Proceedings

THE FOURTEENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1969

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

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THE FOURTEENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

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HERMETIC AND VACUUM SEALS FOR DIFFICULT ENVIRONMENTS

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Whenever a permanent joint between a metal and an insulator is needed, thoughts usually turn to a glass-metal combination and logically so, since glass-to-metal seals are usually the undisputed choice from ease of fabrication, versatility, permanence, economy, or almost any other aspect for which one can conceive. That this generalization is true has been adequately proven by the billions of glass-to-metal seals used in electric lamps, radio tubes, and a myriad of hermetically sealed containers housing capacitors, transformers, relays, switches, and solid-state devices, to name a few. With such a wide variety of glasses from which to choose, it is almost inconceivable that some form of a glass seal possessing the desired property to fulfill any requirement cannot be found.

Nevertheless, scientific progress has succeeded in uncovering various applications for hermetic seals that cannot be successfully met with glass or fabricated by the customary techniques of melting or fusing glass to a metal. What is usually requested is an extension of a particular property beyond practical or physical limits to meet some mechanical, chemical, optical or electrical end usage.

The mechanical demands on seals are often tied to temperature constraints. Many seals for high temperature environments can be met with ceramic compositions, either the pure oxides or compounds, such as alumina, beryllia, silicates, borides, nitrides or cermets. If the requirement is for high strength at high temperature, alumina is satisfactory. If high thermal conductivity is needed, beryllia is in a class by itself. For low thermal conductivity or low thermal expansion, fused silica is indicated. For high thermal expansion, magnesia may be the answer. Ceramic compositions that can be readily joined to pyrex-type glass by fusion include zircon compositions. Thus, in choosing an insulator for these high-temperature applications, the overall environment must be examined in detail, and the best compromise between insulator, sealing techniques, and structural metals must be selected.

Silver-based brazing alloys are to be avoided for high-temperature environments, i.e., above 500°C because of the transparency of silver to oxygen. Palladium-cobalt alloys have proven to be useful for temperatures up to 1000°C. Structural metals to withstand these high temperatures are the main limiting item.

In the area of seals resistant to adverse chemical environments, the alkali metals such as sodium, potassium, lithium, cesium, or solutions of the hydroxides of these elements present a formidable challenge. Nuclear and aerospace energy sources often utilize these caustic elements. Sapphire

or high purity alumina ceramics are resistant to these materials, but a new problem is encountered — that of joining sapphire to metal. The usual brazing alloys and metalizing compositions are also attacked by these alkaline elements. One alternative is to attach a resistant sealing metal directly to the ceramic by means of minute amounts of an active element to serve as a wetting agent. Figure 1 is a photograph of a group

Figure 1

of feedthrough seals that have proven resistant to corrosive environments. The insulator is pure alumina, and the structural metal is pure nickel.

There is no fixed rule to be followed in specifying a seal to survive vicious chemical environments. The many possible chemical reactions that can take place almost automatically limit the choice of sealing materials and components. From this limited choice, it becomes a matter of judgement as to which joining system and technique will most economically meet the requirements of reliability, life, ease of manufacture, and survival under various other environments, such as temperature extremes or nuclear radiation.

Optical requirements that cannot be met with classical glass compositions generally fall into two classes: high temperature and extended spectral transparency. If the environmental temperature is beyond the useful range of glass, possible substitutes are the transparent oxides of silica, alumina, magnesia, yttria, thoria, or more complex compounds such as silicates, fluorides, zirconates, etc.

Silicon dioxide can exist in either the crystalline form, or as a supercooled liquid known as fused silica or more commonly "quartz glass". Fused silica has an almost zero thermal coefficient of expansion, and this property gives it a very high resistance to thermal shock. Among its other

unique properties are its very low dielectric loss, low thermal conductivity, and high transparency to ultraviolet radiation (Figure 4). It is thermally stable to about 1000°C, and has found extensive use in radiant healing elements.

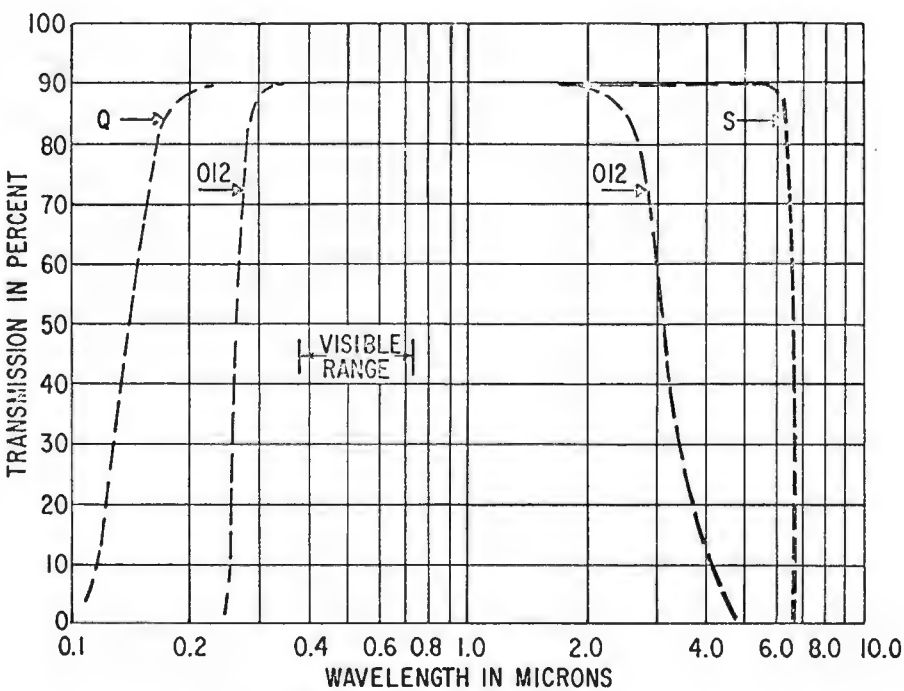
You are probably all well acquainted with the sealing problems encountered in joining a metal to a low expansion, high melting point material such as quartz glass. Thin ribbons of molybdenum or tungsten can be successfully sealed to quartz, and such seals are used in ultraviolet lamps or other lamp applications. It is not practical to make massive seals to optical surfaces of fused quartz by the ribbon techniques. Other fabrication methods have been developed for specific requirements.

Quartz can be joined to a low yield point metal such as silver or gold by brazing techniques. In these seals, the quartz is strong enough to plastically deform the sealing metal under temperature excursions. Pure gold is completely malleable and does not work harden. Pure silver re-anneals at temperatures as low as 300°C, and stress relief occurs automatically. Figure 2 illustrates various quartz assemblies made by brazing techniques.

Figure 2

When high temperature operation is not a requirement, quartz can be joined to a low expansion alloy, such as invar, by low temperature soldering techniques. Invar has low expansion properties up to 200°C. Between 200°C and 300°C, it undergoes a rapid change in expansion properties. Thus, if invar is soldered to quartz with an alloy having a melting point below 300°C, low stress seals can be made. Figure 3 is a

Figure 3



Q = QUARTZ GLASS
S = SAPPHIRE
012 = DUMET SEALING GLASS

Figure 4
Spectral Transmission

photograph of large diameter quartz windows fabricated by soldering. These are used in vacuum apparatus employed in plasma studies requiring U.V. transmission properties.

