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Techniques for Ruling and Etching Precise Scales in Glass and Their Reproduction by Photoetching With a New Light-Sensitive Resist

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Techniques for Ruling and Etching Precise Scales in Glass and Their Reproduction by Photoetching With a New Light-Sensitive Resist

Raymond Davis and Chester I. Pope

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Techniques for Ruling and Etching Precise Scales in Glass and Their Reproduction by Photoetching With a New Light-Sensitive Resist

Raymond Davis and Chester I. Pope

Two methods are described for the making of very precisely graduated circles for theodolites. In one method the graduations and numbers are ruled in a wax resist coated on the glass circle by means of a ruling engine followed by etching. In the other method the circle is coated with a light-sensitive resist and exposed in contact with a glass master negative followed by etching. The requirements of precise circles and the mechanics of engraving the resist on both circles and reticules are discussed. The development of resist coatings and their application on the glass and the methods of glass etching are reviewed. A new mild etching solution containing phosphoric acid and hydrofluoric acid was developed. The synthesis of phenol-formaldehyde resin for use as a light-sensitive resist coating and the procedure for its use are given in detail.

1. Introduction

Instruments used for the measurement of angles are equipped with a reference scale graduated in degrees, minutes, and seconds, or in grads and its subdivisions. Sometimes only a part of a circle (an arc) is graduated, as in the case of the sextant. With other instruments, such as the theodolite, a complete circle is graduated. The graduated portion of a circle is commonly referred to as the limb. It has been the practice for many years to use brass with a silver inlay for the graduation of arcs and circles. In recent years aluminum alloys without the silver inlay have been used for this purpose, and also certain of the stainless steels have been recommended [1].[1] The precise graduation of circles on different materials, the techniques used, and the operation of the dividing engine have been discussed by Page [1].

A type of precision theodolite, having glass circles with the graduations etched in the glass, has come into use during the past 20 to 30 years. Only a few experimental models of these isntruments have been made in this country. One of these experimental theodolites is shown in figure 1. The supply of such instruments is limited to a few European manufacturers. Theodolites equipped with glass circles have several advantages over the older types. They are smaller than conventional instruments of equal accuracy; they have greater compactness of design; and, in most cases, are appreciably lighter in weight. Moreover, illumination of the graduations of the circles and micrometer scales is superior, and the graduations have higher contrast with the background than is generally obtained with metal limbs. The most important feature is the simplicity of reading both circles with the micrometer microscope (magnifications up to × 40) located alongside the eyepiece of the telescope. Some instruments have separate micrometer microscopes for the horizontal and vertical circles. Each reading of the optical micrometer gives the mean of two diametrical points of the circle, thus automatically correcting for eccentricity of mounting of the circles [2, 3, 4, 5,

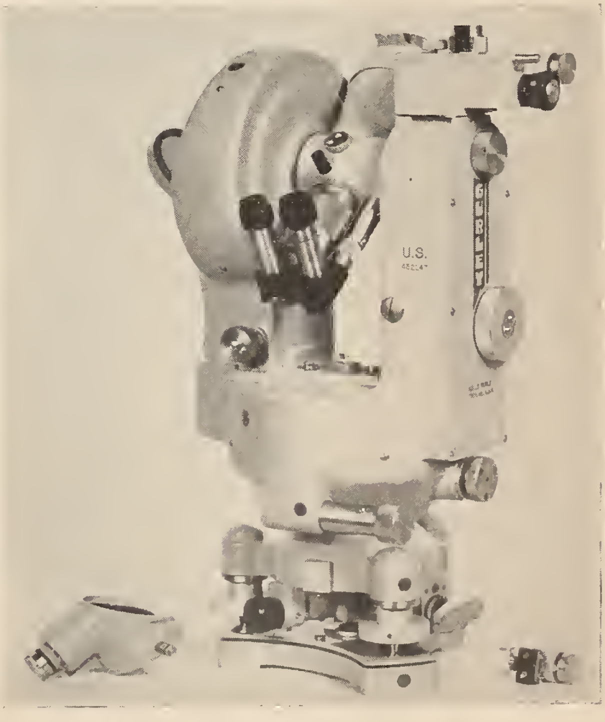

Figure 1. *Pilot model of a one-second theodolite.*

This theodolite was made for the U. S. Army Engineer Board by W. & L. E. Gurley, Troy, N. Y. These instruments were equipped with glass circles made at the National Bureau of Standards by the processes described in this paper.

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[1] Figures in brackets refer to literature references at the end of this paper.

6, 7]. Theodolites with circles 3.5 to 5.5 inches in diameter, graduated to 20 minutes, may be read to 1 second and, in some cases, estimated to 0.1 second. Larger instruments with 10-inch circles, graduated to 2-minute intervals, may be read directly to 0.1 second [8]. It should be pointed out that the production of graduated circles having errors not exceeding the resolution of these optical micrometers poses a problem because such accuracy is not common. An error of 1 second of angle on a circle 4 inches (10 cm) in diameter would amount to a displacement of a graduation by 0.00001 inch (0.25 μ).

Graduated glass circles and scales also have been used in other fields. Dividing heads, indexing tables, cam-rise gages, and other units for machine shop use are now available, and it is expected that the use of glass circles and scales with etched graduations will find wide application in precise work.

Sometime ago the Army Engineer Board requested the National Bureau of Standards to make a limited number of precise glass circles and reticules and to develop a method for their production, with particular emphasis on a photographic method of reproduction that would facilitate quantity production. However, no light-sensitive coating was known that, under suitable exposure and development, would form a mask, or resist, that would also withstand the action of hydrofluoric acid used to etch the graduations into the glass. The project was undertaken and the immediate needs of the Engineer Board were met. However, the techniques used were not fully satisfactory, and further work was done toward a more satisfactory solution of the problem. The details of methods used by manufacturers for producing these circles have not been made generally available. However, examination of a number of graduated circles of European manufacture indicated that each is an original, separately coated with a resist, engraved, and etched.

The production of circles require the making of master circles, engraved on a circular dividing engine and etched in a more or less conventional manner; the development of a satisfactory photosensitive resist; and a contact-printing and etching process to produce replicate circles of the required accuracy. The production of reticules involve similar techniques and the design and construction of a ruling machine. Work on the project was divided between the NBS Length Section and the Photographic Technology Section. The former was responsible for engraving graduations and numbers on the master circles and testing the master circles and the replicas for accuracy [1]. The remainder of the work, that is, the development of resists and of techniques for applying them, design of the master circle blanks, construction of a pantograph for numbering the graduation lines on the master circles, production of replicas; and the production of precise reticlues, was the responsibility of the Photographic Technology Section.

This publication discusses the problems that were encountered and the techniques devised in the production of a limited number of experimental glass circles and reticules. Circles of the desired accuracy have been produced and the major problems have been solved. In quantity production of such circles, modifications in minor details are, of course, to be expected. The first six sections of this paper deal with the production of master circles, theodolite circles and reticules by engraving wax resists, etching the glass, and filling the etched graduations.

Section 7 deals with the production of etched-glass limbs, etc., from a master by photoetching techniques. Some of the observations and techniques are discussed at greater length than would be necessary if similar information were available in the technical literature.

2. Design of Graduated Circles and Master Circles

2.1. Graduated Circles

Two graduated circles, one horizontal and one vertical, are required for each theodolite. The horizontal circle is usually somewhat larger than the other because greater precision of measurement is required in the horizontal plane for geodetic triangulation, and, furthermore, a larger vertical circle makes the instrument more bulky, or less "streamlined." In one well-known instrument, the diameter of the horizontal circle is 3.5 inches, and the vertical circle is 2.7 inches, although both have the same 20-minute graduations and can be read to 1 second with the optical micrometers. The specifications for the graduated circles will, of course, be dictated by the design of the instrument. This design will include the position, length, and width of lines; position, orientation, and size of numbers, as well as the dimensions of the glass, type of etching, and other pertinent information.

All graduation lines should be of equal width, usually between 5 and 10μ. With one exception, in all of the circles of European manufacture examined, the degree lines were longer than the 20-minute subdivisions and were numbered. The numbers were about 0.005 inch high. The thickness of the glass was found to be about from ⅛ inch (3 mm) to slightly over ¼ inch (6 mm) for circles of from 2.5 inches (64 mm) to 4 inches (102 mm) in diameter. Figure 2 shows a much enlarged view of about 1°20′ of a 3.5-inch (89 mm) circle with 20-minute graduations. Two types of graduations were found: (1) more or less deep-etched

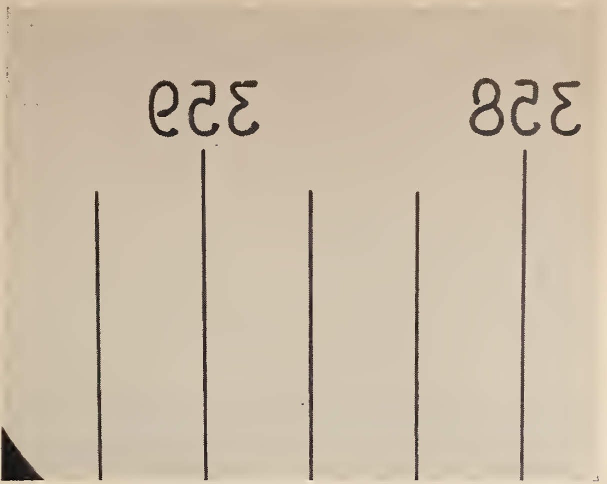

FIGURE 2. *Enlarged view of graduations on a master circle.*

Photographic reproductions were made from these master circles with graduations etched into the glass. These graduations, at 20-minute intervals, are subdivided with an optical vernier to 1-second intervals.

and filled lines on clear glass, (2) frosted, usually shallow-etched lines of fine texture, not filled, but mirror-silvered on the etched side. The silvering either covered the whole surface of the circle or only a narrow band, or ring, covering the graduations. Circles with silver over the etched graduations are viewed through the unsilvered side of the glass. Figure 3 shows a horizontal circle and its mount, disassembled, and also a vertical circle in its mount. Another type of circle examined was a small (2.5 inch) ring of relatively thick glass (¼ inch) with etched graduations on the outside edge of the ring. Obviously, this design would not be a satisfactory one for photographic duplication by contact printing.

One maker of theodolites uses a double line (two lines slightly separated) for each graduation. The circle may have been first graduated as usual with a single-point engraving tool, then the glass circle turned nearly 180 degrees on the dividing engine and a second set of lines engraved close to the first set. Alternatively, both graduations could have been made simultaneously with two tools set nearly 180 degrees apart. These double-line graduations should have the effect of reducing the dividing-machine errors by a factor of 2, provided both sets of graduations are used.

Selected plate or spectacle crown glass can be used for making blanks for the circles, and also for reticules, except, of course, where the specifications require the use of an optical glass, such as borosilicate crown. The blanks are annular rings cut from sheet glass with tube cutters. They are accurately ground on the outside diameter, then they are fitted into a special lathe collet, and the inside diameter is ground to exact size with a diamond grinding wheel on a tool-post grinder. The diameter of the hole is checked with a plug gage before removing the blank from the collet. Following this, the front and back surface of the rings are ground and polished and the edges are beveled.

FIGURE 3. *Horizontal and vertical circles from a theodolite of European manufacture.*

In the foreground is the vertical circle with its clamp ring. In the back, on the left, is the horizontal circle. The band, or ring, just inside the edge of the circle is mirror silvering, which covers the graduated area. In the center is the mount for this circle, and on the right is a clamp ring used to hold the circle in position.

The quality of the glass surface required for reticules and etched scales is higher than that necessary for lenses. Very small imperfections, such as occasional pits or scratches, which are relatively unimportant on the surface of most optical components, are disturbing on surfaces containing scales or fiduciary marks because in use considerable magnification may be required for the observing or measuring operations for which they were designed. Further, if the tool runs into a pit or similar imperfection in the glass during the engraving, both the work and the tool are almost certain to be ruined.

As already stated, the physical dimensions of the glass for circles will be specified by the instrument design in which the completed circle or reticule is to be used. However, thick glass (about ¼ inch) is preferable to thin glass (for example, ⅒ inch). Uneven or local pressure in clamping a circle to the dividing engine table or in mounting it in the instrument in which it is to be used may cause distortion of the circle and thereby introduce several seconds of error. With thicker glass the errors from this cause will be smaller, other things being equal. In the instrument a thick glass has the further advantage that any dust or specks on the back side of the glass will be more completely out of focus.

2.2. Master Circles

The master circle consists of a thick clear glass disk, somewhat larger than the theodolite circle, with etched and filled graduations. Its purpose is similar to that of a photographic negative used for contact printing. (The details of contact printing from the master are discussed in sections 7.3 and 8.1.)

Glass blanks for master circles were made of either spectacle crown or borosilicate crown glass. Those for master circles 4 inches (102 mm) or smaller were made ½ inch (12.7 mm) thick and 6

FIGURE 4. *Storage box and clamping plug for master circle.*

The box on the left is used for safely transporting and storing the master during all stages of its graduation and while not in use. On the right is a master with its centering and clamping plug in position.

inches (152 mm) in diameter. Figure 4 shows a glass master and its centering plug in its storage case. In the center of the glass disk a 60-degree conical hole was drilled and ground, having its larger diameter (about ¾ inch) at the top surface of the glass. The cylindrical steel centering plug is ¾ inch (19 mm) in diameter and about the same length, with a ¼-inch (6 mm) hole through its center. One end of this plug was machined to a 60-degree taper for about ⅜ inch (10 mm) of its length. The plug was fitted to the conical hole in the glass blank by lapping with suitable abrasives. Follwing this, both sides of the glass blank were ground and polished, the face side to a good optical plane free from scratches. Freedom from scratches is important, as very small ones not ordinarily noticed will fill about as well as the etched graduations, thus spoiling a master. The glass must also be free from seeds and bubbles in the vicinity of the graduations.

The steel plug is used to clamp the master blank, by means of a knurled-head screw through the hole in the plug, first to the table of the numbering machine for the engraving of the numbers and then to the table of the graduating engine for the engraving of the graduations.

The master blank is centered by means of a sensitive dial indicator in contact with the plug. Both centering and leveling are very important for accurate graduating. The centering and leveling screws on the table of the graduating machine provide this adjustment. The glass blank is leveled optically by lowering the ruling point until it is a few thousandths of an inch above the coated surface and by observing the ruling point and its image from the surface of the blank with a microscope at near grazing incidence (about 30 degrees). When the blank is level (at right angles to the axis of the spindle), the space between the ruling point and its mirror image remains constant while the table of the ruling or numbering machine is rotated. The back side of the glass blank is prevented from touching the metal table by a paper washer.

As mentioned in section 2.1, two types of graduations on the theodolite circles are in common use: (a) etched and filled lines on clear glass, and (2) frosted etched graduations, mirror-silvered on the etched side. When planning to engrave the master circle for contact printing, one must remember that the engraving on the master should be a mirror image of the graduations for type (1) circles. On the other hand, because type (2) circles are viewed through the glass, the graduations on the master will be the same as that on the finished theodolite circle.

3. Resists

3.1. General Composition and Characteristics

The term "resist" is commonly used in several industries, for example, calico printing, electroplating, photoengraving, and glass etching. A resist is a coating that protects the areas it covers from chemical, electrical, or physical action.

Several publications [9, 10, 25] describe processes used for the production of etched glass scales and reticules in a general way. However, no publication was found with specific information in regard to the composition of the resist. The subject is generally so lightly dealt with that several assumptions can be made: first, the whole matter is so simple that no difficulty should be expected; second, the composition and coating details are trade secrets; third, none of the resists is completely satisfactory. Probably both the second and third assumptions are true. Another factor that must be considered is that in some instances the materials (asphalts, waxes, resins, and the like) used in making resists are of unknown composition, identifiable only by trade name. Furthermore, natural materials frequently vary in properties according to the source, and synthetic materials may also vary because of differences in manufacturing and purifying processes. Finally, some materials cannot easily be obtained.

Resists used for engraving and etching of designs and scales in glass with hydrofluoric acid are usually made from a combination of such substances as asphalts, beeswax, paraffin, Burgundy pitch, and rosin. These materials are resistant to the action of hydrofluoric acid. Waxes are the basis for most resist formulations because of their inherently good ruling characteristics. Other ingredients (asphalts, resins) are added to improve this latter characteristic and to promote adhesion to the glass. Further modifiers sometimes used include oils, fats, varnish, and pigments. Most, if not all, of the ingredients mentioned are obtainable in several grades, which may differ in hardness, melting point, color, purity, and solubility, and one grade may not always be a substitute for another. This is particularly true with waxes and asphalts, because, in addition to the natural products, a wide variety of synthetic materials is available.

In planning resist formulations, compatibility of the components must be taken into account and if a solvent is used, all components (except pigments, if any) must be readily soluble in the solvent. Compatibility is, of course, related to the rule that materials of similar composition are miscible with one another. Certain waxes are incompatible with other waxes, resins, asphalts, or other material [11]. In some cases compatibility of a mixture is obtained by the introduction of a third material that is compatible with the other materials. Compatibility is a relative term expressed in different cases as "excellent", "good", or "poor." The subject of compatibility, solubility, and other properties of waxes is too involved to be more than mentioned here, and reference should be made to the books by Bennett [11] and Worth [12].

Most waxes are poor adhesives, although they are among the best resists for hydrofluoric acid. The adhesiveness can, in some cases, be improved mixing with other materials such as rosin, resins, pitches, and asphalts.

If given sufficient time, waxes will absorb hydrogen fluoride. For example, wax bottles (mainly ceresin), which have been used for hydrofluoric acid, will not lose all of the absorbed acid even after washing and boiling the wax in water.

The asphalts available have a wide variety of properties. In general, asphalt from any one geographic location is likely to be fixed in composition, appearance, melting point, etc. To a large extent natural asphalts for many commerical uses have been displaced by coal-tar pitches, petroleum asphalts, etc., derived from the oil industry. For specific information the reader is referred to Abraham [13], who gives a detailed history, description, and sources of various asphalts, both natural and synthetic.

Resists are sometimes applied to the glass hot, no solvents being used. More often they are dissolved in a solvent, and this solution is applied by several methods, which will be described in another section. Several solvents are available that will dissolve waxes, pitches, and asphalts. The solvent should have a rapid rate of evaporation. Benzene is considered one of the best because of its good solvent power and desirable rate of evaporation. Carbon tetrachloride is a good solvent, but it has a tendency to introduce moisture, thereby spoiling the bond between the glass and the resist. As both of these solvents are very toxic, care must be taken to avoid breathing the fumes. The use of a hood with an exhaust blower is strongly recommended. Turpentine and chloroform are sometimes mentioned in the literature as suitable solvents. Such resists coated on glass will not dry completely but will retain a small quantity of the solvent for an indefinite time; therefore, the ruling characteristics may change with time. Resists containing turpentine would be expected to increase in hardness with age.

In practice a thin layer of the resist is coated on the glass to be etched. The thickness of the layer depends to a large extent upon the type of work to be done. For very coarse work, where the line or pattern is observed without magnificaton, the resist can be as much as 0.1 mm in thickness, but for lines of 1 to 6 μ in width, it may be only about the equivalent of 1 or 2 wavelengths of light in thickness. There is no standard or gage to use for determining the proper thickness for a specific job; it will vary with the composition of resist, the etching techniques, and the user's experience and judgment.

The most important qualities of an ideal resist may be itemized as follows:

(1) Impermeability to either gaseous hydrogen fluoride or to hydrofluoric acid for a length of time at least equal to the time required for etching.

