Proceedings

THE THIRTEENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1968

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

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THE THIRTEENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

Sponsored by

THE AMERICAN SCIENTIFIC
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STATLER HILTON HOTEL
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THE AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY
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POWDERED GLASS FLAME SPRAYING

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ABSTRACT

A brief background of the powdered flame spraying technique is given. The use of commercial metal flame spraying equipment and their shortcomings is discussed.

The developmental and production work done by the author is reviewed. Construction of torches as well as the glass powder metering equipment is shown.

Several applications of the powdered flame spray process are covered. These include large diameter seals and heavy wall build-ups for flanges.

Powdered flame spraying is the technique of passing powdered glass through a flame to accomplish glass working operations normally too difficult by conventional methods. The transportation of powdered materials through a flame is not new. In 1904 Vernulli[1] described his now classic vertical build-up process for producing sapphire boules. Figure 1. In this method the powder was contained in a wire mesh basket within the top end of the torch. This end was closed by a one hole rubber stopper through which passed a metal rod that supported the wire basket. By tapping the external end of this rod, powder could be introduced into the oxygen flow. The torch was a conventional blast burner with the back section water cooled. As the powder passed through the flame it softened and accumulated on a refractory support rod. This rod was slowly lowered to produce an elongated boule. The basic idea is still in use today with only minor improvements in the manner of introducing the powder. Figure 2. In this drawing by Shankland[2] a water cooled burner is provided and the powder is premixed with part of the oxygen flow. Powder flow is accomplished by solenoids, as shown. Figure 3. On the left side of this patent by Lester et al[3] is shown another arrangement for powder flow with an enclosed solenoid. A water cooled oxyhydrogen burner is shown on the right side and provides another approach to the fusing technique. Figure 4. This drawing is from a patent by Barnes[4] for producing gems. He introduces powder by a cam actuated mallet. A multiple tip burner is used and is shown on the upper right side of the drawing.

Powder flame spraying has also been used to a great extent in the manufacture of fused quartz by the powder build-up method.[5] Figure 5. In this operation a screw feed is used to deliver the powder into the gas-oxygen flame. Here again, the softened material accumulates on a rotating support which retracts at a speed related to the rate of material build-up. Fused quartz manufactured by this process is characterized by the near absence of bubbles.

The technical and patent literature over the past 30 years has periodically shown methods for dry powder glass flame spraying. These ap-

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plications have ranged from patching hot furnace wall brick to applying glass beads onto Kovar metal wire. Without doubt, broader use of the technique has been limited by the absence of standard equipment. Several powder flame spray guns are commercially available. These guns, however, were originally designed to spray metals for building up worn shafts or applying hard surface coatings. One typical unit is basically a welding torch which is fitted with a small funnel shaped material hopper. The metal powder enters at the vacuum side of a Venturi mixer and then into the gaseous stream. We have found that this unit does not work with powdered glass because the glass particles are non spherical and clog the feed passageway. Another more popular pistol grip metal spray gun has been used with powdered glass. The disadvantage with this unit is that the abrasive glass powder rapidly wears the internal parts and contami-

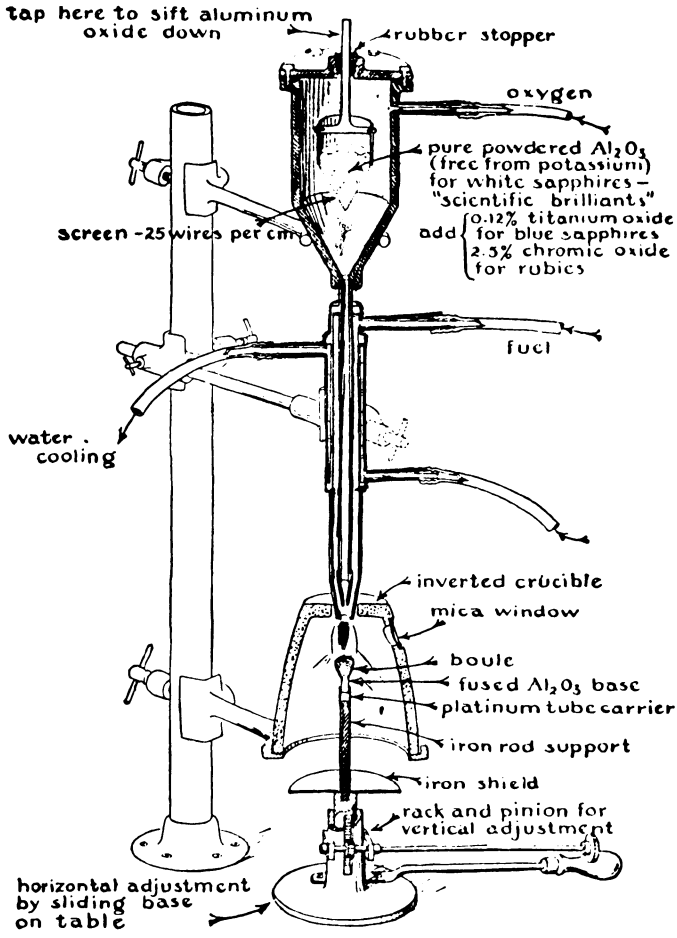

Figure 1

nates the powder. This metallic contamination alters the physical properties of the glass and the wear from abrasion increases operational costs.

As a result of the absence of flame spray equipment for powdered glass and because of the problems with available metal spraying equipment, we set out to build our own unit.

Much of the development work was done about five years ago and at the present time we are installing larger equipment based on this early work.

One of our first powder glass feeds is shown. Figure 6. The powder glass hopper was constructed from a 2 inch O.D. pipe nipple with reducers at each end. Continuous powder flow is assured by the air vibrator strap-

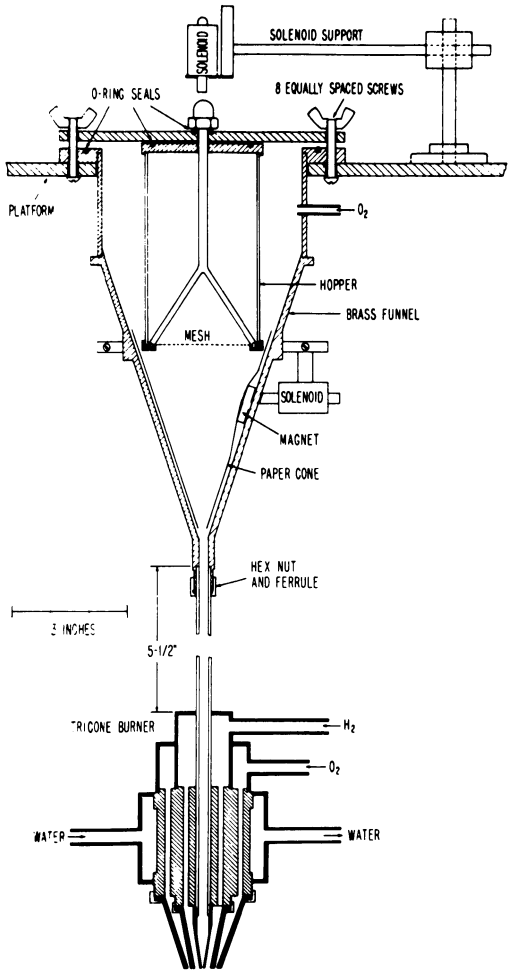

Figure 2

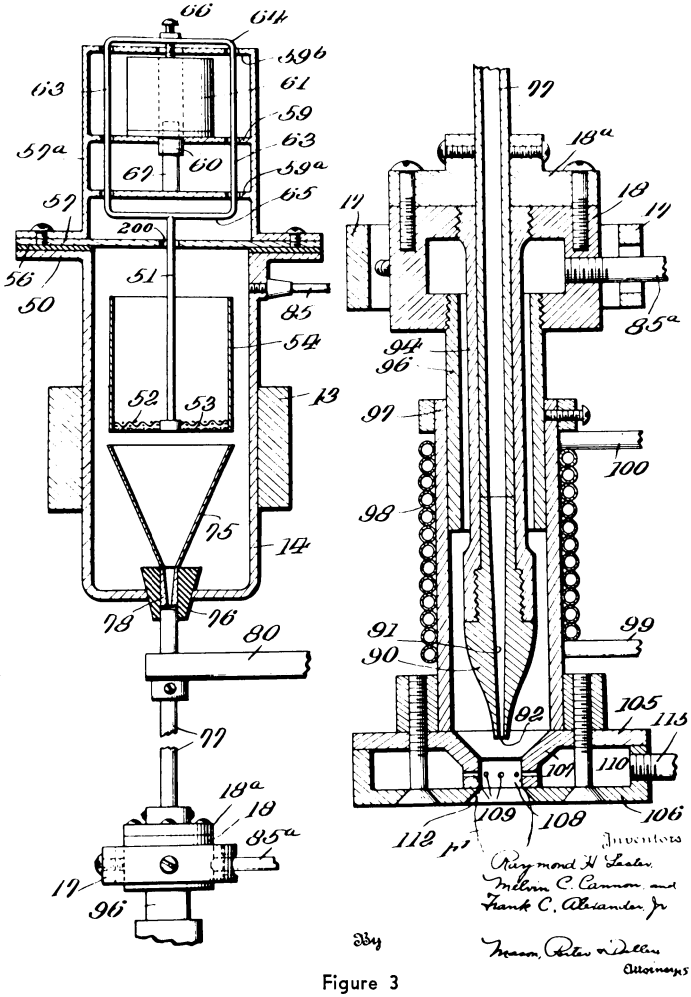

Figure 3

ped to the side of this pipe. The powder filling hole at the top was stopped by a pipe plug that had been drilled and tapped to receive a vacuum gauge. The powder is supported by a wire mesh screen at the lower end of the hopper. Pressure is equalized across the hopper with a by pass made from small bore pipe. The housing for the screw feed has an inside diameter with ample clearance for the screw which was constructed from a wood drilling bit. A test tube brush with helical wound fibers was also used successfully for the screw. The bearing surface is sealed and protected from abrasion by a Wilson type seal having flat rubber washers. The rate of powder flow is controlled by a 0-40 R.P.M. variable speed motor. In operation, a partial vacuum is created in the powder feed system by the oxygen flowing through the Venturi mixer. This negative pressure in the hopper allows refilling with powder while work is in progress.

Screw feed mechanisms are popular for trouble free movement of powders. However, for our diversified type of work which ranges in size from half inch to twelve inches in diameter we required a more versatile powder feed. An improved method for controlling the flow of powder was found in a standard S.S. White sandblasting machine.[6] Figure 7. This unit was used occasionally in our shop for cutting thin wall tubing. Figure 8. The abrasive sand blasting grit was completely cleared from the machine and replaced with fused silica powder. Oxygen was used instead of air. The hopper which sits on top of a vibrator keeps the powder free flowing. The standard sandblasting nozzle is of hard tungsten carbide and is connected to the burner tip. This assembly provided a packaged unit

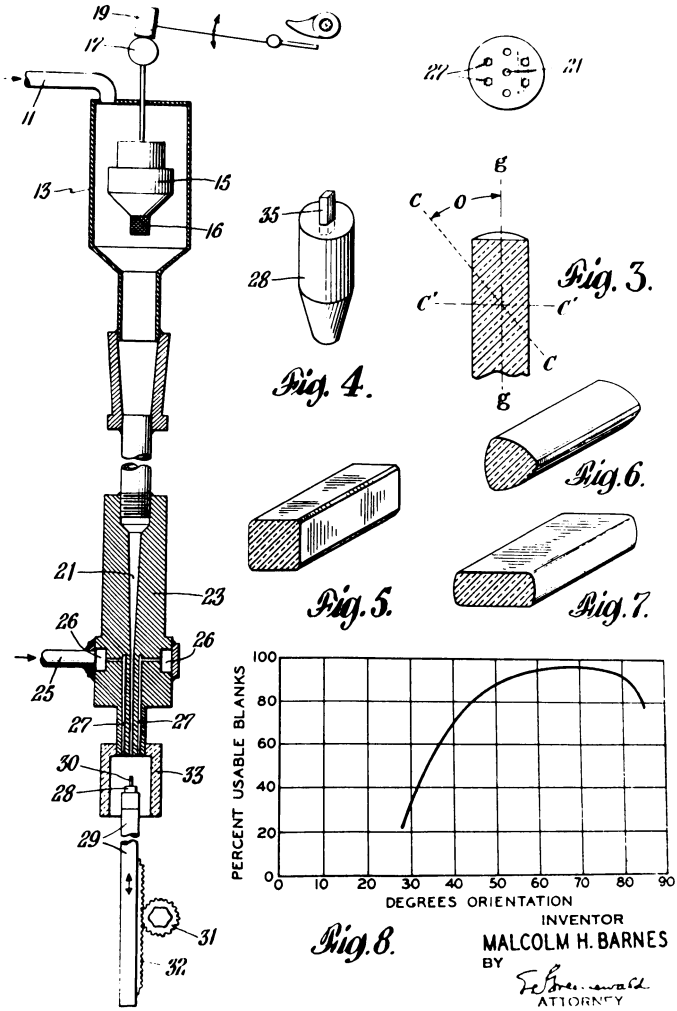

Figure 4

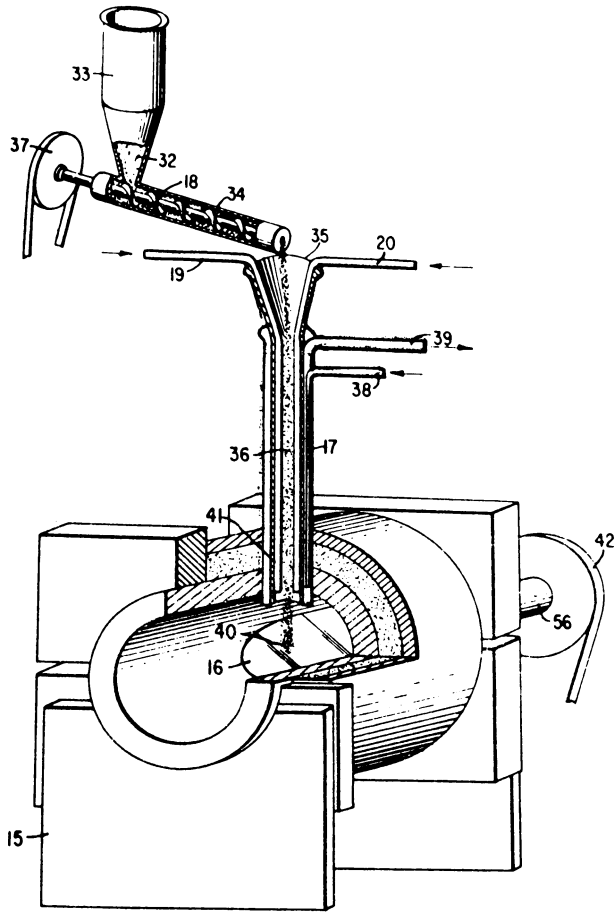

Figure 5

with controls for metering the glass powder. Perhaps of greater importance is that it was designed to handle abrasive materials. The flow diagram is shown in Figure 8.

The torch and tips were our next problem. We had previously experienced a considerable drop in flame temperature when the powder flowed through a single tip torch flame. To overcome this, a five tip manifold was constructed. Figure 9. The first two stainless steel piloted tips were used to preheat the work area. The center welding torch tip was isolated from the other burner tips by a pipe welded through the manifold. This center tip had separate controls for gas and oxygen and carried the powdered glass coming from the S. S. White machine. The last two tips assured complete fusion and flow of the deposited powdered glass.

A new unit for large work is near completion that will allow diameters up to 30″ to be flame spray welded. Figure 10. The oven at the top

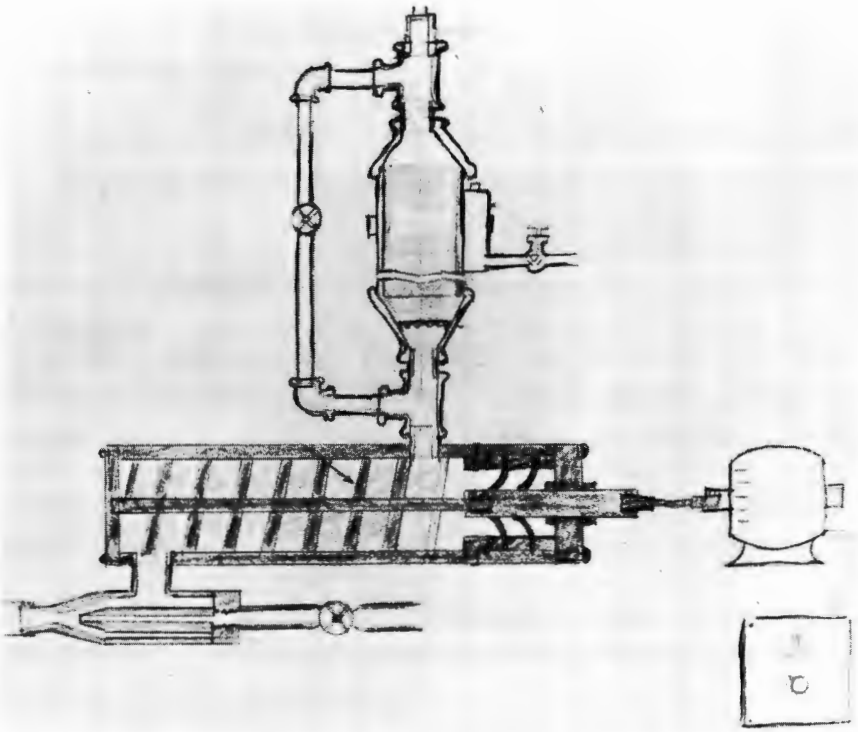

Figure 6

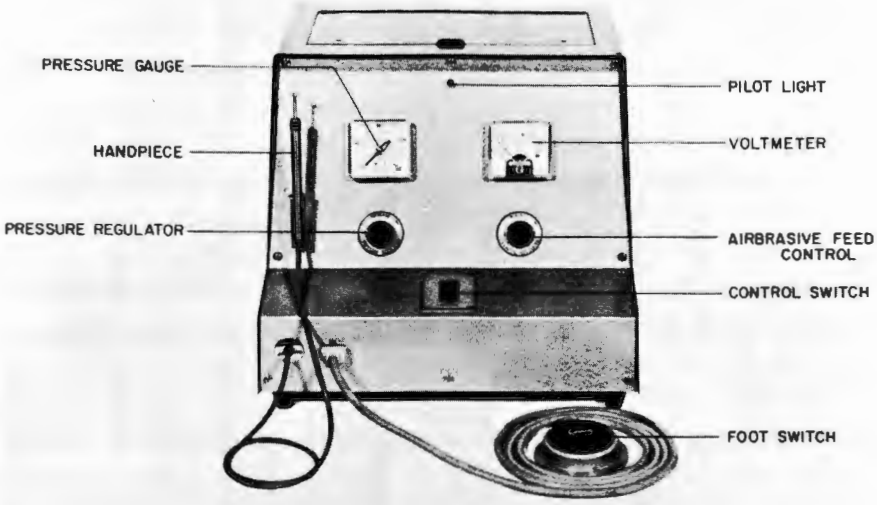

Figure 7

AIR AND AIRBRASIVE FLOW DIAGRAM
S.S.WHITE INDUSTRIAL AIRBRASIVE UNIT
MODEL "F"

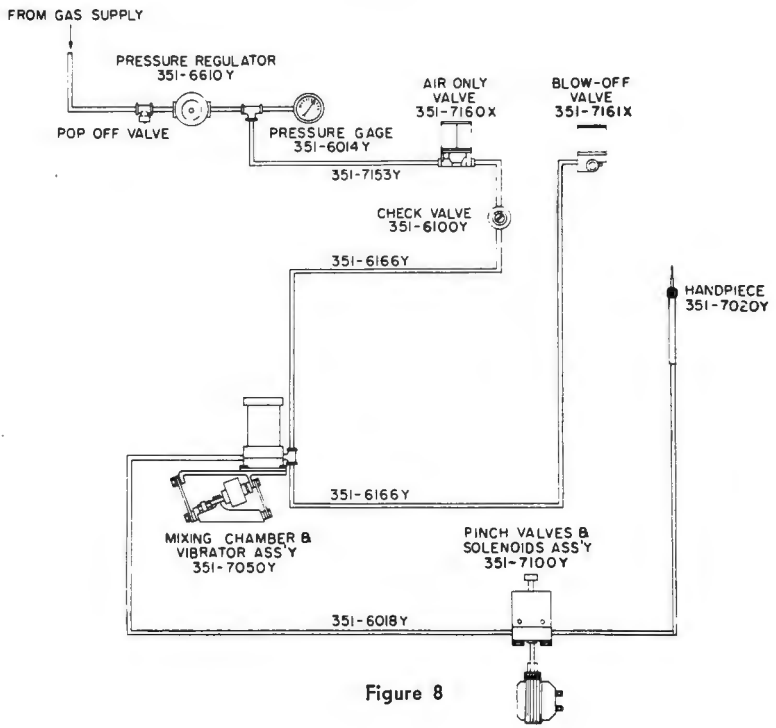

Figure 8

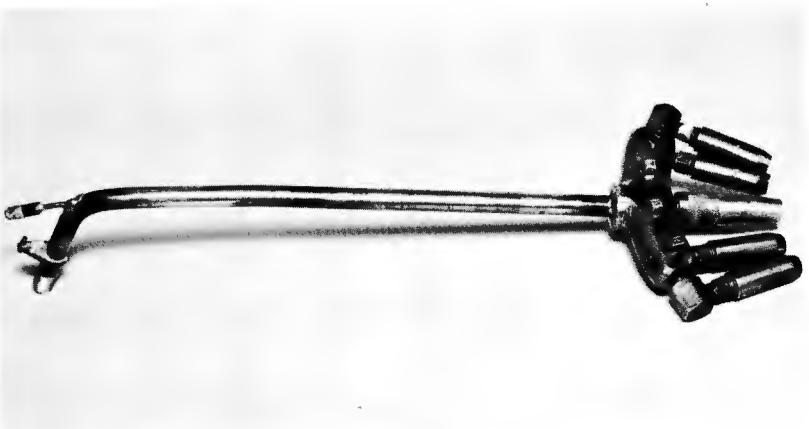

Figure 9

is gas-air fired using Selas radiant burners. The work support table is motor operated for vertical travel and rotation. In the raised position the work is preheated and then lowered out of the hot oven to the powder flame spraying position (not shown). Upon completion of the joint the work is again raised into the hot oven for final annealing. Figure 11 shows the necessary safety equipment and control panel for operating the gas-air furnace burners.

A typical operation is the fusing of a molded round bottom onto a large diameter silica tube. The tube is mounted on the turntable and the end closure placed in position on the open end tube. The surfaces to be fused

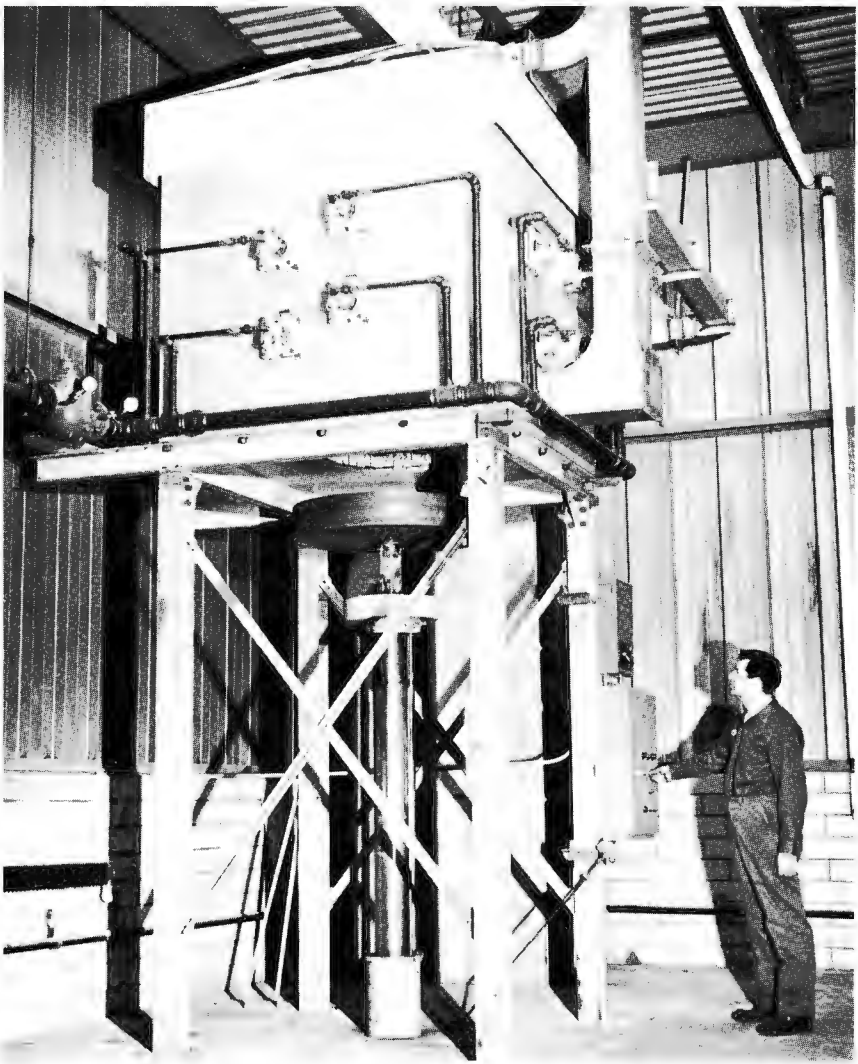

Figure 10

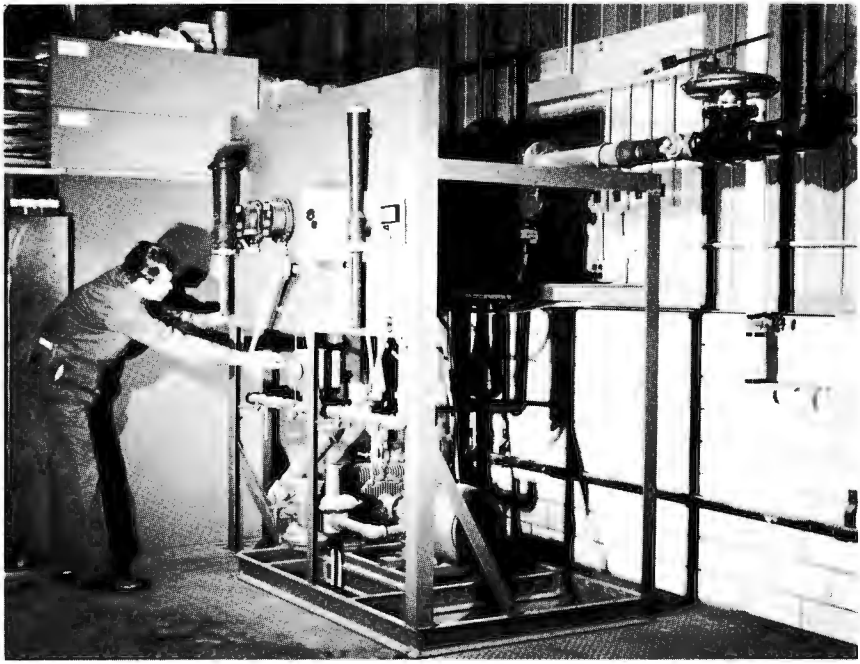

Figure 11

are chamfered to provide greater depth of weld and therefore a strong joint. Burner tips are placed about two inches from the work. After the work is preheated and lowered into the flame spray position soft fires preheat the rotating tube and the work temperature is gradually increased by the addition of gas and oxygen. When the fusing zone is sufficiently preheated the flow of powder through the center burner is started. The speed of rotation, flame size and powder flow are adjusted to assure complete fusion of the powdered glass. When the "V" groove formed by the chamfered ends is filled the flow of glass powder is stopped and the part is oven annealed.