For optical applications at long wavelengths or infra-red spectra, synthetic sapphire is used extensively. Figure 4 is illustrative of the transmission characteristics of sapphire. Lenses made from sapphire are used in many infrared detectors and guidance systems in heat seeking missiles.

Sapphire is a true crystal, and has different properties along the different crystal axes. For optical applications, it is customary to cut lenses or windows with symmetry along the "C" axis. This automatically gives equal expansion coefficients in the X and Y axes, and simplifies the sealing problems. The coefficient of expansion in a plane perpendicular to the C axis is 7.7×10^{-6} at 500°C.

There are metals, structural ceramics, and glasses that approach the thermal expansion to which sapphire can be hermetically sealed with active alloy brazes, with various glasses, or with glass solders such as Corning's Pyroceram.

High purity translucent alumina ceramics are finding uses as envelopes in the high intensity arc lamps because of their resistance to sodium vapor. At first glance, these alumina tubes appear to be rather opaque. This deceptive appearance is caused by the dispersion of a light beam, since each of the minute randomly oriented crystals acts as tiny lens. The actual overall transmission is about 90% for sections ½ mm in thickness. These high efficiency light sources are finding applications in street and stadium lights, and in illumination of golf courses for night playing.

For most electrical uses, glass has proven to be an adequate insulator. It is again that only when glass is subjected to extreme environments, such as high energy concentrations at microwave frequencies, high temperature, or combinations of both, that glass is unuseable.

The electrical resistance of glass falls rapidly as it is heated. For most glass compositions, the conductivity doubles for each 15° to 30°C increase in temperature. The joule heating resulting from electric currents flowing through the glass is an additional heat source tending to make the seal run still hotter, with accompanying increased conductivity. Thus, an unstable or run-away situation is generated, and the glass melts. If the voltage across the seal is not high enough to cause melting of the glass, it may cause electrolysis, and the bond between the glass and the metal is slowly destroyed, leading to ultimate failure.

High power microwave generators are vacuum tubes, such as klystrons or magnetrons. The microwave energy must be brought outside the envelope through some vacuum barrier or window. No dielectric material is completely transparent to electrical energy, and the energy that is absorbed by the window appears as heat. The window is a vacuum barrier usually placed inside a waveguide section or a coaxial line, and is inaccessible for surface cooling. All the generated heat must be removed by edge cooling.

The actual heat generated in watts in a dielectric can be calculated from the relation

$$P = .550\ (10^{-12})\ f\ \frac{A}{D}\ E^2\ K\ \tan\ \delta$$

where f = frequency in cycles per second; A = the area in cm^2; D = thickness, in centimeters; E = electric field in volts per centimeter; K = dielectric constant, and δ is the angle formed by the resistive component of current divided by the capacitive or charging component. If A and D are chosen as unity, then "P" is power in watts per cc absorbed by the dielectric.

In choosing a window material and window design to transmit the ultimate power, one is faced with an intriguing and challenging set of values. It is desirable to keep the adsorbed energy as low as possible; hence, a dielectric with the lowest loss factor is indicated. Second, since the heat is removed only from the edge, a dielectric with high thermal conductivity is desirable. Third, since the center of the window will be at a higher temperature than the edge, a low thermal expansion material is advantageous. Fourth, a high strength material is indicated to resist fracture from stresses set up by temperature gradients; and fifth, the window should have high dielectric strength to resist insulation failure and puncture from the high electric fields existing inside the waveguide.

ALUMINA	DIELECTRIC CONSTANT	TAN δ AT 10 GC	THERMAL COEFFICIENT OF LINEAR EXPANSION X 10^{-6} 0 X 0 500°C	THERMAL CONDUCTIVITY CAL/SEC/CM^2/°C	STRENGTH TRANSVERSE
Coors AD94	8.9	.001	7.7	.043	51,000
Coors AD995	9.7	.0001	8.5	.065	46,000
G.E. Lucalox	9.7	.000025	7.9	.065	40,000
G.E. 923	9.28	.00067	7.8	.064	55,000
G.E. AT100	9.98	.000007 (at 10^7 Hz)	7.8	.065	40,000
Wesgo AL300	9.53	.00077	8.5	.064	46,000
Wesgo 99.5	9.58	.00009	8.5	.070	62,000
Sapphire ⊥ to C Axis	8.6	<.0002	7.7	.065	(60 to 100) X 10^3
Beryllia (Coors BD-98)	6.5	.00056	9.44 (0 to 1000°C)	0.45	36,400
Quartz Glass	3.75	.00005	0.55	.0033	7,000 (Tensile)

Figure 5

Figure 5 is a table of the properties of some of the candidate materials for microwave windows. At first glance, it would appear that quartz glass is the outstanding choice due to its low dielectric constant, its low expansion, and its low loss factor. However, quartz has low thermal conductivity, and the heat generated, even if it is low, cannot be rapidly conducted away by rim cooling. In actual test, at a frequency of 10 gigahertz, quartz windows in an X-band waveguide melted at an average power level of about 75 kilowatts — a value that agrees well with calculated performance.

Low loss alumina, because of its superior mechanical properties, will transmit power up to about 600 kilowatts before fracture occurs. Beryllia with a higher loss factor, but due to its high thermal conductivity, is capable of transmitting equally high power densities. As was shown in the expression for power loss in a dielectric, the total heat generated is a function of the volume. However, making the window very thin does not help, because all cooling must occur at the edge. If the window is made half as thick, heat generated will be half, and the edge area will be half, so that nothing is gained. Making the window thick has some advantages. If the window is exactly half wavelength thick, the internal power reflected from the front and back surfaces of the window is 180° out of phase with the transmitted wave.

These reflected waves tend to cancel each other, resulting in the situation where the power at the center of the window is actually lower than at the surfaces; thus, the power lost per unit volume in a massive $\frac{\lambda}{2}$ window is less than in that of a thin window.

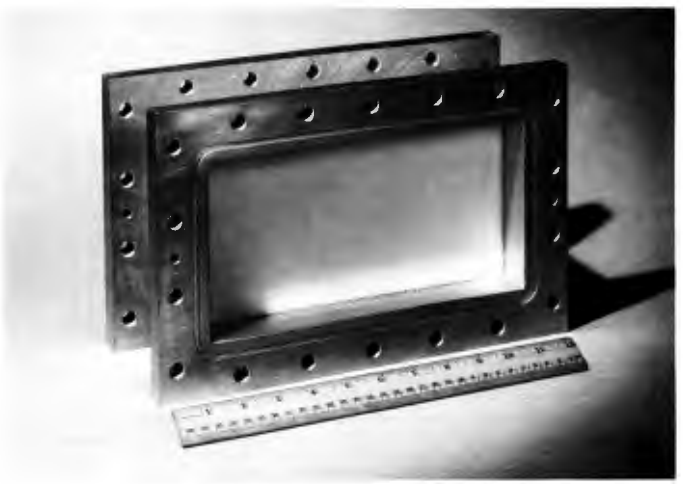


Figure 6

Figure 6 is such an approach to a window designed for a frequency of 805 megahertz at power concentrations up to 1,000 kilowatts. The resonant alumina block is roughly 10 inches long, 5 inches high and 2½ inches thick. The complete window, with flanges, weighs about fifty pounds.