(2) Firm adhesion to the glass surface.

(3) Insensitivity to changes in the mositure content of the atmosphere (relative humidity).

(4) Ability to be engraved cleanly (that is, not be soft and stick to the tool, giving a line of variable width, or be hard and brittle, producing a ragged-edged line).

(5) Retention of its characteristics for at least a week after coating.

(6) Retention of its engraving characteristics over a moderate range of temperatures.

(7) Resistance to loosening of its bond with the glass under moderate thermal shock (10 deg).

The listing of these desirable characteristics will give the reader an idea of the nature of the difficulties commonly encountered with resists. The following is a brief discussion of difficulties, given in the same sequence as the desirable qualities were enumerated.

(1) *Permeability to hydrogen fluoride or hydrofluoric acid.* Practically all of the ingredients and solvents previously mentioned will take up several percent of hydrogen fluoride if given sufficient time; however, the rate of permeability is so low that no difficulty is likely to be encountered. Certain synthetic waxes, such as chlorinated naphthalenes, are so permeable to hydrogen fluoride that only a light etching can be made before the whole surface of the glass is mildly etched. Considerably better etchings can be obtained if hydrofluoric acid is used instead of the dry gas.

(2) *Lack of a good bond to the glass.* This is a common defect, and when present to a small degree is sometimes overlooked. After etching, it can be observed with a microscope as a gradual sloping of the surface of the glass toward the etched line, or as a rounding of the edge of the etched line

at the surface of the glass. It should not be confused with the tapering sides of a deeply etched line. We have termed this defect "surface undercutting." Surface undercutting appears to be caused by a progressive lifting of the resist during the etching, probably a weakening of the bond due to stress during the ruling or engraving. Another form of undercutting is the normal removal of the glass in deep etching so that the resist layer extends beyond the side of the deeply etched line, the adjacent surface of the glass being free from etching. This is illustrated in figure 5.

(3) *Adverse effects of moisture.* Moisture on the surface of the glass or within the resist reduces the adhesion of the resist to the glass. Most resist materials are moisture-permeable or moisture-absorbent to some extent [11, p. 160]. The ruling characteristics of very thinly coated resists containing materials with appreciable hygroscopicity may be expected to change if subjected to an atmosphere of high humidity.

The difficulty of obtaining a strong bonding of the resist coating to the glass is probably due in part to a layer of moisture at the surface of the glass. Hubbard, Cleek and Rynders [14] have definitely established that glass surfaces exposed to water have a measureable hygroscopicity which varies with the kind of glass. It is very likely that this taking up of water is not merely an adsorption on the surface, but involves chemical combination within the surface layer of the glass. Indications are that the amount of water in glass surfaces follows changes in the relative humidity. Heating a glass to drive off moisture is only temporarily effective; when the glass is allowed to fall to room temperature, the moisture is again taken up in some proportion to the relative humidity.

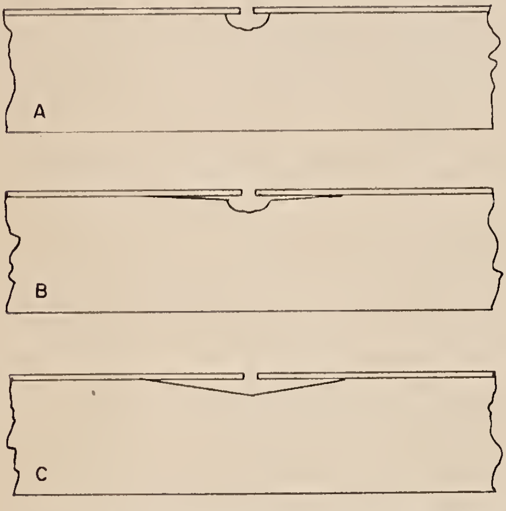

Figure 5. *Sketches showing three kinds of etched lines.*

The sketches were drawn as sectional views from visual impressions received with the microscope by observing normally to the wax resist coating. The top view, A, indicates a good etching of a deep line with normal undercutting of the wax resist. The resist coating retained its adhesion to the glass during the etching. The middle figure, B, indicates "surface undercutting." The adhesion of the wax resist loosened progressively during the etching, which resulted in a gradual slope of the surface of the glass toward the etched line. The bottom figure, C, represents an "excessive", or "abnormal", undercutting, resulting in a very widely etched area that slopes toward the etched line so excessively that the boundary of the etched line is sometimes difficult to find. Resists that have a poor bond to the glass will show this effect.

(4) *Unsatisfactory engraving or ruling quality of a resist.* This is of the greatest importance, since the quality of the final product, the etched lines, is dependent upon it. Faulty positioning of the engraving tool can, of course, spoil the work after a good resist coating has been applied. The point to be made here is that the resist layer must not be too soft or it will stick to the tool, giving a nonuniform line which changes in width somewhat periodically. Furthermore, at intersecting lines trails can be seen that show plainly which line was ruled last. On the other hand, a resist coating is sometimes too brittle. In this case the edges of the lines are ragged, giving a saw-toothed effect. In extreme cases flakes of resist are broken out, sometimes to a considerable distance (several line widths) from the line. Paradoxically, the same resist can sometimes show the effect of being both too hard and too soft; that is, the rulings show both effects to a small degree. This condition is generally due to a change of ruling speed; at low speeds, the resist tends to behave as if soft, and at high speed, it tends to behave as if brittle. Toughness is another characteristic sometimes encountered in resists. Such a resist can be satisfactorily engraved with a sturdy, properly shaped tool, but not equally well with a stylus or a delicately pointed round tool. Toughness can sometimes be remedied by addition of a plasticizer or a soft component.

(5) *Change of the ruling properties of a resist with time.* When a volatile solvent such as benzene is used it will evaporate rather quickly, but, while the resist may be ruled shortly after its application, it appears preferable to let it season a few hours or overnight before ruling. Resists containing drying oils behave like paint and are slow in drying: the best time for ruling has to be determined by trial. Compositions containing mainly soft asphalts often flow, causing the engraved lines to close up slowly; consequently, they cannot be used when the engraving requires several days to complete. Such a resist could be used when both ruling and etching can be completed in a short time, as in some reticule work.

(6) *Change of the ruling properties of a resist with temperature.* When resists contain a high percentage of wax the quality of rulings is markedly affected by the temperature at the time of ruling. It is, of course, desirable to have a resist that can be engraved well at room temperature (22° to 25° C), but this has proved to be a difficult problem. A resist that is too soft to be engraved satisfactorily at ambient temperature is sometimes much improved by lowering the temperature 2 to 5 deg. In general, compositions containing much soft wax can be engraved best at temperatures somewhat below 15° C. The addition of a compatible hard ingredient will usually improve a resist that is too

soft to rule at room temperature. However, too much of a hard material may make the resist sensitive to thermal shocks, resulting in some loss of adhesion, as explained in (7).

(7) *Loosening of the resist from the glass caused by large (10- to 20-deg.) changes in temperature.* The harmful effect of large fluctuations in temperature can be readily understood when one bears in mind that few, if any, of the wax-containing resist coatings are bonded very tightly to the surface of the glass, that the rigidity of these coatings increases with a decrease in temperature, and that the coefficient of expansion of waxes, asphalts, and resins is much larger than that of the glass on which it is coated. These factors combine to cause a reduction and, in extreme cases, a complete loss of the adhesion of the resist to the glass. Data on the coefficients of linear thermal expansion of waxes and asphalts are meager and widely scattered in the literature, but the examples in table 1 give some idea of their relative magnitudes. These data may not apply precisely to all samples of wax or asphalt.

TABLE 1. *Coefficients of linear thermal expansion*

Substance	Temperature range	Coefficient of expansion
	° *C*	
Plate glass [1]	0 to 100	0.089×10^{-4}
Beeswax (white)[2]	10 to 26	2.3
Paraffin [2]	16 to 38	1.3
Spermaceti [3]	25	3.2
Asphalt [4]	------------	[5] 2
Halowax,[6] No. 1014	------------	0.49
Halowax, No. 1013	------------	.64
Halowax, No. 1012	------------	.82

[1] Handbook of chemistry and physics, 34th ed., p. 1901 (Chemical Rubber Publishing Co., Cleveland, Ohio).
[2] Smithsonian physical tables, 7th ed., p. 219 (Smithsonian Institution, Washington, D. C.).
[3] A. H. Worth, Chemistry and technology of waxes, p. 489 (Reinhold Publishing Co., New York, N. Y., 1947).
[4] Handbook of chemistry and physics, 34th ed., p. 1906 (Chemical Rubber Publishing Co., Cleveland, Ohio).
[5] One-third of cubical expansion.
[6] H. Bennett, Commercial waxes, p. 118 (Chemical Publishing Co., Brooklyn, N. Y., 1944).

Use is made of the difference in expansion between glass and pitch in optical shops to remove reticule blanks from the pitch plate after polishing. This plate, covered with a number of reticule blanks, is placed in a refrigerator, and when sufficiently cold, the glass blanks will become detached from the pitch.

Some resists are much less sensitive to thermal shocks than others. For example, Halowax is much less sensitive to thermal shocks than beeswax; ceresin is about the worst in this respect; on the other hand, Halowax is much more permeable to hydrogen fluoride than ceresin. Except in extreme cases, no evidence of loosening of the bond to the glass is observable visually. Apparently the bond becomes so weakened that the stress caused by the engraving tool in cutting through the resist breaks the bond in the immediate vicinity of the engraving. Then upon etching, this area will exhibit "surface-undercutting."

In an attempt to secure stronger adhesions of wax resists to the glass, several substrata were tried but without much success. Waterproofing the glass with Amino Silane prior to coating gave lines with sharper edges. This method was used on circles; details are given in section 3.2.

3.2. Cleaning and Waterproofing the Glass Surface Before Applying the Resist

The glass must be cleaned with the same degree of care as in mirror-silvering. In the work under discussion, chromic acid cleaning solution (30 g of powdered potassium dichromate in 1 liter of concentrated sulfuric acid) was used. Some systematic method for handling the glass during the cleaning is needed, as otherwise the surfaces are likely to become scratched and nicked. For handling glass rings, tripods with glass legs were constructed from glass rod and rubber stoppers, as shown in figure 6. A ring blank was mounted on the tripod by squeezing the legs together and putting them through the hole in the ring. Upon releasing the pressure, the legs separate and hold the glass. The feet on the legs of the tripod prevent the ring blank from falling off and keep it from touching any flat surface on which the tripod may rest. After the cleaning solution had been washed off, the ring was placed under distilled water and swabbed lightly with absorbent cotton. After a final rinsing, it was placed on a whirler [2] and spun until dry. When dry, if the glass circle was to be waterproofed, it was placed in an oven at room temperature and heated to about 100° C. The circle was then removed from the oven and

FIGURE 6. *Glass tripods.*

Tripods with rubber (stopper) heads and glass legs used for handling of rings during cleaning and other operations.

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[2] The whirler was similar to that described in footnote 4, except that the circle holder consisted of a disk of methyl methacrylate 3¾ inches in diameter and ½ inch thick. The top of the disk was reduced in diameter to slightly less than the inside diameter of the circle (3½ inches) for a depth of ⅛ inch, to form a shoulder upon which the circle blank rested during the whirling. The disk, fitted with a central bushing, was mounted directly on the motor shaft.

immediately waterproofed, by exposing it, while hot, to the vapors of Amino Silane[3] for 90 seconds. This was done by suspending the tripod and ring in a large desiccator at room temperature, with the surface of the glass about 3 inches above the surface of the Amino Silane. It is not considered necessary to waterproof the glass to get good results, however, it was found to improve the results. The magnitude of the improvement resulting from the use of Amino Silane is demonstrated in section 5.4.

3.3. Methods of Applying Resist Coatings

In the experimental work that preceded the adoption of specific formulas for resists, the coating of the glass was done by flowing the resist solution on the glass while it was spinning on a whirler;[4] this method is rapid and gives a coating of uniform thickness. However, it was concluded that withdrawing the glass from the resist solution at a constant rate was a superior method because less trouble was experienced with trash and lint.

The withdrawing, or "pull-out," method is no more difficult than the whirler method when used for reticule coating. A small (500-ml) jar or can, having a tight closure, half-filled with resist, is kept in readiness in an incubator at 45° C. The container is removed from the incubator, the top opened, and the reticule, in a holder attached to one end of a rod, is dipped into the resist and, after a moment or two, is withdrawn slowly with a uniform motion. When large pieces of glass are to be coated, it is advisable to use a mechanical withdrawing method to avoid coating irregularities. The mechanical method used in later work will now be described.

The mixture of beeswax, gilsonite, and Burgundy pitch (formula P–1), described in section 3.5, was filtered into a clean stainless-steel tank 3½ by 7 by 20 inches, having a flat top fitted with a plate-glass cover, as shown in figure 7. In use, the stainless-steel tank was immersed in a constant-temperature bath maintained at 45° ±1°C. A completely inclosed reduction-gear synchronous motor, mounted above the tank, was used to drive a V-pulley, which pulled the glass circle blank or master circle blank out of the resist solution. The glass blank was supported by a wire hook fastened to one end of a cord. On the other end was fastened a counterweight, the cord being supported by the aforementioned pulley, as shown in figure 7. Before being coated, the glass blank, supported on a tripod, was submerged in filtered benzene, gently swabbed with cotton, and rinsed with filtered benzene; it was then immediately placed on the wire hook attached to the cord and completely immersed in the resist solution. A two-piece glass tank cover, each piece with a small notch cut in the center of one edge, was put in place with the edges butting (that is, with notched places together so that the supporting cord could pass through without touching the glass cover). The glass covers protected the tank from drafts and helped to maintain a high concentration of benzene vapor above the resist solution; these conditions were necessary to obtain uniform and reproducible coatings. After the glass blank had been completely immersed and the tank covered for a period of about 3 minutes, the motor was started and the glass drawn out of the solution at a uniform rate of approximately 1 foot in 80 seconds. The circle should not twist or turn when it is being drawn out of the resist solution as this may cause variations in the thickness of the coating. The motor was stopped just before the glass touched the tank covers. The tank covers were removed and the resist-coated glass was lifted out

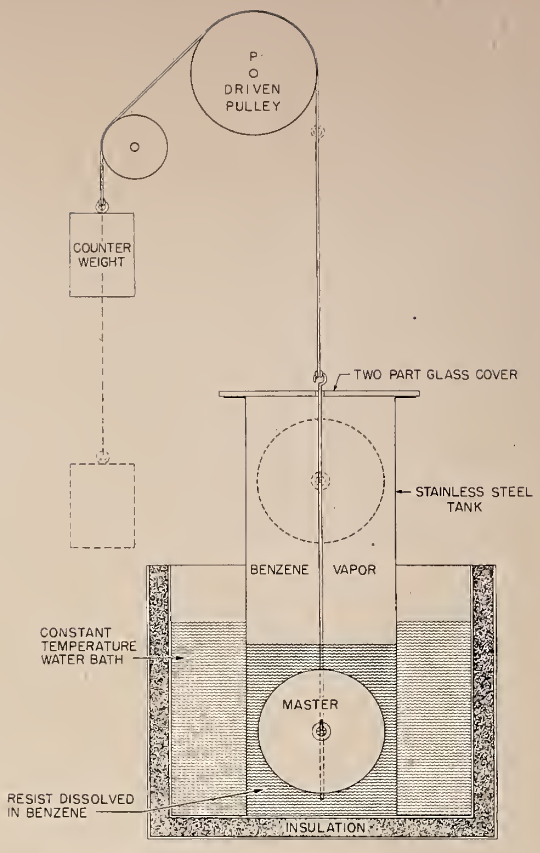

Figure 7. *Schematic view of the apparatus used for coating the glass with wax resist by the pull-out, or withdrawing, method.*

The glass, immersed in a solution of the wax resist, is withdrawn by the pulley, P, driven at a uniform rate. The speed of the pulley, the temperature of the solution, and its composition control the thickness of coating.

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[3] The chemical composition of Amino Silane is di-tert.-butoxydiaminosilane. See Miner et al, Ind. Eng. Chem. **39**, 1368 (1947).

[4] The whirler, used for coating the master with a resist, was made with four arms 6 inches long, 90 degrees apart, each with an adjustable stop. The position of the stops was adjusted to hold the glass in the center of rotation. The arms were attached directly to the shaft of a 110-volt, ⅛-horsepower, shunt-wound, direct-current motor. The motor was mounted with its shaft vertical; thus the glass rotated in a horizontal plane. The field of the motor was connected across the line. A slide-wire rheostat of about 150-ohm resistance was also connected across the line. One of the armature leads was connected to one side of the line, and the other armature lead was connected to the rheostat slider. By adjusting the position of the rheostat slider, any speed from zero to full motor speed (1,750 rpm) could be obtained.

FIGURE 8. *Bakelite holders for resist-coated circles.*

The right-hand figure shows the method of placing the circle into the Bakelite holder preparatory to ruling, numbering, and etching. In the background, the circle is positioned in the holder. The metal plate with center peg and three pins, on the left, is used to remove the circle from the holder. After the etching is complete and the resist has been dissolved off the glass, the holder and circle are placed on the metal plate. The three pins fit into three mating holes in the holder and push the circle out of the recessed groove.

of the tank. This procedure gave very clean and uniform coatings. The resist solution may be used for an indefinite period before it needs refiltering. If the resist solution becomes too cold on standing without the temperature control, the beeswax will precipitate; it is then necessary to warm the tank of solution on the steam bath to about 60° C until it is certain that the beeswax has redissolved before replacing it in the constant-temperature bath. If the temperature of the resist solution rises to 50° C during coating, the resist becomes sticky; this is evidently due to an increase in the concentration of beeswax coating out on the glass. Because of the poisonous nature of benzene, the coating should be done in a well-ventilated room, preferably under a hood. Because benzene is highly flammable, care must be taken that no flames are near and that no sparking electric devices are operating in the immediate vicinity.

If the glass was a master, it was removed from the hook by grasping it at the edge of the glass with the fingers; if a circle, a tripod was used to take it off the hook [5] and to place it in a Bakelite holder designed to contain the circle during the engraving and etching. This Bakelite holder, ½ inch thick and 6 inches in diameter, is shown in figure 8. It had a recessed band milled out as a seat for the ring. The depth of this band, or groove, was about 1/16 inch less than the thickness of the ring. Consequently, the surface of the circle was slightly above the surface of the holder. The circle was fastened in this holder with 3 or 4 small pieces of wax, which were melted at the inside edge of the glass, using a short, electrically heated, U-shaped piece of resistance wire on a handle.

Resists are also applied to the glass hot without the use of solvents. This method is best suited for small-sized glass such as reticules. The resist ingredients are melted and well mixed (see formula H–1, section 3.5). The glass is heated in an oven or over a Bunsen burner, and a small amount of resist is spread over the surface of the glass while hot. A strip of paper somewhat wider than the reticule is placed on top of the melted resist, then slid off with a continuous motion. The glass is then reheated (not too hot) and finally placed on a warm, level surface to allow any fine streaks in the resist to level out. When cooled to room temperature, it is ready to rule. Some excellent etched lines have been made with this kind of resist.

3.4. Procedure Followed in Developing and Testing Experimental Resists

The general procedure used for finding suitable resists was to make up solutions, composed of one or more of the ingredients in a suitable solvent, to coat them on glass, and to test the resist for its ruling and etching properties. The principal solid materials used in this work were:

Asphalts	Resins	Waxes
Asphaltines	Burgundy pitch	Beeswax.
Gilsonite	Congo resin	Candelilla wax.
Roofing asphalt	Coumar resin	Ceresin.
Trinidad asphalt	Pine tar	Halowax.[a]
Asphalt paints	Rosin	Ozokerite.
	Piccolyte resin	Paraffin.
		Spermaceti.