The powdered glass used for flame spraying is commercially available. For most jobs 200 mesh is suitable with finer mesh sizes preferred over coarse material. Powder may be prepared from clean scrap glass or tubing when conventional pulverizing equipment is available. However, crushers, ball mills and all parts in contact with glass should be of steel construction. This will allow impurities to be removed from the powder by an overnight soak in hydrochloric acid. After several tap water rinses the powder is flushed with distilled or demineralized water and oven dried in clean trays.

The powdered glass flame spray process is ideal for large diameter work because the operator is not in the intense heat area. On the other hand, the technique is equally effective for smaller work such as making heavy wall sections, flanges and repair work. We have produced micro spheres of fused quartz by setting two welding torches up as a cross fire.

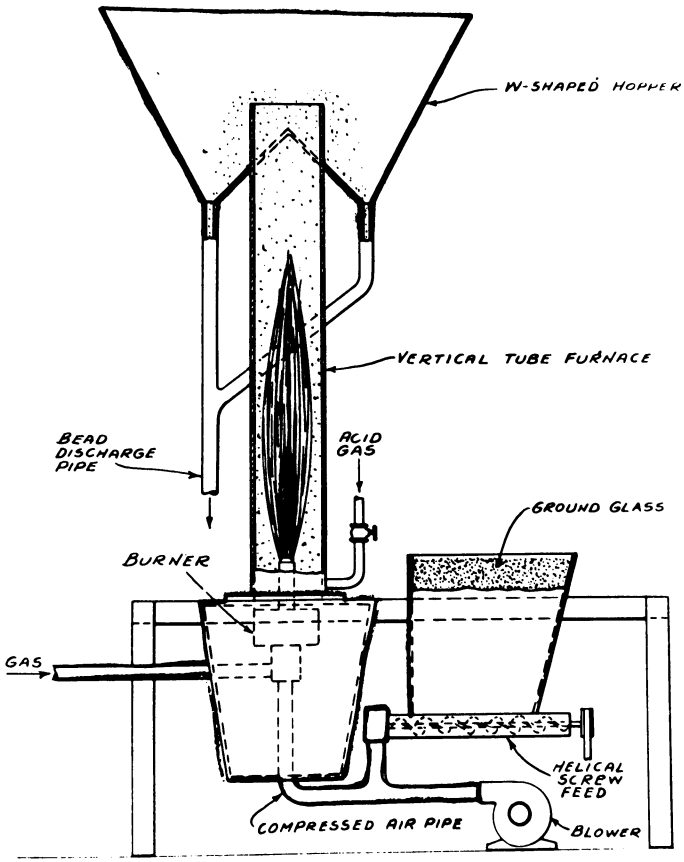

Figure 12

One torch spewed the powder through the flame into the blast of the opposing torch. The spheres were collected on fine wire mesh as they dropped out of the thermal current. The same effect is produced with softer glasses as shown in Figure 12. This patent drawing[7] shows powdered glass delivered to the gas stream by the conventional screw feed. The powdered glass sphereodizes as it passes through the burner and thermal currents carry the beads into a receiving area. By spraying different glass type powders a graded seal effect can be accomplished[8] as shown in Figure 13. The powder in this case is applied electrostatically but is equally effective when sprayed through the burner flame. Flame spraying has also been used for applying 7052 beading glass in controlled thickness to Kovar metal.

The powdered glass flame spray technique is just one more tool for the scientific glass blower. The method should be exploited in your own shops as applications arise.

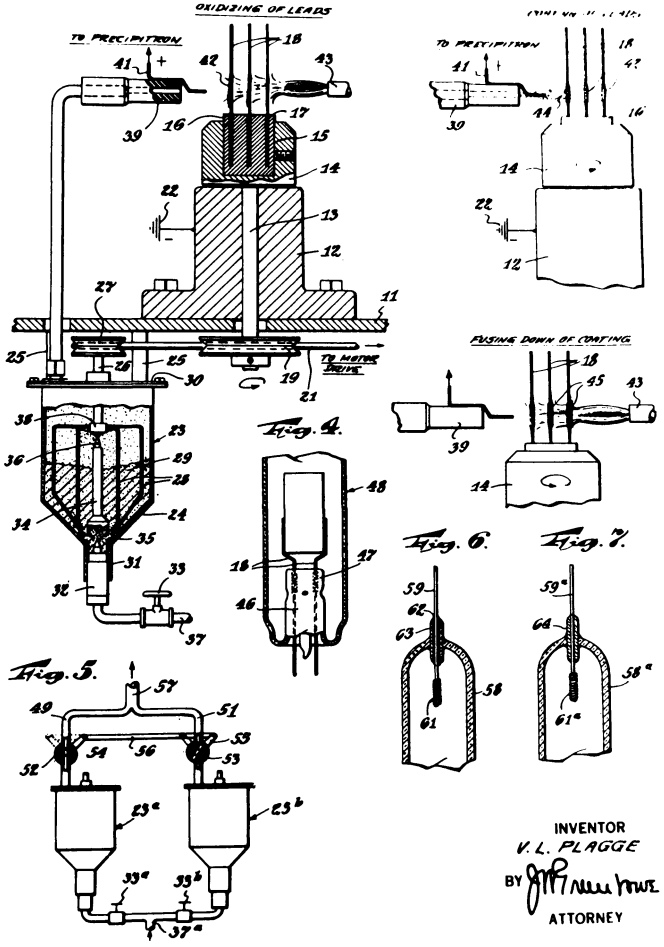

Figure 13

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POWDERED GLASS TECHNOLOGY

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ABSTRACT

The basic principles of sintering glass are presented. A simple laboratory process is useful for educational and experimental operations; thus, requiring a minimum of capital outlay. This simple process will benefit the scientific glassblower, and it should create further interest in the field of powdered glass technology. References with more information on special phases are listed.

PART ONE: SINTERING PROCESSES

1. INTRODUCTION

Powdered metallurgy is a well established field; the relatively new field of powdered glass technology is a parallel. Many of the procedures and methods used for sintered glass are in a textbook on powdered metal.[1] The field of ceramics supplements this technical knowledge.[2] The first commercial use of glass powder other than for glazes and enamels was by G. F. Huttig (1924) to make fritted filters.[3] The Schott and Genossen, U.S.A. patent (1927) covers the preparation of filters; *viz.*, "a porous body of fritted glass particles".[4] This report will give the reader an initiation into this new field of Powdered Glass Technology. The process outlined will be for the novice rather than the skilled technologist. The subject matter and theories are controversial, and the task is not to be considered completed with this publication.

2. THEORY

Glass is sintered by point to point contact of two adjacent particles, forming a "neck" between the particles by viscous flow. The theoretical science of sintering has been published by Kingery[2] for those interested in a detailed explanation.

While a relatively simple principle is involved, the complete reproducibility is very exacting. All details of the process are important. When glass powder is heated at or near the softening point for a short period of time, a piece of glass results, containing a system of glass particles joined together, with entrapped gases giving a translucent appearance. The basic rule never to be violated is that the process must be controlled throughout the entire production phase in order to obtain the best and uniform quality.

3. MATERIALS

3.1. *Glass Preparation*

The basic raw material is massive glass, to be ground into the powder. Careful selection for the finest quality material is necessary.

The usual form is tubing, or water-fritted cullet; this does not include glass from a scrap pile. The glass must be free from stones, abrasive, iron rust, oil and all other contamination, including glass of different composition.

The raw glass is crushed to pass a No. 8, U.S. Sieve. This crushing is necessary for a controlled grinding schedule for the pebble mill. The pebble mill is lined with dense alumina, and dense alumina balls or cylinders are used. The charge of the mill is one half of the volume as grinding media, and one fourth of the volume as minus 8-mesh glass. The rotating speed of the jar is the recommended speed for the particular size mill. The time of grinding for a hard, borosilicate glass is ten hours; one obtains a powdered glass that 70% minus 325 mesh, U.S. Sieve. All coarse particles, over 100 mesh U.S. Sieve, are screened out. The grinding time is critical and determines the particle size of the product. A helpful source of information on grinding is the Paul O. Abbe Company's *Handbook of Ball and Pebble Mill Operation.*[5]

Particle size determination is made by wet sieve analysis. The sieves used are 100, 140, 200, 270 and 325 mesh sizes. The W. S. Tyler Company's *Handbook on the Use of Testing Sieves*[16] is followed.

The average particle size determination is made with a Fisher Scientific Company, Sub-Sieve Sizer, with this 50 percent point used for process control. Sedimentation data based on Stokes Law, using an Andreasen Pipet, is recommended for the fine particle sizes. A good reference for particle sizing is Irani and Collis.

Ground glasses prepared to your specifications require the type of glass, particle size distribution as well as other specific properties. The glassblower with limited facilities and time is requested to state his desires.

3.2. *Binders*

Many binders are available, and each technologist has his preferred binder. The perfect binder is not as yet known; but when it is available, it should meet the following requirements:

Impact high green strength to the compact

Be non-abrasive to avoid excessive die wear

Be free of inorganic salts or metallic ions which will not burn out in the firing process

Decompose or oxidize readily during firing at relatively low temperatures.

Will not adhere to punch faces

Be non-hydroscopic

Disperse in the formation of the granulations to coat each particle of glass

Lubricate the punch and die as well as the grains of glass

The testing of an unknown binder is relatively simple. A clean glazed crucible is filled with 5 grams of the binder. The crucible and

material are placed in a burn-out furnace and observed for melted wax, carbon and ash. Acceptable binders leave the crucible as clean as it was before the test started.

Binders found for glass sintering are the nitrocelluloses, biphenyl, Nopco ORP, Holowaxes, polyvinyl alcohols, and polyethylene glycol (Carbowax). Many users prefer carbowax, or polyethylene glycol.

3.3 *Sagger Plates*

The pressed compacts are placed on sagger plates or tiles for sintering. It is necessary to use a release agent to prevent the compacts from sintering to the fireclay sagger plates. This release agent is a suspension of equal parts of kaolin and fine ground alumina hydrate. A slurry of these powders is made with "Mobilicer-X"™ binder and water. The slurry is brushed or sprayed on in a thin coat on the sagger plate. The plates after coating are dried for 16 hours, or preferably over a weekend in the open room. The dried plates are processed through the sintering cycle without pressed parts to cure the release agent. This coating should be smooth and without flake-off. If trouble is encountered in coating the plates, a sodium phosphate detergent sold as "Calgon"™ or "Climalene"™ should be incorporated in the binder composition to develop a glass bond between the release agent and the sagger plate.

4. Special Equipment

4.1. *Presses*

The compacts are pressed with a hydraulic press, (Figure 1), such as the Carver Laboratory Press or a Wabash Hydraulic Press. The press should have sufficient capacity to press the area of the desired compact at 5000 psi. In a large automatic operation, power presses of the Stokes, Coulton, Kux and other types are used.

4.2. *Punch and Die Sets*

The forming tools for the compact are a simple punch and die set as shown in Figure 2. The metal for the two punches and die is hardened alloy tool or die steel. The yellow label tool steel, BR-4, or D-2 alloy have been used. The punches and die are hardened to a Rockwell 60C and then ground to final dimensions. A series of spacer rings, 0.750″, 0.500″, 0.250″, 0.125″, and 0.065″ thick are used to drop the lower punch to the desired depth of fill.

4.3. *Ovens and Furnaces*

4.3.1 Drying Oven

A drying oven with a circulating fan and exhaust is needed to dry the granulated frit. Any oven with a thermostat regulator may be used, provided the temperature can be controlled at 66°C. or 150°F.

4.3.2 "Burn-Out" Oven

The "burn-out" oven is an electrical hot plate surrounded by insulating brick (Figure 3). This electrical hot plate is actually a spare heating element for the sintering furnace. The hot plate is covered with a Transite or stainless steel sheet about two inches above the heating element. In the back of the furnace a checker work is

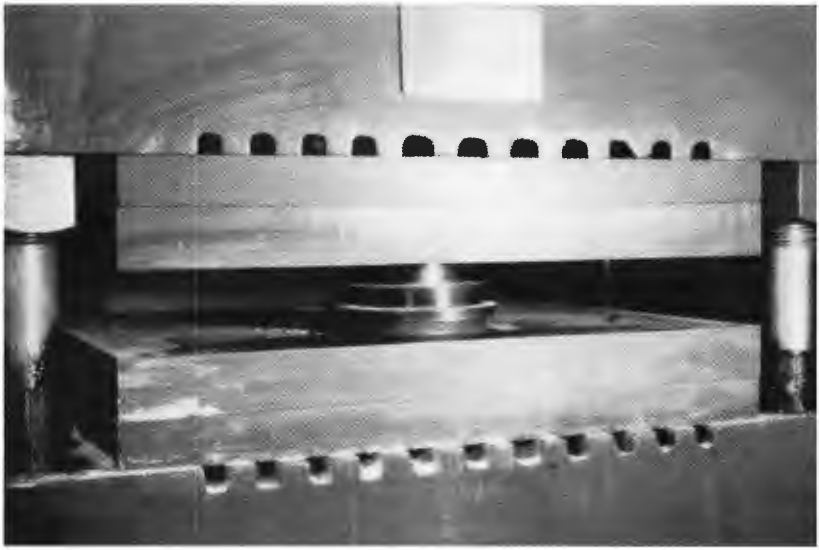

Figure 1
Wabash Press set up.

Figure 2
Punch and die set.

made of cut brick to permit fumes to escape. The door on the front of the furnace can be a Transite or fireclay plate leaned against the brick. A control thermocouple is inserted in the top of the furnace and connected to a potentiometer with an "on-off" control. This "burn-out" furnace is designed to enable the fumes to escape freely into a ventilating system or hood around the oven.

4.3.3 Sintering Furnace

A box furnace of the muffle type with a maximum temperature range of 1850°F. is used. This furnace should have a working space of 7″ x 12″ minimum. The instrumentation usually furnished with this furnace should be disconnected and the circuit rewired for a first-class indicating potentiometer with an "on-off" relay for temperature control. The thermocouples should reach into the furnace and record the temperature about 1″ above the samples.

5. Processes

5.1. *Introduction*

The glass type and particle size distribution should be standardized for good reproducibility. The methods of sintering must be explored for the best application to the product. The basis of glass sintering is to consolidate grains of glass by a time-temperature cycle. Producing sintered glass ware includes may special applications, with varying methods for fabrication depending upon the desired characteristics of the finished ware. Ware may vary from a porous sintered part, as a fritted filter, to a maximum density item as illustrated by glass headers for electronic tubes. Even the use of solder glasses is a

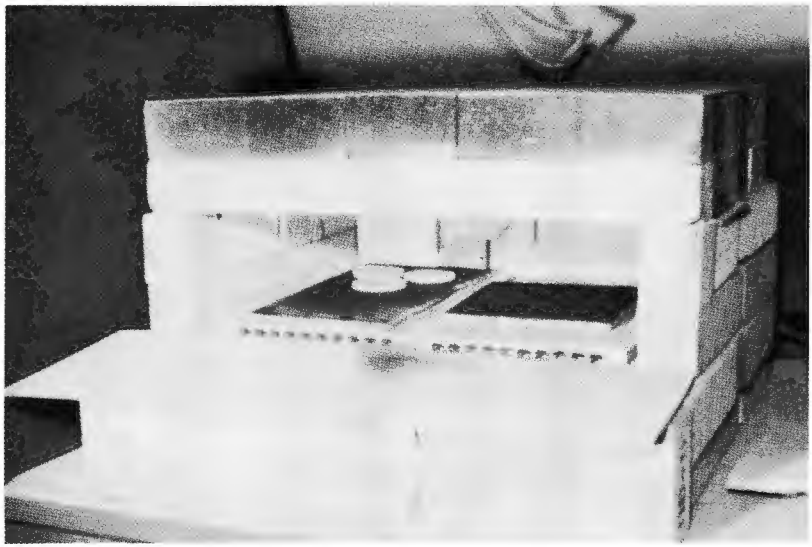

Figure 3
Burn-out furnace with plate and part.

type of sintering. The three basic sintering procedures are outlined below to illustrate the difference in processing.

5.2 *Porous Bodies*

Sintered glass for fritted filters requires uniform round grains. The size of the pores in the sintered filter depends upon the grain size, distribution, shape and the pressure used to compact the filter before or during firing. The grains of glass are sintered in molds, or as compacts, with the processing conditions carefully controlled. The sintering temperature is equivalent to a $\log_{10}$ viscosity of 8.8 poises with the time depending upon the size of grains, the required strength, hardness and porosity of the filter. The sintering time is usually a compromise to control these variables.

5.3 *Philips' Technique*

The Philips' Glass Sintering Technique[8] has been used extensively in the electronics industry. Glass powder is cast in a mold with the metal parts assembled in their correct positions. The mold is covered and passed through a controlled atmosphere furnace. The temperature for sintering this type of part is usually above the softening point of the glass, or at a $\log_{10}$ viscosity of 6.0 poises.

5.4. *Sintered Compacts*

The third process is dry pressing and sintering of compacts. The glass is mixed with a liquid binder, then dried and granulated. The binder-glass granulation is dry-pressed into shape and then heated to remove the binder. A dense part is formed in the ensuing time-temperature sintering cycle. The resulting vitreous body has roughly the same properties as the parent glass; however, it will be translucent rather than transparent because of the remaining tiny voids. This process is of major importance to the glassblower.

PART TWO:

DETAILED PROCESS FOR SINTERING COMPACTS

1. Introduction

The preparation of the powdered glass and a general description of sintering were presented in Part One. It is now necessary to describe the sintered compact process in detail. In the following discussion, it is theoretically presented as the preparation of five test cylinders.

2. Granulation Preparation

Since there are only five sintered cylinders required, a small hand granulation of TM-7® glass will be described for an example. A wax solution of 31.6 grams of Carbowax 20M in 250 ml. of water or acetone is added to 600 grams of TM-7® powdered glass in a 400 ml. beaker. The mixture is stirred for 10 or 15 minutes, with a heavy stirring rod, to coat each particle of glass. The proper mixing is indicated by no glass sticking to the sides of the beaker, and the mixture appears to be similar to a wet paste. The pasty mixture is spread in a tray and placed in a drying oven at 150°F. to dry into a material with a consistency capable of forming a grain. This stiff paste is then gently forced through a No. 12, Tyler stain-

less steel sieve. The granules formed by the sieve screen are dried in a tray at 150°F. to the minimum moisture content possible. On a larger scale, the commercial ceramic industry granulation process equipment is used.

The granulation, after drying at 150°F., is inspected for lumps of material, and passed over a No. 16 stainless sieve to remove these lumps. The screened granulation is now sealed in a glass bottle for storage prior to testing and use.

3. Pressing

The compacts are pressed with a hydraulic press at 500 psi. The forming tools for the compact are the simple punch and die set shown in Figure 2. A series of five test cylinders are usually pressed and fired to obtain design data for the process. The test die set is ¾ inch in diameter, or has a face area of 0.4418 square inch. Then the area times the 5000 psi gives a 2,200 pound pressure that must be applied at platen of the press. A larger spacer ring 0.750 inch thick is placed on the press platen, and the die is placed on the spacer. The lower punch is dropped into the die, and the depth of fill is measured with a depth micrometer. The depth of fill is recorded. The assembled die and punch is loosely filled with the granulation and leveled to the top of the die with a spatula, and the upper punch is carefully inserted by hand. This assembly between the plates of the hydraulic press is pressed until the gage of the press indicates the required pressure of 2,200 pounds has been reached after a short period of dwell. The pressure is now released and the die with punches in place is removed, and put on a work table or heavy plate. The upper punch is carefully pulled out of the die, and a pressure with the thumbs on the

Figure 4
Part ejected from die

die ring will eject the pressed part from the die. By careful manipulation, it is possible to slide the compact off the punch onto a pancake turner for transfer to the firing plate, or to the analytical balance for weighing.

It is recommended that in the preparation of test samples, a careful record of data be logged in a laboratory notebook. The first entry at this stage was the depth of fill. The pressed part is then measured for height and diameter with a micrometer reading in thousandths of an inch. An analytical balance is used to weigh each sample to at least one hundredth of a gram.

The pressed compacts are transferred to a coated sagger plate, with the samples on end in the middle half of the plate, avoiding areas of the door and rear of the furnace.

Figure 5
Part on sintering plate.

4. "Burn-Out" and Sintering

The plate with the samples is placed in the burn-out oven at 1000°F. for 15 to 30 minutes, or until the samples are not discolored with the decomposed binder. The binder should not burn out with a flame. After the binder has been expelled from the compact, the temperature of the burn-out has started a slight tacking together of the particles sufficient for transfer of the plate and cylinders to the sintering furnace. The cylinders are sintered on the plate in the furnace for 15 minutes at 1140°F. After the sintering cycle, the plate of cylinders is removed from the furnace and cooled to room temperature on a sheet of Transite™.

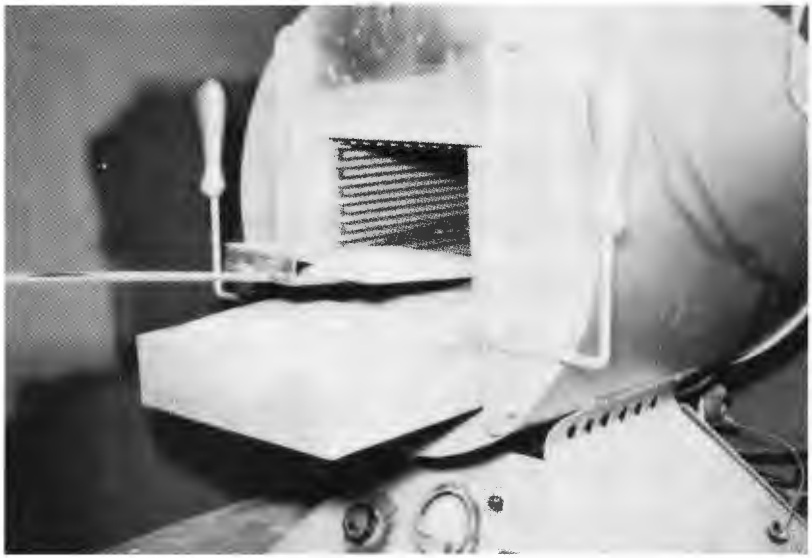

Figure 6
Sintering furnace with plate and part.

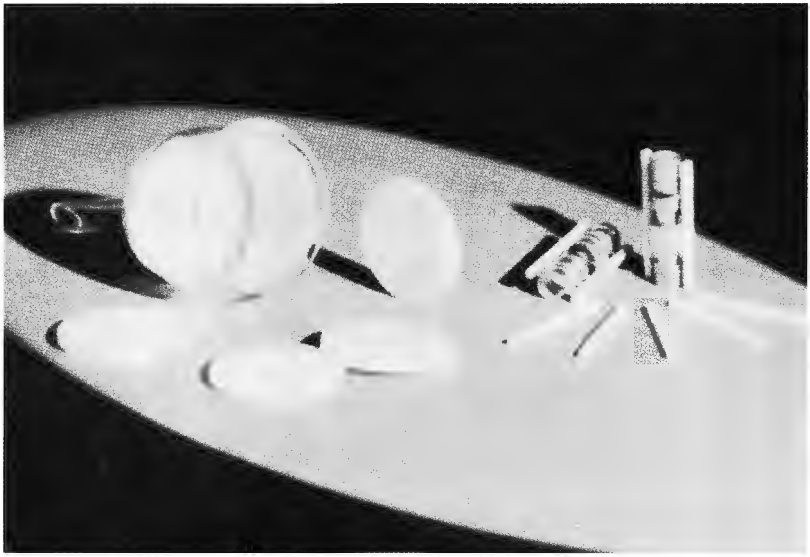

Figure 7
Display photograph side rods, perforated discs, fritted filters.

5. Test Procedures

The cylinders after sintering are weighed on the analytical balance to determine their loss in weight. The cylinders are also measured for height and diameter with the micrometer. When sintered at a temperature that destroys the sharp edge of the cylinder, repeat the firing at 25°F. lower temperature until a sharp edge is obtained on the test cylinder, with a strong structure developed in the part.

The press pressure used to sinter glass is 3000 to 7000 psi, with 5000 psi as the desired pressure for dense sintered parts. The press gage reading is easily obtained by:

(1) Square inch area of punch face $\times$ pressure (psi) = press pressure.

A group of three samples is recommended for a minimum test lot at a given pressure. The data obtained from the test cylinders are used to design the punch and die set of the desired part.

The compaction ratio of the granulation should be constant from one lot of granulation to another for automatic pressed.

$$(2)\quad \frac{\text{Depth of fill}}{\text{Green Height}} = \text{Compaction Ratio}$$

The shrinkage of the part is obtained by:

$$(3)\quad \frac{\text{Green Dimension}}{\text{Sintered Dimension}} = \text{Shrinkage Factor}$$

This shrinkage factor times the sintered dimension will give the dimension required for the punch and die design. The diameter factor is the most reliable factor to use.

The percent weight loss, which indicates the percent binder in the granulation is obtained by:

$$(4)\quad \frac{\text{Weight of Green Part} - \text{Weight of Sintered Part}}{\text{Weight of Green Part}} \times 100 = \text{Percent Weight Loss}$$

6. Conclusion

In conclusion, this paper has been intended to outline a step-by-step process for making sintered parts. It is possible, with careful procedures and good laboratory practice, to make prototype parts by this dry press process. The principles outlined have been used in pilot plant operations with the suitable facilities for increased volume.

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FRACTURE ANALYSIS FOR GLASSWARE

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When we analyse a piece of broken glassware for its failure cause, we seek answers to the following questions:

1. What is the principal fracture pattern?
2. Where and what is the primary fracture origin?
3. What are the residual stresses in the glassware?

Figures 1, 2 and 3 are examples of a fracture pattern that discloses the answer to the first question.

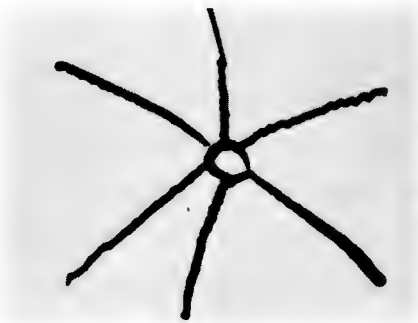

Figure 1

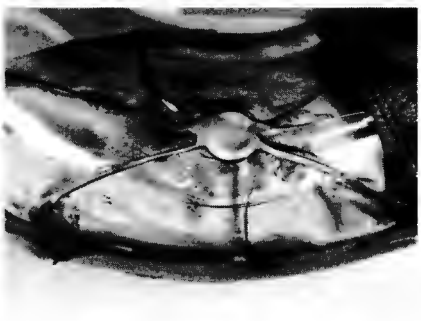

Figure 2

These figures illustrate a radial or star fracture pattern, which obviously resulted from either a severe impact or an excessive point load on one of the surfaces.

Also, this particular fracture pattern shows that the failure started in the center or vortex of the pattern.