The above examples are illustrative of a few approaches to seals for tough environments. Every seal design must fulfill some set of conditions imposed by the end usage. In choosing the materials and sealing system to meet any new and difficult demand, one must, above all else, have a thorough knowledge of the physical properties and limitations of all the components involved before a satisfactory piece of equipment can be procured.

DEVELOPMENT OF CORNING SAFETY WINDSHIELD

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INTRODUCTION

Documented field studies of actual automobile crashes show the windshield ranking third behind the steering column and the instrument panel in producing injuries.

It is the leading cause of injuries to the head.

The windshield is a laminated construction of two pieces of annealed glass firmly bonded by a plastic interlayer. Injuries occur when the occupant's head hits and breaks the glass, exposing sharp edges.

Prior to 1966, the plastic interlayer was .015" thick. It was often penetrated and the occupant's face or scalp contacted stiff, sharp edges with sufficient force to cause severe, disfiguring lacerations. In 1966 the thickness of the plastic interlayer was increased to .030". The result was a marked decrease in the number of penetrations, and the frequency of deep facial lacerations was correspondingly reduced. Although the number of interlayer ruptures are less, the injuries sustained are still bloody, painful and disfiguring.

A new type of windshield has been developed by Corning Glass Works called "The Corning Safety Windshield", and it will be available on a limited number of 1970 model automobiles. Its feature is that it eliminates lacerations while not compromising any good feature of today's windshield.

BODY

The safety windshield inner pane is .070" thick, slightly more than half as thick as the inner pane of a conventional windshield. It is strengthened by chemical tempering, making it sufficiently strong to bend to a small radius without fracture.

The plastic interlayer is the same .030" polyvinyl butyral used in present windshields. The outer pane is .105" annealed glass. The complete windshield is 30% lighter than the conventional.

The new windshield has proved its performance in full-scale impact tests performed by the Biomechanics Department of Wayne State University in Detroit. Anthropomorphic dummies were hurled at windshields mounted in full-size car bodies (Figure 1). The results showed a dramatic improvement in resistance to penetration, concussion and, in particular, laceration.

Such testing is expensive and time-consuming, so for the early stages of this development a faster and more economical approach was desired. A skull impact machine was built with which 2' x 3' windshield modules were impacted the same as a real occupant would hit a real windshield in an accident.

The skull impact machine consists of a test bench on which is mounted a vehicle supporting a dummy head (Figure 2). The vehicle travels horizontally along the bench, guided by steel rails. The head is mounted on a neck extension which pivots forward in a 9″ radius from a point on the carriage. The carriage is propelled forward by action of rubber shock cords fastened to its forward side. The carriage is initially

Figure 1
Car body test arrangement at Wayne State University

Figure 2
Skull Impact Machine

held fast at the end of the bench by a pin connection while tension is put in the cords by stretching them. When the pin is released the cart proceeds along the bench toward where the windshield module is mounted. The vehicle is stopped abruptly by impact with hydraulic shock absorbers. The neck pivots forward with the head striking the glass module (Figure 3).

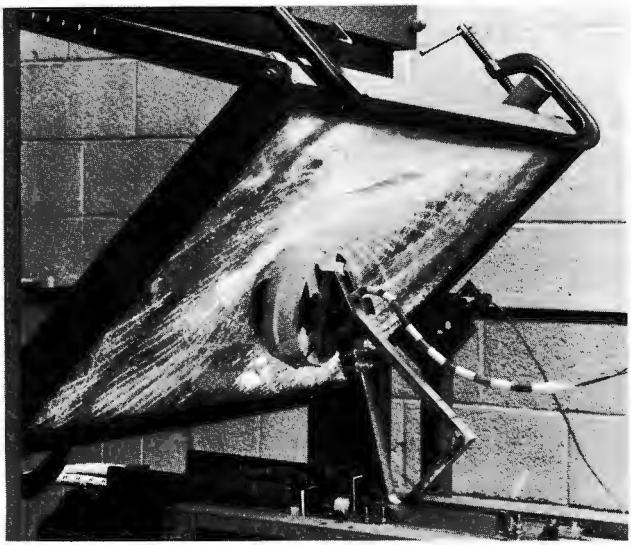

Figure 3
Skull Form against Impacted Module

The dummy head is covered with chamois to simulate human skin. The laceration potential of a windshield construction can be determined by observing the condition of the chamois after test.

Accelerometers are mounted in the dummy head to record the forces the head experiences upon impact.

Head-to-glass speed can be reliably predicted by measuring the amount of stretch in the cords.

Test results from the impact machine correspond faithfully with those of the full-scale test. The machine has been extremely useful for the following purposes:

1.) Screening out glass and plastic compositions to find the best one.
2.) Evaluating performance under conditions not easily available with full-size testing.
3.) Finding the effect of variables that would not be apparent in a limited number of full-size tests.
(The impact machine has a rigidly controlled trajectory and the effect of a change in a test sample is not obscured by variations in the action of the dummy.)

The improved laceration performance of the safety windshield is due chiefly to the strength and the thickness of its inner pane. It develops a high bending stress before breaking under the impact of a head. In this condition there is sufficiently high strain energy in the glass released at the moment of fracture so that the resulting break pattern in the area of impact is entirely blunt tiny fragments. These fragments have dull edges and very little cutting potential. This is due to the surface compression induced by the chemical strengthening, which causes the sharp corners of broken fragments to spall off, in conrast to the large sharp-edged particles of unstrengthened glass.

Laceration potential of various glasses is difficult to measure objectively and results reported here are necessarily based on judgment and photographs. An arbitrary rating scale of chamois damage has been prepared to report results, 10 being the most severe and 0 being virtually no damage (Figure 4).

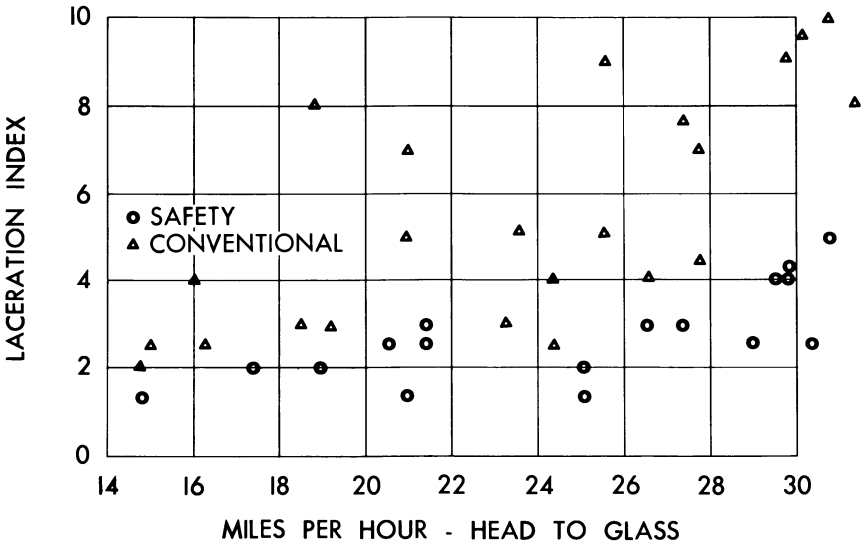

Figure 4
Laceration Results

Note the safety windshield had no laceration above degree 3 (minor) until head-to-glass speed reached 29½ mph where it went to 4 (moderate). In contrast, conventional windshields begin to cut heavily at 19 mph and began to cause very serious damage at 26 mph (Figure 5).