[a] Chlorinated naphthalene.

In addition to those listed above, a number of waxes synthesized from petroleum were tried, but these proved too insoluble to be of use. Carnauba and candelilla waxes are soluble only after heating, and Halowax [11, p. 117] is toxic.

Benzene was used as the solvent in most of the work, because of its good solvent power and its rapid evaporation from the resist coating. Other solvents tried were carbon tetrachloride, ethylene dichloride, toluene, turpentine, and xylene.

Most experimental formulations contained approximately 6 g of solid material per 100 ml of solution. Each formulation was coated on a 3¼- by 4-inch glass plate by pouring from 3 to 5 ml of the resist solution onto the center of the glass plate while it was rotating at from 400 to 600 rpm. The resist dries almost immediately, and, in most cases test rulings can be made in a few minutes, but it is preferable to test the resist after a lapse of a few hours and to retest it after storage overnight to note any changes caused by aging. If the resist had good characteristics, additional tests were made after further aging.

Test lines were engraved in the resist with the reticule-ruling machine. The ruled patterns generally consisted of 6 or 8 lines about 1 cm long, spaced about 100 μ apart; a second set of lines was ruled through the first set of each pattern at an angle of 90 degrees. Each such pattern was

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[5] The area to be engraved on circles was about ⅛ inch from the outside edge. Consequently this edge should not be touched with the hand.

numbered (by hand scribing) for identification. The patterns were examined with a microscope (16-mm objective and a ×10- or ×15-eyepiece) for quality of lines, with particular attention to edges, the beginning and ending of lines, and trails at intersecting lines. After this examination, the individual patterns on the glass were treated separately with experimental etching solutions or with dry hydrogen fluoride. The etched patterns were again examined with the microscope, the observations being compared with those previously made. Inspection also was made for any new defects and for surface-undercutting. This latter defect can be seen, when present, by adjusting the microscope in and out of focus on the surface of the glass at and near the edge of a line. If the surface of the glass slopes toward the etched line and the edge is not sharp, surface-undercutting is present.

3.5. Formulas Adopted

Some very high-quality lines were ruled and etched on masters in the beginning of this work with a Halowax and gilsonite resist. This resist was coated on the master with the whirler at 600 rpm. The etching was done with dry gas, using the wax pot described in section 5.2. The particular sample of Halowax used was very old, and its source could not be identified. This resist, thinly coated (about 0.00001 inch thick) had one fault; it was somewhat permeable to the hydrogen fluoride, and the glass surface was faintly etched. However, this mildly etched surface was easily removed by polishing. Polishing of the glass was necessary when lead sulfide was used to fill the lines and is described in section 6.1. The following resist is equivalent to that mentioned:

Resist Formula W–1

Halowax No. 1014	33.5 g.
Gilsonite	22.5 g.
Burgundy pitch	3 g.
Benzene	1,000 ml.

This resist can be used with liquid etch No. 2, section 5.3, to etch lines considerably deeper than can be obtained with gas etching.

Beeswax is one of the most commonly used substances of those investigated. It bonds to the glass somewhat better than most waxes and is not attacked by the etching solution, but it is too soft to use by itself. Beeswax is compatible with asphalts and resins. Gilsonite, one of the asphalts of fixed composition is less likely than other asphalts to vary appreciably from one lot to another.[6] It was found that a mixture of about 40 percent of white, bleached beeswax and 60 percent of gilsonite engraved well when the temperature was not higher than 22° C, but was improved by the addition of about 5 percent of Burgundy pitch. The Burgundy pitch used was soluble in ethyl ether, ethyl alcohol, benzene, acetone, 10-percent sodium carbonate solution and 10-percent borax solution. Hard pine tar may be substituted for the Burgundy pitch but it not quite as satisfactory. The following resist formula has a concentration of ingredients suitable for coating the glass by the whirler method:

Resist Formula W–2

Gilsonite	34 g.
White bleached beeswax	21 g.
Burgundy pitch	3 g.
Benzene	1,000 ml.

This resist was not attacked by the etching acid, could be engraved without sticking to the tool, did not become brittle on storage for several weeks, and bonded well to the glass.

A 6-inch disk of glass, coated at 600 rpm with resist W–1, had a coating about 0.00001 in. thick. Resist solution W–2 gave a coating thickness of about 0.00002 inch under the same conditions.

The thickness of coating may be adjusted to individual needs by changing the proportion of solvent to solids of the resist formula or by changing the speed of whirling. Dilution of solutions and higher whirling speeds produce thinner coatings. The size of the glass to be coated is another factor to be considered. Small glasses require higher speeds than large ones. For example, ½-inch-diameter reticules were coated at 1,800 rpm, whereas 6-inch glass was run at 400 to 600 rpm with the same resist.

A number of theodolite circles were coated with a modification of this resist by drawing them from the solution at a uniform rate, as explained in section 3.3. The formula for this modified resist is:

Resist Formula P–1[a]

Gilsonite	103 g.
White bleached beeswax	63 g.
Burgundy pitch	9 g.
Benzene	1,000 ml.

[a] The temperature of the solution at the time of use should be 45° to 46° C (see section 3.5).

The temperature at the time of ruling has a decided effect on the ruling characteristics of any wax resist. A temperature of 25° C or above will cause the P–1 resist to become soft and stick to the tool, and a poor engraving will result; at 18° to 20° C excellent results were obtained. Resist P–1 gave a coating about 0.00004 inch thick.

In reticule work the coating, ruling, and etching is usually completed in a short time, an hour or two at most; consequently, requirement (5) in section 3.1 can be relaxed. Additional formulas, which can be used for reticules, are given hereinafter. Formulas W–3 and W–4 are intended for the whirler method of coating.

Resist Formula W–3

Piccolyte S–85	27 g.
White bleached beeswax	7 g.
Burgundy pitch	27 g.
Benzene	1,000 ml.

---

[6] Any asphalt sold in the powdered form is almost certain to be gilsonite. The gilsonite (fusion point 125° to 135° C) was obtained in lump form.

Resist Formula W–4

Gilsonite	30 g.
Rosin	20 g.
Roofing asphalt	10 g.
Copper oleate	10 g.
Beeswax	2 g.
Benzene	1,000 ml.

The following formula is intended for the pull-out or dipping method of coating:

Resist Formula P–2 [a]

Gilsonite	87 g.
White bleached beeswax	58 g.
Burgundy pitch	7 g.
Copper stearate	7 g.
Benzene	1,000 ml.

[a] Coating temperature, 45° C.

A hot method has the advantage of ease of application of the resist with a minimum of equipment. On the other hand, it is more difficult to obtain uniform thickness. Further, the variety materials that can be used is somewhat restricted because some materials that are compatible when dissolved in a solvent may not be compatible when melted together. An example is the mixture of asphalt and wax prescribed for resist formula W–2. Glass to be coated by the hot method is heated over a Bunsen burner or, preferably, in an oven to a temperature somewhat higher than that required to melt the resist. A small amount of resist is applied and spread over the surface. Next, one end of a strip of paper somewhat wider than the glass is laid on the resist and slid off with a continuous motion in the direction of the plane of the glass. Following this, the glass should be reheated and placed on a level surface, so that any small streaks, created when the paper was pulled off, can level out. The following formula makes a satisfactory resist for hot application:

Resist Formula H–1

Gilsonite	12.5 parts by weight.
White bleached beeswax	4.5 parts by weight.
Ceresin	58 parts by weight.
Stearic acid	25 parts by weight.

4. Ruling and Engraving the Resist

4.1. Engraving Engines and Machines

Engraving wax resists is a step in the process used in the production of a wide variety of articles, ranging from metal nameplates for manufactured articles, on the one hand, to very precise scales read with high magnification, on the other. Obviously, graduations to be read with little or no magnification need not have the accuracy of placement or the quality of line necessary for scales intended for measurements of the highest possible precision. Jones and Hammond [9] have described machines and processes used for nameplates and scales for both general and precision use. Their article gives an interesting survey of the manufacture of etched metals, glass scales, etc., and includes a description of a number of instruments, including the circular dividing engine, the linear dividing engine, and the pantograph.

In the work described in this paper a circular dividing engine, which has been described in detail by Page [1], was used to graduate the master circles and theodolite limbs; a pantograph of original design was built and used for numbering graduations; and a specially designed engine was constructed and used for ruling reticles. The reticule-ruling machine is shown in figure 9. Figure 10 shows a typical pattern of the precisely ruled lines obtained with this machine; the accuracy of placement of the lines was ±1 μ. As discussed above, the reticule-ruling machine was also used for testing experimental formulations of resists. When many reticules of the same design are to be made and the utmost in precision is not required, use of the pantograph is to be recommended. With a pantograph of suitable design and a large metal template engraved with the desired pattern, 10 or more recticules can be engraved at one time; curved lines, circles and characters can be made with equal facility.

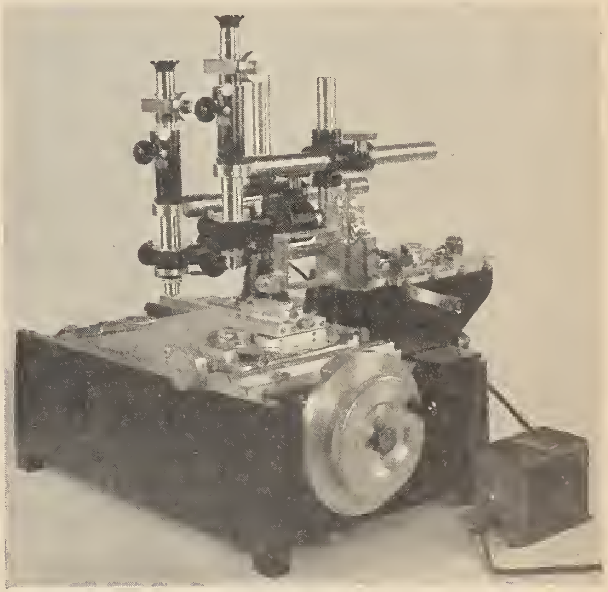
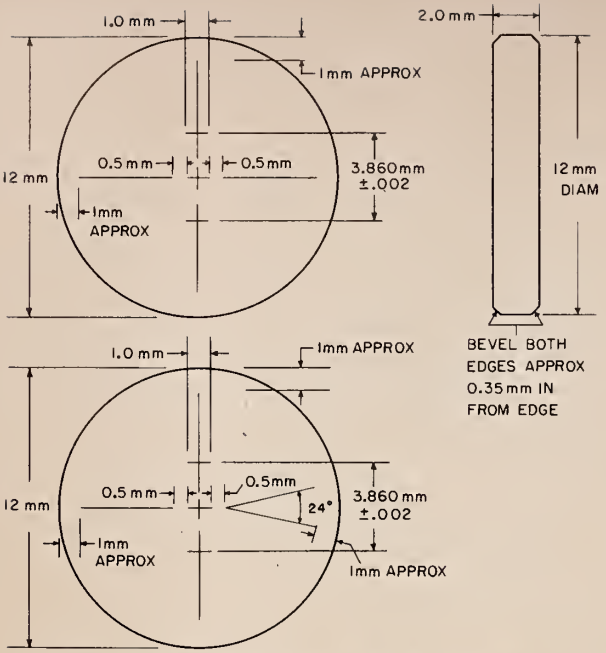


FIGURE 9. *Reticule-ruling and measuring machine.*

This apparatus, designed for laboratory use rather than for production of a large number of reticules, has an accurately lapped screw of 1-mm pitch. The graduated drum adjoining the hand wheel is fitted with a vernier and may be easily read to 1 μ. Equipped with microscope eyepieces and filar micrometers, as shown, it may also be used as a measuring instrument of high accuracy. The table attachment for holding reticules has longitudinal and crosswise adjustments, as well as a divided circle with vernier and tangent screws for angular positioning. The ruling point is supported on a light-weight frame, or yoke, with flexure plates instead of the usual pivots. A dash-pot controls the lowering of the ruling tool onto the work. The length of lines ruled with this instrument is controlled by a star wheel with adjustable stop screws.



ETCHED LINES 4 MICRONS WIDE, UNFILLED CENTRAL INTERSECTION WITHIN 12 MICRONS OF CENTER OF GLASS DISC.

Figure 10. *Two reticule patterns.*

The numbers for the graduations of a theodolite circle of 4-inch diameter are usually about 0.006-inch high. The numbers on the scribing template are 0.5 inch high and, by suitable adjustments, numbers in the range 0.004 to 0.007 inch can be produced. The numbers 4 and 8 were designed without "cross-overs," to avoid the trails so often shown at intersections of etched lines. The unique feature of the pantograph is that either coordinate of the motion of the tracing stylus in relation to that of the scribing needle can be reversed independently; by changing the position of two pins, the engravings can be made to be any one of the four possible mirror images of the scribing template.

4.2. Ruling Tools

One of the difficult problems in engraving fine lines and numbers in a resist is to obtain satisfactory tools to remove the resist cleanly and not wear out after a few rulings. Because the literature is particularly meager on the subject of engraving and scribing tools, the subject will be discussed in a general way, including a description of the method of making the scribing tools. It should be pointed out that much of this work was done under wartime pressure, and the most expeditious rather than the best way of making these steel tools had to be adopted.

a. Diamond Tools

The shaped diamond is, of course, the best tool because of its hardness and wear resistance, but it can easily be damaged by careless handling or improper use. Finding a source of supply is difficult, as most lapidaries are not prepared to furnish diamond tools with suitably sharp edges. The very small flats (3 to 6μ wide), necessary on the bearing surface to obtain a line of the desired width, are also an unusual requirement. The shapes of diamond tools, and their adjustment in the circular dividing engine, have been discussed by Page [1]. It is appropriate to mention here that the late Frederick Knoop, while a member of the Interferometry Section of the Bureau, worked out the techniques for the production of the diamond tools of exceptional quality used in this and other Bureau work.

It may be noted that the tools described by Page have a negative rake, which is necessary for ruling metal to prevent the tool from hogging (digging into the work), since the tool is not otherwise constrained in its motion to and from the work during the ruling. Although these tools gave satisfactory results in the ruling of resists on glass, it is believed that tools with a positive rake (leading face sloping backward) would produce cleaner engraving because the removed resist would be less likely to pile up on the face of the tool. To make such tools might create a problem for the lapidarist as, in order for the diamond to be lapped at the proper angle, it would have to be mounted so that a part of it would project beyond the side of the shank. It would be preferable for the face of the tool to be concave (that is, a section of a cone), with the axis inclined sufficiently to produce about a 10-degree positive rake. A tool of this shape would act somewhat like "chip-breakers" in cutting the edges of the engraving, and would also tend to funnel the carved wax out of the groove.

b. Steel Tools

Steel tools were used in engraving the resists on reticules, as well as in numbering the graduations of circles. They are much less expensive than diamond tools but wear out much faster. However, they are relatively simple to make and are easily resharpened. The engraving tools for reticule work were made from high-carbon steel (drill rod) 0.107 inch in diameter and 2 inches long. These were put on a surface grinder and 0.010 inch was ground off on one side, the full length of the tool, thus making a flat surface, which was used to clamp and position the tool. The tool blanks were heated to about 1,450°F (bright cherry red) and quenched in brine or mercury.

A relatively simple device was constructed to shape and sharpen the steel tools. This consisted of a small, shunt-wound, 120-volt d-c motor, mounted with the shaft vertical, as shown in figure 11. A steel hub with a sleeve was fastened to the motor shaft by a setscrew. A small abrasive wheel with a ⅜-inch hole was clamped to the hub with a flange and nut as shown. The wheels used were ceramic-bonded alundum, about ⅛ inch thick by 4 inches in diameter; 120-grit wheels were used for roughing out, and 200-grit for finishing the rough grinding. At the right of the motor was a steel post about 1¼ inches in diameter and 5 inches high, having a ⅜-inch hole drilled through its longitudinal axis; the lower end of this hole was threaded for a cap screw to fasten the post to the base. A forked bracket on a ⅜-inch steel rod fitted into the post without any sidewise play. A clamping collar, with thumbscrew on one side and a 3/16-inch rod handle about 3 inches long on the other, served to position the height of the fork and permitted it to be turned with the handle as required. The tool holder consisted of a ⅜-inch steel rod 3 inches long, with a longitudinal hole about 1 inch deep in one end and a thumbscrew for clamping the tool. Near the other end were two steel pins, ⅛ inch in diameter by 1½ inches long, pushed halfway through the rod. One of the pins was parallel to the axis of the thumbscrew, and the other was perpendicular to it. A second tool holder, also shown in figure 11, differed from the one just described, in that it had pins on an adjustable collar, which permitted the adjustment of the grinding angle of the tool. These pins (in the form of a cross) supported the grinding fixture in the fork. The elevation of the fork controlled the included angle between the two sides of the tool.

After the tools had been hardened, they were ground on two sides (180 degrees apart). A low speed (about 600 rpm) of the wheel is desirable, but the wheel need not be wet, as at this low speed there is very little heating of the tool. During grinding, the tool is moved back and forth across the section of the wheel, which is rotating away from the tool. This prevents wearing a groove in the wheel and produces a smoother surface on the tool. The pressure of the tool on the wheel was of the order of 15 g (½ oz), and the angle of the tool above the plane of the grinding wheel was about 22 degrees. Grinding was continued, the tool and its holder being turned through 180 degrees occasionally, until a sharp edge was obtained.

For the final finishing of the edge of the tool, the abrasive wheel was replaced with a heat-treated, aluminum alloy disk, 5 inches in diameter by ⅛ inch thick, charged with 304 corundum. The aluminum lap was laid on a flat surface and sprinkled with No. 304 corundum powder before being mounted on the motor, then wetted with a small amount of water. A small piece of mild steel with a flat surface, such as a ¾-inch hex nut, was used for charging the lap. The whole surface was ground by rubbing the nut with a circular motion until the disk was a uniform gray. The charged lap was washed with soap and water, dried, and then mounted on the motor-shaft hub. The tool-holder fork was elevated about ¼ inch higher than in the rough grinding, so that the angle of the tool above the plane of the disk would be 28 to 30 degrees. The lapping was done with the same techniques as in grinding. The tool must be lowered gently on the lap to avoid damage to both the tool and the lap. A speed of about 300 rpm is recommended. The tool and holder were turned 180 degrees after 5 to 10 seconds of polishing. A 10-power jewelers loupe was used to follow the progress of the lapping. It is unnecessary to polish the tool more than ¼ mm back from the edge. When the edge appeared perfectly smooth, sharp, and bright, the tool-holder fork was lowered all the way, to obtain an angle of about 12 degrees between the tool and the plane of the lap. The tool and holder were then put in the fork so that the rounded side of the tool (90 degrees from previous polishing) was in contact with the lap. The polishing procedure was continued until a face ½ to 1 mm in length was obtained.

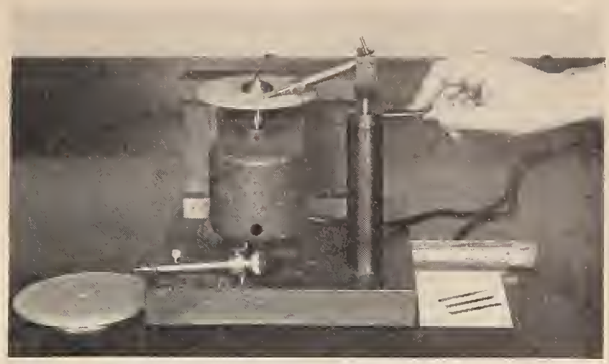


Figure 11. *Tool-grinding and lapping apparatus.*

Steel tools used for making reticules with the apparatus shown in figure 9 were shaped on this simple device. The disk on the bench to the left is an aluminum-alloy lap charged with very fine abrasive for finishing the edge of the tool.