Additional examination usually discloses the surface on which the failure started. Figure 4 represents the cross-section of the vortex around

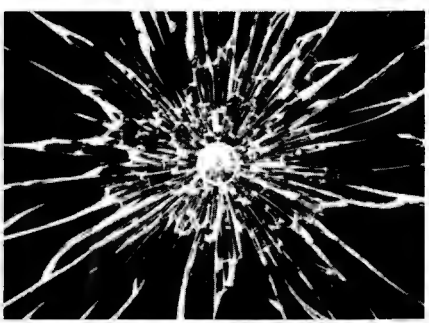

Figure 3

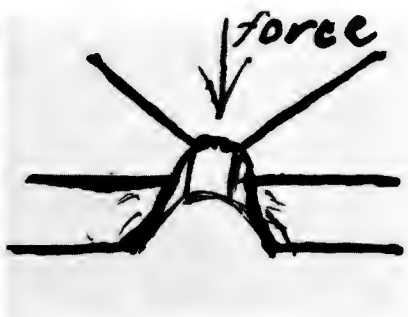

Figure 4

a radial fracture caused by impact. A shape called a Hertzian cone is usually punched out of the glass, and the shape of the hole it leaves identifies the impacted surface. In Figure 3—a closeup of the vortex of a radial fracture—the Hertzian cone was held in place because the fractured plate was laminated to another plate that didn't break. Again, the direction of the impact force is apparent.

Figures 5 through 10 illustrate another basic fracture pattern that is helpful in fracture analysis. This characteristic pattern, called the bending-moment pattern, occurs when a piece of flat glass or tubing is bent to failure. Lab workers produce this kind of fracture when they score tubing with a file and then break the tubing.

The fracture origin is the surface damage caused by the file. When the damage is sharp and new, a clean, single fracture occurs, as shown in Figure 5. A poor file mark, or even a good one several days old, causes a bending-moment fracture in a pattern illustrated by Figure 7.

The complex fracture pattern of Figure 9 results when you bend a piece of tubing until it breaks when surface damage at the origin is very slight—such as you would normally find in a piece of tubing taken from stock.

Figure 11 shows a piece of drainline pipe that broke in an installation where the fill above and around the drainline had not been properly settled after the drainline was put into the ground. The bending-moment pattern tells us that this piece of pipe failed because it was subjected to an excessive bending load resulting from the unsupported weight of the soil above it.

Recognizing the bending moment fracture pattern is important because the fracture pattern for most internal pressure failures is the bending-moment pattern.

Figure 12 shows a culture tube that failed under a relatively low internal pressure, and Figure 13 shows a Corex Brand centrifuge bottle bottle that failed under a high internal pressure. Note how similar these fracture patterns are to the pattern of the drainline failure.

The pressure failures occurred because the tubes were literally bent out of shape by the internal pressure—so much so that the glassware failed.

Failures in tubing from too severe and uneven clamping show the same kind of fracture pattern, but the degree of splintering is usually less for clamping failures and, often, you have only one half of the pattern, as when the failure starts at one end of the tube.

Failures in flat glass, like those in constrained windows that are subjected to a too severe temperature gradient from one face to the other, also are usually bending-moment failures. These failures are usually simple as regards to the degree of fragmentation—often only a single fracture and seldom more than two or three fractures, as is shown by Figure 8. As the hotter side expands more than the cooler side, and as the glass is constrained, the hotter side is put into compressive stress and the cooler side, as a result, is literally pulled into tensile stress. When the stress

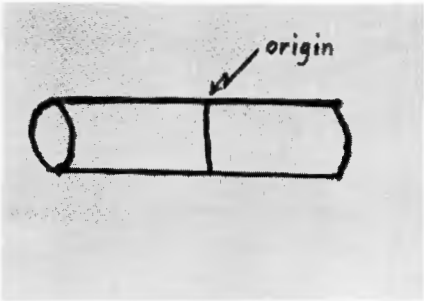

Figure 5

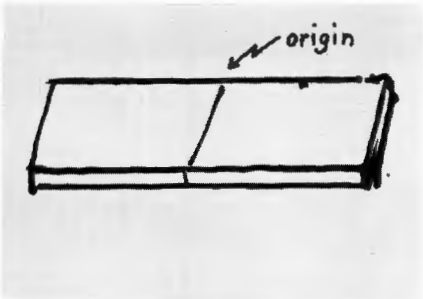

Figure 6

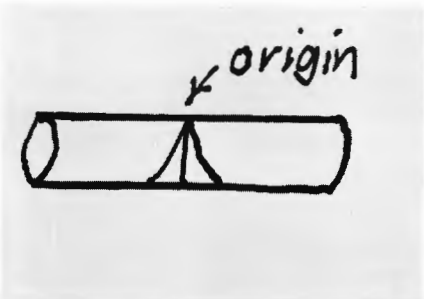

Figure 7

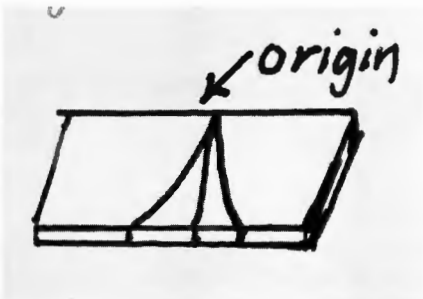

Figure 8

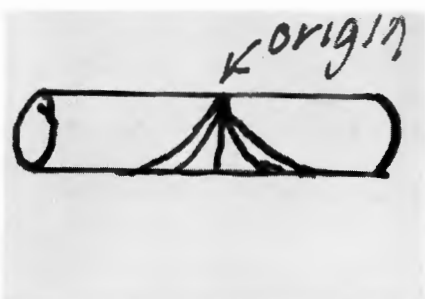

Figure 9

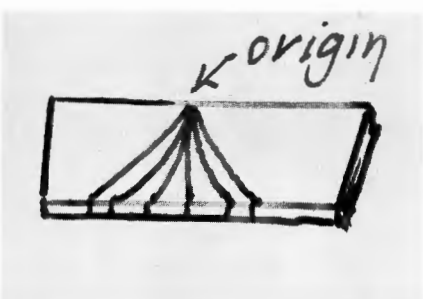

Figure 10

is great enough to cause the glass to fail, the resulting fracture pattern is usually a typical bending-moment type that has been thermally induced.

Figure 14 shows an example of another basic fracture pattern called a thermal fracture pattern. It is representative of the kind of failure that results when a piece of glassware such as a beaker when it is heated too fast after the surface has been severely damaged by too vigorous a use of a stirring rod. When we see this kind of a pattern—almost a lack of pattern as it were—we know we have a thermal failure.

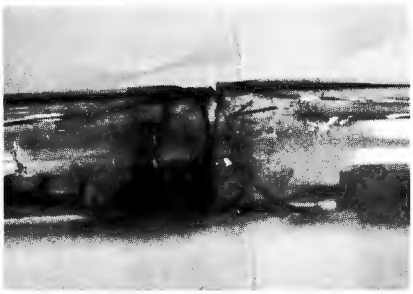

Figure 11

Figure 12

Now this kind of failure is a good example of the reason we need two other tools to study glassware failures—the use of fracture flow lines to locate the fracture origin, and the use of polarimetric means to study the residual stresses in glassware. I'll discuss the use of fracture flow lines first.

When a stone is dropped into a placid pool of water, ripples are produced in the surface spreading out from the place the stone was dropped. Figure 15 shows the pattern of the ripples when the stone strikes the center of the pool; Figure 16 shows the change in pattern when the stone falls next to the edge of the pool. If these ripples could be frozen into the surface of the pool, you can readily see how you could locate the point

Figure 13

Figure 14

from which the disturbance started by observing the curvature of the ripples. Fortunately, when a piece of glassware fractures, ripples in the fracturing surfaces are usually produced; and by locating them and observing their curvature, the direction of the fracturing can be determined. Then by working backwards so to speak, the origin of the fracturing can be precisely determined. The location of this origin is often an essential clue to what caused the glassware to fail. Figure 17 is a photograph showing flow lines of the kind we look for in the fractured surface of a piece of glass. As the origin was in one of the surfaces, as is usually the case with glass failures, the ripples in this figure are analogous to the ripples in Figure 16.

Consider Figure 14 again. By flow lines we were able to locate the fracture origin in a bruise check in the inside surface of the bottom of the beaker. This tells us that the beaker broke while being heated when the inside surface was appreciably cooler than the outside. A measurement of the wall of the beaker at the origin shows the wall to have been good for normal thermal service. The bruise check while not extensive was quite deep. The greater the depth and the freshness of a check, the greater the weakening effect of the check. Since this beaker exhibited no residual stresses, we concluded this failure to be one caused by fairly bad surface damage from a stirring rod or some other agent combined with hard thermal usage.

Glass failures that result from poor annealing are well known. Also glass failures result from inducing bad residual stresses by heating the glass too near or above the strain point. In each case the resulting fracture pattern is usually the thermal fracture pattern of Figure 14, though often even more erratic and more fragmented.

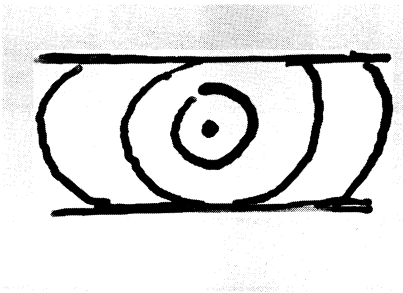

Figure 15

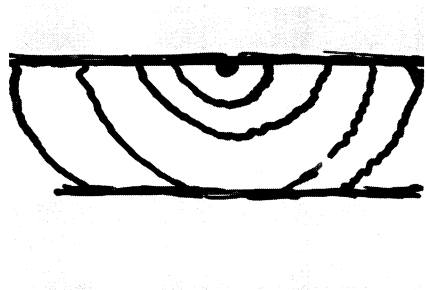

Figure 16

A good example of a potential failure from bad residual stresses is illustrated by Figure 18 which shows a dangerous residual stress condition in a piece of pipeline that was poorly flame-annealed after beading the end of it. This stress condition was observed by means of a Friedel polarimeter and with the pipeline immersed in a mixture of oils of the same index of refraction as the glass. Using this mixture, the surface reflections from the glass are eliminated and we can clearly see through the side walls of the pipe. As indicated by the polarimeter, the outer surface

of the pipeline, a short distance back of the bead, is in a fairly high tensile stress condition, so much so that only minor surface damage plus a mild thermal shock would be required to cause it to ring off.

Figure 17

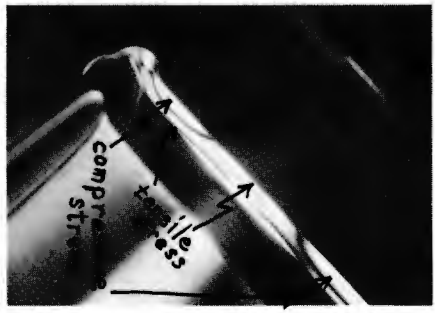

Figure 18

When I said we try to get the answers to three important questions when we do a fracture analysis in our laboratory, it is apparent by now that the need to get all three answers varies appreciably from problem to problem. Often in the case of failures from impact or from bending-moments we do not need to study the residual stress condition of the ware that failed. Our major problem is the reconstruction of the fractured glassware to identify the type of failure and to determine the surface in which the failure originated. Failing to be able to reconstruct the glassware, we are still able as a rule to find the primary origin and this together with shape and size of the fragments associated with it determines what caused the glassware to fail.

On the other hand, with thermal type failures, it is usually essential to employ all three of the tools we use—the reconstruction of the glassware, the determining of the fracture origin by tracing out the flow lines in the fractured surface, and the study of the residual stresses.

While we do have a few glass fractures that cannot be resolved by the methods discussed in this paper, they are the exceptions, so I trust this discussion will be of value to you as a practical guideline for helping you analyse most of the glass failure problems you will encounter.

One last word—when we do have failures with fracture patterns that do not fit the ones I've discussed, we try to duplicate the failure by laboratory experiments that subject the kind of glassware that failed to conditions in the laboratory that simulate the service conditions the glassware was known to have been subjected to. Our successes from this approach are often valuable in two important ways. First of all we convincingly establish why the glassware failed and, secondly, we acquire new and valuable knowledge for future failures analyses.

ADDENDA

Some notes on the kinds of surface damage contributing to failures in glassware.

Since, in our fracture analysis the identification of the surface damage or weakness is often essential, our laboratory thoroughly examines fracture origins for surface flaws. We usually find that one of the following five surface flaws is involved.

1. Bruise Checks—like those produced by glass to glass impact.
2. Checked Scratches—like those produced with a file mark or a glass stirring rod.
3. Fire Checks—like those produced in a glass surface when it is momentarily struck with a hot and intense source of heat such as a sharp flame from a lampworkers fire and is not quickly flame annealed to spread out and reduce the resulting highly localized surface residual stresses.
4. Glue Spalls—like those produced when a strong, nonelastic adhesive peels or cracks away from a glass surface.
5. Poor Glass to Glass Seals—of one of two kinds: one, a seal contaminated with bits of a high-expansion refractory material; the other, a seal made with a severe reentrant angle.

Any one of the foregoing weaknesses can be sufficiently bad to be the principal cause of the glass failure.

This point emphasizes the frequent need to locate fracture origins, especially those occurring from a mild thermal or mechanical shock—like the dropping off of the foot of a cylinder because of a slight jar or the thermal failure of a piece of glassware in normal cleaning and drying procedures.

As an aid to your examination of surface damage we highly recommend the use of a dilute hydrofluoric acid etch—2 to 3 minutes in a 5% hydrofluoric acid solution at room temperature—followed by thorough rinsing and drying.

SAFETY CONSIDERATIONS OF STRAIN IN GLASSWARE

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ABSTRACT

Scientific Glassblowers can be a source of safety knowledge to the users of scientific glass apparatus. This paper describes a talk and demonstration which has been presented by the Dow Glass Fabrication Department to numerous plant and research groups within The Dow Chemical Company. It is hoped that the presentation of this talk to a group of glassblowers will suggest ways in which you may make a meaningful and worthwhile contribution to the safety effort of your own company.

Glassware having uncontrolled strain is much more likely to fail in use than is annealed glass, and could result in a serious safety hazard. After glass has been worked in a flame to produce fabricated glassware at the Glass Lab., it is oven annealed to remove strain. The amount and type of strain left after a glass weld is made, depends on the wall thickness and shape of the article as well as the skill of the person doing the welding. Even though the immediate use of a piece of glassware does not involve heat, pressure, or toxic materials, it could become a "booby trap" for the next person using it who may not know its history.

Scientific glassblowers can and should be a source of safety knowledge to users of scientific glass apparatus. The fact that strained glass, either thermally or mechanically induced, looks the same as unstrained glass under ordinary light sets the stage for possible "booby traps." Every scientific glassblower has had the experience of having a piece of glassware brought into his shop which has had some unprofessional glassblowing work done on it. This work usually consists of some attempt to repair or alter the apparatus with a hand torch. Usually no consideration has been given to possible strains produced. The experienced chemist or engineer is well aware of what can be done in the fabrication of scientific glassware; the fact that glass can be shaped and welded in a flame. Whether the absence of annealing results from a lack of ability or a lack of knowledge on the part of the non-glassblower, frequently a total lack of appreciation of the weakening effect of uncontrolled strain is to be found.

Recognizing the existence of the problem, what can the professional glassblower do about it? At The Dow Chemical Company we put together a program. For the program we made up some test pieces, had colored slides made with polarized light, gathered some examples of amateur glassblowing, and worked out some demonstrations of the effects of strain on glassware.

After making an announcement that the program was available for group safety meetings, we were amazed and gratified at the response. During the past three years over forty plant groups consisting of over

1600 people have seen the program at Dow. After the initial announcement, the only publicity was word of mouth. In the course of these talks, the advantages of thermally tempered safety glasses, tempered glass shower doors, etc., are discussed so that even secretaries and other non-technical personnel present at some of the meetings have been interested. This kind of response indicates a very real need for this type of information by users of glass which you, as professional glassblowers, may take for granted.

Some interesting fallout has resulted from these meetings. At the Midland, Michigan location of Dow, gate-to-gate wearing of safety glasses is required. During the course of our discussions, many people inspected their safety glasses with our portable polariscope and we have discovered at least three individuals wearing glasses provided by the company that somehow had not been tempered by the manufacturer. In each case, these were prescription glasses. Since this discovery all prescription safety glasses are individually checked with a polariscope before issue by the Safety Department. We also looked at one pair of glasses that had been worn during a metal cutting operation with oxy-acetylene. Small bits of slag were embedded in the glass and concentric strain rings appeared around each bit. We recommended that safety glasses having scratches severe enough to catch a finger nail be replaced.

The first slide shows a piece of 38 mm. tubing with a 13 mm. side arm, no attempt was made to anneal this piece. One can see the strain

Slide 1

Slide 2

Slide 3

Slide 4

rings produced where the ends were fire polished and also the strain from welding the side arm. The next slide shows an identical piece which has been carefully flame annealed with a large bushy flame. The sharpness of the strain lines has been lessened and the amount of strain left is reduced. The third slide shows another identical piece which has been oven annealed and is essentially strain free. These pieces were purposely made this size to show glassware too large to do an effective job of flame annealing with a hand torch. It is important to stress the advantages of fire polishing and how it seals up the small cracks leading back from the end of a cracked-off tube. However the strain rings shown in the first slide serve to point out the need for good annealing after fire polishing.

The next two slides show a three-liter baffle flask after an attempt to

alter it by an inexperienced person. It is felt that someone decided to add hooks to the joints and probably attempted to do so with a hand torch. This flask is obviously too large to do any glass blowing on it with a hand torch, but let us assume this individual did get the hooks on and the flask did not break. Now he has produced a "booby trap" for himself or for a fellow worker who sometime later may use the flask with a hazardous material not knowing its history. We have been talking about the weakening effect of uncontrolled strain. It is possible to use strain to advantage to make glass stronger. The last slide shows a piece of one-inch tempered glass pipe. The glass has been heated to near its softening point and then quickly chilled, causing the surface to contract and become rigid while the interior mass is still hot and somewhat plastic. As the

Slide 5

glass continues to cool the surfaces are stressed in compression with the balancing tensile stresses in the interior. When glass fails or breaks, it always fails in tension and from a surface flaw. The force required to break thermally tempered glass must first exceed the compressive stress in the surface and then added to that, the tensile strength of the glass.

One can illustrate the strength of glass in compression and the weakness of glass in tension with the so-called "Prince Rupert Drop" and the "Baloney" tube. The former is made by heating the end of a piece of soda-lime glass and letting a drop of molten glass fall into a beaker of ice water. These drops are strong enough to be struck a good blow with a hammer without breakage. By scoring the tail of the drop and breaking it off, the whole drop shatters into a powder. It is a characteristic of tempered glass that the number of pieces resulting from fracture is proportional to the amount of compressive stress built into the glass surface, and that the pieces are somewhat cubical and are not sharp. This is a safety bonus of high tempered glass such as automobile windows, shower doors, etc. It not only takes a harder blow to break the glass, but when it does break, the pieces will not cut. The broken "Prince Rupert Drop" can be

Slide 6

rubbed between the fingers like sand or sugar. The "Baloney" tube is made by blowing a thick walled bulk about 2 inches in diameter on a piece of ¾-inch heavy-wall borosilicate tubing. While the bulb is red hot it is quenched by inserting in ice water. The outside surface of the bulb

is chilled and ends up highly stressed in compression, but the inside surface is not in contact with the cold water and ends up stressed in tension. It is possible to use a bulb like this to pound a nail into a board. The breakage of glass in tension at a surface flaw is dramatically illustrated by dropping a tiny carborundum crystal into the bulb. Glass broken under these conditions produces very sharp edges.

Mechanical stress due to misalignment in mounting a glass manifold can present a safety hazard even if proper annealing has been done. Glass tubing can be sprung when clamping but in so doing tensile stress is introduced at the outside of the bend and all that is needed is a surface flaw at that point and the glass is easily broken.This can be demonstrated by flexing a length of tubing while looking at it with polarized light. If the tubing is scratched and flexed so that the flaw is in compression, the tube is still quite strong. If it is flexed with the flaw in tension, the glass breaks quite easily.

Glass is basically a very strong material and when careful consideration is given to its properties, hardly deserves its reputation of fragility. When the use of the glassware is going to involve extremes of temperature or pressure, two factors become very important; its surface condition and its thermal history.

If you have experienced the problem of glassblowing being attempted by non-glassblowers in your company, you may want to use some of the ideas discussed here. Presented as a part of a safety meeting we have found that this program has been very well received and that specific knowledge of strain in glass is lacking on the part of most users of scientific glass apparatus. It should become an opportunity for the glassblower to enhance his prestige as a professional as well as make an important and meaningful contribution to the overall safety effort of his company.

CONSTRUCTION OF A THREE-STAGE MERCURY DIFFUSION PUMP

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The purpose of this paper is to show a means of constructing a glass three-stage Hg diffusion pump. It is not the only way of constructing such a pump, but *one* way.

From past experience I have found that no two glassblowers working side by side will work exactly the same. There is always present a competitive spirit to improve on, or to do it just a little differently than your colleague. I am sure that this is good, so again I say, this is one way to construct a three-stage Hg pump. I am sure that there are, in this audience, some who find other means of construction a little easier.

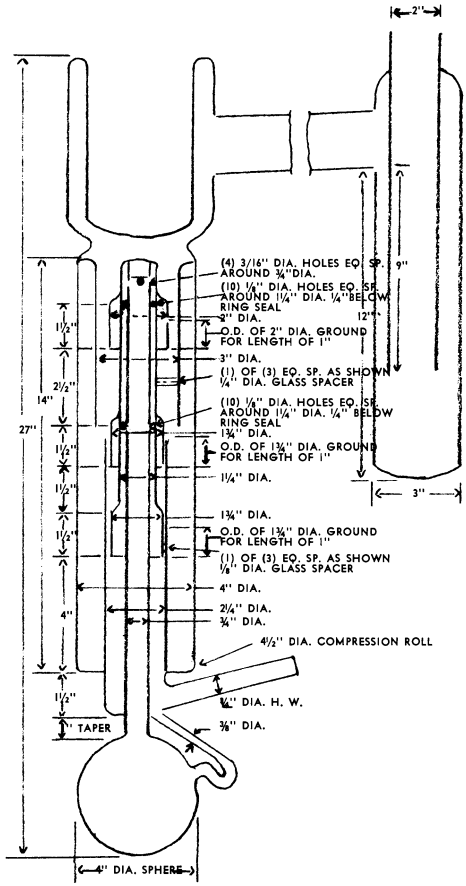

Figure 1

This figure shows all the glass that is necessary to build the three stage Hg pump.

Figure 2

This figure shows the glassblower rolling a slight flare on the 3/4" tube. This 3/4" tube is the tube through which the Hg vapors will rise from the boiler to the umbrella type jets.

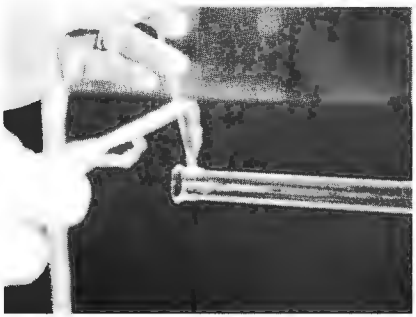

Figure 3

This figure shows the glassblower picking the holes in the 3/4" tube. These holes are approximately 1/4" diameter and placed around the circumference of the tube at 90° intervals. The Hg vapors rising from the Hg boiler will pass through these holes into the jet assembly.

Figure 4

The fourth figure shows the 3/4" tube with the flare and 1/4" holes. This tube is now complete.

Figure 5

This figure shows the part of the jet assembly consisting of the 1 1/4" tube sealed to the 1 3/4" tube. The glassblower is measuring the bump in the 1 1/4" tubing. This bump is made in the 1 1/4" tubing in preparation for the ring seal which will form the umbrella for one stage of the pump.

Figure 6

Glassblower making the 1/8" diameter holes in jet assembly. There are approximately 10 holes around the circumference of the 1 1/4" tube. Hg vapors will pass through these holes, strike the cooler surface of the umbrella, are deflected to the colder surface of the water jacket and are condensed to droplets of Hg to return to the Hg boiler.

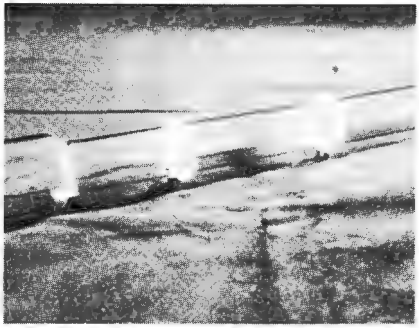

Figure 7

Inside part of the jet assembly with holes for jets, bumps for ring seals.

Figure 10

Glassblower making top umbrella ring seal. This forms the top stage of the pump.

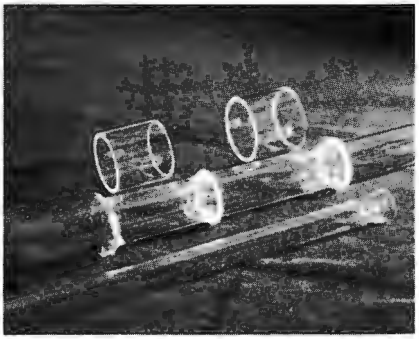

Figure 8

All the glass parts for the jet assembly—¾" supply tube, outside of jet assembly, umbrella parts for middle and top umbrellas.

Figure 11

Another figure showing the same procedure as the previous figure.

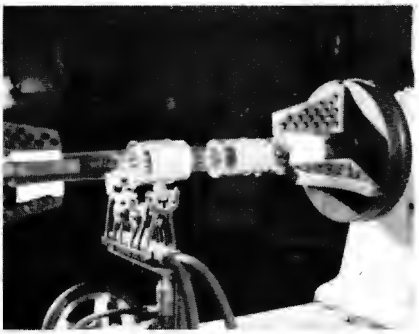

Figure 9

Jet assembly wrapped and ready for ring sealing.

Figure 12

Making the top ring seal between the ¾" supply tube and the outside of the jet assembly.

Figure 13

Completing the top ring seal with 1/4" rods sealed to outside of jet assembly. These rods will aid in supporting the jet assembly inside the water jacket and prevent excessive vibration of the jet assembly. Excessive vibration could snap the 3/4" bottom ring seal holding the jet.

Figure 16

Shows the flaring of the 2 1/2" tubing. This flare is the beginning of the bottom ring seal and the water jacket.

Figure 14

Shows the completed jet assembly.

Figure 17

Shows the inside water jacket.

Figure 15

Is the sealing of the 3" tubing to the 2 1/2" tubing, making up the inside of the water jacket.

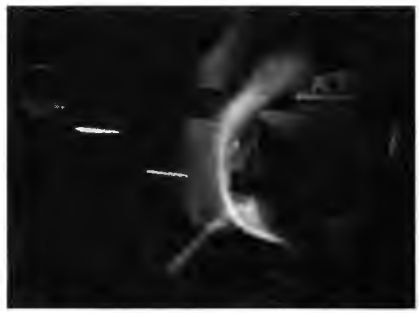

Figure 18

Is the 4" tubing being worked down in preparation for sealing the 2 1/2" tubing. This is the beginning of the outside water jacket.

Figure 19
Sealing the 2½" tubing to the 4" tubing.

Figure 22
Shows the completed outside of the water jacket.

Figure 20
Making the expansion ring in the 4" tubing.

Figure 23
Shows the outside and inside parts of the water jacket and the jet assembly.

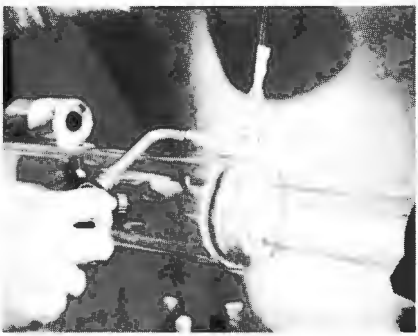

Figure 21
Sealing the water inlet tube to the water jacket.

Figure 24
Shows jet assembly wrapped and ready to be inserted into the inside part of the water jacket.