The safety windshield resists tearing and penetration to a greater degree because its blunt fragments have less tendency to initiate tears; they also allow the interlayer to stretch more easily because they are so small.

Experience with conventional windshields has not shown that they present danger from concussions. Any new construction, regardless of

how well it reduces lacerations, must of course avoid increasing concussive forces.

The accelerometers mounted in the dummy head sense g forces that can be read as a function of time on an oscilloscope screen. The term "Severity Index" represents a number derived from integrating the area under the curve as a function of time. It has been found from laboratory tests that S.I. of 1,000 represents danger to life.

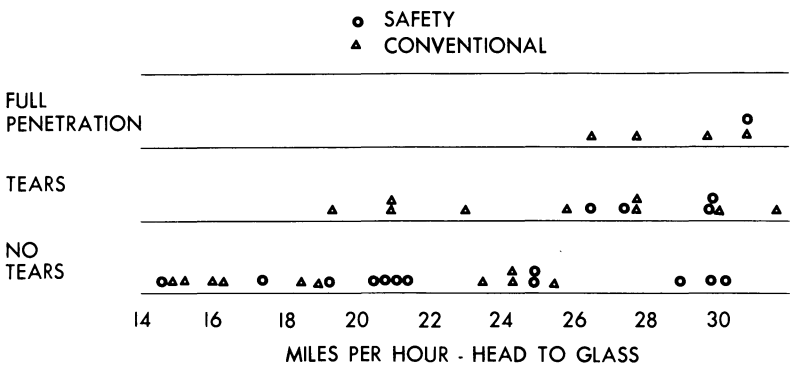

Figure 5
Tearing and Penetration Results

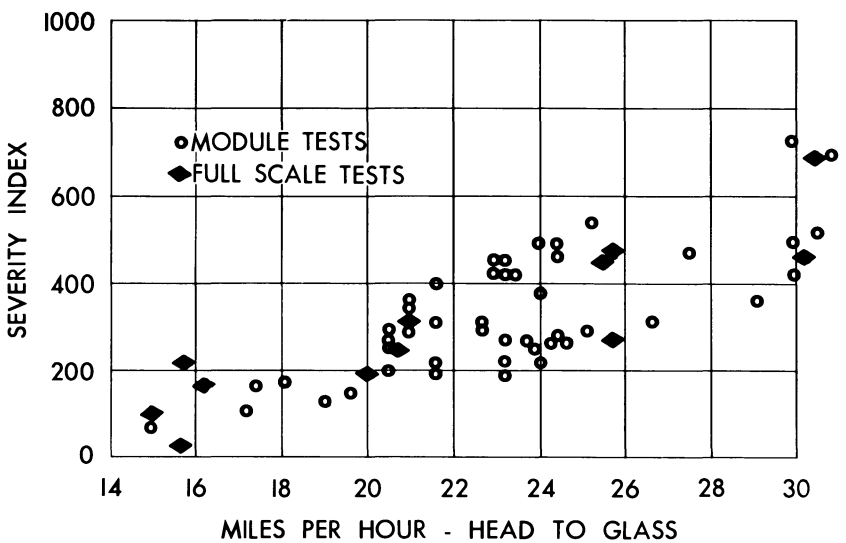

Figure 6
Severity Indexes, 2' x 3' module tests compared with full-size tests at Wayne State University

The data plotted in Figure 6 shows S.I. values on CGW windshield modules and those found on full-size windshield tests with dummies at Wayne State.

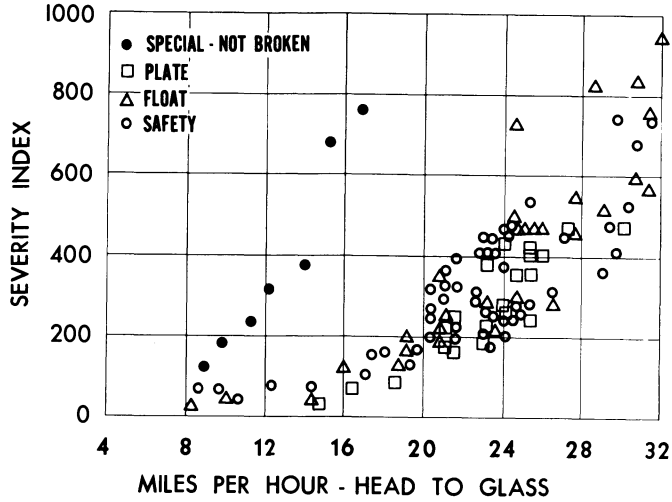

Figure 7
Severity Index—CGW and conventional glass

The plot of test values, Figure 7, indicates no increase of S.I. values with the new windshield over those found with conventional glass.

CONCLUSIONS

A new safety windshield construction has been developed that reduces lacerations and limits concussive forces to acceptable levels.

A small skull impact machine has been designed and built to explore windshield performance. Results on a 2′ x 3′ modules correspond closely with full-scale tests.

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SOLID STATE DEVICES FOR THE GLASSBLOWER

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ABSTRACT

The first portion of this paper will briefly give background information on the simplified theory covering operation of solid state devices and their operating parameters. Several of these devices as well as handling and mounting techniques will be discussed and illustrated by the author. Various types of heat sinks will also be illustrated for the higher power units.

The author plans to conclude the presentation by illustrating ways in which these units may be used to control electrical currents associated with scientific glassblowing such as by (1) reducing heater power input by 50% using a diode, (2) using a common dimmer switch for variable power control, (3) using a diode bridge circuit for a d.c. power source and (4) replacing a mechanical relay with its solid state equivalent.

INTRODUCTION

The scientific glassblower today has many solid state devices that can be used in conjunction with the equipment he designs and constructs. It is intended that this discussion will encourage the glassblower to use these devices as the opportunity permits. Just knowing how these devices work in general, will be all that is required on the part of the glassblower. The theory, for the most part, will be left to the electronic technician and engineer. Since there are so many different types of solid state devices, I will limit my discussion to the common diode and common transistor.

GENERAL DESCRIPTION

When the term "solid state" is used it is synonymous with the word transistorized; however, it is also used to imply that the most recent innovations in electronics are being used. Solid state devices are an outgrowth of the development of the transistor. When vacuum tubes were replaced with transistors the unit was said to be transistorized. The time came when everything became transistorized and while this was happening the technology developed which now allows the transistor manufacturer to build the circuit in the same case with the transistor which is commonly known as an integrated circuit. This development will make it possible in the near future for non-electronic oriented persons to pick out a particular unit that will perform the task at hand and will not have to be concerned with why and how to design the circuit. While the electronic industry is currently working on these new developments, it might be beneficial to make use of some of the devices already available.