Worn tools, if not damaged, may be reconditioned once or twice by relapping before regrinding is necessary. The lap should be recharged with the 304 abrasive when wear (bright areas) appears. This recharging of the lap by its grinding action helps to keep it free from ridges and grooves.

c. Scribing Tools for Numbering Graduations

For numbers or other irregular designs in wax resists, it is desirable that the tools have conical points, so that the width of lines will be the same, regardless of the direction of scribing. Because of the brittleness of the diamond, points made of this material must be in the shape of a blunt cone, with an included angle of 90 degrees. Perfectly conical diamond points are, however, exceedingly difficult to make. The tools must also be relatively thick, so as to be able to withstand stresses during lapping. Blunt, thick tools collect too much wax to be usable for the scribing of a resist, although they are satisfactory for scribing directly into metal surfaces. Further, the diamond crystal has certain planes that are so hard that it cannot be cut in these directions. Consequently, it is difficult to shape it to a symmetrical cone with a sharp apex.

Diamond chips or splinters have been used for microscopic writing directly on glass, but it is doubtful they would be satisfactory for scribing through a resist. Sometimes the effective point, usually a corner, is so close to neighboring parts of the diamond fragment that much of it would rub on the resist adjacent to the scribed area. If this is the case, it would be likely to break off. McEwen [15] describes selecting a writing point and describes his pantograph. One of his writings of the Lord's Prayer (56 words) is in an area 0.0016 inch long by 0.0008 inch wide. Some of the problems of ruling microscopic scales and reticules are also discussed by Nichols [16].

As diamonds of a suitable size and shape are not usually available, a steel point is generally used. After some experience is acquired, a point with the required sharpness can be made from a steel phonograph needle in about half an hour. A satisfactory point should appear sharp when viewed at 100 diameters with a microscope (16-mm objective, 10-power eyepiece).

The steel needle was chucked in a collet of a small lathe. With the lathe running at about 200 to 400 rpm, a small, *natural* oilstone of fine texture is brought up under the needle with light but firm pressure and moved back and forth at a small angle to the needle so as to make a cone for about one-fourth the length of the needle and ending in a sharp point. Considerable care is necessary to avoid breaking the point during the final stages. The progress of this operation should be observed with a 10-power loupe.

The next operation is a slight reshaping and putting a high polish on the point. A microscope slide or similar piece of glass is wet with rouge and water for about three-fourths of its length on one side. The extreme end of the slide is grasped firmly between the thumb and forefinger and the glass brought up under the needle with a light pressure at an angle of about 30 degrees to the needle and moved, in a crosswise direction, back and forth a distance of about an inch until a sharp, highly polished point is obtained. The point is examined frequently with a 10-power loupe to determine when it is ready to be taken out of the lathe and examined with the microscope. To clean the point for this examination, push it carefully through a small piece of tablet paper or newsprint. If this examination shows that the point was broken off, start over again with the oilstone.

d. Positioning the Ruling and Scribing Tools in Ruling Machines

Preparatory to ruling or engraving, the ruling or scribing tool is mounted in the ruling machine, or pantograph, as nearly as possible in the correct orientation. Needle tools should be vertical. Ruling tools must be carefully adjusted so that the sharp V-edge is exactly parallel to the direction of ruling and also with 1 or 2 degrees of clearance. It is necessary to use at least a 10-power loupe or preferably a low-power (×50) microscope to properly make this adjustment for clearance. The tools should rest on a level glass surface, and the weight on the point should be at a minimum. The contact area of these tools is very small, and a load, or weight, of 1 g may exceed the elastic limit of the steel, and the point will be deformed unless precautions are taken to prevent it. Table 2 gives the pressure on the tool point produced by a 1-g load on specified contact areas.

After the tool has been properly positioned, a little water and rouge are put on the glass around the tool, and a small flat is lapped on the tool by moving the glass or, preferably, by moving the tool with its mechanism back and forth through the rouge a few strokes until the desired width of contact is obtained. This width is determined by ruling lines in the wax resist and measuring the line width. Lapping is also necessary on needles and the same procedure is used.

TABLE 2. *Contact pressure on tool points*

Contact area of tool	Contact pressure of 1-g load on tool point per—	
	Square centimeter	Square inch
μ^2	*kg*	*lb*
½	200, 000	2, 844, 680
1	100, 000	1, 422, 340
2	50, 000	711, 170
4	25, 000	355, 585
8	12, 500	177, 792
16	6, 250	88, 896
32	3, 125	44, 448
64	1, 567	22, 224

It is difficult to state specifically the load to be used on a tool for engraving the wax because the actual contact area is usually unknown. Further, tools from the same batch are not always uniformly hard, and the elastic limit will vary correspondingly. The stress in the part of these tools in contact with the glass is always higher than that considered good engineering practice. In fact it is remarkable that they function as well as they do. The conditions of use may be considered as a "special case," and no engineering data appear to be available on the behavior of metals of such small dimensions under such heavy loads. Of course, the support, or backing, of the contact area by much thicker sections contributes materially to their strength. The fact that the glass is not fractured is, no doubt, also due to the support or backing of the glass in the immediate vicinity, elastically absorbing the strain. If one could observe the contact area of the tool and glass with sufficiently high magnification, the expected elastic movements of both glass and steel during the ruling would make an interesting study.

High-carbon steel, which could be hardened to around 60 on the Rockwell C scale, was tried and found to work satisfactorily. Consequently, no systematic study was made to find the relative merits of the various steels for ruling tools. Tungsten carbide might be better than any of the steels because of its hardness and high compressive strength.

With steel tools, it was possible to rule lines in wax of 1 to 2μ in width and to etch these to a width of 4μ. The steel needles used to scribe numbers were positioned in the numbering machine, and a small, flat surface, about 3μ in width, was lapped on the point, as previously described. Sometimes as many as six circles were numbered (a total of 2,160 graduation lines) with one needle before the point was worn too much for further use.

The useful life of a ruling tool, exclusive of accidents and wear, is also dependent upon the impact on the tool point by the ruling mechanism in setting the tool down on the work. The use of a rugged, heavy, rigid frame on pivots and a counterweight to reduce the load on the tool point to the desired amount is common practice. Many of these heavy fixtures were designed primarily for scribing, or engraving, relatively heavy lines in metal where the force required is much larger than is necessary for ruling in wax on glass. When a fixture of this type is used, the mass of the counterweight, as well as the pivoted frame and all other parts, which rotate about the pivots as a unit, contribute to the energy that is absorbed by the tool point at the instant of contact with the glass. Of course, the tool is lowered by a cam and levers so that the velocity is low. However, there are no springs between the tool and the arm and counterbalance framework to lessen the impact. It is fortunate that the wax resist helps to "soften the blow". However, for these fine lines, the mechanism should be designed to reduce the impact to a minimum.

5. Etching the Graduations

5.1. Examination of Engraving

Before etching the glass, the engraved lines and figures in the resist should be examined with a microscope. Note particularly the ends of lines for "pick-outs" caused by wax adhering to the tool; crossover points in numbers for wax trails; irregularities at edges of lines, small conchoidal fractures indicating brittleness; wax piled up on one side of line, indicating the tool was not set square with the direction of ruling, the heel of the tool was dragging on one side; small pieces of wax "chips" in lines or lying across lines; scratches or "digs" in resist; oil drops on resist, and other defects. If the defects are serious, the glass should not be etched because of its cost. A light repolishing is necessary before it can be recoated with resist because an invisible amount of glass is sometimes removed by the ruling tool. After the glass is etched, it should be reexamined, making use of the notes made of defects appearing in the ruled resist, because this is the only way that the importance of the various defects can be ascertained.

5.2. Methods for Etching

Glass etching is done with hydrofluoric acid because it attacks glass quite rapidly either in solution or in the gaseous state. It is also potent on human beings and will destroy living tissue [17]. If it is handled with the fingers, it will cause hard-to-heal sores and will work its way under the fingernails, where it is hard to get at to neutralize. If some should get on the skin, wash it off, and bathe immediately in lime water or borax solution or other deactivator. Keep a container of antidote conveniently at hand at all times. Protective gloves should be worn while working with it, and further, all operations should be carried out under a chemical hood with forced-draft ventilation to the outside. The gas, or vapors, are extremely irritating to the lungs. The glass to be etched should be held in tweezers, tongs, or special fixtures during the etching and washing operations. The apparatus and physical operations should be planned to reduce the hazard to a minimum.

For the class of work discussed in this paper, the glass may be etched by either of two methods: (1) hydrogen fluoride (gas), or (2) hydrofluoric acid (liquid). The gas form of etching can be done (a) with the presence of water vapor, or (b) with the dry gas without water vapor. With method 1–a the liquid acid is contained in a lead, wax, or other suitable container, and the glass being etched is held over the acid for a suitable time, usually from 10 to 60 seconds or more. In method 1–b, acid is mixed with sulfuric acid in a suitable container, which is kept closed at all times. In a closed container, the sulfuric acid takes up practically all water vapor in the space above the acid solution. The glass to be etched is subjected to the hydrofluoric acid gas (hydrogen fluoride) preferably by methods which will not require complete uncovering of the pot. Etching times are about the same as for method 1–a. These methods give a matte etch and are used principally for fine-line etching not intended for pigment filling. Vapor, or gas, etching has some advantages in that the etching times are longer than for most etching solutions, thus giving better control of the amount of etching. Chips of resist from rulings lying across lines (bridging) do not interfere with vapor or gas etching, and the method is clean and easy to operate.

Liquid etching solutions are more often used than the gas or vapor. These may be classified roughly into two groups: (a) solutions giving a clear etch, and (b) those giving a frosted etch. Clear etching is obtained with straight hydrofluoric acid (2–a). Dilute solutions up to a maximum strength of 48 to 60 percent are commonly used. Solutions giving a frosted (matte) etch (2–b) contain salts that promote the formation of insoluble fluorides of calcium, barium, or lead, depending upon the composition of the glass. The insoluble products formed during the etching interfere with the etching, thus causing a rough, or matte, surface. With a given kind of glass, the degree of matting and the size of grain are controlled by the composition of the etching solution. A résumé of glass etching given by Schweig [18] should be consulted for further details.

Another method, known as "dry-etching" or "powder-etching", used principally for etching trade-marks and sometimes for etching graduations in volumetric glassware, was not studied because of a lack of sharpness at the edge of the etching. The active agent is a fluoride salt, such as ammonium bifluoride, in the form of a fine powder. Details of this process are given by Jones and Hammond [9] and elsewhere [19].

5.3. Vapor Etching of Masters and Reticules

After some study of etching methods, it was decided to etch the masters with the dry gas (hydrogen fluoride). This method was chosen because, with the large size of masters (6 inches in diameter), it was believed that a more uniform etching could be obtained than with the hydrofluoric acid. Further, the etching time required with the dry gas was about 60 seconds, compared with ½ to 1 second with 48-percent hydrofluoric acid, thus giving better control.

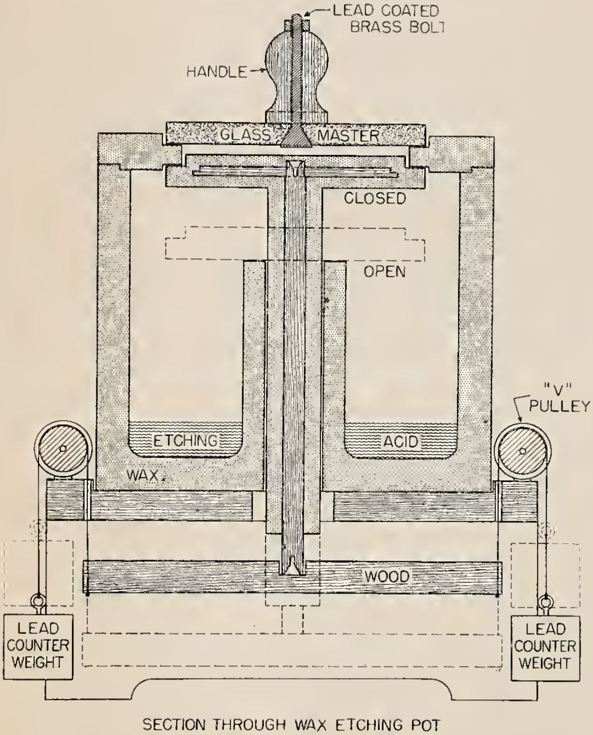


Figure 12. *Wax pot for vapor or gas etching of masters.*

The glass master, shown in position for etching at the top of the pot, is exposed to the etching vapors by lifting the two counterweights simultaneously. This causes the center unit to be lowered to the position shown by the dashed lines · Lowering the counterweights closes the pot.

Vapor etching of masters was done in a wax pot designed specifically for this purpose. Figure 12 shows a section through the pot, and its accessory fittings. The pot is cylindrical, 9⅛ inches in diameter by 8½ inches high. It was cast of ceresin, and the component parts were machined in a lathe [7] so that they fitted together accurately. The central piece has a round, wood stem with a plywood disk at one end for reinforcing the wax. The wood stem had centers drilled at the ends for turning this part to size on a lathe. This central unit rests on a small wooden beam; the beam is supported at the ends by cords that run over pulley wheels to lead counterweights. The counterweights are slightly heavier than the combined weights of the beam and the central or closure unit. The etching solution consisted of 500 ml of concentrated sulfuric acid to which was added (in the pot) from 10 to 20 g of calcium fluoride, depending upon the activity desired. This etching mixture should stand overnight to come to equilibrium. If desired, straight 48-percent hydrofluoric acid may be used. This will etch faster than the sulfuric acid mixture, and the etching will be nearly clear (only slightly matted).

In use, a wooden handle was attached to the master to be etched, and the master was placed face down on the pot in the recess provided for it, as shown in figure 12. The etching vapor had access to the master when the post closure, which opened inward, was lowered by lifting the two counterweights simultaneously. When the closure was lowered, a draft of vapor from the etching acid swept across the master from the edge toward the center. When the etching time had expired, the counterweights were lowered, thus closing the pot, and the master was removed and washed in a stream of water to stop the etching.

Excellent line quality was obtained by this method. The lines were of sufficient depth to be filled with lead sulfide but not deep enough to be filled satisfactorily with pigment by hand application. As previously mentioned (section 3.5), the resist used, principally Halowax and gilsonite, was somewhat permeable to hydrogen fluoride. The surface of the glass was faintly etched. However, the polishing required to remove the surface layer of lead sulfide also removed this surface etching. It may be of interest to mention that this pot, made 12 years ago, is much discolored but is still in good working order.

The same general etching procedure was used successfully in making about 500 precision reticules having line patterns, as shown in figure 10.

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[7] The wax pot and the ring part of the cover were fastened to a wood disk attached to the face plate of the lathe. Holes were drilled in the bottom of the pot and also in the wax ring. Wood screws with iron washers were used for fastenings. After turning, the holes in the wax pot and cover ring were closed by filling with melted ceresin.

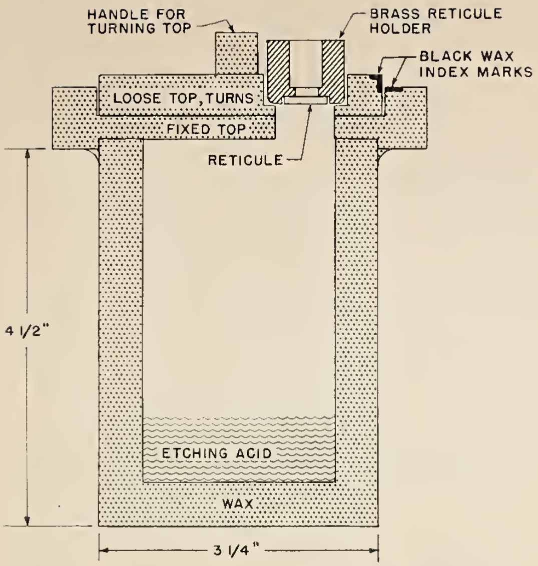

FIGURE 13. *Wax pot for vapor or gas etching of reticules.*

This sectional view of the pot shows a reticule in a brass holder in position for etching. Mating holes in the fixed top of the pot and in the rotatable top when in coincidence exposes the reticule to the etching vapors. Turning the movable top closes the pot.

The resist, mainly beeswax and gilsonite, was coated on the reticules with the whirler rotating at 1,800 rpm. The rulings were 1.5 μ in width and, when etched, were from 3 to not exceeding 4 microns in width. For the etching of reticules, a ceresin wax pot, approximately 4½ inches wide by 6¼ inches high, was constructed, as shown in figure 13. The main body of the pot, 3⅛ by 4½ inches, contains the etching acid. The top of the pot was permanently fixed on by sealing with hot ceresin. This top was recessed to provide a place for a disk, also of ceresin, which could be turned (rotated) in this recess. A hole, drilled off center through both the fixed cover and the disk, served as a gate valve and, when opened, provided access for the hydrogen fluoride to reach the reticule. The reticule, in a brass holder, rested on a shoulder in an enlarged part of the hole through the movable disk. Turning this disk about 90 degrees closed the pot.

The large etching pot (fig. 12) also can be used for etching a number of reticules at the same time by making an adapter consisting of a disk 6 inches in diameter of either ceresin or, preferably, of methyl methacrylate. This disk is drilled with holes of suitable size to support the reticules in their holders. This disk would be placed on the pot in the same position as the master.

These etching pots provide a clean, convenient, and safe method for vapor etching of glass. They could be made of lead or Monel metal. However, wax (ceresin) has some advantages in that the pots are relatively inexpensive, and their surfaces are always dry because the acid does not "crawl" on the wax. This is not the case with metal pots, particularly after they become old and the surface has become oxidized, corroded, or dirty.

5.4. Liquid Etching

Etching with aqueous hydrofluoric acid solutions is done by dipping the glass directly into the etching acid or by pouring the acid onto the engraved wax side of the glass. Of course the glass must be completely covered with resist, or otherwise protected, so that only the engraved areas of the glass are exposed to the action of the etching acid.

The resist does not limit the width of the etched line to that of the engraved line. In general, the width of the etched line exceeds the width of the engraved line by an amount equal to twice the depth of the etching. This approximate relation between the width of the engraved and etched line and its depth does not hold if the resist does not remain tightly bonded to the glass during the etching. A little reflection will show that an etched line that is narrow with respect to its depth can be filled more easily with a pigment than one that is wide with respect to its depth. As the width of an etched line cannot be less than twice its depth plus the width of the engraved line in the resist, it is obvious that the engraved line should be as narrow as other factors permit.

Experience indicates that the resist and etching techniques should be tailored to the particular job. A resist that works well on one kind of glass with a given etching solution may fail completely on a different kind of glass. Of course, one resist may be more versatile than another, but the requirements for etched glass scales and reticules are so varied that one combination (resist, glass, and etch) will not suffice.

As mentioned in section 3.1, materials used to compound resist coatings are, in general, nearly but not completely inert to either water or hydrofluoric acid or hydrogen fluoride. Some, like ceresin, paraffin, and beeswax, are better than others, such as coumar resin, rosin, and Halowax. Sometimes the water or acid is absorbed, and in other cases chemical reaction takes place or the resist is permeable. When these materials are coated on the glass in a thin layer, sometimes only a few hundred thousandths of an inch thick, it is to be expected that they will be troublesome at times. If the coating is made too thick, the etching acid may not wet the resist, and consequently, surface tension may prevent it from getting through a finely engraved groove to the glass, resulting in an etched line of irregular width and depth. Successful resists are usually a compromise of several factors.