Figure 25

Jet assembly inserted in the inside part of the water jacket, the inside water jacket wrapped and ready to be inserted in the outside of the water jacket.

Figure 26

Assembly ready to be put in lathe for ring sealing of water jacket and Hg supply tube.

Figure 27

Making 2½" ring seal, completing bottom of water jacket.

Figure 28

The 2½" ring seal has progressed.

Figure 29

Starting to round off the 2½" tubing to ring seal the ¾"Hg supply tube.

Figure 30

Sealing the Hg boiler to bottom of pump. We use a 500 ml. bulb. It is more convenient and the heating mantle is used as a heater for the Hg. The heating mantle for the Hg boiler is connected up in series with a Variac, and the temperature is maintained at about 160°C. We have found that at this temperature maximum pumping speed is achieved with a minimum of back diffusion. The liquid nitrogen dewar on top of the pump should also eliminate or keep to a minimum back diffusion of Hg.

Figure 31
Sealing the ¾" tube to the section of 2½" tubing between ring seals. This is the tube connection to the mechanical pump.

Figure 32
Sealing on the Hg return tube.

Figure 33
Sealing of Hg return tube has progressed.

Figure 34
Completed bottom of pump. Note the loop in the Hg return tube. This loop forms a trap, so that when the Hg fills this trap it prevents the Hg vapors from entering the bottom part of the pump.

Figure 35
Pump is in machine and the top ring seal has been made, completing the water jacket. Remember at this point, that in setting up the job it is necessary to blow into both sections of the pump, that is the water jacket and the jet assembly.

Figure 36
Sealing on the top which had previously been made.

Figure 37
Sealing on water outlet tube.

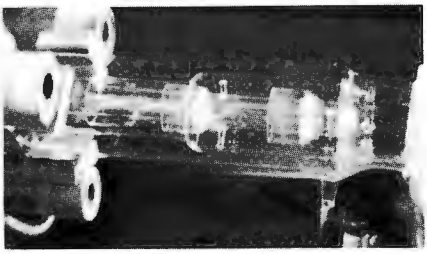

Figure 38
Flame annealing the top ring seal. After removing from the machine, the completed pump is set up and annealed in an oven. It should be set up with a vertical position, otherwise the weight of the jet assembly could cause the jet to sag a little out of center in the water jacket.

Figure 39
Pump is completed.

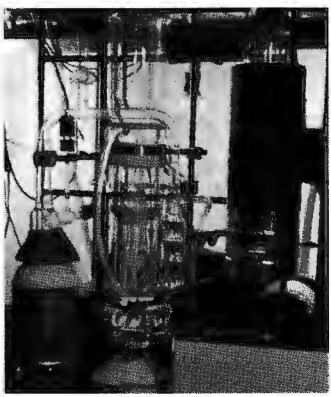

Figure 40
Pump installed in a vacuum station. We have a water condenser and a cold trap in the line going to the mechanical pump. On the high vacuum side we use a 3" O.D. cold trap; also the dewar on top of the pump prevents back diffusion of Hg into the 3" cold trap.

OPERATION

This pump gives excellent service on systems requiring absolute freedom from hydrocarbon contamination. Operated with a liquid nitrogen trap in the foreline and a liquid nitrogen trap on the high vacuum side, pressures of 10^{-12} Torr are attainable provided the system is completely bakeable to the top of the pump. Pressures of 10^{-12} Torr are obtainable using double liquid nitrogen traps on the high vacuum side (both of which are baked). These pressures have been obtained on well designed systems of the order of 1 - 5 liter volume in 24 hours. With care, pressures of 10^{-14} Torr have been obtained.

VITREOUS COATINGS

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INTRODUCTION

Generally in glass sealing, a relatively larger and more massive glass body has sealed to it, thin metal wires, fine metal parts, or small metal or ceramic pins or caps. In the case of vitreous coating, more frequently the reverse is the case.

Typically with vitreous coatings, the massive substrate consists of a heavy cast or molded metal part or metal sheet which is many times the thickness of the coating. It is the vitreous coating which is the minor member, ranging in thickness from a fraction of a thousandth of an inch to several thousandths. In some applications, as in decorating or marking, the thin vitreous coating may be fused to a solid glass substrate and special techniques are required.

In this paper, the fusing of vitreous coatings to metals, ceramics, and glass will be described. Characteristic problems arising from the differing properties of the vitreous coating and the substrate will be discussed as well as techniques for dealing with them.

Aside from the use of vitreous coatings for refrigerators, domestic appliances, sanitary ware and metal signs, an extensive use is also found in scientific and in industrial equipment. It is essentially to this use that this paper is directed. Applications to glass, ceramics, and metal substrates will be discussed.

VITREOUS COATINGS ON GLASS SUBSTRATES

Vitreous coatings for glass objects have been used mainly for labelling and trade marks on glass bottles and containers. More recently this use has been extended to include calibration and scale markings. An excellent example of the use of the vitreous coating to perform a multitude of functions is the tapered bore flowmeter tube illustrated in Fig. 1.

In the flowmeter tube the accuracy of flow measurement depends not only upon the bore size, which is precision controlled during the glass reforming operation, but also upon the accuracy with which the decal scale has been reproduced. Additional functions performed by the decal on this tube are trade mark display, identifications numbers, and even illuminator to facilitate reading of scales using reflected light only.

In Fig. 2 are illustrated decal scales on paper backing. The scales are made by photographic reproductions from master drawings. The filmed pattern is then actinically printed on a sensitized silk screen which is fixed and mounted in a printing frame. Using a rubber squeegee to wipe the "paint" across the screen and also the backing, the process here resembles poster printing, except for the paper that is used to receive the "paint", and the composition of the "paint" itself.

The paper backing is a higher quality stabilized type and extremes of temperature and humidity have to be guarded against to avoid dimensional changes in the paper since this would affect the accuracy of the scales. To permit the ready transfer of the painted material to the glass object to be marked, a thin gelatine coating is applied to the paper be-

Figure 1
F & P flowmeters with decal scales and reflectors.

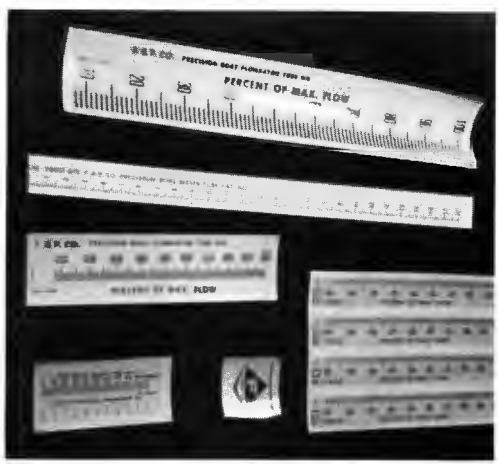

Figure 2
Decals on paper backing.

fore silk screening. The silk screening then actually takes place on the thin gelatine film which is on top of the paper backing. Of course, temperature and humidity precautions are especially necessary here because of the extreme thermal expansitivity and hygroscopicity responses of gelatine.

For "paint" a conglomerate of powdered glass frit, vehicle, solvent, opacifier, coloring stains, drying agents and others are intimately milled. In this operation it is important to secure small particle size and homogeneity of mix or lack of color uniformity and improper fusing will take place after firing.

The completed decal is then seen to be essentially as powdered glass composition printed on a gelatine coated paper backing. To transfer the decal to the glass, the paper decal is immersed in a water bath until the gelatine is softened. Then the thin gelatine film with the printed scale is slid onto the glass surface and positioned over a diamond scribed reference line. The gelatine film is then hand pressed to the tube to remove air pockets that might blow up during firing. After complete drying, the glass ware and applied decals are placed in an oven for firing.

Insofar as the firing temperature of the glass frit must be below the temperature at which the glass tube will distort, special low melting, and eutectic glass compositions are used for the frit. Insofar as reducing conditions cannot be tolerated, vapors and gaseous combustion products, during firing, must be removed by adequate ventilating provisions. Bleached and chalky decals are evidence of inadequate furnace ventilation.

Due to the extremely small thickness of the decal (about .001") the matching of expansion coefficients is not very critical. However, too extreme a difference in expansivity between decal and glass substrate will result in crazed decals. Good decals that have been properly fired show bright color, are glossy and have good adherence.

The chemical corrosion resistance of a decal is generally not as good as that of the glass substrate. This is a consequence of the necessary low fusing temperature that is required in a decal. This condition constrains the composition of the glass frit to one of low silica and relatively high flux content, and hence lessens corrosion resistance.

However, in actual use, the decal is generally on the outside of the vessel and not in contact with corrosive chemicals. Commercially available decals have retained color, brightness, and gloss after years of service in very severe environments.

This vitreous powdered glass frit, vehicle, and solvent are also used to seal or cement glass parts. These coatings can also be applied by brushing, printing or even with coated tapes.

VITREOUS COATINGS ON CERAMIC SUBSTRATES

Ceramic electric substrates, laboratory ware, industrial fittings (Fig. 3) and thermocouple tubes are frequently given a vitreous coating to provide moisture and corrosion resistance, and gas impermeability.

In the case of the ceramic substrate, a more favorable situation exists

Figure 3
F & P vitreous lined ceramic fittings.

with respect to latitude of composition of the vitreous coating. This derives from the difference in structure between ceramics and glass bodies. The ceramic object, which is to be vitreous coated, is usually either 100% crystalline or mostly crystalline, with a minor amount of glossy phase. Compositionwise, it consists mainly of high refractory oxides. Consequently it does not have the extended low temperature softening range which is characteristic of glass and which limits the maximum firing temperature to the annealing range.

This permits the use of vitreous coating composition having higher fusing temperatures and better resistance to chemical corrosion. Since the vitreous coating applies to ceramic substrates may be fairly thick (.002" to .012"), a close match in thermal expansivity is required. Fortunately the latitude in composition permits a latitude in thermal expansitivity of available glass frits for ceramic substrates.

Although ceramics do shrink a small amount on firing, they can be fired to very high temperatures without slumping. Since the shrinkage is symmetrical it can be compensated for in fabrication. Also, if the ceramic has been fired before the application of the vitreous coating, the firing of the vitreous coating will produce negligible shrinkage.

When vitreous coatings are applied to ceramic bodies, an aqueous medium is used instead of the oil or plastic vehicle and solvent combinations used for decals or tapes. The vitreous coating is applied as a thin aqueous slurry known as a slip, consisting of about 90% powdered frit and the rest kaolin, clays, coloring stains, and electrolyte. The purpose of the additives is to impart good flow and uniform coating characteristics to the slip.

The ceramic body may be coated with slip by dipping, spraying or brushing. It is permitted to dry and then put in an oven for firing. This

operation is not as critical as with glass substrate since a wider temperature range is possible. Care must be taken in cooling that cracking due to thermal shock does not occur, especially for thicker objects. For high production, the firing may be done in continuous lehrs.

Since a wide latitude of composition is available, even hard borosilicate glass may be used as the frit for the vitreous coating of low expansion ceramic ware. Internal coated ware, as in Fig. 3 may be used with highly corrosive liquids.

VITREOUS COATING ON METAL SUBSTRATE

With metal substrate a vitreous coating ranging in thickness from .003″ to .030″ may be used. This requires a good match in relative thermal expansivities between the coating and the metal. Insofar as glass is stronger under compressive strain than tensile strain, the expansivities of the metal should be a little higher than that of the glass frit to avoid tensile strains during cooling.

Before any coating is applied, the metal must be thoroughly cleaned. This operation may vary from just a baking and sandblasting to a complete and highly controlled chemical cleaning with washing, pickling, neutralizing, nickel coating and other specialized techniques.

The slip is chosen for compatability with the metal and for the required function of the finished part. This might be corrosion resistance, oxidation resistance, insulation protection, low coefficient of friction, or a host of other properties that a vitreous surface can impart. Application of the coating is done by spraying, dipping, brushing or slushing.

Upon drying, the ware is put in an oven and fired at a temperature determined by the properties of the particular metal used. Such metals could include cast iron, low carbon steel, inconel, hastelloy, titanium,

Figure 4
F & P vitreous lined cast iron fittings.

stainless steel, etc. In Fig. 4, a vitreous lined cast iron fitting for a flowmeter is illustrated. Figs. 5 and 6 show an F & P Magmeter with stainless steel, inconel, and platinum electrode parts coated with the vitreous lining.

In the dry process powdered glass frit is scattered on the red hot metal part which has been removed from the oven. The glass grains which are kept fairly coarse, adhere to the hot surface and then the unit is returned to the hot oven for firing. In both the wet and dry processes greater thickness can be built up by multiple coatings.

Figure 5
F & P vitreous lined magmeter spool.

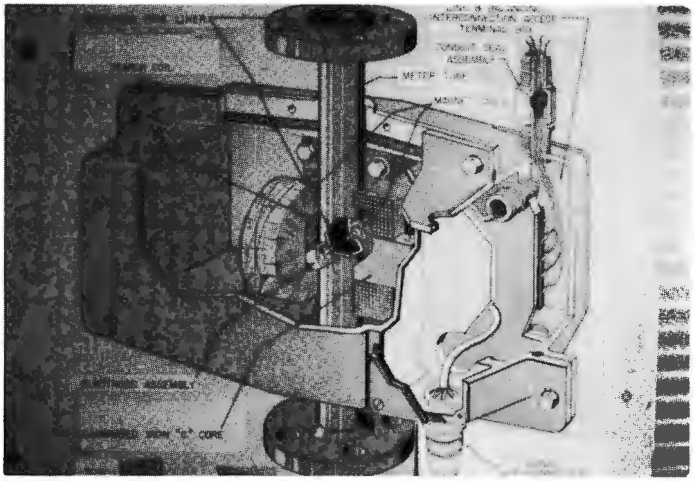

Figure 6
Magmeter cut-away.

Good corrosion resistance can be obtained with vitreous linings used for coating metal. However, the vitreous lining, because it is essentially glass, has a similar type of limitation as far as resistance to hydrofluoric acid, hot alkalies, and high pressure steam is concerned. Vitreous lined metal fittings and magnetic flowmeters give years of service under typical industrial corrosion flow conditions. A worn vitreous lined body can then be salvaged by recoating.

SUMMARY

Glass ranks as a very stable and corrosion resistant material. Techniques for applying and firing thin vitreous coatings on glass, ceramic and metal objects have been discussed. The use of such coatings for lettering, scales, sealing and protective coats against corrosion oxidant and electrical leakage, has been described.

SENSITIZED FLUORESCENCE IN ALKALI VAPORS

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ABSTRACT

Collisional transfer of excitation between the two resonance states of alkali metal atoms can be easily detected using techniques of sensitized fluorescence. The standard method is to optically excite an alkali atom to one resonance state and then detect the fluorescence of the other state that has been sensitized by collisions with foreign-gas atoms or other alkali atoms in the containing vessel. A straight forward interpretation of the results of such experiments is possible only if the fluorescence photons are not trapped in the alkali vapor. Trapping can be avoided by keeping the alkali densities below about 10^{11} atoms per cm^3 but this severely reduces the intensity of the atomic fluorescence and makes detection difficult. Specialized glass containers have, however, been developed which eliminate the trapping problem but maintain high fluorescent intensity levels.

INTRODUCTION

There has been a remarkable renewal of interest in atomic collision phenomena in the last few years and the main reason for this is not hard to find. Technological developments—the laser being a well-known example—have required knowledge of atomic collision cross sections and several laboratories, including our own, have been trying to provide the necessary information.

The kinematics of atomic collisions can be easily described in classical physics but within this framework no mention is made of the detailed nature of the collision process. When we try to elaborate on this point we are immediately faced with the problem of how close two atoms must approach to produce a collision. For classical particles the answer to this question is obvious—the colliding particles must touch one another. However, the electron cloud surrounding an atom does not have a definite boundary, and there is a small probability of the atomic electrons being located far from the atom. Consequently the electron clouds of atoms can "touch" even though the atomic nuclei are far apart. We therefore define a cross section for atomic collisions which can be larger than expected on the basis that atoms behave as rigid spheres of radius equal to the atomic radius which is on the order of 10^{-8} cm. for most atoms.

The effective cross-sectional area for an atom is the area that the atom appears to have on the basis of applying classical theory to experimental measurements of the number of collisions. We would not expect that an atom would interact in exactly the same manner with an electron as it would with another atom; nor would the interaction with one atom be

the same as with other atoms. Consequently the effective cross section of an atom will depend on the relative velocity V of the colliding atoms and if two different species are involved in the collision the effective cross section Q can be obtained from the equation

$$Z \text{ (experimental number of collisions)} = n_1 n_2 V Q$$

where n_1 and n_2 are the concentrations of the two species.

Inelastic collisions between atoms, where the total energy is conserved but some kinetic energy is converted into internal energy of one of the particles, has long been of interest to physicists. Atoms may be electronically excited by the direct absorption of light but it is also possible to electronically excite an atom utilizing the energy of another excited atom in an inelastic collision. This process is known as energy transfer and often occurs with an extremely large cross section. In other words excitation energy may be collisionally transferred from one atom to another even when the two atoms are very far apart. In the following sections we shall discuss a type of experiment that has provided some of the background for the modern idea of energy transfer, giving special attention to recent innovations in apparatus and experimental technique.

SENSITIZED FLUORESCENCE

Consider a gas consisting of two different kinds of atoms and assume that we know the complete absorption and emission spectra of the two components of the mixture. The mixture is now irradiated with light that can only be absorbed by one of the components. In certain cases the resulting fluorescence contains lines from the atoms that did not absorb light in the first place. This type of fluorescence is called sensitized fluorescence. It is not caused by direct optical excitation but rather by a collision process that involves the participation of other excited species. The observation of sensitized fluorescence provides direct confirmation of the concept of energy transfer during collisions, and it also provides an experimental tool that can be used to obtain precise details of collisional and energy transfer processes.

Sensitized fluorescence is not restricted exclusively to multicomponent gases. It can also be observed in single component systems as the result of transitions which normally are not permitted but which can be caused to occur during collisions. These collisionally induced transitions can be detected in alkali vapors and there has been a long history of such measurements.[1] The alkalis readily lend themselves to experimental studies of collision induced energy transfer as the excited levels involved are close to one another and well removed from other levels which might perturb the process. We shall use sodium as the vehicle for discussing sensitized fluorescence in alkali vapors.

The two lowest levels of the sodium atom are depicted in Fig. 1. Atoms in each of the excited levels $3^2P_{3/2}$ and $3^2P_{1/2}$ can undergo transitions to the $3^2S_{1/2}$ ground level giving rise to the familiar sodium D-lines. In the diagram the $3^2P_{1/2}$ level is shown being selectively excited by absorption of D_1 radiation. The excited state will persist for a very short time called the mean lifetime which is on the order of 10^{-8} seconds for the alkali atoms. If during this short period the excited atom collides with a

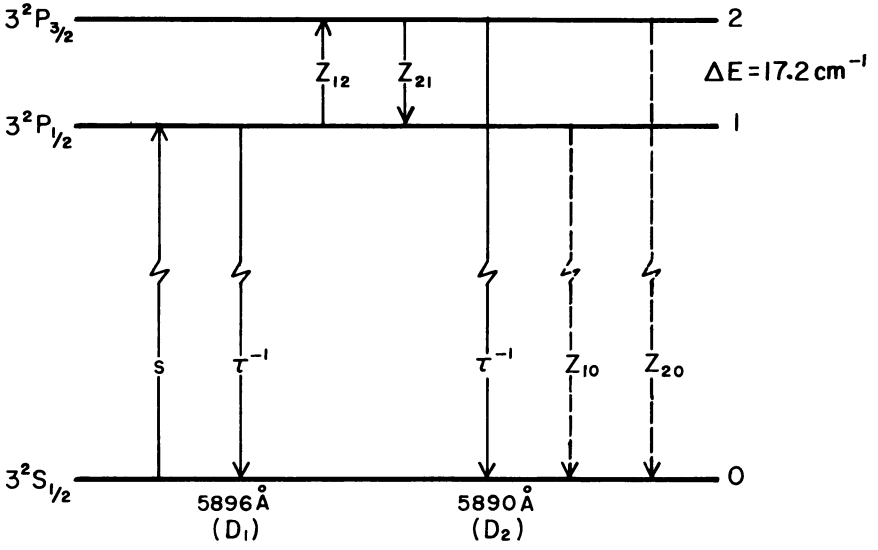

Figure 1

The lowest excited levels of the sodium atom showing the origin of sensitized fluorescence in sodium vapor. Solid arrows indicate transitions giving rise to sensitized fluorescence and the broken arrows represent quenching transitions. T is the mean lifetime of the excited levels.

foreign-gas atom or another sodium atom in the containing vessel, one of two things may happen. First, the excitation may be collisionally transferred to the $3^2P_{3/2}$ level with the subsequent emission of the sodium D^2 line. In this case, fluorescence is sensitized by the collision through a radiationless transfer of energy between the excited levels. Thus the following reaction may occur during a collision between an excited sodium atom Na* and a perturbing atom A:

$$\mathrm{Na}^*(3^2P_{3/2}) + A \rightleftarrows \mathrm{Na}^*(3^2P_{1/2}) + A + \Delta E,$$

where ΔE, the energy difference between the two excited levels, is supplied or carried away by the kinetic energy of relative motion of the colliding partners. The second possibility is that the sodium atom will be completely deexcited by the collision. This process, called quenching, can be represented by the following relation:

$$\mathrm{Na}^*(3^2P_{3/2,1/2}) + A \rightarrow \mathrm{Na}(3^2S_{1/2}) + A + \Delta E',$$

where the energy released, $\Delta E'$, is equal to the excitation energy of Na*. If neither of the above effective collisions occur, the excited sodium atom will optically decay emitting the absorbed D_l radiation. It should be noted that the transition $3^2P_{3/2} \rightarrow 3^2P_{1/2}$ is quantum mechanically forbidden so that radiative transmissions between these two levels cannot occur with high probability. If the D_2 radiation is observed, it must be the result of an energy transfer collision. To detect these collisions we require an experiment in which only one of the sodium levels is excited in order to observe whether one or both of the sodium D-lines appear in the emission spectrum.

Figure 2 shows the required experimental arrangement. Light from a sodium lamp is passed through a grating monochromator and the dispersed light is made to fall on a narrow slit. The dispersion is such that only one of the D-lines can pass through the slit. The monochromatic beam is then focussed into a vessel containing sodium vapor at a known temperature and pressure. The light is absorbed and a few sodium atoms are raised to an excited state. Fuorescent light from the vapor that is emitted 90° to the incident beam is then analyzed for the D_1 and D_2 lines by a pair of narrow band interference filters and focussed on the cathode of a photomultiplier. The photocurrent is either registered with a high-speed picoammeter and a strip-chart recorder or pulses in the anode circuit of the photomultiplier are counted using electron-pulse-counting techniques. A vacuum and gas handling system must also be provided to evacuate the containing vessel to at least 10^{-7} Torr and to admit to it controlled quantities of foreign gases as required.

If energy transfer collisions do occur in the sodium vapor the intensity of the sensitized fluorescence will usually be very weak, often as low as 10^{-17} watts which corresponds to about 40 photons per second incident on the photomultiplier. Counting rates of 2 counts per second and anode dc currents of 10^{-13} amps are not uncommon. In order to detect such small signals it is essential that the photomultiplier be cooled to liquid nitrogen temperatures so that the tube's internal noise will be reduced. It is also necessary to employ specially developed radio-frequency light sources[2] to ensure a high density of excited atoms. Even with these devices detection of the sensitized fluorescence is usually difficult. The fluorescent intensity can be substantially increased simply by increasing the concentration of sodium atoms in the containing vessel. However, at high concentrations the fluorescent photons are absorbed and reemitted many times

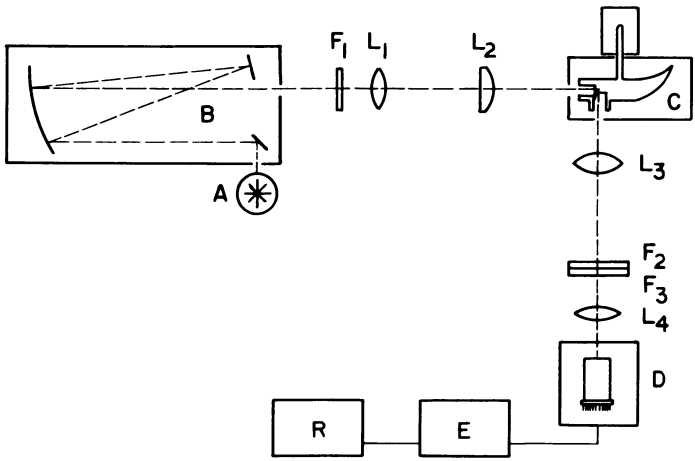

Figure 2

Apparatus used in the studies of sensitized fluorescence: A, Rf lamp; B, monochromator; F_1, F_2, F_3, interference filters; L_1 - L_4, lenses; C, vessel containing alkali atoms; D, photomultiplier; E, picoammeter; R, recorder.

before they leave the vessel and are detected. The primary result of this "photon trapping" is an increase beyond the mean lifetime of the time available for a collision and an apparent increase in the energy transfer cross section. To avoid this effect the alkali concentration must be kept well below 10^{11} atoms per cm^3. Forced to work with such low concentrations we must have a containing vessel which makes maximum use of the absorbing power of the alkali vapor.

When a beam of *D*-line radiation enters a vessel containing alkali vapor, most of the absorption originates at the point of entry. The maximum fluorescent intensity is therefore obtained by observing the fluorescing vapor as close as possible to the entrance window. An observation point one centimeter away from the entrance window receives only 20% to 30% of the available fluorescence, whereas at a distance of a millimeter or less, almost 90% of the available fluorescence is observed. The optimum design of the containing vessel is therefore one in which the entrance and exit windows are joined at a right angle so that observation of the fluorescing alkali vapor may take place as close as possible to the entrance window. Such a vessel has been constructed and is shown in

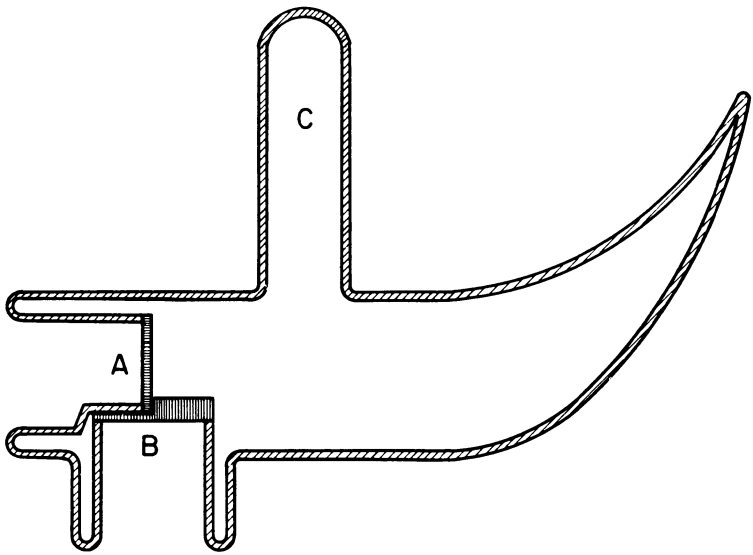

Figure 3

A fluorescence containing vessel that meets the optimum design characteristics specified in the text. The exciting radiation enters at A and sensitized fluorescence is observed at B. The side arm C contains the alkali metal.