The common diode has just two terminals and may be thought of as an electron check valve. Figure 1a illustrates a cross-section of a check valve and Figure 1b illustrates the electronic symbol for a diode. Electrons

will pass through the diode in the forward direction, however, while in the reverse direction, very few electrons will leak backward. To illustrate

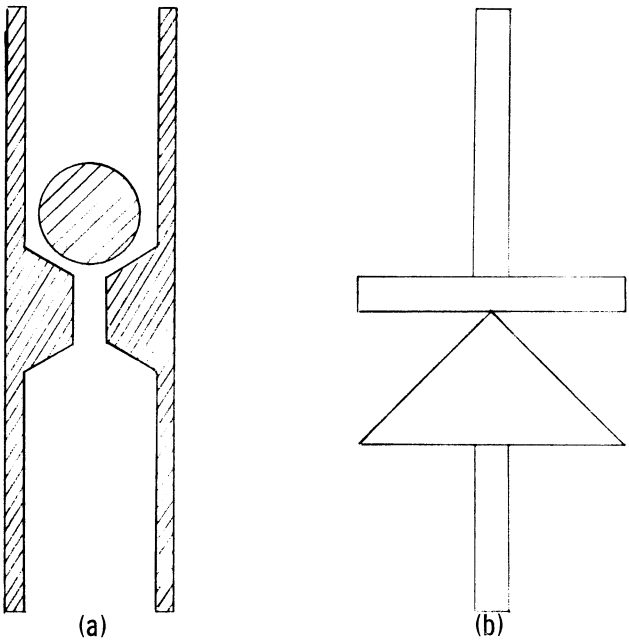

Figure 1a and 1b
Check Valve and Diode

this, a 6 volt battery, two diodes and two 6 volt bulbs are connected as shown in Figure 2. Bulb (a) is not lit because the diode will not pass electrons in this direction, or it may be referred to as being in the "off" position. Bulb (b) is lit indicating that electrons are going through the diode. It can be said that this diode is in the "on" position.

Rectifier circuits using diodes are common. It should be kept in mind that diodes have many other uses, and if you will think of them as electron check valves you will discover many of them for yourself.

The common transistor has three terminals, identified as an emitter, base and collector. It is similar to a triode vacuum tube, relay, or of other units capable of amplification or switching. In Figure 3 the transistor and its relay equivalent are compared. One side of the relay coil and one of the relay contact leads are connected together to represent the transistor emitter terminal. Passing a current through terminals 1 and 2 on both the transistor and its relay equivalent will permit the current to flow from terminals 1 and 3. Another minor difference between the two to be noted is that the transistor has an arrow as part of its symbol. This indicates in which direction the current is intended to flow. The transistor will control current in only one direction while the relay coil or contacts are not polarity sensitive.

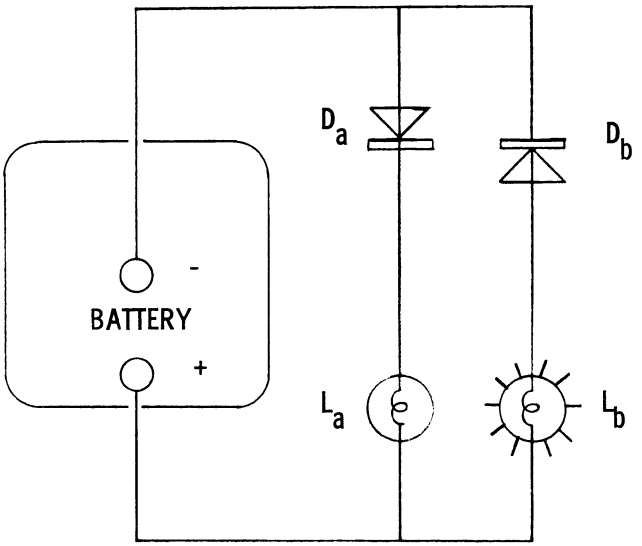

Figure 2
Diodes in On and Off Positions

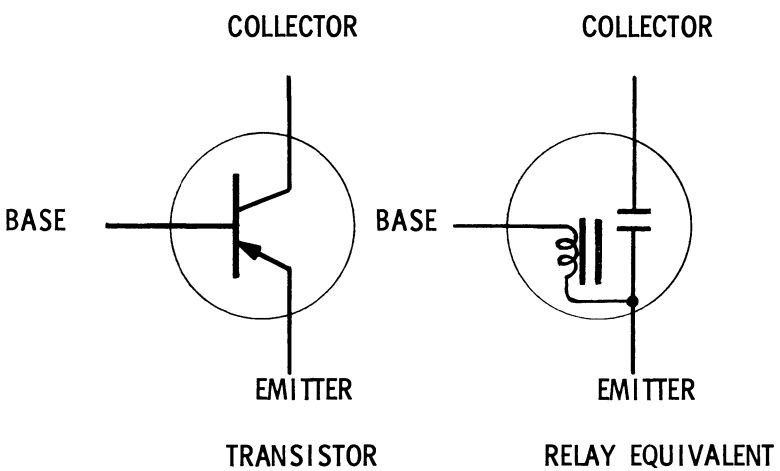

Figure 3
Transistor-Relay Comparison

Transistors are available in a variety of electrical ratings and intended usage. It may be used as an on-off type device much like a very sensitive relay without any moving parts. As can be seen in Figure 4, bulb (a) is lit while bulb (b) is not. It is necessary for bulb (b) to be in the circuit if we expect bulb (a) to light. To confirm this, bulb (c) has been

disconnected as illustrated in Figure 4; however, note that bulb (d) is not lit. It can be concluded from this that the current passing through bulb (b) is not sufficient to light it but enough to operate the transistor which in turn will turn on and light bulb (a). In order to accomplish this, the current going through bulb (b) was amplified to a level sufficient to light bulb (a).

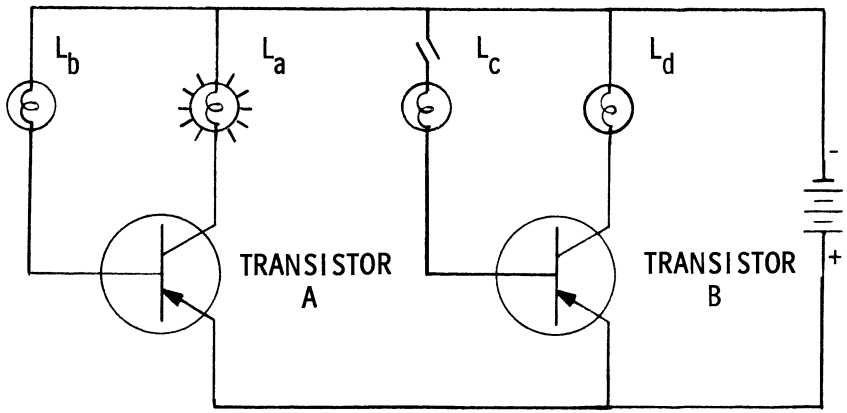

Figure 4
Transistor in Operation

Diodes and transistors have maximum operating limits that must not be exceeded. Furthermore, permanent damage may result when these conditions are exceeded, the most common cause of which is heat. Small diodes and transistors dissipate this heat by conduction to the surrounding air and through the lead terminals to cooler surroundings. When soldering transistors and diodes of this type, heat from the soldering iron must not be allowed to reach the unit. This may be done by using a pair of pliers to hold the lead wire while soldering or, an alligator clip can be attached to the lead wire before it is soldered, then removed after the soldered connection cools. As the power ratings increase, more elaborate methods of cooling are required such as cooling fins or heat sinks. Many of the higher power rated diodes and transistors are designed to be mounted on the metal box used to contain the other components used in the circuit. The objective of any type of mounting is to transfer the heat being generated in the transistor or diode to an area where it cannot cause any problems.