Resists that are not inert to hydrofluoric acid or hydrogen fluoride (gas) are not suitable for deep etching. In some instances deep etchings can be obtained by repeated etching. For example, in one instance with a light-sensitive resist, the depth of etching was considerably increased by etching lightly, then washing off the etching acid, drying, and then reetching. This cycle could be repeated several times. The same result was obtained with a Halowax-gilsonite resist when etched with a liquid etching solution containing hydrofluoric and phosphoric acids (formula EP–1). In another instance, with the same Halowax-gilsonite resist and etching with hydrogen fluoride (gas), this procedure did not work; washing in water removed the resist.

Dilute etching solutions and some containing salts, such as those described by Schweig [18] for etching glassware, etch the glass more slowly than the concentrated 48-percent hydrofluoric acid. However, they are not always useful in the etching of fine lines because of a tendency of the etching acid to get between the resist and the glass and thereby produce an unusually wide etched line (abnormal undercutting). The same effect, only more pronounced, was observed with 48-percent hydrofluoric acid diluted with an equal volume of water. Concentrated 48-percent hydrofluoric acid etched rapidly and usually produced sharp-edged lines with no signs of abnormal undercutting. The principal difficulty with this strong acid was that the etching time for fine lines (10 μ or less) was too short to control accurately.

In section 3.2 mention is made of the use of Amino Silane for waterproofing the glass as a means of preventing abnormal (excessive) undercutting during the etching. Some resist formulations, when coated on glass, show abnormal undercutting during the etching; also some kinds of glass, particularly some of those having a fire polish, exhibit abnormal undercutting even with a resist that is satisfactory on other kinds of glass. Further, some etching solutions have a strong tendency for abnormal undercutting. The least satisfactory glass found is a particular lot of lantern-slide cover glass, and the etching solution with the greatest propensity for abnormal undercutting is etching formula ET–10 given below. This combination was used for testing resists and the effectiveness of waterproofing the glass with Amino Silane.

To illustrate the effectiveness of the Amino Silane treatment on the bonding of the resists to the glass and the effect of different etching solutions, the following experiment is described. Two lots of glass were chosen, (1) lanter-slide covers, and (2) plate glass known to be fairly good. After cleaning with chromic acid solution, one-half of each of the two lots of glass was treated with Amino Silane for 90 seconds, as described in section 3.2. All of the glasses were then coated with resist (resist formula W–2) on a whirler at 450 rpm. Test patterns were ruled in the resist on all of the glasses with the reticule-ruling machine. The pattern consisted of two sets of parallel lines about 1 cm long, one set ruled on top of the other at an approximate right angle, thus producing a small grid.

Six etching solutions were used in this test. The compositions of these and their identification is as follows:

Etching Solution EP–1

Phosphoric acid (85%)	100 ml.
Water	50 ml.
Hydrofluoric acid (48%)	25 ml.

Etching Solution EP–2

Phosphoric acid (85%)	150 ml.
Hydrofluoric acid (48%)	25 ml.

Etching Solution EP–3

Phosphoric acid (water removed by distillation)	100 ml.
Hydrofluoric acid (48%)	20 ml.

Etching Solution ET–10

Hydrofluoric acid (48%)	100 ml.
Water	100 ml.

Etching Solution EC–5

Hydrofluoric acid (48%)	qs

Etching Solution ES–7

Water	65 ml.
Ammonium bifluoride	100 g.
Sodium fluoride	11. 5 g.
Hydrofluoric acid (48%)	50 ml.

The first three formulas, EP–1, EP–2, and EP–3, are solutions of phosphoric and hydrofluoric acids, which differ principally in their water content. The solution containing the most water gives the least matte in the etching. These etching solutions were developed primarily for use with a photographic resist described in section 7. Their use with wax resists is recommended. Formula EC–5 is a 48-percent hydrofluoric acid solution. It etches rapidly and in most cases deeply etched lines of good quality can be obtained with it. Formula ES–7 is an etching solution containing salts to promote the formation of insoluble compounds during etching, such as the fluosilicates, which form particles that lie on the glass and interfere with the etching, thereby promoting an irregular etch or matte surface.

The results of these experiments are summarized in tables 3 and 4 and illustrated in figures 14 and 15. It may be noted in table 3 that the lantern-slide cover glass, untreated, gave good quality of lines without any signs of undercutting with the first three etching solutions and that the other three solutions produced unsatisfactory etches, all of which were severly undercut. The same glass treated with Amino Silane showed no under-

Table 3. *Effect of waterproofing on the quality of etching of lantern-slide glass*

Sample number in figure 14	Etching formula	Etching time	Quality of lines		Type of etch			Depth of etch			Edge of lines	
			Good	Poor	Clear	Matte	Coarse matte	Light	Medium	Heavy	Sharp	Undercut
Untreated												
		sec										
1	EP-1	20	×	------	×	------	------	------	×	------	×	------
2	EP-2	30	×	------	------	×	------	×	------	------	×	------
3	EP-3	30	×	------	×	------	------	×	------	------	×	------
4	ET-10	10	------	×	×	------	------	------	------	×	------	×
5	EC-5	5	×	------	×	------	------	------	------	×	------	×
6	ES-7	20	------	×	------	------	×	------	×	------	------	×
Waterproofed with Amino Silane												
7	EP-1	20	×	------	×	------	------	------	×	------	×	------
8	EP-2	30	×	------	------	×	------	×	------	------	×	------
9	EP-3	30	×	------	×	------	------	×	------	------	×	------
10	ET-10	10	×	------	×	------	------	------	------	×	×	------
11	EC-5	5	×	------	×	------	------	------	------	×	×	------
12	ES-7	20	×	------	------	------	×	------	×	------	×	------

Table 4. *Effect of waterproofing on the quality of etching of plate glass*

Sample number in figure 15	Etching formula	Etching time	Quality of lines		Type of etch			Depth of etch			Edge of lines	
			Good	Poor	Clear	Matte	Coarse matte	Light	Medium	Heavy	Sharp	Undercut
Untreated												
		sec										
13	EP-1	20	×	------	×	------	------	------	×	------	×	------
14	EP-2	30	×	------	------	×	------	×	------	------	×	------
15	EP-3	30	×	------	------	×	------	×	------	------	×	------
16	ET-10	10	------	×	×	------	------	------	------	×	------	×
17	EC-5	5	×	------	×	------	------	------	------	×	×	------
18	ES-7	30	------	×	------	------	×	------	------	×	------	×
Waterproofed with Amino Silane												
19	EP-1	20	×	------	×	------	------	------	×	------	×	------
20	EP-2	30	×	------	------	×	------	×	------	------	×	------
21	EP-3	30	×	------	×	------	------	×	------	------	×	------
22	ET-10	10	×	------	×	------	------	------	×	------	×	------
23	EC-5	5	×	------	×	------	------	------	------	×	×	------
24	ES-7	30	× [a]	------	------	------	×	------	------	×	×	------

[a] Etching solution is the type used for frosting glass. Consequently rough edges are expected.

cutting and the etchings were all satisfactory. In table 4, the results obtained with untreated glass show that all of the etching solutions except ET–10 gave good results. The same glass treated with Amino Silane again gave good results with all of the etching solutions. Not shown in these tables is the effect of the Amino Silane on the quality of the etching. In all cases the quality of the etch is definitely improved, even for those solutions that gave good line quality without its use. Also it should be mentioned that the amount of etching of the treated glasses is slightly less (possibly 10 percent) than of the untreated glass. That the improvement noted is not due to slightly less etching has been verified by other tests. Other experiments have shown that the waterproofing treatment also gives a similar improvement in vapor etching.

There are several products on the market for waterproofing by fuming or bathing with silane and silicone compounds. These waterproofing compounds were not tried, but it is believed that they would be effective. Some of these would require the use of a special cabinet.

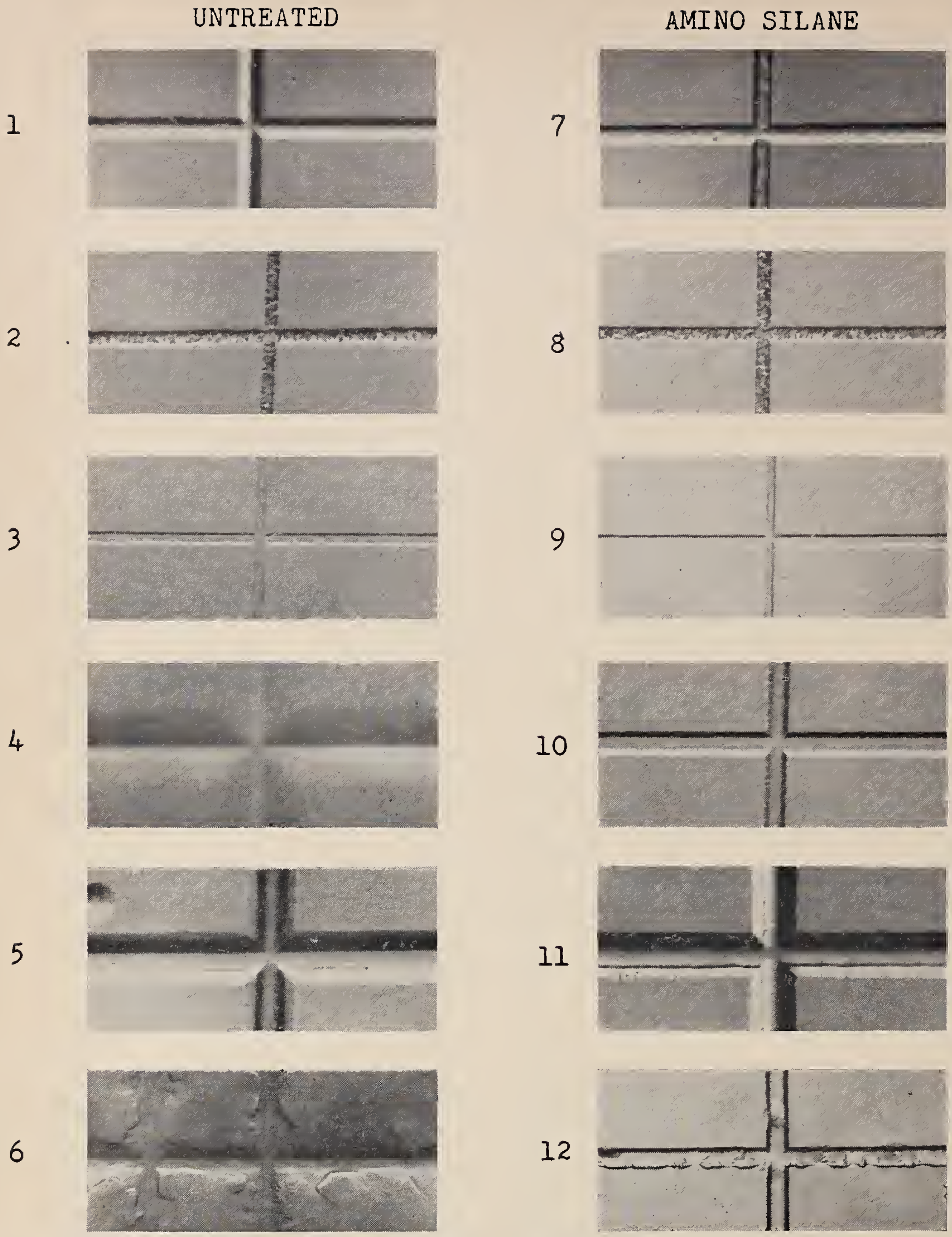

FIGURE 14. *Photomicrographs of etched glasses listed in table 3.*

The magnification is such that 5 μ equals 1 mm in the illustrations.

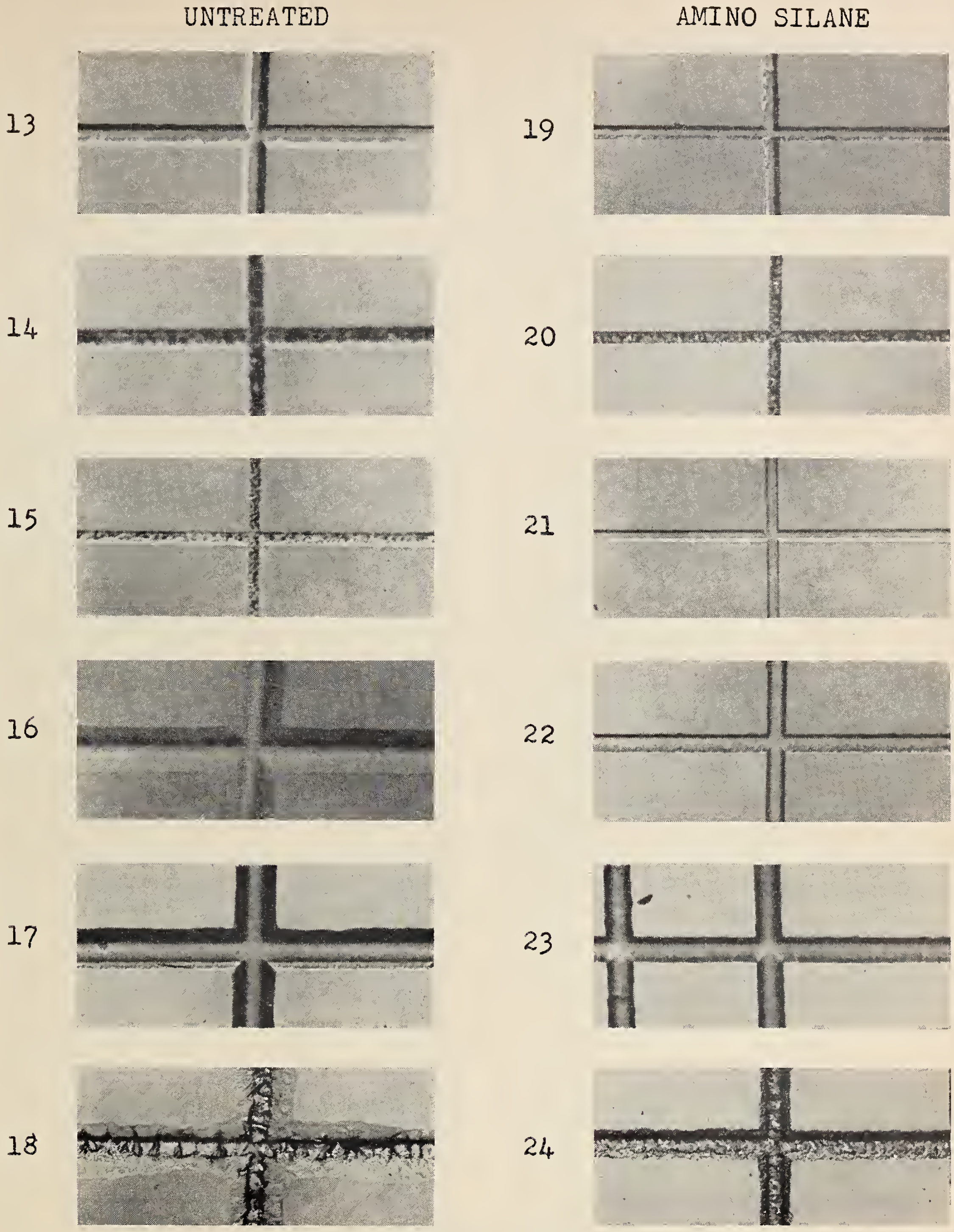

FIGURE 15. *Photomicrographs of etched glasses listed in table 4.*

The magnification is such that 5 μ equals 1 mm in the illustrations.

6. Filling of Etched Graduations

6.1. Filling With Lead Sulfide

Shallow etching, which produced narrow lines, was used on many masters and circles, and as the etched lines were not of sufficient depth to be filled with pigment, lead sulfide filling was used. The lead sulfide was deposited chemically on the surface of the glass in much the same way as in mirror silvering and then it was polished off, thus leaving it only in the etched areas.

The formulas found in the literature for depositing lead sulfide on glass proved difficult to use as a precipitate always formed on mixing the solutions and heating was usually necessary. The following formula was developed which gave satisfactory results:

Solution A:

Lead nitrate	10 g.
Distilled water to make	1 liter.

Solution B:

Thiourea	20 g.
Distilled water to make	1 liter.

Solution C:

Potassium hydroxide, 85% assay	23.5 g.
Distilled water to make	1 liter.

The sulfiding solution is prepared by taking equal volumes of each solution. Combine solutions A and B and add solution C to the mixture. When first mixed the solution should be clear. If a slight whitish precipitate persists, add just enough of solution C to make it disappear. Best results are obtained with stock solutions made up just before use, but they are usable for about 3 days. The time required for the coating to start depositing on the glass gradually increases with the age of the solutions. Experiments showed that the presence of sodium silicate inhibits the reaction and and prevents the deposition of the lead sulfide. Thus, the increase in time required for old solutions to work is caused by the dissolving of silicate from the glass bottles in which solutions are stored. As the concentration of the silicate increases, the time for deposition also increases and eventually heat must be applied to start and continue the reaction. The use of polyethylene bottles is suggested for storing these solutions.

The glass to be coated should be cleaned with chromic acid solution (see section 3.2) and not allowed to dry between cleaning and coating with lead sulfide. Pour the sulfiding solution into a dish containing the glass to be coated. When the stock solutions are new, the sulfiding solution is clear at first and in from 1 to 5 minutes it begins to deposit lead sulfide on the glass at room temperatures of from 25° to 30° C. With fresh solutions, the precipitation is continued for about 10 minutes. Three coats are applied, rinsing the glass and dish with distilled water between coats. During the deposition period, the glass surface should be swabbed gently with a tuft of absorbent cotton to prevent particles that form in the solution from adhering to the surface. When the coating is complete, the glass is washed in distilled water, dried on a whirler, and then placed in an oven at 50° C (120° F) and left until it is approximately at oven temperature. After this, it is removed and the graduated area is painted with some of the beeswax-gilsonite resist (formula W–2) to protect it during the following operation. The glass is next immersed in a 20-percent solution of ferric chloride to remove the lead sulfide except where protected by the wax resist. This is done to simplify the polishing off of the sulfide from the surface of the glass with a lap. The glass was dried on a whirler and the wax masking removed by warm carbon tetrachloride (60° C) under a well-ventilated hood. The lead sulfide was polished off the surface of the glass, leaving a coating of lead sulfide in the lines and numbers.

Polishing was done on a beeswax lap charged with USP magnesium oxide. The customary pitch lap could not be used as it seemed to seize to the lead sulfide. The lap consisted of a 6-inch disk of cast iron about ½ inch thick, machined flat on one side. The other side had a boss in the center of the disk. The boss had a threaded hole to take a steel rod that was used to clamp the disk to a bench or vise. The flat side of the lap was covered with a sheet of honeycomb foundation (beeswax) by coating the metal surface with some wax masking solution and pressing the wax foundation into contact, using a piece of plate glass, and left until dry.

The lap was fastened to the bench, face up, and charged by sprinkling it with a small amount of powdered magnesium oxide, followed by a little distilled water. The lap was conditioned, or broken in, by taking a glass similar to a master and moving it in the usual manner until the lap was charged and the top edges of the honeycomb cells were brought into a plane. When this was completed, the master or circle was put on, additional water and magnesium oxide applied, if needed, and the lead sulfide polished off the surface.