Fig. 3. The side-arm (*C*) contains the liquid alkali metal and its temperature determines the alkali concentration in the main body of the vessel. A somewhat different vessel has been developed for use in experiments employing magnetic fields where three mutually perpendicular axes are of interest, namely, the incident direction and the directions that are parallel and perpendicular to the magnetic field. This design, shown in

Fig. 4, incorporates three windows joined at right angles to one another. In both vessels the exciting radiation is focussed to form an image of the monochromator slit in the corner between the windows as shown in Fig. 5. In this way the maximum fluorescent intensity is observed and "photon trapping" is avoided.

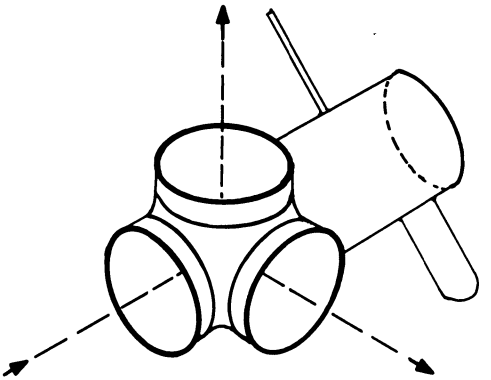

Figure 4
A vessel used in magnetic fields that has three mutually perpendicular windows. The arrows indicate the directions of excitation and of observation.

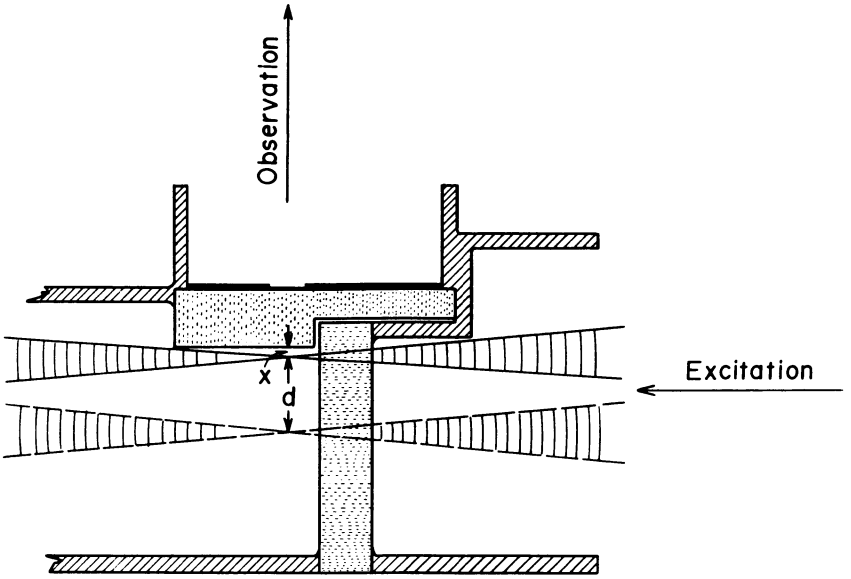

Figure 5
The window section of the alkali containing vessel. d represents the distance available for lateral movement of the image of the monochromator slit (1.0 cm.) and x is the minimum distance between the slit image and the exit window (0.05 mm.).

ENERGY TRANSFER CROSS SECTIONS

The cross section for energy transfer between the first excited levels of the alkali atoms can be obtained from measurements of the relative intensities of the two *D*-lines present in the fluorescent light. Sensitized fluorescence experiments such as that described above have recently been completed for all the alkalis[3] and a few of the measured energy transfer cross sections are given in Table I. The effective cross sections for the

TABLE I

CROSS SECTIONS FOR $^2P_{3/2} \rightarrow {}^2P_{1/2}$ ENERGY TRANSFER INDUCED BY COLLISIONS BETWEEN ALKALI ATOMS

Collision Partners	*Cross Section* (cm^2)	ΔE (cm^{-1})
Na* - Na	28×10^{-15}	17
K* - K	25×10^{-15}	58
Rb* - Rb	7×10^{-15}	238
Cs* - Cs	37×10^{-15}	554

collision induced $^2P_{3/2} \rightarrow {}^2P_{1/2}$ process are equal to or larger than the kinetic cross sections, illustrating the extremely efficient nature of the long-range energy transfer process. It is also apparent that the effective cross sections decrease as ΔE increases. Quantum mechanics predicts that the maximum interaction between two atoms occurs when their excited levels are at the same energy. Since the energy transfer cross section depends on the strength of the interaction during a collision, the observed inverse dependence of ΔE is to be expected on theoretical grounds.

The effect of ΔE on the effective cross section is even more striking when inert gas atoms are used to induce energy transfer in the alkalis. Table II contains the effective energy transfer cross sections that have been measured as the result of alkali-helium collisions. The cross sections

TABLE II

CROSS SECTION FOR $^2P_{3/2} \rightarrow {}^2P_{1/2}$ ENERGY TRANSFER INDUCED BY ALKALI-HELIUM COLLISIONS

Collision Partners	*Cross Section* (cm^2)	ΔE (cm^{-1})
Na* - He	5×10^{-15}	17
K* - He	4×10^{-15}	58
Rb* - He	1×10^{-17}	238
Cs* - He	4×10^{-20}	554

are much less than the kinetic values indicating that many classical collisions must occur before energy is transferred within the alkali atom. As was noted above, the induced transition $^2P_{3/2} \rightarrow {}^2P_{1/2}$ was most efficient when the two levels were of the same energy. The results in Table II point out still another reason why the energy transfer efficiency is sensitive to the energy gap ΔE; the highest probability of electronic energy transfer occurs when the least amount of kinetic energy is created during the process.

CONCLUSIONS

It appears possible to make reasonably accurate experimental determinations of the various energy transfer cross sections using the technique of sensitized fluorescence. It is also possible to understand, at least qualitatively, the collisional interaction mechanism. There are, of course, many questions left to be answered. We are actively purusing this line of research in the hope of obtaining at least a vigorous if not a rigorous understanding of the energy transfer process.

ACKNOWLDGMENTS

I would like to acknowledge the expertise of Master Glassblower Wolfgang Eberhart who designed and constructed the fluorescence vessels which played such an important role in this research.

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EXAMINATION OF GLASS AND CERAMIC MATERIALS WITH THE SCANNING ELECTRON MICROSCOPE

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ABSTRACT

Utilizing the combined advantages of high resolution, large depth of focus, and minimum specimen preparation, the scanning electron microscope (SEM) can be used to great advantage in the delineation of microstructures of glass and ceramic materials. The principles and operation of the SEM and its application to glass and ceramic materials are described. Typical applications are studies of surface finishes of glass, fracture morphology of glass and ceramics, characterization of particulate matter, phase separation in glasses, chemical compositional differences, and devitrification of glasses.

INTRODUCTION

The first application of secondary emission phenomena to microscopy was made in 1935 by Knoll,[1] who recorded the emitted current as a function of position on a specimen. In 1938 von Ardenne[2] constructed the first true scanning microscope with electromagnetic lenses. Zworykin *et al.*[3] employed a facsimile recorder synchronized with the secondary emission electrons from a very fine probe. A resolution of 500 Å was attained, but only after long exposures and great difficulty in focusing. Following World War II, Leauté in France built a scanning microscope on which Brachet[4] and Davoine[5] made notable contributions. By far the greatest impetus to the development of scanning electron microscopy has been the activities of the Engineering Laboratory of Cambridge University, where work was initiated in 1948 under Professor Oatley. McMullan[6] incorporated new features such as a relatively noise-free system for collection and amplification, separate display channels for visual and photographic recording, double deflection of the electron probe, and the use of a high-energy electron current for the enhancement of contrast. The resolution achieved was approximately 250 Å. This fundamental construction, coupled with other improvements emanating from Professor Oatley's group, led to the production of the first commercial SEM in 1965. Additional information on the development and operation of the SEM may be found in articles by Smith,[7] and Oatley *et al.*[8] as well as in a book by Thornton.[9]

GENERAL DESCRIPTION AND OPERATION

Figure 1 shows the overall view of the operating console and electron optical column of the Stereoscan SEM which was used in the present

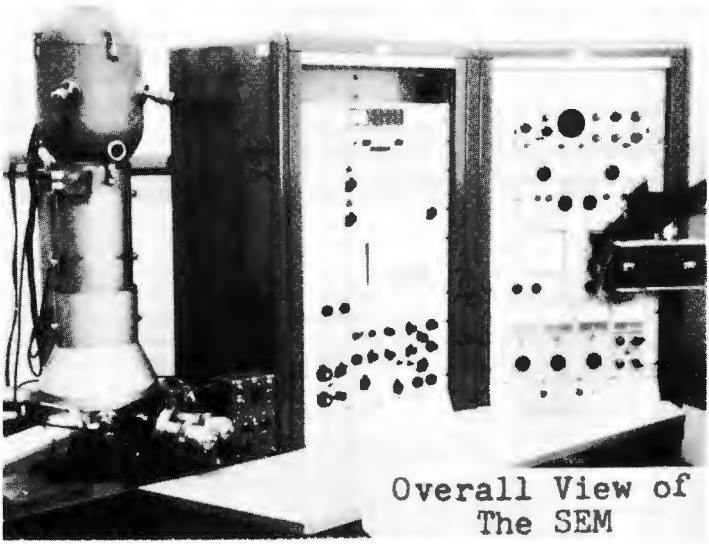

Figure 1
Overall view of the Stereoscan Scanning Microscope showing the electron optical column (left) and operating consoles (center and right).

study. Not shown are additional power supply components, line voltage regulator and variacs placed some distance from the electron optical column to eliminate any field interferences to the SEM. This particular instrument is equipped with two visual and one photographic cathode ray tube (CRT) channels.

Figure 2 is a schematic diagram of the SEM. A beam of electrons is generated by a hairpin tungsten filament in the electron gun. The beam is directed down the column and is demagnified to a spot size of approximately 100 Å at the specimen by three electromagnetic lenses, two condenser and one objective. Secondary electrons and back-scattered primary electrons are generated when the beam strikes the specimen. A collector consisting of a phosphor-tipped scintillator in a Faraday cage attracts and detects the low-energy secondary electrons but not the high-energy primary reflected electrons that are produced at the specimen surface. The light generated at the scintillator tip passes through a light pipe and through a photomultiplier tube. The signal is then amplified and transmitted to a CRT which scans in synchronism with the electron beam as it traverses the specimen.

Three modes of operation are possible with the SEM. The emissive mode utilizes the secondary electrons to form the image and is used to discern surface topography and chemical composition differences. Detecting and analyzing the current generated by the electron beam when it strikes the sample defines the conductive mode which is invaluable in the study of conducting and semiconducting phases. Luminescent and phosphorescent phases may be detected by the cathodoluminescent mode whereby the light produced by the electron beam is recorded by the SEM.

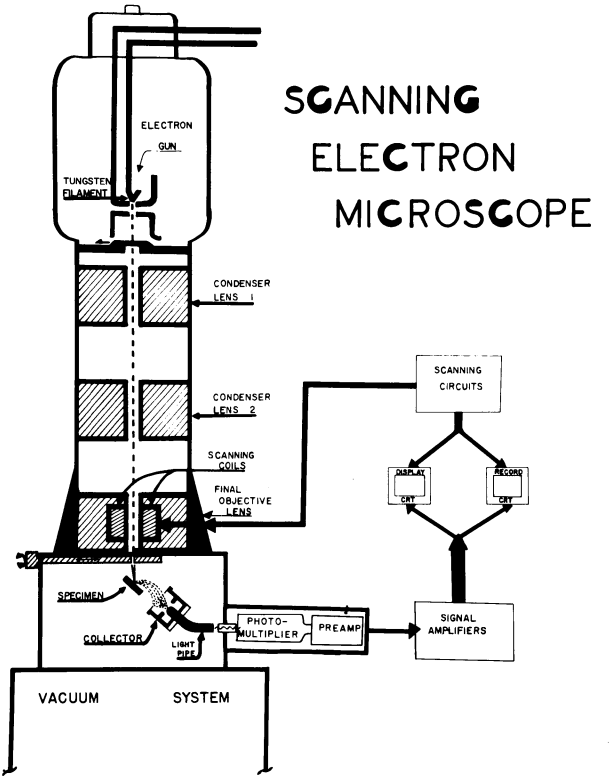

Figure 2
Schematic diagram of the Scanning Electron Microscope.

To place the SEM in its proper perspective, its advantages and disadvantages may be compared to those of other microscopy techniques. A comparison of optical, scanning electron and transmission electron microscopy (TEM) is given in Table I. One of the main features for comparison is the limit of resolution. The practical limit of resolution on commercial instruments is approximately 2000 Å for the light microscope, 200 Å for the SEM, and 2 Å for the TEM. Therefore, resolution of the SEM is one order of magnitude greater than the optical microscope but is two orders of magnitude less than the TEM. Comparison of the depth of focus shows that the SEM is about 500 times better than the optical microscope. A distinct advantage of the SEM over the TEM is the ability to examine surfaces of material directly. In TEM, extremely thin specimens ($<$1000 Å) must be prepared or replicas made before materials can be studied. Thus, the resolution of the SEM, coupled with its great depth of focus and minimum amount of specimen preparation, gives the SEM a prominent place in the field of microscopy.

Photomicrographs of a glaze-ceramic interface comparing optical microscopy, SEM and TEM are shown in Figure 3. Resolution of the

TABLE I

COMPARISON OF OPTICAL, SCANNING AND TRANSMISSION ELECTRON MICROSCOPY

Comparison Factors	*Optical Microscopy*	*Scanning Electron Microscopy*	*Transmission Electron Microscopy*
Magnification Range	1 to 1200X	50 to 50,000X	500 to 250,000X
Resolution Possible	2000 Å	200 Å	2 to 50 Å
Type of Observation	Direct	Direct	Mainly Replica, Direct Difficult
Sample Preparation Time	Minutes to Hours	Minutes	Hours to Days
Electrical Potential Differences	No	Yes	No
Depth of Focus	1	500	—

SEM (lower left) is much better than the optical microscope (upper left). However, the TEM (upper right) has much better resolution and shows crisper detail than the SEM (lower right).

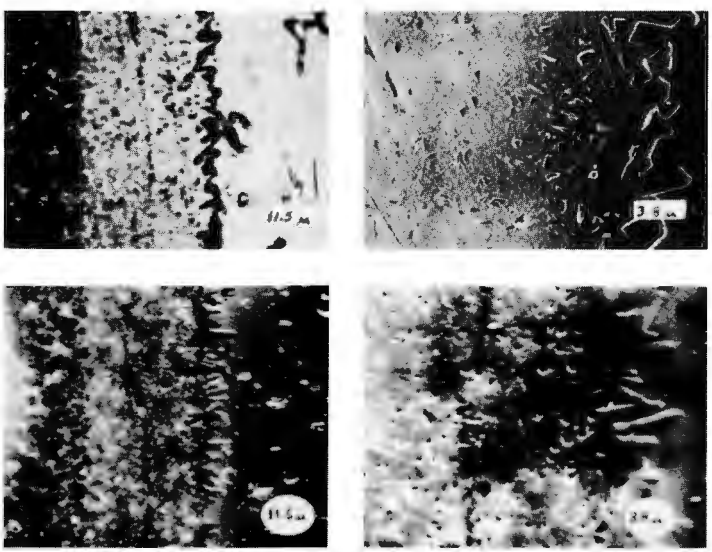

Figure 3

Comparison of resolution of the light microscope (upper left) with SEM (lower left). Also comparison of transmission electron microscope (upper right) with SEM (lower right). Note the resolution of the crystals growing from the ceramic (left of each picture) and glaze (right of each picture).

EXPERIMENTAL TECHNIQUES

For SEM examination, specimens which are nonconductors must be covered with a vacuum-deposited layer of conducting material, approximately 300 Å thick. This thin coating permits a drainage of the electrons from the specimen, thus preventing a surface charge buildup that would affect contrast when the primary electron beam strikes the surface. An evaporated film is chosen on the basis of high electrical conductivity and good secondary-electron characteristics. Aluminum satisfies these essential requirements and, in addition, is easily evaporated at a relatively low temperature. Other conductors such as gold, platinum, palladium, and carbon may be employed. Specimens which are electrical conductors, such as metals, naturally do not require special surface treatment. The ease with which samples can be prepared for SEM examination is one of its main virtues.

APPLICATIONS

The SEM is useful in examining a wide variety of materials and devices. In this respect the SEM is comparable to the light microscope and much more universal than the TEM. In Table II are listed some of

TABLE II

APPLICATIONS OF SCANNING ELECTRON MICROSCOPY

1. Physical Topography of Surfaces
2. Fractures, Cracks and Crazes
3. Particulate Matter
4. Composition Variations in Materials
5. Potential Gradients
6. Semiconductor and Integrated Circuit Analysis
7. Photoconductive Mapping
8. Cathodoluminescence
9. Stereoscopy

the applications of the SEM. To indicate the marked versatility of the instrument, a variety of samples investigated in our laboratory will be presented. A previous article [10] on the application of the SEM for the characterization of ceramic materials describes other applications.

The SEM is an ideal instrument for studying the finishes resulting from abrasive grinding and polishing of glass. Figure 4 shows the surface finish of a glass that was subjected to successive polishes of 60 micron (μ) silicon carbide (left), 6μ diamond paste (center), and 1μ diamond paste (right). Another example of the effectiveness of the SEM to delineate surface topography is given in Figure 5, which shows the microstructure of a glass (left) bonded to a metal (right). In this case an oxide layer (black arrow) defines the boundary between the etched crystal

pattern of the metal and the smooth surface topography of the glass. The SEM also resolves the scratches and highly disturbed surface of the metal.

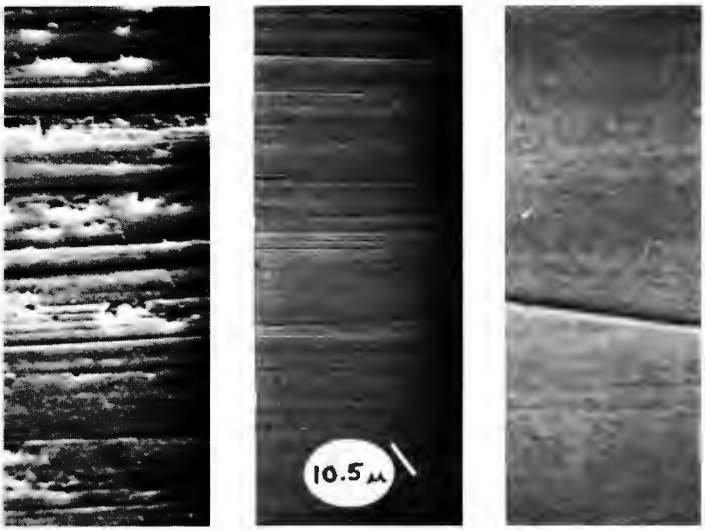

Figure 4
Polished glass surfaces using 60μ silicon carbide (left), 6μ diamond (center), and 1μ diamond (right).[10]

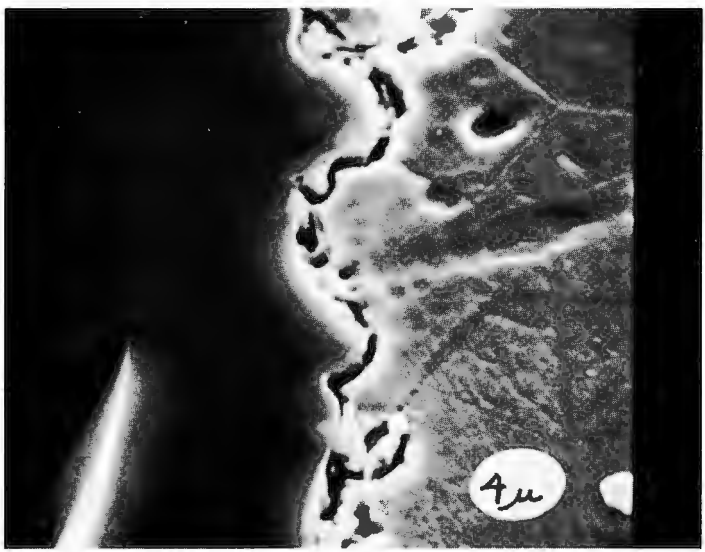

Figure 5
Oxide layer (arrow) formed by a bond of glass (left) and metal (right).

Figure 6
Typical break source pattern of a soda-lime glass rod broken in tension.

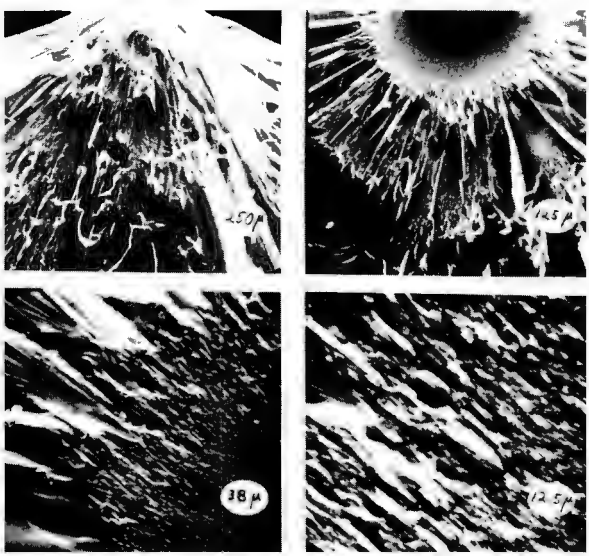

Figure 7
Higher magnification micrographs of regions of fracture from Fig. 6.

The SEM provides an excellent tool for the examination of fractured surfaces. A typical fracture pattern of a 6-mm. soda-lime glass rod, broken by tension, is shown in Figure 6. Successively increasing magnifications

of the various areas of a representative break source are shown in Figure 7. SEM micrographs of mirror radii of varying sizes from a series of break sources are shown in Figure 8.

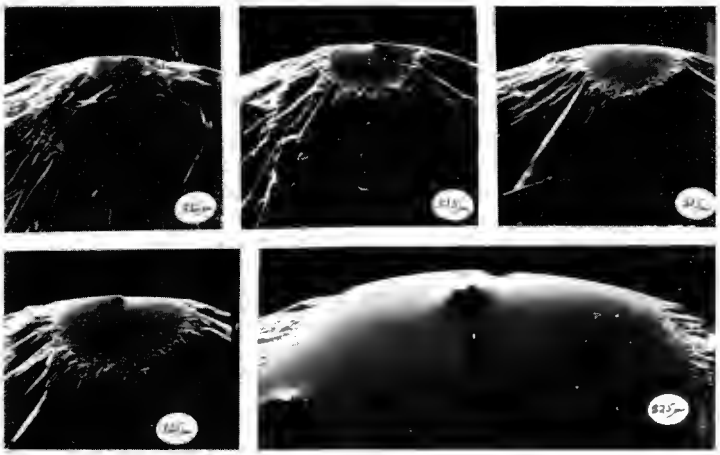

Figure 8
SEM micrographs of mirror regions of various sizes.

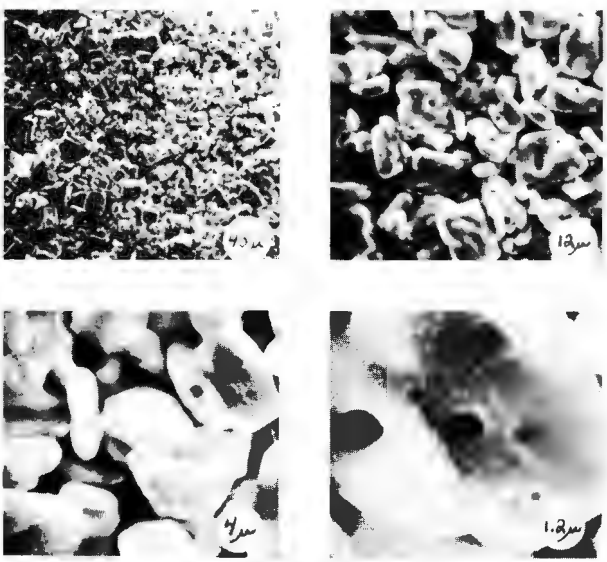

Figure 9
Phosphor powder from fluorescent lamp at various magnifications. Note the well-defined, three-dimensional nature of each particle and the pores present in each particle.

In the study of particulate matter, the SEM is able to give a three-dimensional aspect to the particles. Figure 9 is a series of micrographs of a phosphor powder at magnifications ranging from 315X to 10,500X. This type of micrograph is ideal for studies of particle size and count. The high-magnification micrograph (lower right) shows the structure of the binder material on the surface of the phosphor particle as well as structure of the inner surface of the pores. A SEM micrograph showing the variation in size, shape and morphology of silver halide crystals is shown in Figure 10.

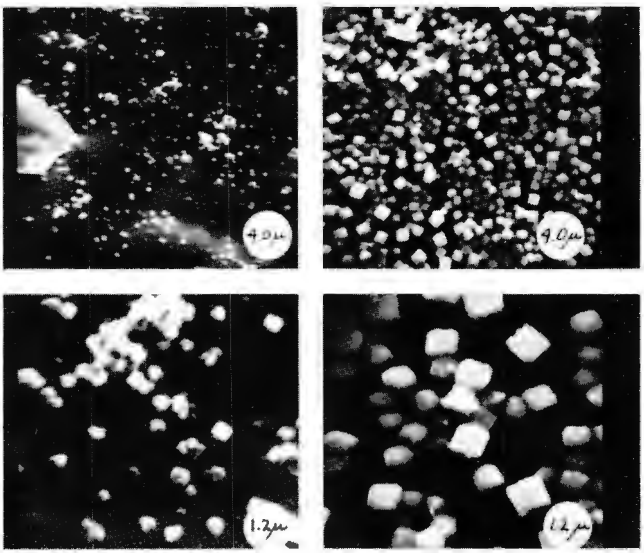

Figure 10
Variation in size and shape of two different silver halide samples.

The red glaze on a piece of Islamic glass made in the 9th century was investigated by the SEM. From an analysis of the glaze by X-ray diffraction it was found that crystalline phases of copper oxide and copper were present. Two morphologies of the copper oxide, dendritic and globular, were delineated by the SEM on fractured and polished samples etched in 1% HF. Crystallization in the dendritic form is shown at the left, and the globular form is illustrated at the right in Figure 11.

Since the SEM has a very large depth of focus, it can be used to great advantage for the delineation of microstructures resulting from complex crystallization processes. Figure 12 shows the original formation as well as the growth of crystals in a specimen of a calcium silicate hydrate material. Both nodular and whisker-like crystal growth, denoting various degrees of hydration, in addition to the original log-like crystals, are resolved in three-dimensional clarity.

Differences in chemical composition may be discerned with the SEM by the variation in secondary emission characteristics of different phase

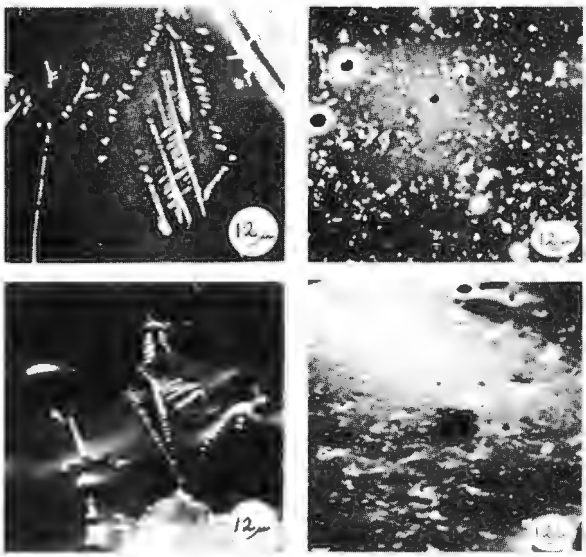

Figure 11
Micrographs showing degrees of crystallization of copper oxide in the red glaze of a piece of 9th century Islamic glass.