Diodes are rated in both maximum voltage and maximum current. To determine the minimum ratings a diode must have, take the operating voltage of the circuit and increase this value by 75% to 100%. The same should be done with the current rating. Ratings obtained in this manner will give a nominal safety factor. Generally speaking, diodes can be used at their maximum rating but the cost of one with the next higher rating is comparatively small thus making it worthwhile to obtain the higher rating.

Transistor ratings are extremely varied making it difficult to pick out one that will work the best in a given circuit. Major manufacturers of transistors have aided the novice and the experimenter with a series of selected transistors. These transistors are made for general replacement and for experimental purposes. They are categorized by intended usage rather than electrical characteristics, making it simpler to pick out a suitable unit. Audio power type transistors are adequate for most direct current and switching applications that glassblowers may encounter. Booklets describing the series carried by your local electronic parts dealer may be found very informative.

Several transistors operating in unison can do some very interesting things; however, this is beyond the scope of this discussion. For anyone who is interested, a list of references is given at the conclusion of this paper.

USES AND POSSIBLE APPLICATIONS

The following four examples are used to illustrate just a few applications for diodes and transistor circuits. Typical electrical values which might be used are also described.

EXAMPLE I — *To reduce the heat being generated in a heating element of 50 watts at 115 volts a.c. to approximately one-half by using a diode.*

Using the previously described method of determining diode ratings, we will use a diode rated at 250 volts at .75 amperes. When this diode is placed in series with the incoming power, it restricts the current flow to one direction thus reducing the average current flow by one-half. Figure 5 illustrates how the circuit could be constructed. When Sl is in the open position the power is reduced; when it is closed, full power is on. It is a

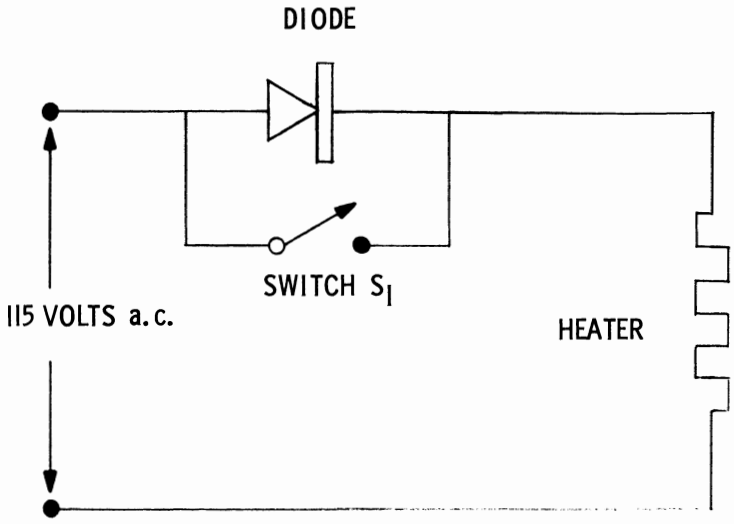

Figure 5
Diode in Series with Power Lead

common trick to use an in-line switch with the diode connected across the switch contacts as shown in Figure 6.

EXAMPLE II — *A Six Volt d.c. Power Supply*

An alternating current may be converted to direct current by using four diodes in a rectifier circuit. Let us suppose we need a 6 volt direct current power source at one ampere. Refer to the circuit shown in Figure 7. Tl steps down the 115 volt line to 6 volts with at least a one ampere rating.

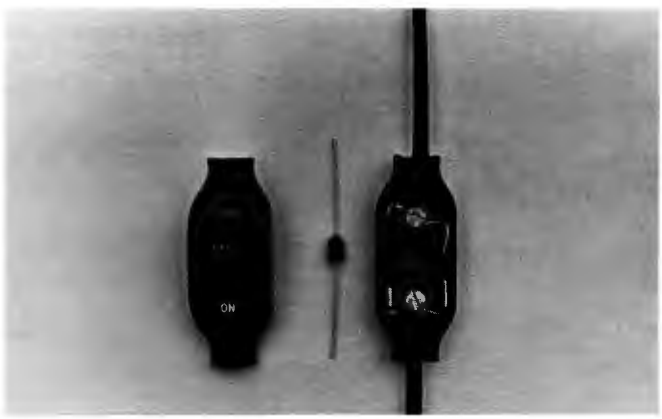

Figure 6
Diode Mounted in Line Switch

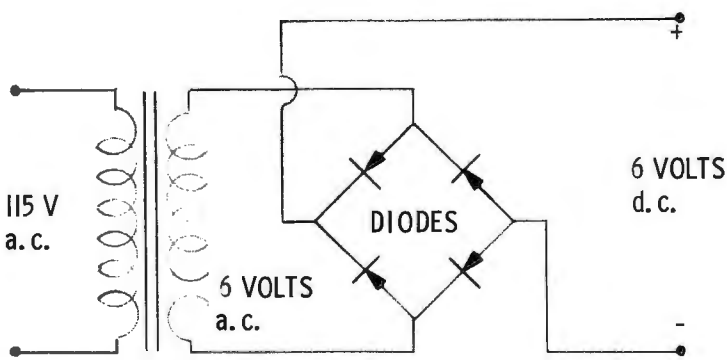

Figure 7
Six volt d.c. Supply

Using the method of diode selection suggested in Example I was found to be more than adequate. The voltage supplied by this circuit will be pulsating d.c., and will have a pulse frequency twice the input frequency. Caution must be used, however, to insure that the diodes are connected in the proper direction.

EXAMPLE III — *Using a Dimmer Switch in Place of a Variable Transformer*

Dimmer switch units sold at the local hardware and electrical supply stores are specially designed diodes. The electrical circuits which make them operate are completely assembled and ready for use. There are many areas where they may be used. For instance, a small diffusion pump contained a heater rated at 300 watts at 115 volts supplied by the manufacturer. It was decided it would be more advantageous for a particular application to operate at a lower power rating. One common method to accomplish this would be to install a variable transformer to provide this function. However, the alternative that was used was to replace the on - off switch on the diffusion pump with a dimmer switch. (Most dimmer switches have at least a 600 watt rating.) This now provides zero to full heater power and turns the pump on and off. This required no additional space and cost less than the variable transformer. Furthermore, it took just a few minutes to install. Figure 8 shows a comparison between the dimmer switch and a variable transformer.

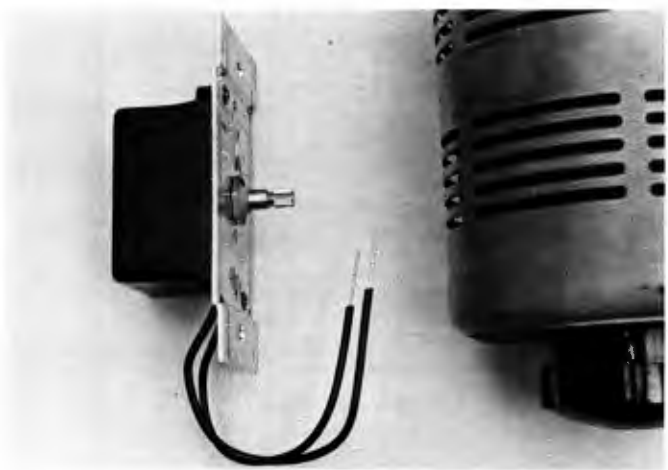

Figure 8
Dimmer Switch Compared to Variable Transformer

These dimmer switch units are very similar to those sold for variable speed control. When used for this purpose, they should not be used at much more than one-half of their electrical rating.