6.2. Filling With Pigments

It is customary to fill deeply etched lines with a pigment. Sometimes a white pigment, such as titanium dioxide or zinc oxide, is used. These pigments are sufficiently opaque to use with transmitted light but will appear white when illuminated for night use. More often the pigment used is lampblack or rouge.

To fill the lines, the glass is clamped by the edges, face up, on a rigid support. A dilute sodium silicate solution is prepared by diluting 1 part of water glass (sodium silicate solution, 40 to 42° Baumé) with 7 parts of water. A few drops of this dilute solution is placed on a piece of glass, and a little pile of the dry pigment is placed nearby. A lint-free cotton or silk cloth is wrapped around the index finger. With the end of this finger, first touch the dilute sodium silicate solution and then the dry pigment. The silicate and pigment adhering to the finger are rubbed on the etched glass with a back and forth and sidewise motion to work the pigment into the etched lines. The excess is wiped off with a rotary motion of the side of the cloth-covered finger as it is moved across the glass surface, thus a clean surface is continually being used in the wiping. Considerable experience is required to fill even a small reticule. The chief difficulty is not in getting the lines filled, but in getting a clean glass surface free from smear. If the sodium silicate drys on the surface of the glass, it is very difficult to remove without scratching the glass.

7. Replicates of Precise Scales by Photoetching Techniques

7.1. Photographic Methods

As mentioned in section 1, a part of this work was the development of a photographic method for the production of etched glass replicates from an original ruled, etched, and filled master circle. Photographic methods employing lenses could not be considered because image distortion resulting from lens aberrations [20, 21, 22] would exceed the small tolerance, ±0.00001 inch (0.25μ), allowed for the position of graduations.

Contact printing with a light-sensitive coating on the glass circle blanks from an optically flat master offers the best promise of freedom from distortion. This light-sensitive coating, after exposure and development, must result in a mask or stencil similar to that of an engraved wax resist and likewise be impermeable and resistant to hydrofluoric acid so that the image of the graduations of the master can be etched into the glass. Unfortunately, as judged by the literature, no light-sensitive resist meeting these requirements was known.

A number of photographic processes have been used for producing reticules and scales of high quality. Rheinberg [23, 24], Geiser [25, 27], and Leistner [26] have reviewed and described a number of these processes.

It may be helpful to point out briefly the principal kinds of light-sensitive coatings used in making glass reticules and scales and follow this with a simple classification of types of reticule processes, including some references to the literature.

The light-sensitive coatings used in reticule work are (1) silver halide emulsions in gelatin, albumen, or collodion having very fine grain, high resolution, and high contrast; (2) a dichromate sensitized photoengravers glue, albumen, shellac (cold top), etc., and (3) iodoform sensitized resins, asphalt, etc. Photographic emulsions (1) are sometimes used for making master negatives or positives, but in recent years they are being used less for making reticules because the clear parts of reticules (where there is no image) are covered with a layer of gelatin, collodion, or other vehicle for the silver halide. The surface between parts of the image is not always perfectly clear and is difficult to clean. The surface is not an optical plane and, therefore, in an optical system it scatters some light, thus, degrading image contrast. Cementing a cover glass on emulsion side will reduce the scattered light and also protect the image. Coatings (2) and (3) do not have this characteristic. These dichromate or iodoform sensitized coatings become insoluble on exposure to light. Development of the image consists of dissolving out the soluble (unexposed) areas with warm water, alcohol, kerosine, turpentine, or other suitable solvent, depending upon the nature of the colloid. Exposed through a negative of a line pattern, the lines are reproduced on the reticule as an insoluble colloid on clear glass. If exposed through a positive, the lines are reproduced as clear glass, thus the resulting image resembles a stencil, or mask. The final image is deposited on the glass through this stencil or the stencil is used as a resist to etch an undercoat or, if it is a resist for hydrofluoric acid, the glass is etched. Following this the stencil layer is removed with suitable solvents.

Dichromate sensitized glue or gelatin containing silver halide or colloidal silver is often used to obtain an opaque image on clear glass. After exposure in contact with a negative, the soluble unexposed areas are removed by developing in warm water, leaving the image as isolated areas, or "islands", on the glass. The silver halide in the image area is blackened with a photographic developer, then intensified, if necessary, with a mercury or silver intensifier as in regular photography. In the case of colloidal silver, physical development and intensification are necessary to make the image black and opaque. Glue images not containing silver or silver halide may also be blackened by alternate treatments with silver salts and reducing agents.

The lack of a light-sensitive coating of the stencil layer type that can withstand the action of hydrofluoric acid necessary to etch the reticule pattern into glass has lead to multiple layer coatings. For example, the glass may be coated with a layer that is not light sensitive but which is inert to hydrofluoric acid. Metallic silver, Bakelite, and asphalt have been used as such an undercoat. The stencil layer may be dichromate sensitized glue or shellac. After developing the stencil layer, the uncovered subcoat is then dissolved away, leaving the glass exposed. When the coating is dry the back and other parts of the glass that are not to be etched are protected by painting them with asphalt or wax. The glass is then etched by exposing it to hydrogen fluoride vapor or dipping it in the etching acid.

For convenience and clarity, the processes available for making reticules and scales may be classified into three main groups as follows: Type I, reticule image on the surface of the glass; type II, image fused in or on the glass, and type III, image etched in the glass. Each type is further classified by the nature or kind of image (continuous, discontinuous, or stencil, etc.) and finally by a process number. Thus each kind of reticule and the process used for its manufacture is approximately identified by three characters, thus type I–A–1 in the table below would represent a reticule made with a silver halide emulsion in which the vehicle layer (gelatin collodion, etc.) covers the face of the reticule. A specific process could be identified by adding another digit, but this is unnecessary for the present purpose. At the beginning of each process description the letter (N) or (P) indicates that a negative or positive is used in exposing the sensitized coating.

TYPE I. IMAGE ON SURFACE OF GLASS

A. Single Continuous Layer Processes

1. (N) Silver halide emulsion in gelatin albumen or collodion. Very fine grain and high contrast required for reticule work, such as obtained with spectroscopic plates type 649 or with albumen and collodion emulsions [26, 27, 28, 30].

2. (P) Diazo image in gelatin layer. Transparent grainless image, many colors available.[8] Several patterns of different colors may be put on same reticule by applying same or different sensitizer to previous image layer and develop with appropriate developer to obtain desired colors. (Experiment with fixed out and washed lantern slide plates. Apply sensitizer with swab of absorbent cotton [36, 37, 38].

3. (N) Blue print image in gelatin, layer gives transparent grainless images [35, 38].

B. Single Discontinuous (Filmless) Layer

(Image as "islands" on glass surface)

1. (N) Dichromate sensitized colloid such as glue or gelatin containing silver halide or colloidal silver. Silver in the colloid image developed and intensified to make it black and opaque [26, 29, 31].

2. (N) Dichromate sensitized colloid, such as glue or gelatin. Image made black and opaque with alternate treatments of silver salts and reducing agents [27]. May also be blackened with lead sulfide [31].

3. (N) Cold top enamel. Dye in developer gives color and increases visual contrast [32, 33].

C. Single Stencil Layer (Metal Image Deposited on Glass Through Stencil)

1. (P) Dichromate sensitized colloid, glue cold top, etc., used to make a stencil layer. The glass and stencil is coated with a metal, such as silver, aluminum, chromium, etc., by vacuum evaporation. Removing stencil layer with solvents; also removes metal overcoat except in image areas where the metal is on the glass [34].

D. Two-Layer Process (Metal Layer Under Image)

1. (P) Glass coated with silver by chemical deposition or by evaporation. Dichromate sensitized colloid coated on top. After exposure and development, the uncovered undercoat is dissolved off with Farmer's reducer. Glue or gelatin image on top of silver may be intensified as in process 1B2 [25].

2. (P) Glass coated with lead sulfide undercoat. Dichromate sensitized glue coated on top of lead sulfide after exposure and development of colloid layer, after baking the glue remove uncovered lead sulfide with hydrochloric acid-bichromate bath [31].

TYPE II. PROCESS, SCALE OR RETICULE PATTERN FIRED OR FUSED IN OR ON GLASS SURFACE

A. Single Discontinuous Image Layer

1. Ceramic transparent [24].
2. Ceramic opaque [24]. (No details available.)

TYPE III. PROCESS SCALE OR RETICULE PATTERN BELOW SURFACE OF GLASS (ETCHED)

A. Single-Layer Process (Ideal Resist)

1. (P) Stencil layer resistant to hydrofluoric acid or to hydrogen fluoride [47]. This paper, section 8.

B. Two-Layer Processes; Resist Undercoat Not Light Sensitive

1. (P) Metal-film undercoat (usually silver). Overcoated with dichromate sensitized colloid. Metal uncovered after developing stencil layer is removed with Farmer's reducer or other suitable solvent. The exposed glass is etched with hydrofluoric acid or hydrogen fluoride [39, 25].

2. (P) Undercoat of asphalt, Bakelite, varnish, etc., overcoated with dichromate sensitized colloid. Undercoat exposed by developing stencil layer, is dissolved out with suitable solvent. The exposed glass is etched with hydrofluoric acid or hydrogen fluoride [40, 41, 42].

C. Two-Layer Process. Resist Overcoat on Stencil Layer

1. (P) Light sensitive undercoat of dichromate sensitized albumen. After exposure, albumen is rolled up with developing ink and developed as usual and dried. Inked surface dusted with powdered asphaltum and heated to fuse the powder with the ink. It is then etched with hydrofluoric acid [42].

D. Two-Layer Process. Fine-Grain Frosted Etch Continuous Permeable Overcoat on Resist Stencil Layer

1. (P) After developing stencil layers having complete or partial resistance to hydrofluoric acid, it is overcoated with dichromate sensitized glue, gelatin, gum arabic, etc., and exposed to harden this layer. This layer is not developed. After protecting back of glass with wax it is dipped in frosted type of etching solution for a suitable time (see section 7.3).

7.2. Survey of Resists for Photoetching

A number of the light-sensitive coatings used in photolithography and photoengraving were tried and found to be unsatisfactory for use as resists for etching the glass directly with hydrofluoric acid. The coatings would invariably crack, undercut, decompose, or become permeable to the etching solution before the etching was complete. Substances coated from water solutions such as glue, albumen, gelatin, gum arabic, polyvinyl alcohol, and cold-top enamel were permeable to the etching solution. With the exception of albumen and cold-top enamel, these materials did not give the sharp, crisp image edges necessary for very fine line (5 to 10 μ) work. Wood [43] and

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[8] Not found in literature, but could be used where colored lines are wanted. The resolution of both diazo and blue print in a thin layer of gelatin is very high.

Smethurst [44] have reviewed many of the coatings used in lithography and photoengraving. Most of the hydrophobic light-sensitive resist coatings were found difficult to develop with the organic developer solutions; clean lines were not obtained without the exposed portion of the coatings being attacked by the developer. For example, methyl ethyl ketone-furfural resin was found difficult to develop as there was the tendency for the exposed part of the coating to be attacked by the developer when the development was sufficient to remove the unexposed portions of the coatings in the fine lines. The amount of exposure and the time and temperature of the developer were so critical that it was difficult, if not impossible, to fully evaluate their usefulness as a light-sensitive resist for etching fine line patterns. Sensitized asphalt [45, 46, 47] has been used as a resist, principally for etching of metals, but its low sensitivity to light and unsatisfactory development makes it difficult to use in production work. Some of these coatings require rubbing with a tuft of cotton during development because the unexposed areas are not sufficiently soluble to dissolve out and it must be removed by friction. This procedure cannot be recommended in the production of fine lines required in theodolite circles unless the adhesion of the coating to the glass is very strong and the resist tough enough so that the edges of the lines are not likely to be damaged.

Processes using an insensitive resist undercoat that is dissolved out through a light-sensitive overcoated stencil layer (type III–B) were considered. In these processes the glass is first coated with some material that is resistant to hydrofluoric acid, such as silver or other metal, Bakelite, asphalt, varnish, etc. For best results this layer should be coated as thin as possible but not so thin that it will lose its resistance to hydrofluoric acid. Further, it must be very uniform in thickness. On top of this subcoat dichromate sensitized glue, albumen, or cold-top enamel is coated with a whirler, exposed in contact with a positive and developed, thus forming a stencil on top of the resist undercoat. Suitable solvents are then applied to dissolve the resist undercoat through the stencil openings. The solvent must not affect the stencil layer. The resist undercoat must dissolve uniformly and completely. If some areas require more time for dissolving than other areas because of variation of thickness, the resist layer will be dissolved out from under the edge of the stencil, thus altering the dimensions of the pattern in the thin areas.

7.3. Photoetched Reflection-Type Circles

When this project was initiated there was an immediate demand for a few reflection-type graduated glass circles for theodolites. Solution of the problem appeared to be the use of a light-sensitive resist in a photographic process whereby the image of the lines and numbers would be printed on the circle blank in contact with a master negative. With a stencil type of resist the clear unexposed developed out areas could then be matte-etched so that the lines and numbers would appear black when viewed with vertical illumination, as explained in section 2.1 for type 2 circles. Several light-sensitive coatings were tested, but all failed as resists.

Further work led to the discovery that if the glass was coated with sensitized and exposed glue during the etching, the glue controlled the grain size of the etching. Used with the matte-etching solution ES–7 the grain size of the matte etch was the finest and most uniform observed in the present work. With mirror silver deposited on top of the etching it appears very white under ordinary white light illumination, but when viewed in an optical system with a vertical illuminator (illumination through the objective) it appears black, and of course the unetched parts (also mirror-silvered) appear white (see fig. 16). Gelatin and gum arabic were also effective, but the grain was appreciably larger than that obtained with photoengraving glue.

It was also found that by overlaying a developed image of an organic stencil layer coating with the glue, that the glue protected the stencil layer coating long enough to give the fine matte etch of the graduations in the glass surface. Cold top enamel was selected as the light-sensitive coating for this work because it develops readily and with smooth, sharp-edged lines. The light-sensitive glue was coated over the developed image of cold top enamel and exposed just long enough to actinic light before etching to make it insoluble in water.

The cold top enamel was sensitized according to the manufacturer's directions and coated by running a small stream of it from a separatory funnel on the glass circle on a whirler at 600 rpm. After drying the coated circle for about 10 minutes it was exposed in contact with the master negative, using an EH–4 mercury flood lamp with a ground-glass diffuser to make the illumination uniform. The exposure time was about 15 minutes at a distance of about 22 inches. The exposed coating

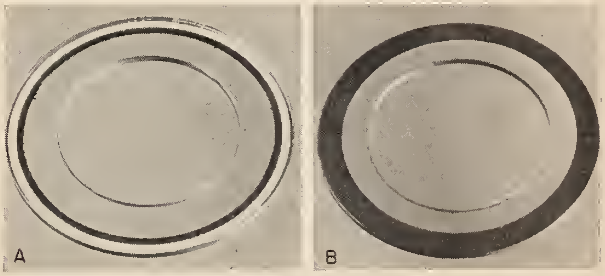

FIGURE 16. *Front and back views of the reflection-type circle.*

The circle (A) on the left shows a white etched band about one-eighth inch wide, the graduations are in the silvered band (dark) adjacent to it. The right-hand figure (B) is the back of a similar circle of slightly different dimensions, showing the copper plating to protect the mirror-silvered area.

was then developed and dyed in the cold top enamel developer (alcohol plus dye), rinsed in ethyl alcohol, and finally in acetone, which dried the coating. The cold top enamel is sensitive to moisture in the air and will not give a good image if exposed to a damp atmosphere too long. The coated glass circle should be exposed and developed as soon as possible after coating and drying. See section 8.7.b, for the effect of relative humidity on cold-top enamel. The developed cold-top image was then coated with sensitized glue on a whirler. With the whirler running at 100 to 200 rpm a small quantity (3 to 4 ml) of sensitized glue was poured over the circle. Then the speed of the whirler was immediately increased to 600 rpm and allowed to whirl until the glue was dry, usually about 15 minutes. The sensitized glue solution had the following composition:

Photoengraving glue	33 g.
Water	120 ml.
Ammonium dichromate	2 g.

This solution was made up as follows: A solution of 90 ml of water and 33 g of glue was heated in the steam bath in a sealed pressure bottle from 6 to 24 hours, or until the solution became clear. Then 2 g of ammonium dichromate dissolved in 30 ml of water was added to the cooled glue solution and filtered.

The sensitized glue was exposed about 8 minutes to a mercury EH–4 flood lamp at a distance of 18 inches. A 1/16-inch-thick piece of ground glass over this lamp was necessary to obtain uniform illumination.

Before etching the glass, the back, edges, and the areas on the top surface, where no etching was desired, were painted with a wax solution. The circle was then etched by dipping in the following solution:

Etching Solution ES–7

Water	65 ml.
Ammonium bifluoride	100 g.
Sodium fluoride	11.5 g.
Hydrofluoric acid (48%)	50 ml.

After etching the circle about 15 to 20 seconds it was removed and quickly immersed in a 10-percent sodium hydroxide solution to stop the etching action and also to remove the cold top and glue.

After removing the wax with solvents it was chemically cleaned and silvered by the Rochelle salts process. A forebath, freshly prepared, of dilute stannous chloride (about 1 to 1,000) followed by rinsing in distilled water prior to immersion in the silvering solution will speed up the mirror silvering. When the silvering solution was spent it was replaced with a fresh one in order to get a heavy coat of silver. After silvering the circle, it was rinsed off, mounted on a fixture, and placed in a copper-plating bath (100 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) per liter), and a layer of copper was electroplated over the silver for mechanical protection, using the procedure given on pages 10 and 11 of reference [48].

The fixture for holding the glass circle during the electroplating was constructed as follows: The circle ring was clamped between two Bakelite disks. These disks cover about half of the width of the ring. The silvered surface on the upper (unetched) side was contacted with spring fingers for the electric connection. It was then immersed in the plating bath with the top surface of the glass just above the solution. The copper was deposited on the edge and on the outside half of the etched side of the circle. After copper plating the circle it was washed and dried. A thin layer of shellac was painted over the copper for protection against corrosion. The appearance of these circles is shown in figures 16 and 17.

Figure 17. *Photomicrographs (×125) showing the appearance of the etched graduations and band of the same part of the circle under different conditions of illumination.*

The top figure (A) was made with diffuse illumination. The lower figure (B) was made by changing the illumination to specular light (illumination through the objective).

Extreme care is necessary in exposing the glue overcoat and an excessive exposure will cause the glue to crack. Too much heat at the time of exposure will also promote cracking by reducing the moisture content of the glue. These cracks may be too fine to see with the eye and also may be confined to a small area. When cracks occur, the etching acid reaches the cold top directly instead of by diffusion through the glue, and breaks through the cold-top enamel and etches the glass, thus spoiling the work. Trash in the glue will also promote break-throughs.

The phenol-formaldehyde light-sensitive resin developed after these circles were produced may be used in place of cold top enamel to produce a similar etching. It is much more resistant to hydrofluoric acid, and consequently the effects described above are less likely to occur.