Figure 12
New crystals of various degrees of hydration formed on original calcium silicate hydrate crystals.

compositions. A BaO - SiO_2 glass system that has phase-separated is shown in Figure 13. The micrographs were taken of a fractured surface (left), a polished surface (center), and a polished and etched surface (right).

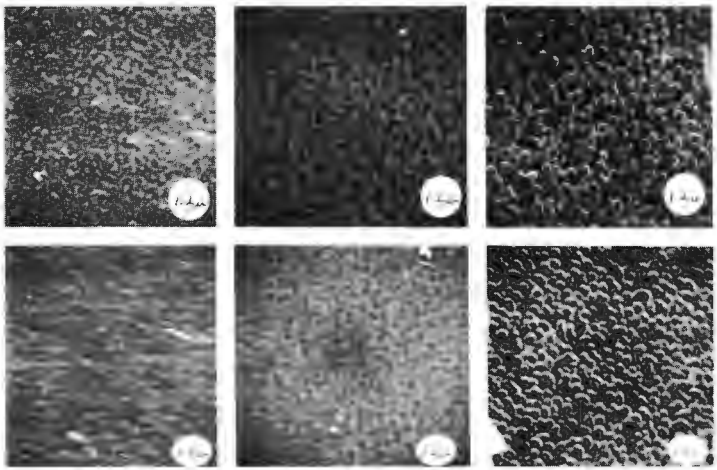

Figure 13
Fractured, polished, and polished-and-etched sections of BaO-SiO_2 glass showing phase separation.

Figure 14
Fused cast refractory showing a spinel phase (light) precipitated in a periclase matrix (dark).[19]

One phase (spherical) is barium-oxide-rich, while the other phase (matrix) is silica-rich. This difference in chemical composition is clearly portrayed in the polished specimen in the center and can be enhanced by etching in 1% HF (right) to develop an additional surface topography in the sample.

Another example of delineating chemical composition differences is shown in Figure 14. A polished sample of a fused-cast refractory is seen to be composed of a spinel phase (light) precipitated in a periclase matrix (dark). A higher secondary emission characteristic of the spinel as compared to the surrounding periclase phase is responsible for the difference in contrast.

A comparison of the secondary emission mode and the cathodoluminescent mode is shown in Figure 15. The micrograph on the left

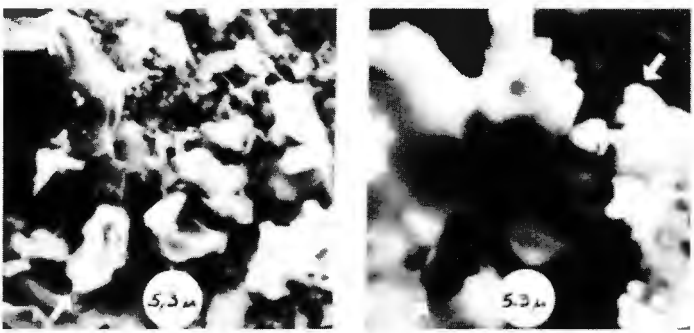

Figure 15
Secondary-electron-emission mode and cathodoluminescent mode of P-16 phosphor.[11]

pictures a P-16 phosphor specimen made up of a number of grains by the secondary emission mode, while the micrograph on the right is the identical field of view by the cathodoluminescent mode. The white arrows point to specific particles which exhibit a wide variation of light emission, suggesting that the SEM may be useful for establishing the efficiency of phosphor particles.

SUMMARY

The great depth of focus and high resolution of the SEM have proven invaluable in the characterization of various materials. A great number

of examples of microstructures of glass, ceramics, and refractories, utilizing the secondary electron emission and cathodoluminescent mode of the SEM, have been described.

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AN ANALYSIS OF ANCIENT GLASS WITH THE ELECTRON MICROPROBE

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ABSTRACT

The electron microprobe provides a quantitative means of chemical analysis on a microscopic scale in which the characteristic X-ray emission is excited from regions of less than 1 micron in diameter by bombardment with an electron beam. The instrument has had many important applications in glass research at Corning but one of the most interesting is the analysis of glass fragments from ancient mosaics recovered from the sea at Cenchreae, Greece. Analysis of the miscroscopic grains of colored opacifiers provided information which helped to determine the date of manufacture of the glass to be between 200 and 400 A.D. In addition, the results suggested to specialists in ancient glass manufacture that some of the glass used in the mosaics had been made by remelting older glasses and adding new coloring opacifiers.

Under a microscope the apparent homogeneity of most materials is replaced by a surprising and sometimes bewildering complexity. A smooth shiny metal object may, when magnified, show itself composed of two or more clearly defined crystal forms that are complexly intergrown. A sec-

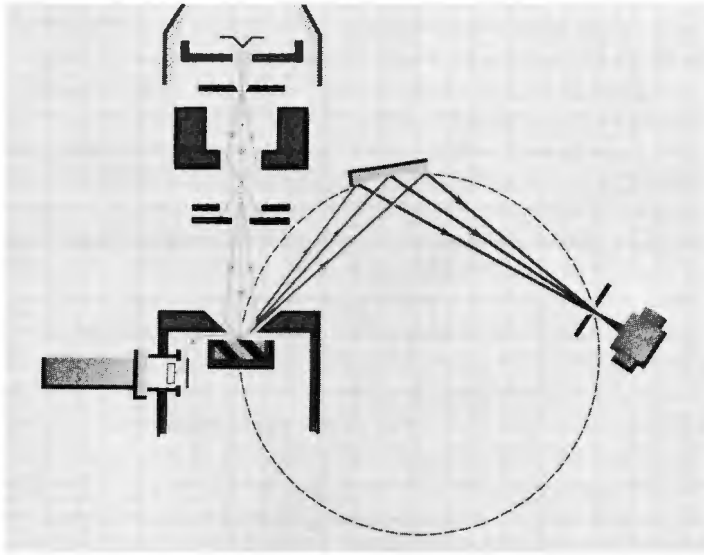

Figure 1

Schematic diagram of the electron microprobe showing the electron and X-ray optical systems. Electron paths are shown in dotted lines and X-ray paths with solid lines.

Figure 2

A modern electron microprobe installation. Systems shown in Figure 1 are boxed in the large evacuated tank in the center of the picture.

tion of corroded glass tank refractory will often reveal a succession of both glassy and crystalline phases on a microscopic scale which reflect the mechanism of failure. The electron microprobe is an instrument which allows the unravelling of the chemistry of these complex problems through the analysis of extremely small sample volumes. It has had very important applications in metallurgy and mineralogy, and much interesting research is being done in the microchemistry of cells and other biological materials.

In the electron microprobe, a very narrow beam of electrons is focused on a highly polished sample. The material under the electron beam emits X-ray spectra which are characteristic of the elements present. Figure 1 is a schematic diagram of the electron and X-ray optical systems of the electron probe. Electrons are emitted from a heated hairpin filament in the electron gun and accelerated down the column under a potential of from 5 to 30 kilovolts. The electron beam is demagnified by two magnetic lenses and focused on the sample surface forming a spot approximately 1 micron in diameter.

The electron bombardment of the area of the specimen causes emission of X-ray wavelengths which are uniquely characteristic of the elements contained in the approximately 5-cubic-micron excited volume. The focusing X-ray optical system allows the wavelengths of the emitted X-rays to be measured with considerable accuracy. This is done by diffracting the X-rays from a curved crystal (shown on the focusing circle) and detecting the diffracted wavelength with a proportional counter tube.

The pulses are counted using quantum counting equipment which provides a quantitative measure of X-ray intensities. The X-ray emission

from the sample is compared with that of a pure element or simple compound standard to provide an intensity ratio. The intensity ratio is then converted by means of rather complex correction procedures to a quantitative chemical analysis. In many cases, however, purely qualitative results will provide answers to difficult questions.

Since an electron beam is used to excite the sample, it is possible to scan the beam over the surface of the sample in a grid or raster pattern much like that used with TV picture tubes. An image can then be formed on a synchronously scanned cathode ray tube which then indicates the distribution of selected elements in the area of the sample surface that is scanned.

The hardware needed to accomplish these operations is both complex and expensive, with a typical research installation costing between 80 and 150 thousand dollars. Figure 2 shows a modern electron probe similar to the one used at Corning Glass Works. We have reached a degree of sophistication in materials science where a minute stone in a glass laser rod will cause explosive failure and a microscopic inclusion may result in the rejection of many thousands of dollars worth of electrical components. The rapid and accurate solution of such problems can compensate the cost of the expensive analytical equipment in a rather short time.

At Corning we have dealt with a large number of modern technological problems, but one of the most interesting problems was a microprobe investigation of glass technology almost two thusand years old.

In 1964 and 1965 an archaeological team from the University of Chicago and Indiana University led by Robert L. Scranton excavated the site of a structure which was partially submerged at the southwestern end of the harbor at the ancient Greek port city of Cenchreae. On a subfloor of the building, the remains of 108 glass inlaid panels were found surrounded by fragments of the original wooden packing cases. On the smooth plaster face of the panels, bits of colored glass were assembled to form a design, as in a stained-glass window. Restoration of these badly damaged panels revealed pictorial scenes showing swamp flowers and birds, nautical scenes with ships, fish and fishermen, and at least two human figures, one identified as Homer and the other thought to represent Plato. Representative samples of the badly weathered colored glasses were collected by Dr. Robert Brill of The Corning Museum of Glass for analysis. When the weathered surface was removed from these samples, brightly colored opaque glasses became visible.

H. P. Rooksby and W. E. S. Turner (1959) have determined that a change in glass manufacturing techniques which occurred between the second and fourth centuries A.D. is reflected in the opacifiers used in producing both yellow and white decorative glass. In the early times, $Pb_2Sb_2O_7$ was used as the pigment to obtain yellow glass, and $Ca_2Sb_2O_7$ was used in white opaque glass. Between the second and fourth centuries, glassmakers began to use $PbSnO_3$ for a yellow opacifier and SnO_2 for the white. Thus, a chemical analysis would allow an approximate date to be assigned for the melting of these glasses. The results of the analysis obtained by Dr. Brill by conventional chemical methods showed the white opacifier to be the $Ca_2Sb_2O_7$ variety which was characteristic of the early glasses. However, the results for the yellow glass indicated significant

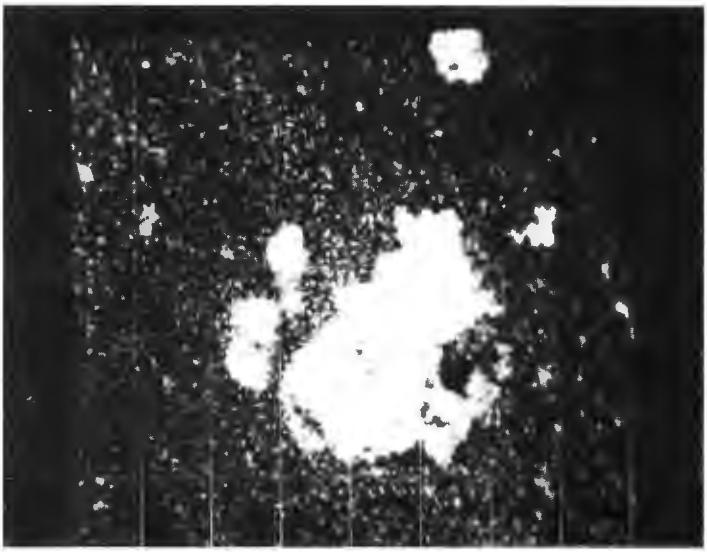

Figure 3

Lead X-ray scanning image of several opacifier grains in ancient glass matrix. The light areas indicate high concentrations of lead. Magnification 300X.

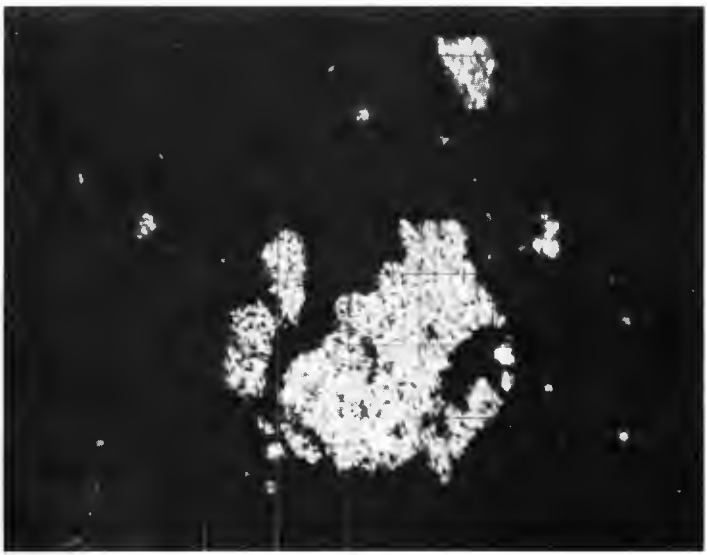

Figure 4

Tin X-ray scanning image of the same area shown in Figure 3. The exact correspondence of the images indicates the opacifier grain is a lead-tin compound. Magnification 300X.

amounts of both antimony and tin which made the interpretation rather difficult, since the use of two yellow pigments in the same glass was not considered probable. At this stage the yellow glass was submitted for microprobe examination to determine the composition of the opacifier grains.

The problem in this case lay in the fact that wet chemical analysis, and most instrumental techniques as well, provides information on the bulk analysis of a material. It was necessary to determine the composition of the opacifier grains themselves and not have the result affected by the composition of the matrix glass. The grains were easily visible by optical microscopy and averaged between 25 and 50 microns in largest dimension. Since the microprobe electron beam focuses down to a one-micron diameter, it was quite simple to excite the exposed opacifier grain and not the surrounding matrix.

The samples were mounted in a conductive bakelite disk, polished, and given a very thin evaporated coating of carbon to make the surface of the glass electrically conductive. Figures 3 and 4 are, respectively, lead and tin X-ray scanning images of an opacifier grain surrounded by the matrix glass. The white areas are indicative of high concentrations of these elements. Figure 5 is an antimony X-ray image at the same magnification which indicates a relatively uniform distribution of the element in the glass matrix. Uniformly distributed areas of antimony concentration are visible, which suggest that opacifier grains originally present have broken up and largely dissolved.

It appears probable that this glass was made by melting together two or more glasses which originally contained both the early type of $Ca_2Sb_2O_7$ white pigment and the $PbSnO_3$ yellow pigment which is characteristic of

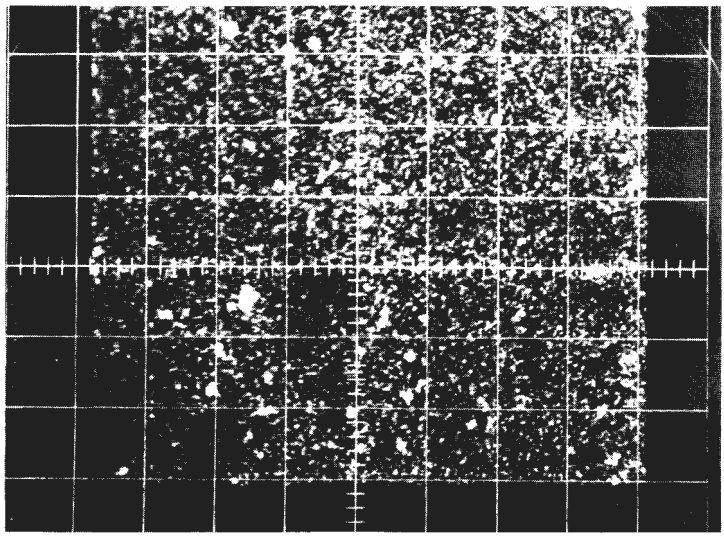

Figure 5

Antimony X-ray scanning image of the ancient glass sample. The rather uniform distribution suggests that the antimony has dissolved in the matrix glass. Magnification 300X.

the later period. In the remelting process, the $Ca_2Sb_2O_7$ opacifier was almost totally dissolved in the glass and, as a result, antimony is rather evenly distributed at a low level of concentration in the glass matrix. The $PbSnO_3$ yellow pigment apparently was insoluble and remained as discrete grains acting as the sole opacifier in the resulting glass. The date of manufacture appears to lie somewhere during the transition period between the second and fourth centuries A.D. This is further substantiated by a carbon 14 date for the wood of the crates of 290 A.D. $\pm$100 years. These early workers would seem to have been very competent artists but not particularly advanced glass workers, for they apparently obtained the colors they wanted by remelting and mixing existing glasses rather than melting glasses from raw batch.

We have found the electron microprobe to be uniquely powerful in investigations of some of both the oldest and newest of glass and ceramic materials. Much of the story of ancient glass lies hidden in the materials themselves awaiting the tools to observe and interpret it.

ACKNOWLEDGMENTS

I would like to thank Dr. Robert Brill for both suggesting the problem and providing invaluable assistance with the interpretation of the results and also Mr. Norbert Binkowski who performed the microprobe analyses.

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ARE WE GLASSBLOWERS?

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ABSTRACT

The author cites the lack of accurate definitions surrounding the term "glassblower," describes his opinions of the reasons for such a lack, and makes recommendations for clarification of definition. He cites the need for development of technical understanding by today's glassblower, speaks about the types of training programs available in the industry and suggests the role the A.S.G.S. might play in the general future of glassblowing and glassblowers.

There has been a recent rash of discussion and written material concerned with training of glassblowers in this country. Quite a bit has appeared in FUSION. Reading and listening suggests to me that we glassblowers need a solution of what I would call "the problem." Until the problem has been defined and some settlement made, I'm afraid that you and I who have trained and worked as glassblowers won't really be sure if we have been successful. You see, the real, basic problem is wholly a matter of definition. What is a glassblower? If I were suddenly confronted by an eminent group of A.S.G.S. members asking, "Are you a glassblower?" I would have to answer, "I don't know. What do you mean by the word 'glassblower'?" If I was then asked to answer the original question and to give my own definition, I would really be face to face with a dilemma. Why? Because my definition might tend to insult one member of such a group and at the same time anger another group member because he felt he did not personally measure up to my definition. I feel that clarification of definition is of vital importance to us as people working as glassblowers, to our employers, and to our government which is vitally interested in the state of our technical manpower pool.

What follows are opinions based solely upon a limited experience of twenty-odd years in and around the glassblowing community. My first premise is that there can be no absolute definition of the term "glassblower" when it is insisted that one definition apply to all glassblowers. Many of us tend to make such insistence however. I would like to propose that a glassblower is, and performs as, an employee who is what his employer says is a glassblower. Therefore, a man who assists in the operation of a bottle-blowing machine, the woman who operates an envelope-sealing machine, the man at the fairgrounds who makes glass novelties, the fellow who mold-blows carboys, and the bench worker employed in industrial research and college laboratories can all be called glassblowers. Yet, they have very different capabilities and their job definitions would describe different activities and knowledge.

I will apply this discussion to the bench glassblower, however, since that is where I am most familiar. Here, too, I will assert that the employer

is still the one who says whether we are or are not glassblowers. After all, the glassblower in question is on the employer's payroll. I feel that the following question must be asked. Does time-in-the-trade and the experience which is supposed to be gained from that time make a glassblower? I don't think that it does and I don't feel this is a heretical statement simply because I apply it to my own profession. I think that there is a goodly number of us who have time-in-trade advantage and yet are not as proficient glassblowers as some of our less experienced fellow glassblowers. As a case in point, let's suppose that you have been taking your automobile to one particular garage whenever it needs repair. Over a period of time several different mechanics there have worked on your car. You have had ample opportunity to observe the comparative abilities of these men and you have probably developed a preference for one mechanic. Might not that preference be made without regard for his time-in-the-trade? Why? Because you find that man more knowledgeable, efficient, and generally competent than the other mechanics. Perhaps he is even more cooperative. I think it is the same with glassblowers, electronics technicians, machinists, doctors, lawyers, or any other craft or profession. Time-in-the-trade is just not a firm factor in determination of who is or is not a good man in his field. And it is not a firm factor in training programs either.

Look at our training programs of today and of the past. They have been operated under widely different conditions and from greatly different philosophies. There have been training programs within private corporations. These trainees were meant to bolster the service force of the company and they were taught by an employee of the company. There have been training programs run by states in vocational atmospheres. They have been intended to supply workers to local industries. There have been training programs run by the federal government in cooperation with state educational systems and local industry. They have been intended to train underemployed citizens in capabilities that the government recognizes as needed for the national good. These programs have covered various lengths of training periods and have had widely different curricula. There is one thing that they have had in common though. They've all been taught by glassblowers, teaching within the requirements of their employer, the private corporation, the state vocational education system, or the federal government. But that teacher is still a glassblower who got his experience someplace. He can teach what he knows but no more than that. If he is an employee of private industry, he teaches what his employer wants taught. In the state vocational system he teaches what local industry wants taught. In the federal government sponsored programs he teaches as an experienced glassblower, it's true, but he is probably preconditioned by what his present or former employers have expected of him as a glassblower. Behind all the forgoing lurks the party, vague in form, who is responsible for the training we had and who continues to be responsible for the development of glassblowers today. He is the employer. He defines for himself and for us what a glassblower is, regardless of how we feel about it as individuals or as a group. If any employer can (and he does) set arbitrary standards defining what a glassblower is, then it is very possible that there is a wide capability gap in our ranks although we are all classified as glassblowers. The same argument applies to trainees

and training programs. Regardless of how the A.S.G.S. feels about it and regardless of how people in other glassblower training programs feel about it, the single training program under consideration is run the way that vague form, the "employer," says it will be run. Don't think that I am suggesting some sinister plot and procedure through which the glassblower is made and controlled by the employer. I don't think that. I simply recognize that the employer is forced to make his own determination of what a glassblower is because no one central authority is prepared to assist him in that determination.

Before I make some general suggestions concerning a manner by which some uniformity of definition could be attained, I would like to say something about the job most of us are doing today. There seems to be a feeling that glassblowers have contributed greatly to the advance of science and technology in the past and are continuing such contribution today. This is always a favorite theme of speakers addressing glassblower conclaves and it always goes over well since it appeals to the ego. I wonder if these accolades will stand the light of day, however. There comes a time when, if you believe your own propaganda, you do yourself a disservice. You fall into a deep, dark trap—the trap of complacency. If you're complacent, you will never rise beyond your present level of ability. If you are not complacent, you will continue to strive, to learn, to grow, and to rise. You will grow in ability to contribute to contemporary development, and you will truly earn the respect that you now only expect. I submit to you that training is a continual, never-ending process. If our training should end, we can no longer expect to contribute to the sciences we profess to serve. With all of the pressures and demands upon today's scientist, it seems only sensible to assume that the less time he must spend doing what could be our job, the more time he will have to devote to his specific and generally more important pursuits. If we become more familiar with mathematics, with basic scientific principles, theory of glass constitution and applications, etc., then we can truly contribute to the success we claim, and we will force glassblowing into a respected position. From a purely selfish standpoint, the glassblower who does learn and grow can serve his individual better interests at the same time.

I have spoken about training programs and about glassblowers, the people who are already beyond the initial training period. How do they tie together? From this point forward I feel that the A.S.G.S. should develop and maintain an influence as the central authority on glassblowing in this country. If it does, it will influence all training programs yet to begin, all glassblowers just finishing initial training, and every mature glassblower on the job. How can the A.S.G.S. accomplish this? There can be no doubt that this Society possesses the capability. With all of its membership, regular, associate, and junior, and with the ability of that membership to gather information on glassblowing in the country, it should be a relatively simple matter. Once the Society gains information about who employs glassblowers, what they do, what they think they should do as a part of their job, and what they think should be involved in training, the Society can develop a program for training and can write a series of job definitions for various types of glassblowers which will have

of glassblowers should also be encouraged. When the job is done, I'm certain that employers will subscribe to the definitions of glassblower real meaning. When this job is started, the assistance of various employers classification and that parties contemplating the training of glassblowers will be happy of Society participation in those training programs. I previously said employers are doing this themselves. But I don't seriously believe they want to do it; and I don't believe that they will forgo the possible benefits of available information, schedules, and programs compiled by a responsible Society. in favor of simple guesswork of their own.

Many of you will say that these proposals lead to certification. Certification of glassblowers has been a bone of contention in the A.S.G.S. for some time now. And it is entirely fair to say that certification could logically grow out of Society efforts such as I have suggested. Many of our older members are afraid of certification. I've investigated my own feelings and am ready to admit that I have some personal fears about certification. But I'm not going to be around as long as the fellow who is just entering glassblowing. I'm not going to be around as long as the A.S.G.S. is. What about the future of the Society and the young glassblower? I've asked myself some questions which I think we all might ask ourselves. You might be interested in them; some of the are . . .

Is the purpose of any training program to make a person *fully* trained?

Should our craft be kept "locked" by the "ins" to the exclusion of the "outs"?

Should we be importing more "foreign" glassblowers?

Should available jobs go begging for the lack of trained personnel?

Should my Society be involved in training?

What is a glassblower?

What can a glassblower be?

Am I happy with what I know as a glassblower?

Would I be better off if I knew more than what I do?

Do I feel satisfied with the possession of mere manipulative talent?

What is a top man as far as I am concerned?

What is a top man as far as many employers are concerned?

Are glassblowers like fishermen? No good except for you and me and I'm not so sure about you?

Would I make a good training instructor for young glassblowing trainees?

Would any of the glassblowers I know make good training instructors? Why or why not?

Would I rather hire a person with some training or a person with none? Why?

How strongly do I disagree with another person's glassblowing method when they get just as good results as I do with a different method?

These questions, and others which will no doubt appear to each of us, can break down some of the "feeling barrier" which each of us sets up to protect us from change and even from thinking. I would like to suggest to each of you that many of the things we enjoy and believe in today came about because some person had the insight to see that something was necessary and went ahead and did it. In closing, it is time to once again ask, "Am I a glassblower?" Each of us working together can assist in an effort to clarify factors which will someday let us answer that question honestly and fairly.

GLASS TUBING MANUFACTURING

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ABSTRACT

"Glass Tubing Manufacturing" consists of two main topic discussions: Tube-Forming processes and Tube Dimensional Nomenclature. In the process section the various methods and processes in use today for manufacturing glass tubing will be discussed. Their peculiarities, advantages and disadvantages with respect to quality and dimensional characteristics will be covered. The processes that will be discussed will be the Danner, Vello, Updraw, Downdraw and Redraw.

In the nomenclature section the paper will cover the various terms, their meanings, and their importance to a buyer and user of glass tubing. All of the discussion in this area will revolve around dimensional characteristics of tubing with respect to outside diameter, inside diameter, wall thickness, out of round and bow. Regarding OD, ID, and wall, we will cover various "gauging limits" to which tubing is manufactured and sold and the types of gauges used to measure to these limits. Concerning OOR we will mention the two types of OOR and methods for measuring them. For bow we will discuss the three types of bow, the errors sometimes made in measuring bow, and suggested methods for measuring these types.

Information gained, in summary, will be a greater knowledge of tube forming processes, gauging techniques, and nomenclature used by the manufacturer which will allow the glass blower to better define his needs to his supplier and thus receive tubing which will supply his needs to the fullest extent.

We have chosen for our subject today "Glass Tubing Manufacturing." Our purpose is to acquaint you with tube-forming processes, gauging techniques of tube dimensions, and the nomenclature used by the manufacturers with respect to tube dimensional gauging. We hope that this will benefit you, the ultimate user of glass tubing, to define your requirements to your supplier in a way that will help you meet those requirements to the fullest extent.

Our first area of discussion will be tube-forming processes. In current use for the manufacture of glass tubing are three basic processes: horizontal, vertical-up, and vertical-down. These can be further defined as Vello, Danner, and Redraw in the horizontal category. The vertical-up type is known as an updraw, and the vertical-down as a downdraw.