EXAMPLE IV — *Replacing a Relay with a Solid State Equivalent*

For the purpose of this example, we will assume that a mercury thermal regulator is to be used to control a constant temperature bath. Since a relay is a satisfactory switch for this application it will be used in this circuit. However, a transistor will be used to operate the relay, while the transistor will be operated by the mercury regulator. By doing this, the mercury regulator will be switching a small fraction of the power

required to operate the relay. This will allow a lower operating voltage and current at the regulator contacts.

A relay that happened to be on hand had a 6 volt coil and operated at .3 amperes. A general purpose medium power transistor can easily handle the power required by the relay for operation. Since it usually does not involve much additional expense, a transistor with more than ample current and voltage rating was used. The transistor used was rated at 90 watts with either 30 volts or 5 amperes maximum ratings. The circuit shown in Figure 9 was used. Resistor Rl is adjusted to turn on the relay when the regulator switch is closed. Once turned on the relay will stay on until the current through the regulator switch is reduced. Rl is adjusted to the minimum current setting that will produce dependable relay operation. Resistor Rl was made adjustable so that transistors with different electrical characteristics could be substituted by simply adjusting the resistor. In addition, this same circuit could be used to operate a solenoid valve instead of the relay coil.

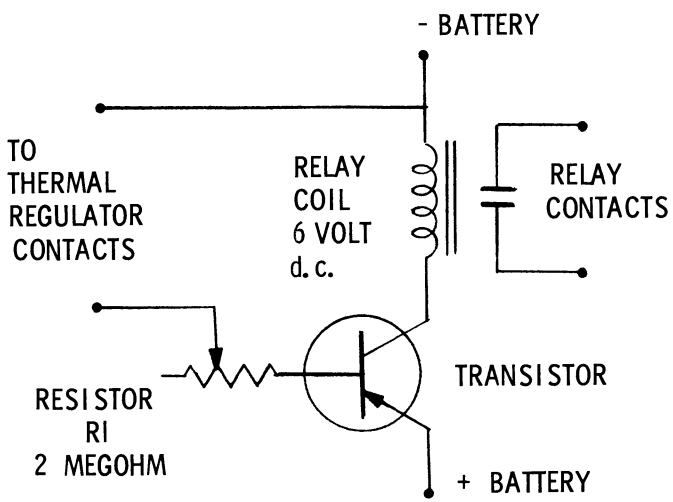

Figure 9
Transistor Operated Relay

CONCLUSION

It is sincerely hoped that the preceding information will stimulate interest in making use of solid state devices in conjunction with scientific glassblowing. For a more thorough study and for special applications the list of references may be consulted.

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PROGRESSIVE ADAPTATION IN PHYSICAL CHEMISTRY TEACHING

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This paper is in the form of a Triplet, that is to say, three distinct items are discussed, their common bond being their application to the broad concept of teaching Physical Chemistry. Basically the principals are well established, being the work of several authors. Some items have been in use for decades in spite of the fact that in some cases they suffer from drawbacks no longer acceptable when one considers the flood of new materials which have appeared on the market during the Sixties. Furthermore, quite apart from the material standpoint the complexity of the units sometimes give rise to the problem that the student has to be overly concerned with making his equipment work rather than being able to use it to learn the scientific principal — the basic reason for his laboratory work. This is a waste of everybody's time.

The subjects covered are:

Liquid/Vapour Equilibria, Ebullometry, and a Material Injector for Gas Phase Kinetic Studies.

These subjects are discussed from the point of view of the Glassblower since he will be the 'Joe' who will have to make them.

SUBJECT A.

MODIFICATIONS TO OTHMERS VAPOUR LIQUID EQUILIBRIUM STILL.

The Othmer Still[1] is utilised for the study of two component systems at boiling point in order to provide data for the study of Raoults Law and the Phase Rule. This apparatus in its commercial form, and a simplified version of it formerly in use at the Lash Miller Chemical Laboratories are shown in Fig. 1. and Fig. 2, respectively.

The simplified version made itself known to me because of the frequency with which it appeared in the Shop for repair, from the remarks which accompanied it the student body had no place for it in their hearts.

After a study of the working procedure it became clear that the main cause of trouble lay in the method used to apply heat. A 250 watt heating mantle is placed somewhat more than angularly against the base of the flask, a situation caused by the boiler drain tube. Not only is this awkward, it also produces a most undesirable thermal distribution, the mixture, being made up of various proportions of Acetone and Chloroform has an uncooperative attitude to poor heating technique, a situation which I will now try to make clear to you.

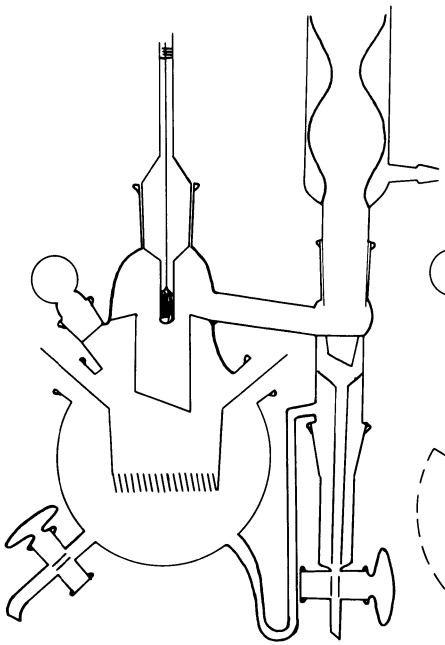

Figure 1

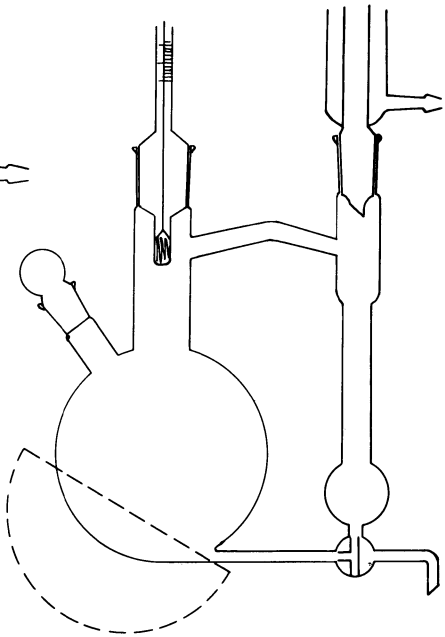

Figure 2

To start things off, 250 ml of Acetone is poured into the flask and the heating mantle is turned on, so far so good. When the boiling point is reached, there is a 50/50 chance that the Acetone will erupt — releasing its pent up emotions by emerging through the top of the condenser. If the operator happens to be holding any part of the equipment when this happens, he usually forgets to let go before heading for the hills.