8. Photoetching with the Phenol-Formaldehyde Resist

8.1. Phenol-Formaldehyde Resin

Phenol-formaldehyde resin was known to be resistant to the action of hydrofluoric acid, and it seemed possible that a thin layer coated on glass might serve as a resist for hydrofluoric acid etching after development of the image. Doelker [49] patented a process whereby phenol-formaldehyde resin was recommended as an etching resist for zinc plates. The resin was dissolved in alcohol and, immediately before coating, was sensitized with ammonium bichromate. The exposed plate was developed with a dilute solution of caustic potash. Beebe, Murray, and Herlinger [50] patented the use of light-sensitive phenol-formaldehyde resin for photoengraving processes. They sensitized the resin with iodine, iodoform, etc., and, after exposure, developed the coating in a solution of about equal parts of alcohol and water. The resin made according to their directions was soft, remained tacky too long after coating, and when sensitized, was low in light sensitivity. Any light-sensitive resin used in contact printing must become tack-free shortly after coating. In the course of the investigation it was found that the softness of the resin was due in part to the presence of methyl alcohol in the formaldehyde solution. The addition of methyl alcohol to trioxymethylene (solid) and phenol in a concentration corresponding to that generally found in 40-percent formaldehyde solutions yielded a soft, tacky resin. Therefore, trioxymethylene was used instead of the 40-percent aqueous solution of formaldehyde for production of the phenol-formaldehyde resin in this work. Also the alcohol-water developer used by Beebe et al [50] was not a satisfactory developer for the resin on glass.

Many organic substances are sensitive to or hardened by actinic light, but it is generally a difficult problem to find a developer solution that will dissolve out the unexposed portions of the resin and not attack the exposed portions. This difficult hurdle was overcome by developing an organic solution that dissolved the unexposed light-sensitive resin quickly and yet did not attack the exposed portion when it had been properly exposed to light even if the development was extended several times beyond the normal developing time. Iodoform was found to be a very good sensitizer. A resorcinol-formaldehyde resin was also made for study. It was found useful as an additive in the phenol-formaldehyde resin. A concentration of 5 percent of the resorcinol-formaldehyde resin improved the sensitivity and resist properties of the phenol-formaldehyde resin, although its presence is not necessary to make the phenol-formaldehyde resin function as a resist for etching glass.

Light-sensitive resists made with phenol-formaldehyde resins will not withstand the action of concentrated 48-percent hydrofluoric acid. However, an etching solution containing hydrofluoric acid and phosphoric acid (formula EP–1, section 5.4) was found that can be used to produce excellent etchings with etching time up to at least 15 seconds.

In the production of the theodolite circles, a 5-second etch was used to keep the lines as narrow as possible, and the etched portions were filled with lead sulfide chemically deposited as described for filling the etched graduations of masters in section 6.1. Even though the resin coating will not withstand a long period of etching, deep lines may be obtained with the special etching solution by etching the circle several times for 3 to 4 seconds and washing and drying it between each etch.

The details for the synthesis of these resins are given in section 9.

8.2. Sensitization of the Resin with Iodoform

Iodine sensitizes the resin to actinic light, but the sensitized solution is unstable and must be used as soon as sensitized. Iodoform proved to be a very satisfactory sensitizer, and the sensitized resin solution was very stable in methyl ethyl ketone when it did not contain water and was free from acid. Iodoform is unique as a sensitizer because the iodine is released by the actinic light during the exposure when the catalytic action of the sensitizer is needed. Both sensitized and unsensitized solutions of the resin should be stored in brown bottles in a dark cool room or preferably in a refrigerator. Sensitized solutions stored in brown bottles in the dark at room temperature over anhydrous sodium sulfate were still usable after 1 year, and when stored in the refrigerator were good after 3 years. Acetone could not be used as a solvent for the resin because the iodoform underwent slow decomposition.

The effect of the concentration of the iodoform on the sensitivity of the resin was determined in the following manner: Four 100-ml solutions of the phenol-formaldehyde resin containing 20 g of resin each were prepared from the same resin batch. To each solution was added different amounts of iodoform. Glass test plates 1 by 3 inches were coated by drawing them out of the sensitized resin solution at the rate of 1 foot per 80 seconds, using a synchronous motor-driven apparatus similar to that described in section 3.3. After storing the coated glass plates in the dark at room temperature and approximately 50-percent relative humidity for 4 hours they were given progressively increasing exposures in contact with a glass master ⅜ inch thick to an EH–4 mercury flood lamp placed at a distance of 11 inches from the glass-plate grid. After development, the minimum exposure time necessary to give a good image was determined by inspection with a microscope at ×80. The exposure times giving the best images were plotted against the concentration of the iodoform in percent, expressed as the percentage of iodoform based on the concentration of the resin. These results are shown in figure 18. Crystals appeared in the dried resin coating when the concentration of iodoform reached about 20 percent, indicating that the iodoform concentration had exceeded the saturation point. A concentration of 10 percent of iodoform as sensitizer based on the resin concentration was selected because it gave good sensitivity to actinic light without getting too close to the saturation point.

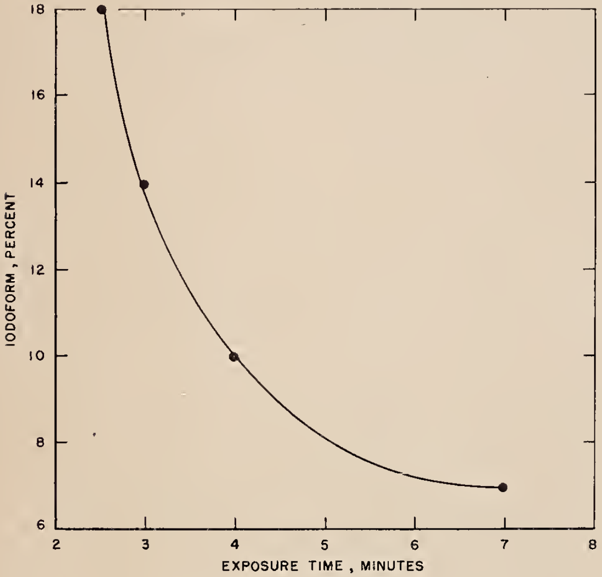

Figure 18. *Effect of the iodoform concentration on the exposure time.*

The following coating formula was used for the production of the theodolite circles:

Phenol-formaldehyde resin, 25% solution	800ml.[a]
Resorcinol-formaldehyde resin	10 g.
Iodoform [b]	21 g.
Methyl ethyl ketone to make	1 liter.

Then add about 100 g. of anhydrous sodium sulfate to the solution, shake occasionally, and allow to stand overnight. Filter the solution through a coarse fritted-disk filtering funnel without pressure.

[a] The concentration of the phenol-formaldehyde solution, which varied from batch to batch, ranged from 22.5 to 30 g of resin per 100 ml of soluton. The volume of solution used was adjusted so that 200 g of resin is used in the above formula.

[b] The iodoform used was Eastman Kodak Cat. No. P–341.

8.3. Coating the Circles

The phenol-formaldehyde coating is somewhat less sensitive to light than cold top enamel. Either of these materials can be used in a room lighted with incandescent lamps if care is taken to protect the dry coating from direct strong light either by shielding or keeping it covered. The circles were coated in a closed cabinet to protect them from drafts, dust, and light during the coating operation. The glass circle was coated by the "pull-out" method described in section 3.3 and shown schematically in figure 7. The sensitizing solution was contained in a glass battery jar 2⅞ inches by 5¼ inches and 7 inches deep (inside dimensions). It was filled to about ¼ inch of the top of the jar with the resist solution. The top edges of the jar were ground flat and when not in use, was covered with a glass plate to prevent evaporation.

The circles were cleaned and dried by the same procedure as that described in section 3.2 for coating the engraving resist, except they were not treated with amino silane (waterproofing agent). The dried circle was placed on a glass tripod (fig. 6) and washed in filtered methyl ethyl ketone by swabbing with cotton, rinsed with filtered methyl ethyl ketone, and quickly placed on a wire hook and immersed in the sensitized resin solution. The wire holder is designed so that the inside of the circle rests on the wire without touching the front or back side of the circle. After immersion, the circle was moved up and down a few times within the solution to remove any bubbles of air that might adhere to the glass. When the surface of the solution became quiet the circle was drawn out with the synchronous motor at the rate of 1 inch per 6¾ seconds. The door of the cabinet was kept closed after the immersion of the circle and opened after it had been drawn from the solution. The circle was clasped with an aluminum-band holder and placed face down over the neck of a 300-ml Erlenmeyer flask. The resin coating on the circle was allowed to dry at least 1 hour before exposure, but 4 hours was found to be better. If this precaution is not observed, there is danger that some of the resist coating may stick to the master.

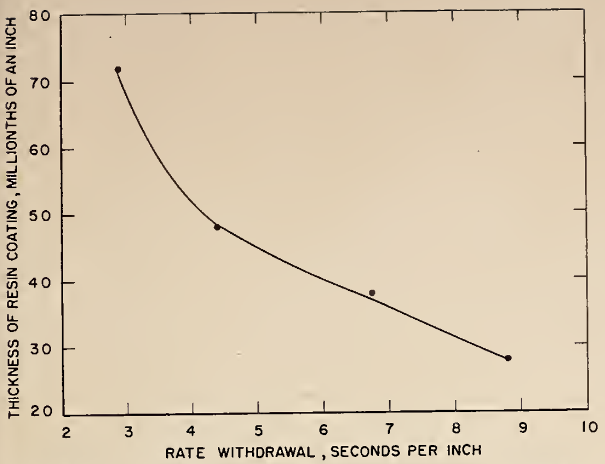

FIGURE 19. *Thickness of the resin coating as a function of the rate of withdrawal of the glass from the coating solution.*

The resin concentration of 21 g per 100 ml of solution, and the rate of withdrawal of 1 in. per 6¾ seconds yielded a thin and very uniform coating on the glass circle, which, after development, measured 38 millionths of an inch thick. The solvent, methyl ethyl ketone, evaporates fast enough at room temperature to leave the desired coating on the glass as it is drawn from the solution. The thickness of this resin coating must be very uniform as a slight change in thickness affected the time of exposure, which decreased with an increase in thickness. During the coating operation the circle must not twist, turn, or touch the sides of the container because variations in the thickness of the coating will result. The thickness of the coating may be changed by varying the concentration of the resin or the rate of withdrawal. The thickness of the developed coating was determined for four different rates of withdrawal. The thickness of the developed samples was measured by the interference microscope, and the results are given in figure 19. A. G. Strang of the NBS Engineering Metrology Section made the measurements of the thickness of the resist images. The withdrawal rate of 1-inch in 8⅘ seconds gave a coating that was too thin. The curve shows that for the solvent used the thickest coating obtainable would be about 50 millionths of an inch at the rate of withdrawal of 1 inch in 4⅕ seconds because beyond this rate the evaporation of the solvent is not sufficiently complete, so that the solution drains off, causing a nonuniform coating. Of course the thickness of the coating is also determined by the concentration of the resist and the temperature.

8.4. Contact Printing and Exposure Effects

The sensitized resin coating is sensitive to the violet and ultraviolet parts of the spectrum, and consequently, light sources having high energy in this spectral region, such as sunlight, carbon arc, and the mercury vapor lamp, are necessary. The light source used for the experimental work was an EH–4 mercury flood lamp. A 3/8-inch-thick glass plate containing filled etched lines 10 μ wide was mounted 11 inches from the face of the lamp. The coated glass plates were 1 by 3 inches, and were exposed in contact with the line image. The different batches of resin synthesized in this work had exposure times varying from 2 to 5 minutes with the above described exposing apparatus. The experimental glass plates were coated by drawing them from the sensitized resin solution with a synchronous motor. An AH–6 high-pressure mercury-quartz lamp, cooled by running water, was used as the light source for the production of the theodolite glass circles. This water-cooled lamp develops a mercury-vapor pressure of 110 atmospheres and operates at 840 volts and 1.4 amperes. The lamp, transformer, magnetic switch, and water solenoid valve were mounted in a cabinet. The master negative ½ inch thick was mounted 19 inches from the light source. A penthouse fitted with a door was constructed on the top of the cabinet. It served to protect the glass master and to reduce the hazard from dust particles. A 25-watt lamp located below and to one side of the glass master was turned on to observe any dust particles that might be present on the master. If present, they were removed or picked off with a camel's hair brush. The circle was removed from the Erlenmeyer flask by means of the aluminum clamp and placed carefully in position on the master around the centering plug and washer, which fits into the hole in the circle glass ring. The circle was pressed down lightly with the fingers and covered with a black felt cloth. The 25-watt lamp was turned off, and the resin coating was exposed to the AH–6 lamp by opening a small door type of shutter located above the AH–6 lamp. After exposure the circle was removed from the master negative with the aluminum clamp and placed on the glass tripod. The exposure time was about 12 minutes.

It was found that the polymerization of the resin continued after the action of the light was stopped. Thus the image of lines may be narrowed slightly (similar to the effects of a more full exposure) by storing the exposed coating in the dark for 15 minutes or longer, but if continued too long, an overexposure effect takes place. When the sensitized resin was given a one-half normal exposure and stored 1 to 3 hours in the dark it generally developed a good image, but a fully exposed plate when stored in the dark too long will become overexposed. While the above effects may be useful in some instances, it is recommended that the exposed resin coating be developed as soon as the exposure is complete. It is also interesting to note that the sensitized resin coating becomes insoluble and cannot be developed if kept in the dark at 50° C for 4 hours. This is due to the thermosetting properties of the resin.

8.5. Development of the Exposed Resin Coating

The unexposed areas of the resin coating were dissolved out (developed), and the exposed areas were dyed simultaneously by means of an organic solution developed for use on this resin coating. The developer solution was made up as follows:

Ethyl alcohol 95 %	1000 ml.
Normal butyl alcohol, bp 117° to 117.8° C	1000 ml.
Methyl ethyl ketone, bp 79° to 80.5° C	200 ml.
Methyl violet	2 g.
Basic fuchsin (aniline red, magenta)	2 g.

The developing solutions were filtered through a coarse fritted disk filtering funnel.

The ethyl alcohol, normal butyl alcohol, and methyl ethyl ketone were of reagent grade and were used without distillation or drying. The developer solution contained about 3 percent of water. The mixture of methyl violet and basic fuchsin dyed the resin coating a heavy blue-purple and was found to be the best combination of dyes tested. Methyl violet dyed the resin coating blue-green; basic fuchsin, red; and malachite green, green. Another developer solution was also made up without the dye for use in washing off the excess dye on the surface that accumulates during the developing procedure.

The exposed resin coating was developed as follows: The circle mounted on the glass tripod was twirled gently for 30 to 40 seconds in the developer-dye solution; then twirled gently for about 3 seconds successively in three developer solutions that contained no dye; and placed at once on the whirler to dry. All solutions were at room temperature. The resin coating becomes soft during development but quickly hardens on drying in about 2 minutes. Although the development took place in 30 to 40 seconds, there were no adverse effects on the resin coating if the developing time was extended for as long as 2 minutes. No rubbing is required because the unexposed portion of the resin dissolves very quickly. This development procedure is very practical because the development of most organic solutions require close control of time and temperature.

The activity of the developer may be increased by increasing the concentration of the methyl ethyl ketone, and this might be necessary in instances where the resin has condensed very close to the critical point due to age and also to temperature being too high during storage. It was also found that if the sensitized resin had condensed so far that it did not give complete development by the normal procedure or by increasing the concentration of the methyl ethyl ketone, that the addition of 25 to 50 percent of a fresh sensitized resin batch made it capable of proper development. Sensitized resin batches were found to be readily developable after storage for 1 year at room temperature. Sensitized solutions of the resin increased slightly in sensitivity on storage at room temperature. One sample of sensitized resin that was stored in a refrigerator developed a good image after 3 years.

8.6. Etching and Filling the Graduations in the Circles

After the development of the resin coating it was baked to increase its resistance to the hydrofluoric acid. The coated circle supported on an Erlenmeyer flask was placed in an oven at room temperature, and the temperature of the oven was raised to 100° to 135° C and maintained at this temperature for 3 hours. The oven was turned off, and the sample was allowed to cool nearly to room temperature before removal. This precaution of heating and cooling slowly was taken to avoid the possibility of breaking the glass due to thermal shock. Concentrated hydrofluoric acid solutions (48 percent) attack the phenol-formaldehyde resin coating. The problem was to find a solvent for the hydrofluoric acid that would delay its attack on the resin coating and prevent the formation of insoluble salts during the etching. Experimentally, the answer was found in using phosphoric acid in aqueous solution with hydrofluoric acid. Also phosphoric acid assists the hydrofluoric acid in etching the glass [18]. The phosphoric acid retards the attack of the hydrofluoric acid on the developed resin and gives a clear etch when sufficient water is added. The following formula was found to be satisfactory:

Etching Solution EP–1

Phosphoric acid (85%)	100 ml.
Water	50 ml.
Hydrofluoric acid (48%)	25 ml.

The phosphoric and hydrofluoric acids were of reagent quality, meeting ACS specifications. This etching solution is the same one used in etching the ruled wax-coated circles described in section 5.4. The etching solution was simple to make up as no noticeable heating took place when the chemicals were mixed. The etching solution may be used as soon as it is made up, and, if stored in a wax pot fitted with a tight cover, it will keep for several months. Decreasing the water in the above formula gave a coarse matte etch, whereas increasing the water and hydrofluoric acid yields a more rapid etching solution, giving a clear etch. Although the theodolite circles were made from plate glass, borosilicate glass etched equally well.

The glass circle was etched by masking the areas not covered by the resin with a mixture of 20 g of gilsonite and 5 g of burgundy pitch in 100 ml of benzene. The fingers must not at any time touch the portion to be etched. The circle mounted on the glass tripod was immersed in the etching solution for 5 seconds with a gentle twirling movement and then immediately immersed in a 20-percent solution of sodium hydroxide solution to neutralize the hydrofluoric acid. Then the

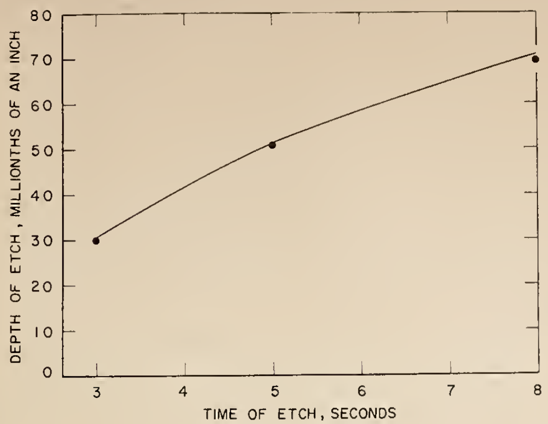

FIGURE 20. *Depth of etch versus time of etch, using etching solution EP–1.*

circle was washed, dried, and the wax masking coating removed with carbon tetrachloride in a crystallizing dish under the hood while mounted on the glass tripod. The remainder of the resin coating was removed by first treating with a 20-percent solution of sodium hydroxide and then with a cleaning solution (potassium dichromate and concentrated sulfuric acid). The etched lines and numbers were filled with lead sulfide, using the same procedure described in section 6.1.

The resin coating withstood the etching solution about 15 seconds at room temperature. This etch is not quite deep enough to fill the 10-μ, lines with pigments as described in section 6.2. However, a deeper etch on the circle was not desireable as it widened the lines. Unlike reticules, the cost of the glass circle was too high to risk damage by scratching. The etching used on the circle was deep enough to fill with lead sulfide by chemical deposition. The etched lines in the circles after filling averaged 1 to 2 μ wider than those in the resist layer. With full exposure the line width in the developed resist layer may be made slightly narrower than those on the master negative. Tests were made on the glass circles to determine the depth of the etch for different etching times. The depth of the etch was measured with an interference microscope, and the results are shown in figure 20. As might be expected, the depth of etch is nearly proportional to the time of etch. However, it was found that a deep etch may be obtained with the phenol-formaldehyde resin coating by etching 3 to 4 seconds several times with the above etching solution. After each etch the etching solution is removed immediately with copious amounts of distilled water and the glass dried at 100° C for about 30 minutes, cooled, and the etching repeated. Three to four such etches were found to give a deep etch that could be filled with pigments.