Horizontal draws manufacture the smaller tubing. Smaller meaning, in most cases, up to and including 32 mm. O.D. Each type of horizontal draw has its peculiarities, thus defining its advantages and disadvantages.

A Vello process yields tubing with such advantages as very little taper—thus tighter O.D. control, no hairpin cord, and good wall and

weight uniformity within the stick and from stick to stick. A Danner process yields tubing which has good bow control, good OOR control, and good wall uniformity within a cross section commonly known as siding. A redraw process differs from the others in that it is a re-melting, and proportional reduction of a larger O.D., heavier wall tube. This process is used to manufacture very tight tolerance and/or very small O.D. tubing. There are also in use today vertical redraw processes, redrawing larger O.D. tubing. The redraw is a slow process which forces the finished tube to be rather expensive. (In the remainder of this paper, redraw will not be included in the general discussion of horizontal or vertical processes.)

Continual efforts are being made to manufacture larger O.D. tubing by the horizontal processes. Due to the support given by the runway, it is possible to pull at a higher rate, reducing the cost, and have much better bow control than in the vertical process.

Vertical draws manufacture the larger O.D. tubing. They also have their peculiarities defining their advantages and disadvantages. The updraw is a process where the glass is pulled from a bowl of molten glass. Its advantages are good bow control and low inside-surface tension with relation to stress in the tube.

In the downdraw process, the glass is pulled straight down from an orifice. Its advantages are better O.D. control and better visual glass quality than an updraw. It also permits a higher pull rate, resulting in lower costs.

Moving on to our second area of discussion, let us consider gauging techniques of tube dimensions and the nomenclature used by the manufacturer with respect to these dimensions. In the discussion of this topic, our aim will be to define various terms pertaining to dimensional tolerances.

First, let us consider the term "gauging limits." There are four gauging limits which define the tolerance to which outside diameter (O.D.), inside diameter (I.D.), and wall are controlled. These are "R" limits, "U" limits, "T" limits, and "S" limits.

With respect to O.D. control, we use three of these: "U," "T" and "S." "U" limits mean that *one* diameter *only,* six to nine inches from each end, must be within specified tolerance. (Fig. 1)

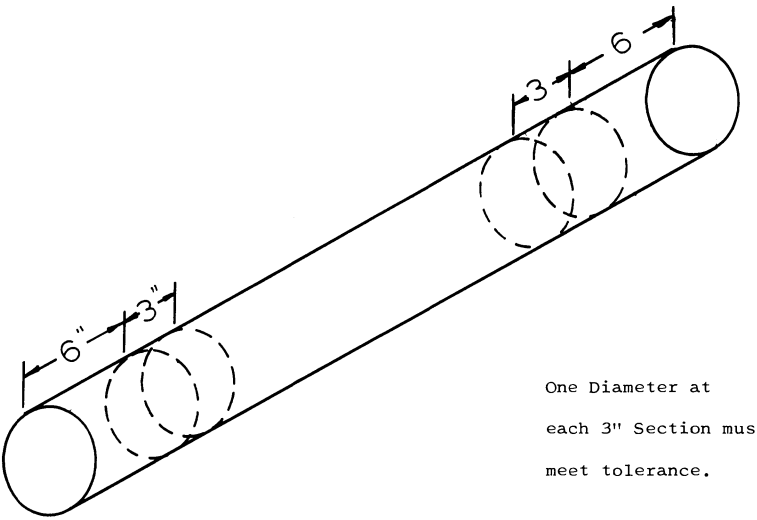
"T" limits mean that all diameters at *one cross section* six to nine from each end, must be within specified tolerance. (Fig. 2)

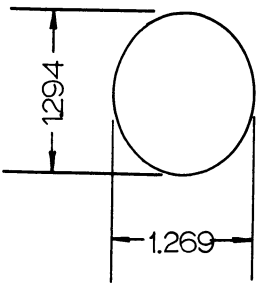
"S" limits mean that all diameters, anywhere on the tube, must be within specified tolerance.

"U" limits will, therefore, allow points on the tube to exceed the specifications in the center of the tube and will even allow points at the particular cross-section six to nine inches from each end to exceed the specification by the out-of-round tolerance. This causes one to wonder why these limits would ever be used, since they are so open. However, they do have a use and can be used to a good advantage. In the first place, if you can find a point within specification six to nine inches from the end, the possibility of any point on the tube exceeding it by more than 2% is not likely. Secondly, then you can specifiy a tight O.D. tolerance to "U" limits which will force the manufacturer to center his process to your

specified nominal O.D., and all diameters on the tube will not exceed those tolerances by more than 2% of the nominal O.D., which is the allowable out-of-round and the expected limit on O.D. variation down the tube as stated above. The key to this is the fact that tighter specified tolerances can be manufactured to "U" limits than to "T" or "S" limits. Tighter by 2% on the total spread of the tolerance as specified. If the actual out-of-round of the tube manufactured was only 1%, instead of the 2%, as allowed, this would guarantee you that your tubing could be more closely centered around the specified nominal O.D. than if the specified tolerance was looser to a "T" or "S" limit.

"T" limits are used when gauging is made necessary because of tight O.D. tolerance. Assuming the required tolerances were tighter than the



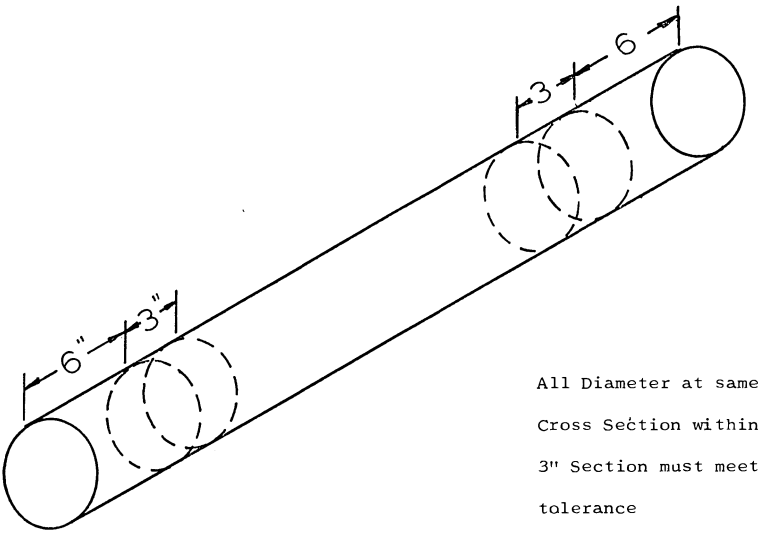


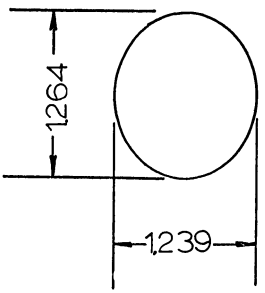
O. D. Tolerance 1.230" - 1.270" 'U'

Actual O. D. 1.269" - 1.294"

Maximum or Minimum O. D. can exceed Spec. by allowable OOR.

Figure 1
"U" limits — 0.0





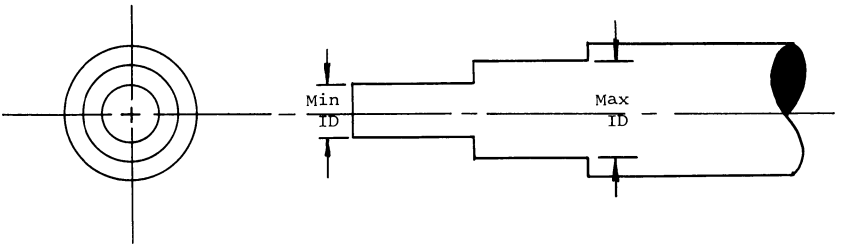
O. D. Tolerance 1.230" - 1.270" 'T'

Actual O. D. 1.239" - 1.264"

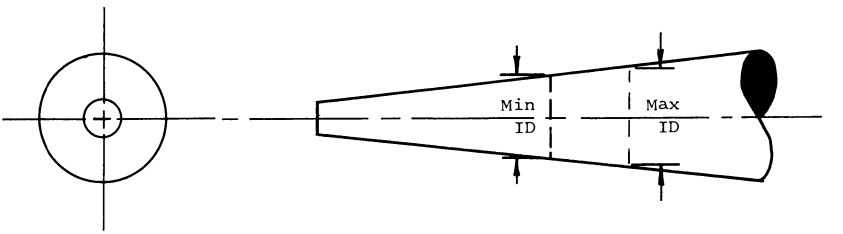
Figure 2
"T" limits — 0.0

process would yield and gauging would be necessary, gauging six to nine inches from each end can be done much easier and more economically than trying to gauge down the entire tube. Gauging machines are in use which gauge the tube six to nine inches from each end, which is the reason these areas were chosen for "U" and "T" limits. Normally, when gauging is necessary for an item specified to "S" limits, the "S" limit tolerances can be reduced 10% and the tubing gauged to "T" limits to guarantee an "S" limit tube.

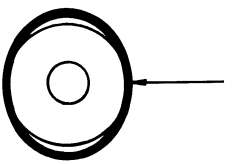
With respect to I.D. control, we use all four gauging limits; "R," "U," "T," and "S." "R" limits mean that the minimum diameter at each end of the tube must be within specified tolerance. A round stepped or



Round stepped plug gauge



Tapered plug gauge



Point of hang up. Therefore, I.D. can exceed specified Max. tolerance by allowable OOR. Min. tolerance will not be exceeded

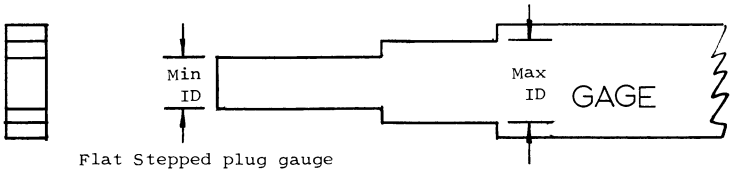
Figure 3
"R" limits — 1.0

tapered plug gauge measures to "R" limits. (Fig. 3) "U" limits mean that *one* inside diameter *only* at each end of the tube must be within specified tolerance. Caliper, inside micrometer, and flat-stepped or tapered plug gauges measure to "U" limits. "U" limits on the I.D. are used for the same purpose as they are for O.D. (Fig. 4-A)

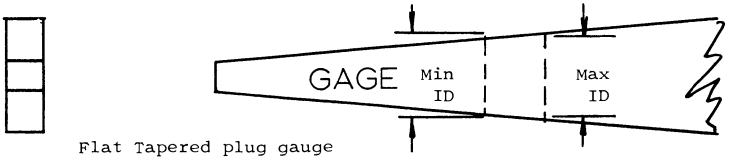
"T" limits mean that *all* inside diameter at each end of the tube must be within specified tolerance. Calipers, inside micrometers, and flat stepped or tapered plug gauges measure to "T" limits. (Fig. 4-B) "T" limits are the tightest gauging limits for I.D.

"S" limits mean that the *minimum* I.D. *only,* the entire length of the tube, must be within specified tolerance. A ball gauge measures to "S" limits. Tolerances for "S" limits are stated in one figure only, such as 1.495″ "S" limits. (Fig. 5)

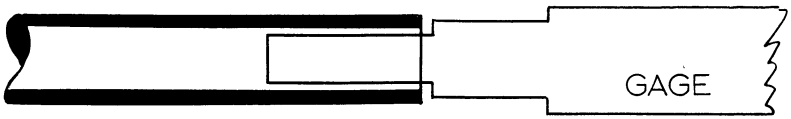
Lastly, with respect to wall, we use two of these gauging limits, "U" and "T" limits. "U" limits mean that *one* wall thickness on the circumference of the tube at each end must be within specified tolerance. "T" limits means that the wall thickness as measured around the circumference



Flat Stepped plug gauge

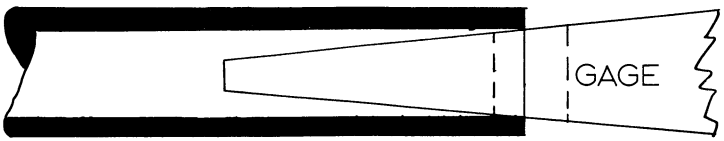


Flat Tapered plug gauge



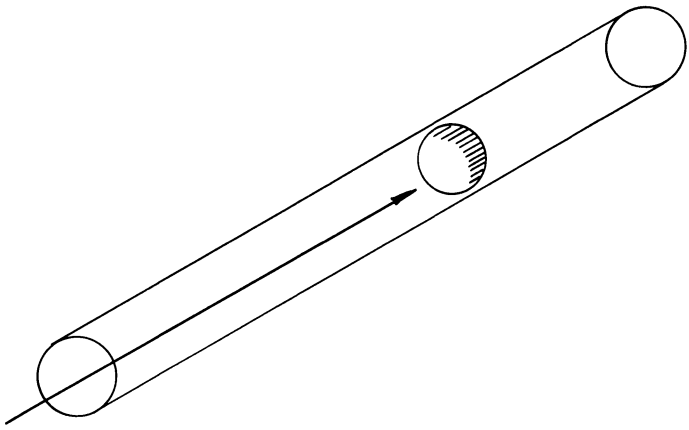
1. For 'T' Limits gauge must enter tube to first step and rotate 180° + and must not go beyond first step at any point as it is rotated.
2. For 'U' Limits gauge need only enter tube to first step at one point and/or not enter beyond first step at one point. Therefore, I.D. can exceed Minimum or Maximum tolerance by allowable OOR.

Figure 4-A
"U" and "T" limits — 1.0



1. For 'T' Limits gauge must enter tube beyond first mark and rotate 180° + while the end of the tube remains between the two marks.
2. For 'U' Limits gauge must enter tube beyond first mark at one point and/or not enter beyond second mark at one point. Therefore, I.D. can exceed Minimum or Maximum tolerance by allowable OOR.

Figure 4-B
"U" and "T" limits — 1.0



A Ball with a diameter as specified must pass through the tube. This guarantees minimum I. D. to be controlled; however, maximum I. D. is controlled by O.D. specification.

Figure 5
"S" limits on I.D.

of the tube at each end must be within specified tolerance. "U" limits on the wall, as on the O.D., allow points to exceed the specified tolerance; and in this case, it could be as much as 12% of the nominal wall which is the normal allowance for siding. Siding being the wall variation within a cross section. Their advantage as on the O.D., is to hold the wall closer to nominal. "T" limits are the tightest gauging limits for wall.

As demonstrated in Figure 6, wall thickness must be measured with a rounded gauging point on the inside of the tube.

The next dimensional characteristic in our discussion is out-of-round. We have discussed out-of-round (OOR) with respect to gauging limits on O.D. and I.D., but there are several other aspects of OOR which bear mentioning. There are two types of OOR—oval and triangular. Triangular is gauged by means of a 60° "V" block with a dial gauge centered above the block. (Figure 7-A) Oval is gauged by means of measuring O.D. with micrometers around a chosen cross section and the difference between the minimum and the maximum O.D. is the OOR. Oval OOR can also be gauged with a dial gauge and a set of rollers; however, the dial gauge must

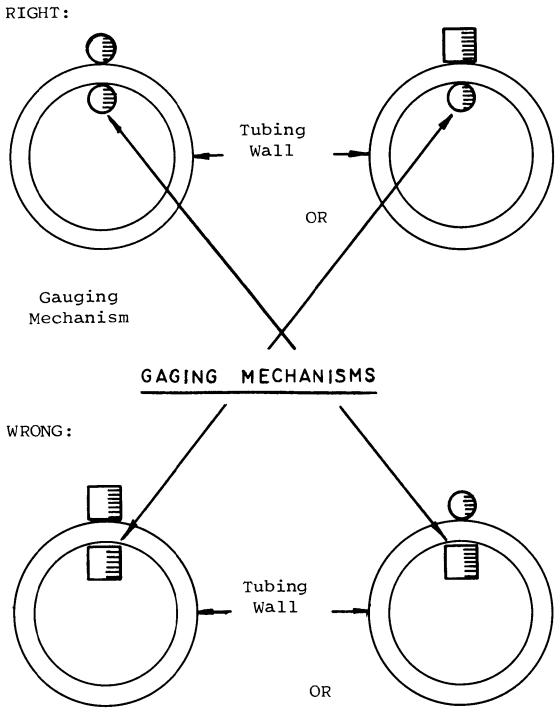


Figure 6

be diametrically opposite the point on the tube where one of the rolls contacts the tube. (Fig. 7-B) It is important that the type of OOR present in the tube be identified prior to gauging; this can be done by feel, since it is possible to get a much better than actual and theoretically a perfect OOR reading by using the oval method to check triangular OOR and vice versa.

As our final point, let us consider bow. Bow is defined as the maximum deviation from a straight line connecting any two points on the tube. There are three types of bow present in tubing. They are: single arc, multiple arc, and cork screw. As in the case of OOR, the type of bow present must be determined before a method of measurement can be specified.

Single arc bow can be measured with a dial gauge at the mid-point of the tube and a set of rollers at each end. The total throw on the dial gauge equals *two* times the bow in the tube and is known as TIR (total indicator reading). It can also be measured by laying the tube on a flat plate and measuring the distance between the bottom of the tube and the plate with the tube lying concave downward on the plate. (Fig. 8) A method sometimes used is also shown in Figure 8, which is laying the tube on the plate concave upward and holding one end of the tube against the plate with the other end rising off the plate. It must be understood that the actual bow in the tube is only one-half the distance between the plate and the raised end of the tube.

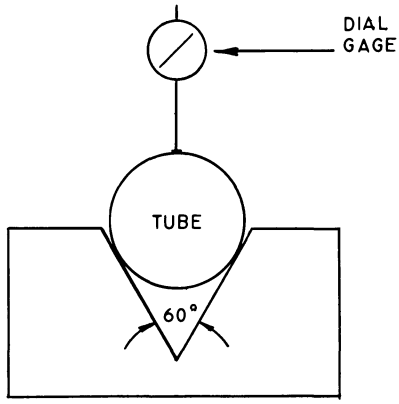


Figure 7-A
For measuring triangular OOR

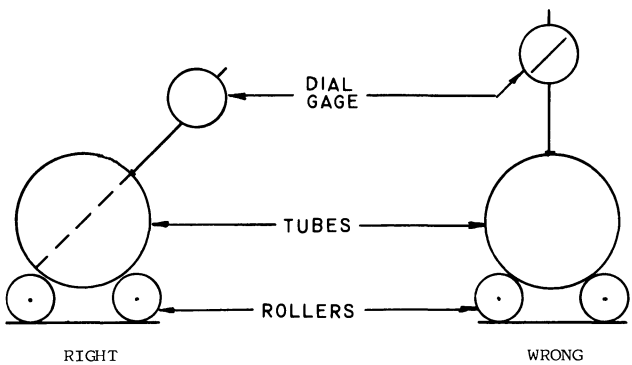


Figure 7-B
For measuring oval OOR

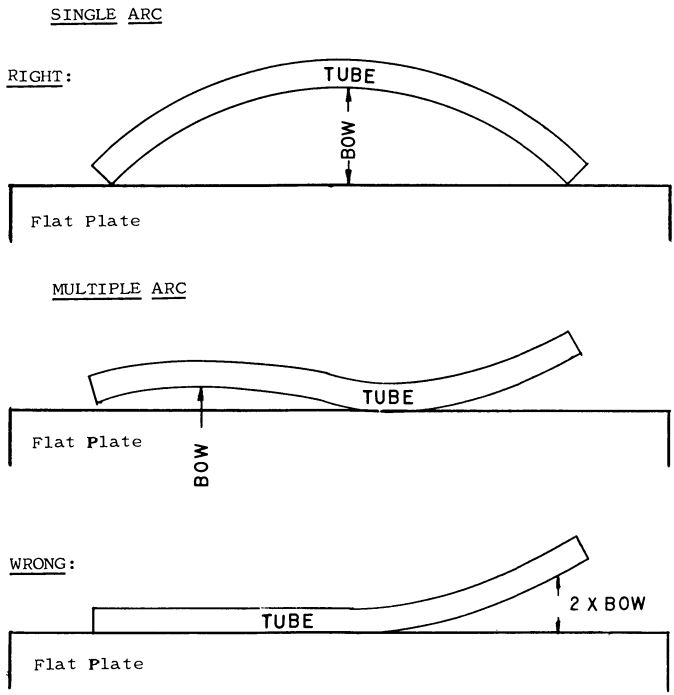


Figure 8

Multiple arc bow, sometimes referred to as "dog leg," can best be measured on a flat plate, measuring the distance between the bottom of the tube and the plate with the arc you are measuring lying concave downward. (Fig. 8) Measuring multiple arc bow with a set of rollers and a dial gauge at the mid-point of the tube, as suggested for measuring single arc bow, can result in a bow measurement of zero when actual bow is extremely bad.

Lastly, cork screw bow, which is common on horizontal processes, is next to impossible to measure accurately. It can best be seen by sighting vertically down the stick while rotating it between finger and thumb.

In conclusion, we hope that a better understanding of the characteristics, as discussed in this paper, will permit you, the user, to better specify your needs to your supplier.

THE CONSTRUCTION OF DEMOUNTABLE ABSORPTION CELLS

J. L. A. FRENCH

and

RESISTANCE MANOMETERS

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This paper deals with two distinct and totally unrelated subjects. However, each in its own field may be useful in the form in which it is herein described, or it may form the basis for other ideas which may be better. If the latter proves to be the case then this contribution has been doubly justified.

Firstly the subject of absorption cells. The field is very wide, and is well catered for by the commercial manufacturers. Indeed, some of these tiny multi-compartment cells are jewels in their own right. They come in all shapes and sizes each with a particular application the demands of which they faithfully satisfy. All would seem well with the world. The glassblower has only to indicate a suitable catalogue to his client and the problem is solved permitting him to return swiftly to his neglected coffee cup. Woe is he who allows such complacency to dominate his mind—"I've had this quartz cell custom made with double thickness windows because I want to study reactions at about 6 or 7 atmospheres." All one can do is wish the fellow luck. Next day he's back. "Could you seal these windows back; they sort of came off?"

This oft repeated experience initiated the investigation the results of which I now present to this assembly, for what they are worth. The problem was not a demanding one. A cell with an internal diameter of 20 mms., and varying in length from 10 to 60 mms. is closed at its extremities by parallel windows composed of various materials. A side arm facilitates filling, provision being made to enclose the cell either by a stopper or by means of a stopcock. So far its first grade stuff, capable of satisfying the demands of all reasonable men. Unfortunately some of our clients belong to a different category with the result that we must oft times think a little. Vacuum, partial or otherwise, is relatively simple because external pressure tends to push things together, a feature which can be turned to our advantage. Pressure, on the other hand, demands more Draconian measures.

The manner in which I solved this particular problem is as follows: A body is fabricated using heavy wall 1-inch O.D. tubing with a side arm of $\frac{3}{8}$-inch O.D. tubing. Care must be taken to ensure that the seal is smooth with no sacrifice in wall thickness. After thorough annealing, the barrel is wet-cut to the desired length. Practice and a good machine will

produce a satisfactory finish in one operation. However, if further grinding is necessary, allowance must be made for the removal of this material. I will describe the next step in conjunction with Figure 1.

The previously prepared barrel is cemented to a stiff, metal plate using hard vacuum wax or similar material. It is important to clamp the assembly so that it sets with the barrel vertical to the plate. An O-ring groove is ground into the end face of the barrel using a diamond core drill or a suitably machined copper tube and abrasive. Irrespective of the choice of drill, the dimensions of the groove will be dictated by the O-ring. Small cross-section Viton rings have been found satisfactory. Depth of cut should be adjusted so that when a smooth finish has been achieved, the O-ring will sit in a little over half way. After thorough cleaning, the barrel it detached from the plate and remounted so that a second groove may be made in the other end. In order to increase strength and reduce damage to the prepared ends of the barrel, the ground surfaces should be carefully glazed.

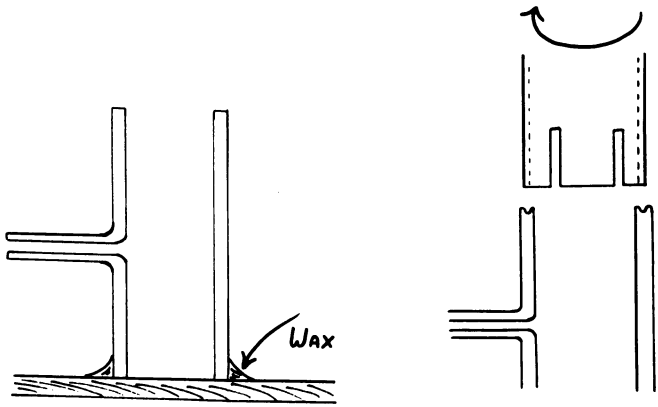

Figure 1

Thickness of the window material will be dictated by the pressure which will develop within the cell. For the higher range, it should be not less than 4 mms. thick and be free from defects. In the event that non-vitreous materials are to be used, it may be necessary to prepare the window as best you can. Some fluoride and chloride crystals can be troublesome, particularly when the time comes to clamp them to the ends of the barrel. A circular disc is the most convenient shape to use, but with a little intelligent modification to the shaping of the clamps, square, or even irregular shapes may be used.

Clamping plates are assembled in the following manner: Metal discs, 1/4 of an inch thick, are bored out in the center to provide a hole equal to the internal diameter of the barrel and beveled to about 45 degrees. The material for the plates is a matter of choice. Brass was used in my own cell. Assuming that 1-inch diameter windows are to be used, the

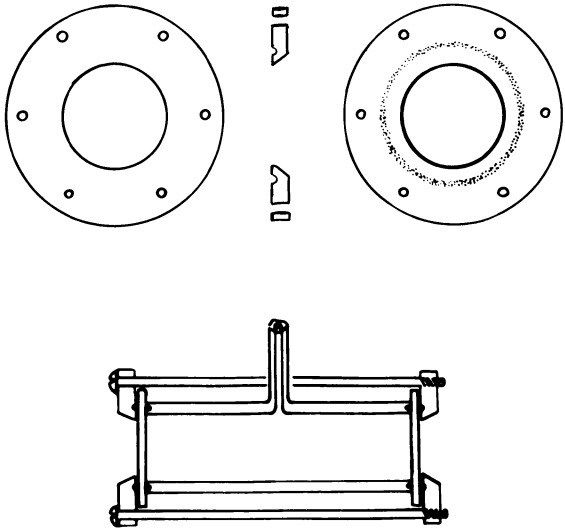

Figure 2

metal discs should be 2 inches in diameter, common sense being the guide where irregularly-shaped windows are to be used. Having prepared the plates thus far, 6 holes are drilled around a circle 1½ inches in diameter in one plate to pass a 10/32 screw. The other plate is similarly marked, but in this case the holes are drilled and tapped to accept a 10/32 screw. Nuts and bolts were tried, but it was found that successful assembly of the cell required three hands—by all means feel free to adopt this method if you have members of your staff who are suitably endowed. The final operation in the preparation of the plates is to machine an O-ring groove of the same dimensions as the one which has been made in the end of the barrel. This groove is located on the opposite side of the plate from the bevel. It has been found that using O-rings of the same material and dimensions produces a satisfactory pressure distribution when the cell is tightened up. See Figure 2.

When maximum pressures are to be used, a careful and thorough cleaning of the internal surfaces will contribute considerably to the strength factor. This matter is dealt with in detail by John Lees in the 11th Proceedings of the A.S.G.S. The system which I follow is immersion of the cell body in fresh chromic acid for 24 hours, followed by several washings with distilled water. Immediately prior to assembly, a 5-minute treatment with HF 10% solution, followed by further water washing and air drying, will complete the preparation of the cell. Optical windows do not enjoy swimming in HF; they should be cleaned with detergent followed by methanol.

