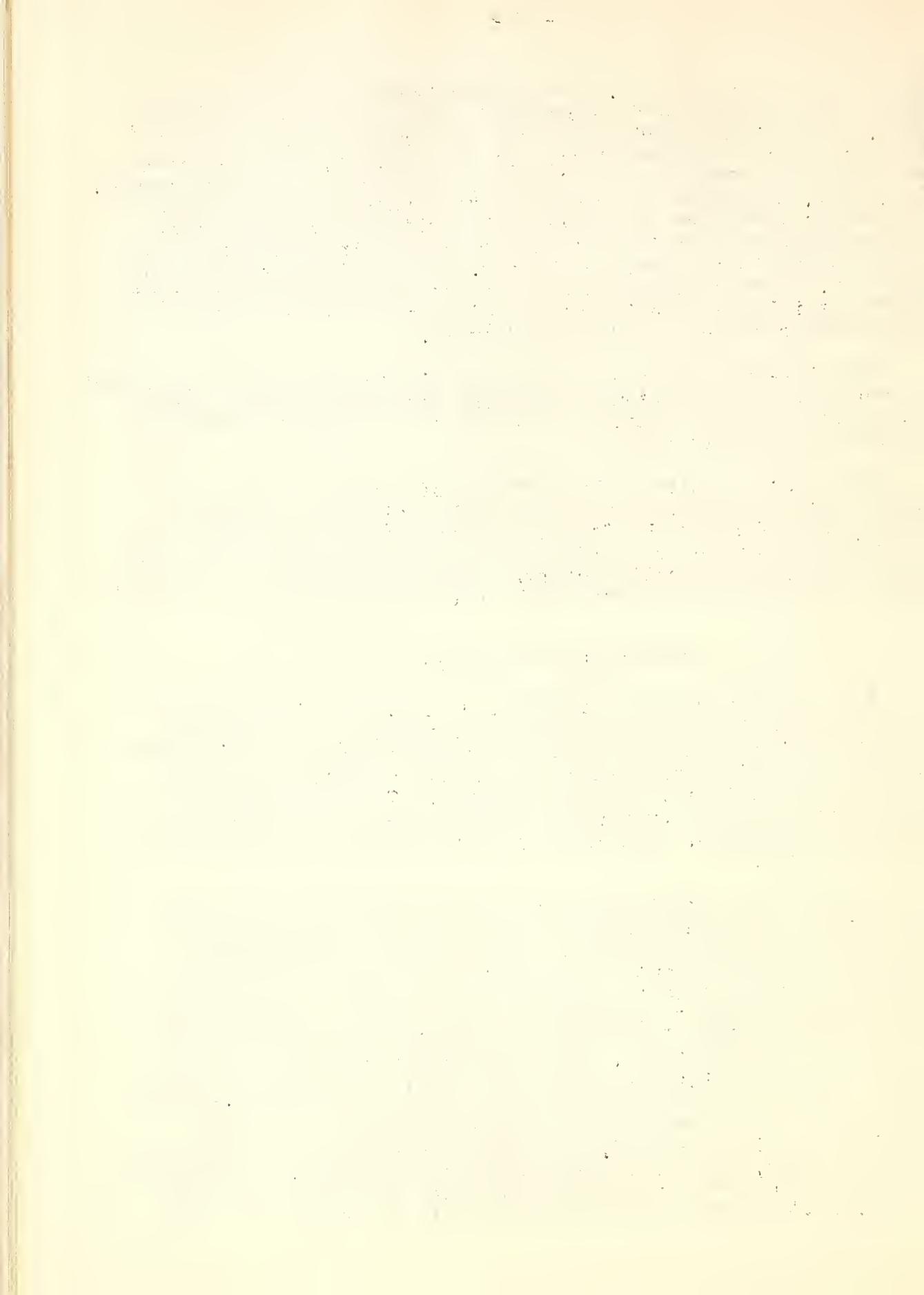
The ink-pad, plate and roller should be kept covered when not in use, and will not require cleaning for several days, after which time the ink is apt to be gummy and the outfit should be cleaned and freshly inked.

The pads are cleaned by brushing off lightly with a small stiff brush - similar to a tooth brush - dipped in benzol or gasoline, preferably the former. Alcohol (or alcohol and benzol) can be used but hardens the pads too rapidly and is for this reason, very unsatisfactory. These liquids are, of course, highly inflammable and must not be used near a flame.

Etching Ink for Glass

Take equal parts of hydrofluoric acid, ammonium fluoride and barium sulphate and mix together carefully, in a mortar. When thoroughly blended, place in a lead, or gutta percha dish and stir in fuming hydrofluoric acid with a pestle, until an impression left on it, quickly vanishes. This fluid can be applied to the glass by means of a steel pen, and needs to act for only 15 seconds. The ink may also be applied by means of a rubber stamp.

Where only a small quantity is required, equal parts of hydrofluoric acid and ammonium fluoride are stirred together in a small wax cup by means of a rod and sufficient barium sulphate is added (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 has given excellent results and requires very little mixing. It is stirred occasionally while in use. A ball pointed steel pen is used, the tip only, being inked. Redip the pen frequently and clean it off from time to time. Warm the glass slightly before applying the ink and also immediately afterward; this after-heating seems to produce a clearer mark, and eliminates danger of spreading. A quantity of the acid and ammonium salt mixture may be made up and kept in stock, adding the barium sulphate only as required, or all



the ingredients may be mixed together at once, and kept for use as 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 and the tops must be sealed with wax when not in use.

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 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.

Colored Stamps on Glass and China

Colored stamps are sometimes applied to glass or china ware by means of a fusion method. The process requires the use of a vitrifiable powder and medium.

Have the glass clean and dry and the powder dry and very fine. A rubber stamp may be used for putting the mark on the vessel.

Spread a thin sheet of the medium on a glass plate; ink the stamp from this and apply it to the vessel. Sprinkle the powder over this impression, with a camel's-hair brush and brush off the excess. Then heat to dull red until the powder fuses with the glass. The powder and medium may be mixed together and applied with a pen, if desired, but the ink may require thinning for this. This method is used for stamping beakers, etc.

The materials can probably be obtained through an artists' supply store.