The appearance of the graduations of a master and a circle made by contact printing with the phenol-formaldehyde resist is shown by the photomicrographs in figure 21. It may be noted that the graduations lines on the circle (B) are slightly wider than those on the master (A) by about 1 μ.

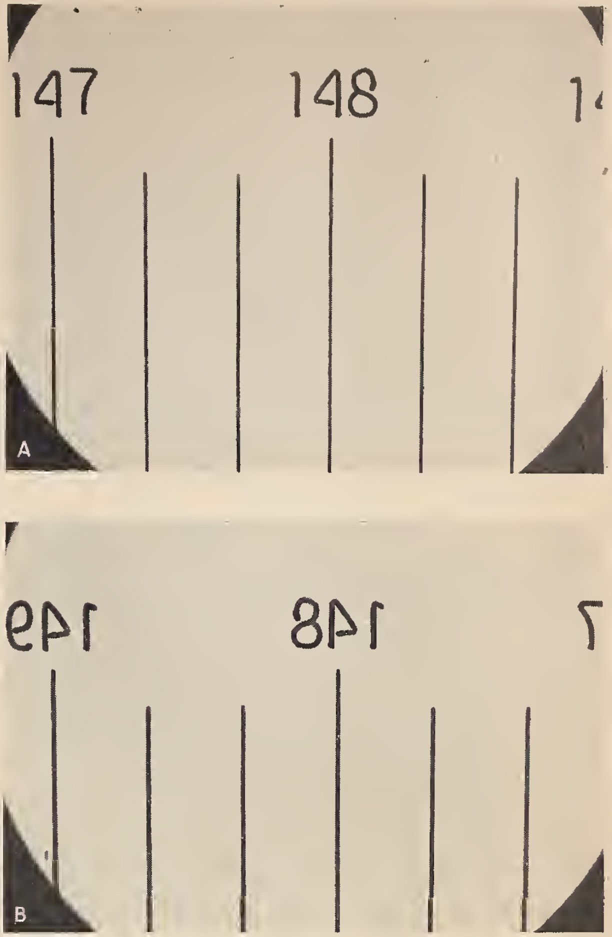

FIGURE 21. *Photomicrographs of master and circle made from it by contact printing, using the light-sensitive phenol-formaldehyde resist.*

A, Master; B, circle. Both have been etched and filled with lead sulfide by chemical deposition.

8.7. Effect of Relative Humidity on the Phenol-Formaldehyde Resin and Cold Top Enamel

a. Phenol-Formaldehyde Resin

It is well known in the photomechanical industry that glue, albumen, cold top enamel, and other light-sensitive coatings are affected by high humidity, and the effects are peculiar to each particular coating. The effect of atmospheric moisture on the sensitivity and developability of the phenol-formaldehyde resin and cold top enamel used in this work was studied. A humidity cabinet having a volume of 7 cubic feet and designed for determining dimensional changes in photographic materials as a function of relative humidity was used to subject the sample coatings to the desired relative humidity. This cabinet is well insulated and is completely moisture tight. A fan on a long shaft (motor outside) drives a stream of air down onto the surface of a tray of saturated salt solution, from which it flows into the partitioned space containing the test samples. The air then passes over the top of the partition and back to the fan, giving a continuous stream of conditioned air. The relative humidity is controlled by using saturated salt solutions, which give the desired relative humidity. This apparatus is efficient and will condition photographic film and paper in about 2 hours.

Tests of the effect of the relative humidity on the sensitivity and developability of the phenol-formaldehyde resin were made at 14-, 51-, 65-, 76-, and 88-percent relative humidity. For each relative humidity, coated glass plates were exposed in contact with a glass master having filled etched lines about 10 μ wide.

At different time intervals samples were removed from the humidity cabinet and given the same exposure and development as that needed for control samples run at the same time. Both the control and tested samples were subjected to room relative humidity (about 50 percent) and room temperature (25° to 30° C) for about 15 minutes after coating. The control samples were exposed and developed 15 minutes after coating. The evaluation of the tests was made with a microscope by noting the quality of the developed image.

The results of the tests are summarized in table 5 and show that at a relative humidity of 50 percent or less the relative humidity has little effect on the sensitized coating and that the effect of relative humidity up to 75 percent is not serious if the light-sensitive resin coating is exposed soon after coating. High relative humidity in the humidity cabinet affected the sensitivity and developability very rapidly, and this was reflected in a weak image with loss of gloss and a partially dissolved or decomposed coating. However, under practical working conditions in still air the deterioration of the sensitivity and developability is not nearly as rapid as that indicated by the tests in the humidity cabinet. Coated glass plates stored in a dark box at room temperature and humidity for 5 days showed only a slight loss in sensitivity and developability even though the weather was damp and it had rained once during the period and the room was not artificially heated.

In the production of theodolite circles no loss of sensitivity and developability was experienced when the coated samples were stored 4 hours before exposure and development. The tests in the humidity cabinet accentuate the difference in the effect on sensitivity and developability on the phenol-formaldehyde resin coating when it is stored in a stream of rapidly moving air as compared to its storage in still air of the same relative humidity.

Table 5. *Effect of relative humidity on the sensitivity and developability of the sensitized phenol-formaldehyde resist coating in the relative-humidity cabinet*

Relative humidity	Time to cause loss of sensitivity and developability as image takes on a dull, weak appearance
%	
4 [a]	Not affected after 55 days.
14 [b]	Not affected after 4 days.
51	48 to 72 hours.
65	About 6 hours.
76	30 to 60 minutes.
88	About 5 minutes.

[a] Sample was stored in a desiccator over anhydrous calcium chloride.
[b] Fan not running.

b. Cold Top Enamel

Experiments similar to those described in the section 8.7, a, were also made with sensitized cold top enamel. Cold top enamel when freshly sensitized is "soft" working and becomes more contrasty with age. Solutions that are about a week old give best results for line work on glass. During periods of high relative humidity it was difficult to get satisfactory development of the exposed cold top enamel. Apparently the presence of moisture in the cold top enamel after coating promotes a chemical reaction that causes a hardening of the unexposed areas with time, rendering them less soluble.

Increasing the relative humidity increases this chemical action, and the image becomes partly or completely undevelopable even if the exposure time is shortened. About 1 hour was about as long as a glass plate coated with cold top enamel could be stored at 60-percent relative humidity and 23° C. The results of the tests made on the cold top enamel are summarized in table 6 and show that increasing the relative humidity causes the coating to become insoluble (undevelopable) and to take on a dull, weak appearance.

Table 6. *Effect of relative humidity on the sensitivity and developability of sensitized cold top enamel in the relative-humidity cabinet*

Relative humidity	Time in cabinet	Effects noted
%	*Min*	
51	30	Lines developed.
	60	Lines incompletely developed.
76	15	Lines developed.
	30	Lines incompletely developed.
95	5	Lines developed.
	10	Lines incompletely developed, coating weak and dull in appearance.

The tests further indicate that cold top enamel when used as a sensitized coating on glass should be handled in an atmosphere of 50-percent relative humidity or less and that the exposure should be made as soon as the coating is dry and developed immediately. To overcome the effects of high humidity, one manufacturer of cold top enamel [33] recommends heating the plate on a whirler to remove moisture from the coating and to prevent sticking during contact printing. It was not found necessary to use heat with relative humidity at 50 percent or lower.

9. Synthesis of Phenol-Formaldehyde and Resorcinol-Formaldehyde Resins

9.1. Phenol-formaldehyde (Stage-A) Resin

Baekeland [51, 52, 53] divided the phenol-formaldehyde reaction during resinification into three stages, A, B, and C, which are characterized by the appearance and solubility of the resin. The A-stage, or initial product, is a low molecular weight condensation product soluble in acetone; the B-stage, or immediate condensation product, is swelled by acetone but not soluble in it; and the C-stage, or final condensation product, is infusible and completely insoluble in acetone. Sometimes the A-stage resin is called a resol; the B-stage, a resitol; and the C-stage, a resite. The resin used in this work is that formed in the A-stage (resol) and condensed to the state where it is just soluble in 95-percent ethyl alcohol. The resin is a thermosetting phenolic that slowly passes into B-stage (resitol) on drying at room temperature. After the condensation reaction was completed the resin was pressed free of as much water as possible, dissolved immediately in methyl ethyl ketone, and dried over anhydrous sodium sulfate. When the resin solution was made up to about 20 g of resin per 100 ml of solution it kept in the dark at room temperature for at least 3 years, provided the solution was dry and free from acid.

Sodium acetate, a weak alkaline salt, proved to be the best catalyst for the condensation of the phenol and formaldehyde. It yielded a resin that had the greatest light sensitivity and that was readily developable by an organic solution. Other salts tested as catalysts were potassium acetate, lithium acetate, calcium acetate, barium acetate, and sodium formate. These resins were low in light sensitivity and could not be as easily developed as the resin formed with sodium acetate. Acids such as hydrochloric acid act as strong catalysts and produce a resin that is not as light sensitive as that produced by the weak alkaline catalysts mentioned above and further the condensation reaction is difficult to control because the resin passes rapidly from the A-stage to the B-stage.

Investigation of the condensation reaction showed that 1 mole of phenol, 3 moles of trioxymethylene, 6 moles of water, 0.3 mole of sodium acetate ($CH_3COONa \cdot 3H_2O$) produced a satisfactory light-sensitive resin that was not too soft. Decreasing the sodium acetate gave a softer resin that was less light sensitive.

The following formula and procedure were worked out for synthesizing the light-sensitive resin used in printing theodolite circles from a glass master negative:

Phenol	282 g.
Water	324 g.
Sodium acetate ($CH_3COONa \cdot 3H_2O$)	122 g.
Trioxymethylene (paraformaldehyde)	270 g.

The phenol and trioxymethylene were USP grade, and the sodium acetate was reagent quality, meeting ACS specifications. Distilled water was used in the synthesis and tap water in washing the resin.

The apparatus consisted of a 3,000-ml round-bottomed flask fitted with a reflux condenser by means of a ground glass joint and mounted on a ring stand. The apparatus should be located in a chemical hood. The chemicals were added to the flask in the order listed in the formula, followed by the addition of boiling chips made from an unglazed porcelain plate. The mixture was heated through an asbestos pad with a Bunsen burner to a gentle boil. The ring stand was rocked gently and frequently with the hand to prevent superheating until the boiling began. The boiling was continued throughout the period of the reaction, and the time required was 2½ to 3½ hours. The temperature of the boiling solution during the reaction before precipitation was 105° C. Toward the end of the condensation reaction the solution became cloudy, and finally opaque to transmitted light about 20 minutes, before two definite phases developed, accompanied by foaming. After the two phases appeared, gentle and frequent rocking of the ring stand was helpful to prevent the resin, which slowly precipitates from the boiling mixture, from sticking to the flask. After the two phases appeared, the boiling was continued about 5 minutes, and the hot reaction mixture was immediately poured into cool water with rapid stirring, thus completing the precipitation of the resin from the hot reaction mixture. The resin was washed and kneaded in about 5 changes of water and tested for degree of condensation. This test was made by taking about 10 g of the resin batch and heating it on the steam bath in a small porcelain dish while stirring with a glass rod and the time noted for the resin to pass into the B-stage. This was observed visually when the resin became rubbery, stringy, or lumpy and is the point at which all or most of the resin becomes insoluble in 95-percent ethyl alcohol. If the resin has condensed close to the B-stage the small sample of resin should become insoluble in 95-percent ethyl alcohol after heating for 10 minutes on the steam bath, and if this is the case, the large resin batch is sufficiently condensed. If the time was greater than 10 minutes, the precipitated resin batch was heated on the steam bath in a large porcelain dish while stirring constantly with a glass rod, and the time of heating was estimated from the time required for the small sample to become insoluble in 95-percent ethyl alcohol. With experience, the operator will find no difficulty in determining the end-point of the condensation. As a safeguard against carrying the condensation too far on the steam bath the resin batch may be cooled with water at intervals and a small sample tested for degree of condensation as described above. The resin passes rapidly from A-stage to B-stage at a temperature of 100° C, and if the resin shows any signs of stringiness or a tendency to be rubbery and lumpy, it should be cooled immediately by stirring in cool water. If a few insoluble particles appear in the alcohol solution, the resin is usable, but if it is essentially insoluble in the alcohol, it should be discarded. The highest degree of light sensitivity along with developability was obtained by condensing the resin as close to the B-stage as possible, without the resin becoming insoluble in 95-percent ethyl alcohol.

After the resin had been condensed to the desired state and cooled, as much of the water as possible was pressed out and the resin dissolved immediately in 700 ml of methyl ethyl ketone (2-butanone) of a good commercial grade, free from acid or any substance that would react with iodoform. Then 500 g of anhydrous sodium sulfate was added and the resin solution allowed to stand for several days, with occasional shaking. After filtering the resin solution, it was ready for sensitizing and use. The amount of resin determined from the dried resin solutions of different batches gave yields of 220 to 300 g. The dried resin solutions contained from 22.5 to 30 g of resin per 100 ml of solution. The concentration of the resin in the filtered solution was determined by noting the volume, evaporating 10 ml of the solution to dryness in a tared 50-ml beaker, and weighing.

Another formula containing ethylene glycol as part of the solvent was developed. This resin was not used in the production of the theodolite circles as the tests on it had not been completed. The resin has the same sensitivity as that produced by the above formula. The resin is easier to produce by using this formula, but a trace of ethylene glycol remains in the resin. Ethylene glycol, because of its hydroscopic nature, causes a slight decrease in the light sensitivity of the resin coating when working at high relative humidities. This effect is nil when working with the resin at a relative humidity of 50 percent or less. The chief advantage in using this formula is that the resin is generally sufficiently condensed when precipitated so that it needs no further treatment on the steam bath. However, it should be tested for degree of condensation as described above before dissolving it in the methly ethyl ketone.

The following alternative formula was worked out for synthesizing the phenol-formaldehyde resin:

Phenol	282 g.
Ethylene glycol	186 g.
Water	270 g.
Sodium acetate ($CH_3COONa \cdot 3H_2O$)	122 g.
Trioxymethylene (paraformaldehyde)	270 g.

The ethylene glycol was of reagent grade. The apparatus and procedure for producing the resin were the same as described for the previous formula. The time required for the reaction was 2 to 3 hours. The temperature of the boiling solution during the reaction before precipitation was 107.5° C. The reaction mixture remained clear until very close to the end of the reaction. The solution became cloudy and the boiling was continued about 3 minutes after it had become opaque to transmitted light. The resin was immediately precipitated from the hot reaction mixture by pouring into cool water with rapid stirring. The resin was treated in the same manner as that obtained from the first formula.

9.2. Resorcinol-Formaldehyde Alcohol-Soluble Resin

The phenol-formaldehyde resin works well as a resist, and this resin was used in most of the experimental work. However, it was thought that the incorporation of other substances might improve the sensitivity and resist properties of the resin coating. Small amounts of shellac in the phenol-formaldehyde resin caused the sensitized solution to become unstable. The resorcinol-formaldehyde resin, because of its reactivity and chemical similarity to the phenol-formaldehyde resin, should improve the sensitivity and resist properties of the latter, and this was found to be true. A resin, soluble in 95-percent ethyl alcohol, was produced from the condensation of resorcinol and formaldehyde. While this resin was light sensitive, it was not possible to develop the image satisfactorily. Like many of the organic resins, no differential solvent was found that would dissolve the unexposed areas and leave the exposed image on the glass. It is somewhat more resistant to hydrofluoric acid than the phenol-formaldehyde resin. The addition of 5-percent of the resin, based on the weight of the phenol-formaldehyde resin, increased the sensitivity about 25 percent, increased the intensity of the dyeing of the image during development, and improved its resist properties slightly.

The following formula and procedure were used in synthesizing the alcohol-soluble resorcinol-formaldehyde resin:

Resorcinol	55 g.
Water	75 ml.
Sodium sulfate, anhydrous	12.5 g.
40-percent formaldehyde solution	41 ml.

The resorcinol was Eastman Kodak Cat. No. P–222, and the sodium sulfate was reagent quality, meeting ACS specifications. The formaldehyde was USP grade. Distilled water was used both in the synthesis and in washing the precipitate. The chemicals were added to a 250-ml Erlenmeyer flask and brought into solution. The reaction mixture was stored without agitation in a constant temperature room at 22° ±1° C. The solution

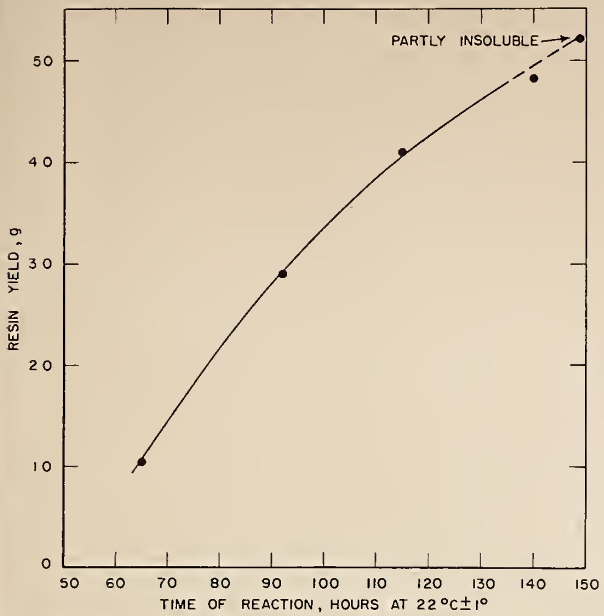

Figure 22. *Yield of resorcinol-formaldehyde resin versus time of reaction.*

was clear after 24 hours, but after 40 hours a precipitate began to settle out. At the end of 140 hours the reaction mixture was diluted to 1,500 ml, and then 100 g of anhydrous sodium sulfate was added. The sodium sulfate salts out the resin during the reaction and also on dilution before filtering. The precipitated resin was removed with suction by means of a Buchner filtering funnel. The precipitate was thoroughly washed, air dried overnight, and finally dried in the dark in a desiccator over anhydrous calcium chloride. The yield of the ethyl alcohol-soluble resin was determined for different times of reaction, and the results are shown graphically in figure 22. The resin became insoluble in 95-percent ethyl alcohol when the reaction time was extended much beyond 140 hours.

The rate of the condensation reaction increases with increase in temperature accompanied by an increase in the yield of an alcohol insoluble resin. At 100° C the reaction is very rapid, and the resin is completely insoluble in ethyl alcohol. It was difficult to obtain a good yield of the alcohol-soluble resorcinol-formaldehyde resin when the reaction was carried out at a temperature much above 25° C.

The dried resin when stored in a dry brown bottle kept in the dark at room temperature was still soluble in 95-percent ethyl alcohol after 2 years. The resin when dissolved in methyl ethyl ketone over anhydrous sodium sulfate at a concentration of about 20 g per 100 ml of solution was still usable after 3 years of storage at room temperature.

The authors welcome this opportunity to express their indebtedness to Benjamin L. Page for the numbering and ruling of the graduations in the wax resists of the master circles and for the calibration of the circles produced in this work, as well as for the many helpful suggestions during the progress of this work. The authors also express their thanks to Emory J. Stovall, Jr. and Henry G. Dorsett, Jr. for their assistance in the production of the reflection-type circles, using cold top enamel.

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