Regarding the problem of sealing, there are two basic methods available: Capillary sealing or the use of a stopcock. In order to effect a satisfactory seal, it is necessary to condense the material if it be in gaseous form, or by an extension of this principle to provide for a reservoir so

that pressure may be exerted in the closed cell by vapor phase components of the material, or by the use of a ballast gas which does not itself participate in the reaction being studied. By virtue of the differential expansion between the glass and the metal screws holding the cell together, direct cooling of the unit is undesirable. The various methods outlined above are illustrated in Figure 3.

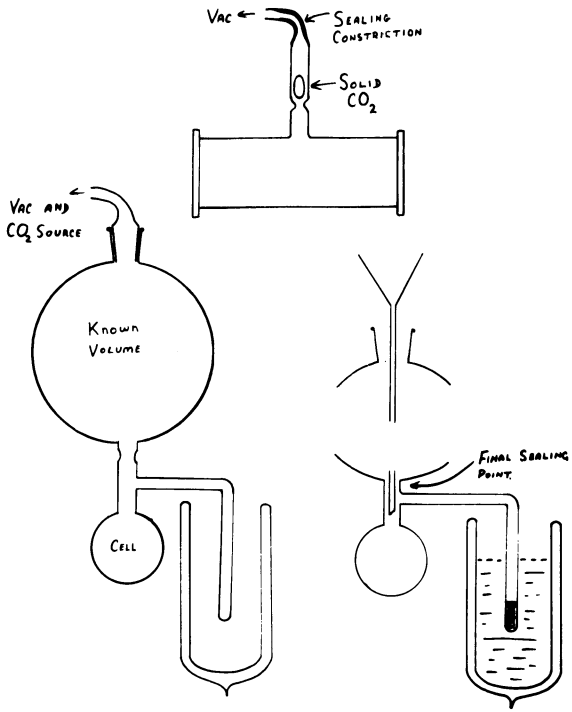

Figure 3

This cell has applications in the teaching field where it is desirable to show the absorption characteristics of various window materials without the expense of purchasing a number of complete cells.

I will now turn to the second part of this paper. From time to time students at Toronto and elsewhere have utilised in its simplest form the recording manometer, which I will now describe to you. My best efforts to trace the originator of the idea have failed. Nevertheless, whoever he or she may be, my thanks.

My research associate and I have been concerned with the feasibility of introducing comparatively advanced physical chemistry techniques into the practical curriculum of the second and third year bachelor courses. We have found that occasionally it is psychologically rewarding to the student to be confronted with difficult problems rather than to be

seemingly forever in a swamp of basic mediocrity for the entire scholastic year. I would hasten to point out that we do not propose a radical departure from the status quo, but a little variety is the spice of life. In our efforts to bring a little sunshine, we brought upon ourselves a problem, namely, the limited interpretive powers of the junior student coupled with a servo automatic biochemical condition which has become more pronounced in recent years due, no doubt, to social emancipation. I refer to the co-ed. Our forefathers were spared these stimuli to day-dreaming, etc. Unfortunately delightful though they may be, in circumstances demanding undivided attention they represent an independent variable for which there appears to be no mathematically calculable error constant. "If you can't beat them, join them." We have endeavored to do this by making the apparatus prepare its own experimental results, leaving the student to carry out the interpretation thereof in less provocative surroundings.

Kinetics is a subject dear to the physical chemist; the temperature/time functions provide interesting exercises not only in the somewhat complex equipment in which they are carried out, but also in the mathematics required to resolve them. In most cases, results are set out in graphic form based upon accurate readings obtained in a laboratory.

To quote from our most recent activity, we have utilised the technique of W. A. Guillory[1]—"Kinetics of the Gas Phase Decomposition of Di-Tert-Butyl Peroxide"—where the reaction is predominantly according to the stoichiometric equation:

$$(CH_3)_3C-OO-C(CH_3)_3 \rightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + C_2H_6$$

D.T.B.P. starts life as a liquid which is vapourised into a closed vessel. Subjected to time and temperature, it breaks down into 2 molecules of acetone and 1 molecule of ethylene, or, in other words, where there was one there are now three. Avogardos Hypothesis tells us that as the volume of the vessel has remained constant, the effect must manifest itself as a threefold increase in pressure.

In the experimental process, the D.T.B.P. vapour in a nitrogen carrier is introduced into an evacuated vessel at constant temperature 170°C., and the decomposition progress measured as a pressure rise during a time period. A 760 mm. mercury manometer works fine, provided you keep looking at it. Coupled with the existing manometer, we have introduced the device illustrated in Figure 4. This simple device was constructed based on general information, it being our intention to pass a small current through the carrier wire, variations in the height of the mercury column altering the voltage drop across the carrier wire. This information is fed to an analog computer programed to the characteristics of the reaction. Investigation is still going on, and the results will be published in due course.

Constructed as illustrated above, the device lacked sensitivity due to the small resistance of the wire. To increase the overall resistivity, it was decided to construct a spiral. The problem was how to support this spiral, which must be at least 76 cms. long, to cover the full pressure

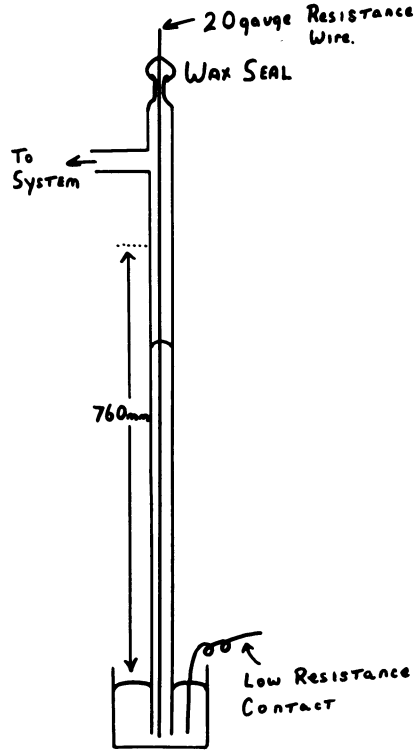

Figure 4

range. The turns must be equally spaced and must remain so if the instrument is to be serviceable. Any support material must be non-conducting. Regularity of spacing requires a machine-cut thread, thus rendering glass unsuitable. A hard polyvinyl chloride rod 4 mms. in diameter was selected and threaded with a machine die having 32 turns to the inch; the resulting thread was rough and in some sections irregular, due to the nature of the P.V.C. Nevertheless, when wound with 40-gauge resistance wire over a length of 76 cms., a total resistance of 600 ohms was registered. There are two ways by which this physical quantity may be measured: At constant voltage, the changes in resistance are recorded by a bridge or ohmmeter, or, alternatively and more satisfactorily, the voltage drop across the resistance is measured on a recording voltmeter. The curve generated on the chart of this instrument represents the graph of the reaction.

So much for the crude beginnings. Further studies of the spiral support resulted in the following technique: Heating the wire while at the same time winding it onto the P.V.C. rod causes the wire to embed itself part way in the rod. Speed of winding and temperature will determine the depth of penetration. Ideally, the wire should be bedded in for half its thickness. The method by which this is achieved is shown in Figure 5.

A length of P.V.C. rod is mounted in a screw-cutting lathe set to cut 30 to 40 turns to the inch. In place of the cutting tool the device I have illustrated is mounted on the tool carriage. The two brass tubes serve to stabilise the rather flexible rod. A few turns of wire are put on to provide the electrical contact with the brass spring loaded pad which serves to complete the electrical circuit to the energising battery or variable transformer. The other part of the circuit is the feeder arm which guides the wire from the spool and at the same time applies tension to it. At a given rate of feed, the penetration of the wire into the P.V.C. is adjusted by means of a rheostat. Practice will determine the amount of current required to produce a satisfactory bedding of the wire. When the winding is finished, time should be allowed for the work to cool down, after which the whole length should be rubbed with emery paper to clean oxides, etc., from the exposed surface of the wire.

In order to have a flat surface on the mercury, the spiral should be mounted in a 20 mm. O.D. tube. If small tubes are used, the meniscus effect of the mercury causes it to climb irregularly, thus making variable contacts with the spiral which result in errors.

The use of large cross-section manometers may give rise to problems where the total volume of the system is critical, or where one or more of the reaction products are condensible at room temperature, since these products will condense in the manometer, thereby removing themselves from the vapour phase of the system so that they will no longer be measured. There is no complete answer to this problem, but best results are achieved when the dead volume of the system is kept to a minimum and the components are heated. This is usually impractical except as a means of barbequing students. A compromise is being studied which seems to satisfy the demands of physics in that the dead volume has been reduced from 200 ccs. to 3 ccs. The body of the manometer is a capillary tube 2.5 mms. bore with a straight resistance made out of Woolaston wire, which is platinum wire 0.0005 inches in diameter made by a special process named after the inventor. This wire is kept under tension by means of a short tungsten spring made from 0.002 inch wire located in the base of the tube. (Figure 6) The cross-section of the wire is so small that it has very little effect on the mercury meniscus. I must confess that making this unit is troublesome unless you like joining a spring too small to handle to a wire that is almost invisible to see.

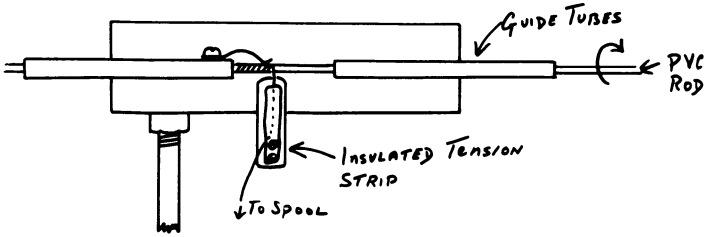

Figure 5

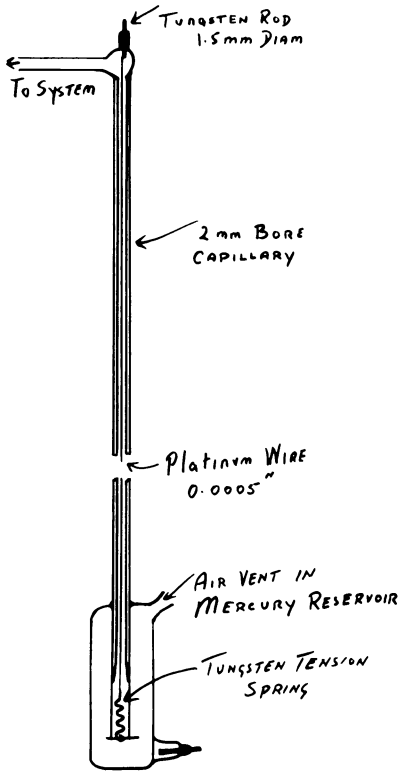

Figure 6

There is still a considerable amount of work to be done before the full potential of this system can be determined, but I will not bore this assembly with the technicalities which I have in mind since they are far removed from the field of glassblowing.

In conclusion, I would like to thank Dr. Leon M. Dorfman of Ohio State University for his interest and support in the development of the absorption cell. I would also like to express the thanks of myself and my colleague, K. Bondrup Nielson, to the University of Toronto for the funds and facilities to study the recording manometer.

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1. William A. Guillory, *Journal of Chemical Education,* Vol. 44, #9, p. 514, 1967.

THE EFFECT OF TRACE WATER CONTENT ON THE WORKING PROPERTIES OF GLASS

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ABSTRACT

This discussion shows that the effect of traces of water in silicate glasses and in fused silica is most pronounced on the annealing and strain points. The glass blower, therefore, must be aware of the water content of the glass in order to properly anneal his wares in an oven. The effect of water on the working temperature is trivial for all practical purposes.

INTRODUCTION

Almost all commercial glasses, including fused silica, which are used in the fabrication of glass apparatus for various applications contain traces of water. The water content may vary from almost nil to about 0.05 percent by weight. The water content depends on the glass manufacturing process, that is, whether the glass is manufactured in an electric or gas heated furnace; and on the type of raw material used in the glass production. In an electric melting process, where the raw materials are nearly anhydrous, and there is no water produced as a product of the chemical reaction, the glass will be practically free of water. On the other hand, a gas-furnace melting process always results in glass containing about 0.03% water.

INFRARED ABSORPTION SPECTRA

The water in the glass is present in a chemically combined state in the form of Si-OH, and as free -OH radicals. Therefore, the presence and the concentration of water in the glass may be readily determined from the infrared spectrum. The free -OH is manifested by an absorption band at around 2.9μ, while the Si-OH shows up as an absorption at about 3.5μ. Scholze[1] and coworkers[2] have made extensive studies on the relationship of water content to various glass properties. These studies showed that the most suitable index for estimating the water content in a silicate glass is the 2.9μ infrared absorption. Scholze[1] obtained a "practical" extinction coefficient of 41 ϑ/mole-cm. for H_2O. This value is an average obtained from the measurement of many silicate glasses, and is accurate to within 20% for predicting the water content. Figure 1 shows an example of the infrared spectra, obtained by us, of a soda-lime silicate glass of composition shown in Table I containing different amounts of water. Only the wavelength region from 2.5 to 4μ is shown since this is the region in which the -OH absorption is most characteristic.

Fused silica is also known to contain combined water in varying amounts. In this material, the infrared absorption is more clearly resolved

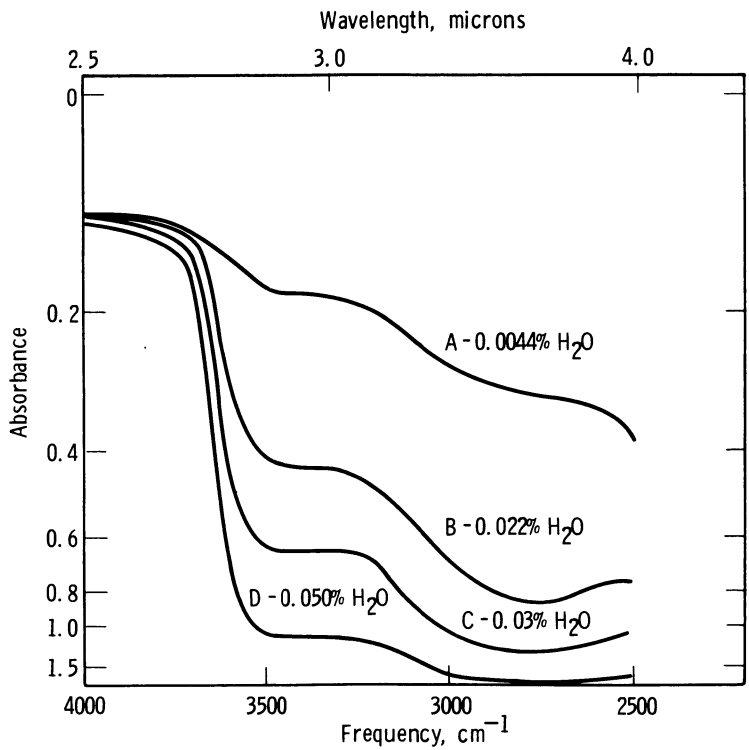

Figure 1
Infrared spectra of soda-lime silicate glass containing H_2O.
Thickness of sample: A, B — 0.126, C — 0.123, D — 0.119 inch

than in the glasses, such as the soda-lime silicate. Figure 2 shows the infrared absorption spectrum of "Spectrosil-B," as reproduced from the paper of Dodd and Fraser.[3] These authors determined the -OH content in this material and have assigned a molar extinction coefficient to each

TABLE I

COMPOSITION OF SODA-LIME SILICATE GLASS

	wt. %
SiO_2	69.8
Al_2O_3	0.53
CaO	7.98
K_2O	0.06
Na_2O	20.61
SO_3	0.14
Sb_2O_3	0.89

band shown in Figure 2. This type of infrared spectrum for fused silica is typical, and the band at 2.7μ, with extinction coefficient of 78 ϑ/mole-cm. for -OH, is a very convenient index for the estimation of the water in fused silica. As shown by Hetherington, Jack, and Kennedy,[4] the water content in fused silica may also be used as a qualitative tool to indicate the process by which the fused silica was prepared.

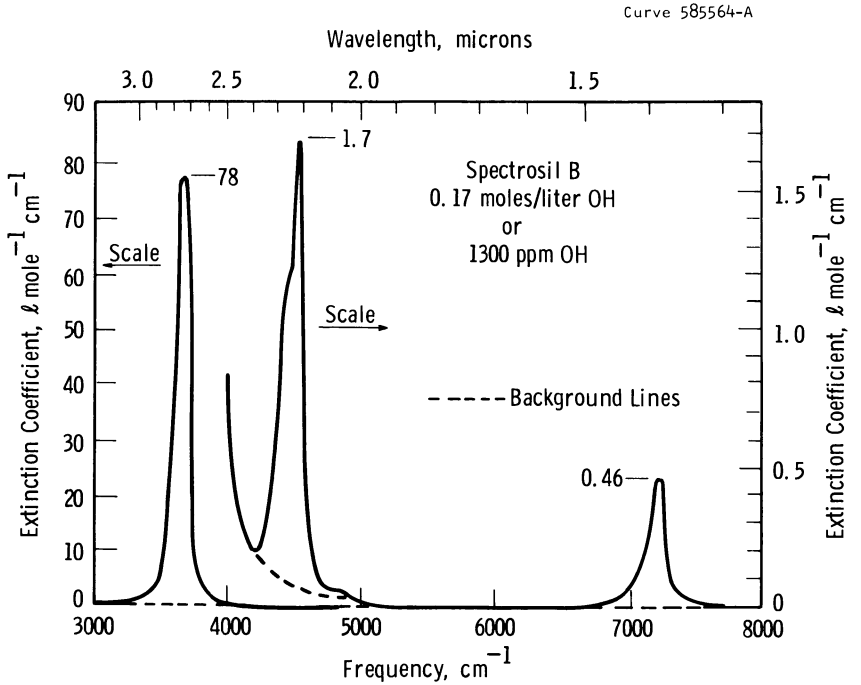

Figure 2
Infrared spectrum of spectrosil B. (After Dodd and Fraser)

RELATIONSHIP OF VISCOSITY TO WATER CONTENT

It has been known[5] since 1926 that small amounts of water in commercial soda-lime silicate glasses will affect the viscosity to a measurable degree. However, it has not been until the last twenty years that definitive work has been reported to show the real effect of water on the glass viscosity. Almost all of the studies reported to date have been concerned with measuring the effect of water on the viscosity in the glass transition region; *i.e.*, in the range of viscosity of 10^4 to $10^{14.5}$ poises. Usually, the Littleton softening point, the annealing point, and the strain point are determined as a function of water content in the glass. The viscosities corresponding to these respective points are $10^{7.6}$, 10^{13}, and $10^{14.5}$ poises. Another viscosity point of interest to the glass blower is the working point, which corresponds to the temperature at which the viscosity is 10^4 poises.

Graff and Badger[6] reported a somewhat qualitative effect which

showed that the water in glass lowered the softening, annealing, and strain point temperatures of a commercial soda-lime glass. These workers found no change in the viscosity at 2500°F., at which temperature the glass viscosity was presumably 100 poises.

The most comprehensive reports of the effect of water on the viscosities of silicate glasses are those of Merker and Scholze[7] and of Poole.[8] The latter showed that the softening point temperature of a flint and an amber glass will be lowered by 17°C. when the water content is

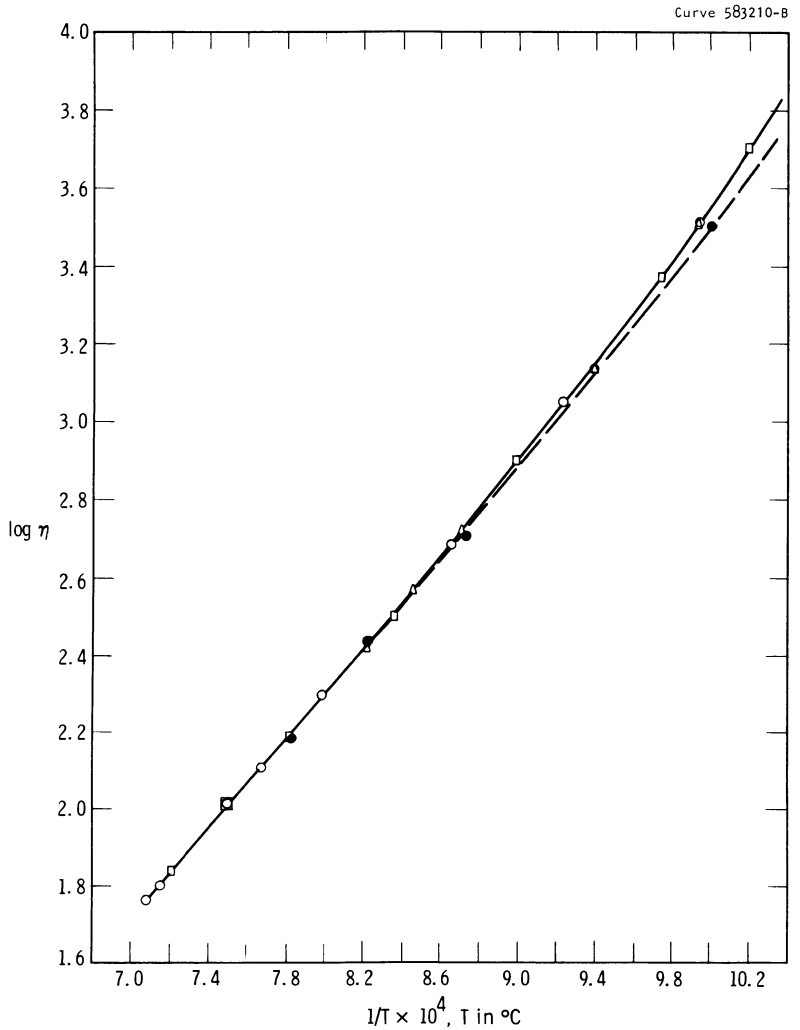

Figure 3

Log viscosity vs. reciprocal temperature for glasses containing:
□ — 0.0044%, O — 0.031%, Δ — 0.022%, ● — 0.050% H_2O

increased from an original value of 0.005% to a wet glass containing 0.03%. Merker and Scholze measured the temperatures for viscosities of $10^{7.6}$ and 10^{13} poises for a soda-lime silicate containing 0.004% and 0.11% water. These authors showed that the difference in the annealing point was about 40°C. lower, and that for the softening point was about 20°C. lower for the glass containing 0.11% H_2O.

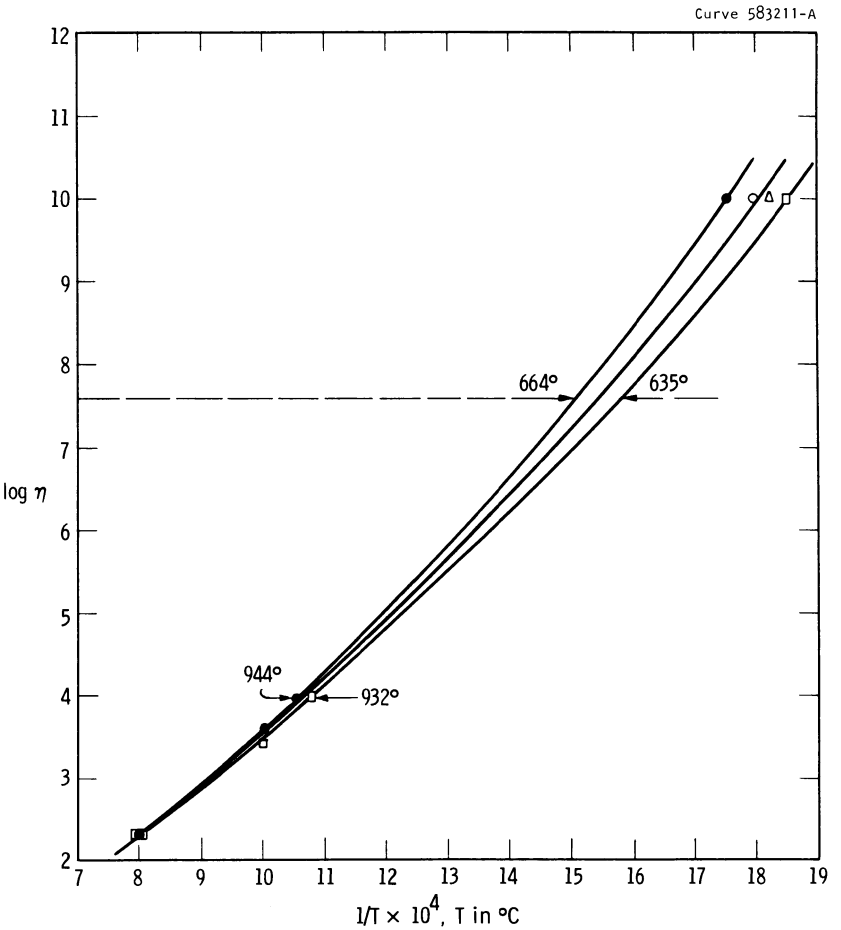

Figure 4

Log viscosity vs. reciprocal temperature.

□ — 0.050%, △ — 0.022%, O — 0.031%, ● — 0.0044% H_2O

In our work, the viscosity of the glass of Table I was measured (by Tiede's method,[9] after calibration with glasses from the National Bureau of Standards) as a function of water content at the low viscosity range of log η less than 4. Here, η is the viscosity in poises. The different water contents in the molten glass were obtained by equilibrating the melt with

an atmosphere of nitrogen and water vapor at different partial pressures of the latter. The measurements were reproducible to log η values of ± 0.02. The water content was estimated from the infrared absorption intensity (see Figure 1) at 2.9μ, and by using Scholze's extinction coefficient of 41 ϑ/mole-cm. Figure 3 shows the viscosity of the glasses as a function of temperature in the form of a Fulcher plot. The "dry glass" refers to the glass which was remelted at a reduced pressure of 9 torr for 4 hours at 1400°C. The "wet glass" refers to the original kilogram batch of glass which was prepared from sodium and calcium carbonate and silicic acid. The glass was fused in a kyanite crucible at 1375°C. for a period of 3 days with continuous stirring. As shown in Figure 3, the viscosity of the glasses was the same at log η below 2.6. At higher viscosities, however, the curves begin to diverge. We carefully determined the sag point[9] temperature on fibers of identical dimensions drawn from each glass shown in Figure 3. This temperature corresponds to a log η of about 10. The latter value was arbitrarily selected, and the curves of Figure 3 were extrapolated to the sag point temperature as shown in Figure 4. The water content of each glass is also shown in the latter Figure. The decrease in viscosity with water content shows similar trends as those reported by others.[7,8]

TABLE II

SOFTENING, ANNEALING, AND STRAIN POINTS, IN °C., OF FUSED SILICA

	I.R. Vitreosil	*O.G. Vitreosil*	*Spectrosil*
OH content, wt. %	0.0003	0.04	0.12
Softening point	1583	1596	1594
Annealing point	1190	1108	1082
Strain point	1108	1015	987

Hetherington, Jack and Kennedy[4] have measured the viscosities of various types of fused silica, manufactured by British Thermal Syndicate, over a wide temperature range. These authors obtained the softening, annealing and strain points shown in Table II. The -OH content for each material is also shown. As seen in the table, the effect of traces of hydroxyl (and water) in the fused silica decreases the annealing and strain points very significantly.

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The following are on record as having attended the Thirteenth Symposium on the Art of Glassblowing held at the Statler Hilton Hotel, Detroit, Michigan, June 12, 13, 14, 1968. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

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