The cause of this trouble is the neglect of a fundamental law of physics. In the absence of nucleii, most fluids will absorb more kinetic energy than is required to promote boiling, as more heat is put in an unstable situation, known as super-heating, occurs. The trouble is that when boiling does occur, the excess heat is gotten rid of very rapidly, vaporization takes place throughout the whole mass and this vapour mechanically transports the liquid with it. If there is an inadequate exit, it will be enlarged.***

Nucleii may be provided by the inclusion of rough surfaces or particles, i.e., porous pot. Unfortunately, these may be inadvertently left out if loose. Therefore, it seems logical to make them a permanent part of the boiler system.

In Othmers Still, use is made of a platinum heating spiral which provides Nucleii for smooth boiling, this is a satisfactory but expensive solution which can only be justified when the unit is to be used for special studies. It gets rough on the tax payer when this type of unit is required on mass for teaching purposes. Bearing these facts in mind, I set about redesigning the system to render it as free of trouble as possible. To begin

with, the heating mantle was replaced by an immersion heater sheathed in glass. This arrangement makes possible the replacement of a faulty heater without disturbance to the unit. At the same time, the sheath is constructed so as to provide ample nucleii. As illustrated in Fig 3, the heater is made by wrapping a glass tube 6 or 7 mm diameter with refractory felt[2] so that it will pass easily into the sheath which is constructed of 18 mm tube. A winding of resistance wire adjusted to give 40 watts at 30 volts is located so that the winding is toward one end of the felt, and the overall length is such that the felt will protrude one inch beyond the external portion of the sheath. In practice, it has been found convenient to have a dummy sheath available to form the shape of the felt so that it will fit into the coned exterior of the sheath. After winding and shaping the heater is dried in an oven to 350°C thereby hardening the refractory. One word of warning, the felt is supplied wet and any surplus must be stored wet.

The sheath shaped as in Fig. 3 is covered with a large number of projections located so as to envelope the wound part of the heater. These projections are 2 mms long and their extremities are rough ground by holding the sheath against the side of a thick wet cut wheel. The rough grind produces millions of nucleii which can't be poured down the sink.

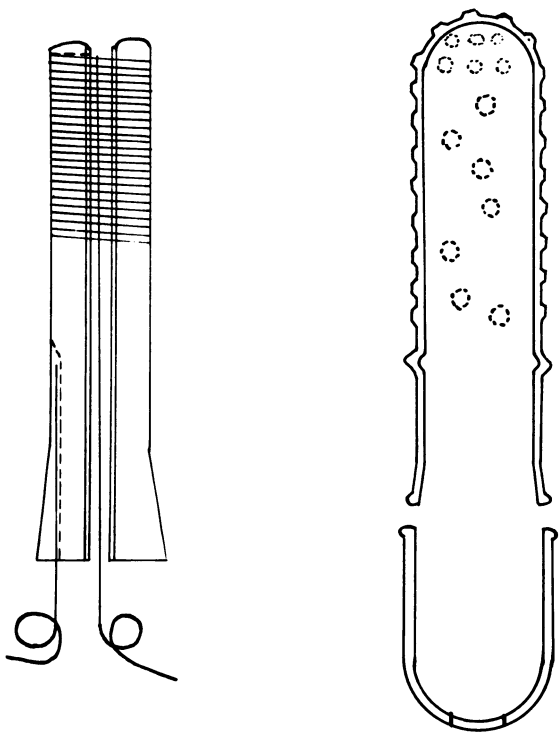

Figure 3

A significant safety factor is provided by the low voltage, and for that matter, the relatively low working temperature of the heater. As a further precaution, a rubber cap is placed over the external part of the heater with the thick lead wires passing through two pin holes in the end of the cap.

As can be seen in the illustration in Fig. 4, the main unit is no challenge to construct. Indentations in the neck act as splash barriers,

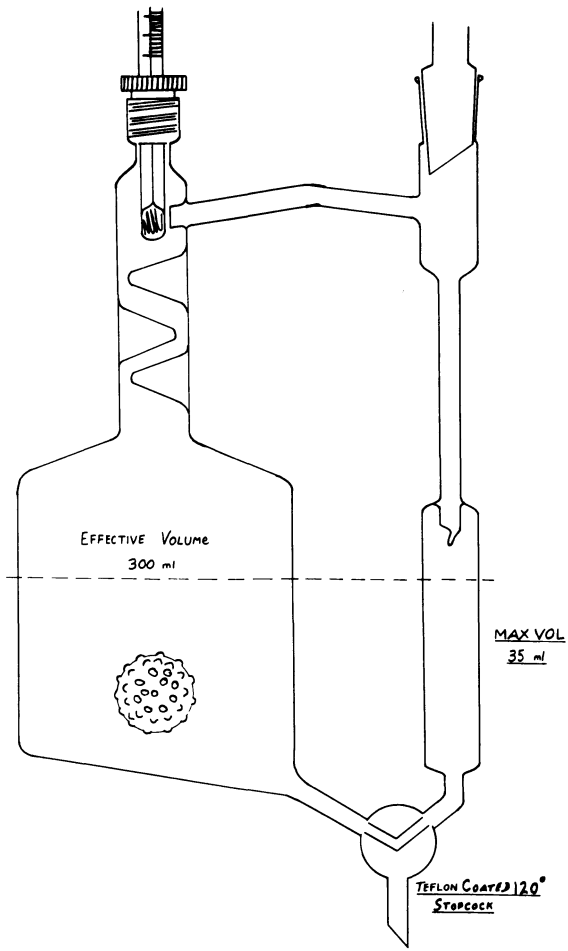

Figure 4

while the neck itself acts as a convenient clamping point. An inexpensive thermometer inserted through an adaptor[3] with a viton O-ring is adequate as part of the experiment is devoted to calibration of the thermometer. The single Teflon coated stopcock[4] 120° pattern is used in order to avoid

seizing which is the bugbear of solid teflon plugs when subjected to thermal differences. In this case, samples are drawn from the condensed material and directly from the boiler. A difference of 70°C.

The general sizes of the unit are based on the units in use at the Lash Miller Laboratories, it is of course, a simple matter to modify them to suit individual needs. Total space requirements of the units including electrical components are minimal being less than the width of an average operator (male).

Six of these units have been in use during a two year period during which time none have given any trouble, the modification may, therefore, be considered as satisfactory.

I would like to acknowledge the assistance of N. N. Holder, and D. Sproat in connection with this project.

Subject B.

EBULLOMETRY — OR IN PLAIN LANGUAGE — BOILING

Boiling points of fluids under controlled pressure conditions, directly or by correction, are used as standards. Pure water at 760 mms boils at 100°C. If the water contains other species its ebulomertic equilibrium will be either above or below the standard value. The reason why this takes place not only in water, but in almost all solvent media, is very complex. It is not my intention to bore you with matters outside of glass-blowers' interests, so let that be enough of it.

From the educational standpoint, ebolution studies are useful attributes to the study of molecular weights, etc. In instruments having thermometric detectors with a resolution of better than 1×10^{-6} degrees, the process becomes a valuable analytical tool.

In all cases, it is necessary to flood the detector with a stream of liquid and vapour in equilibrium. This business of using the mixture is important because of differences in the boiling point of the doped solvent and the vapour, i.e., muddy water would have one temperature but the steam that comes off would indicate that it is pure water.

What we need is a pump which is totally enclosed in the system and which utilizes the energy of the system for its operation. Sounds complicated, does it not? In fact, it's very simple. The design was thought out by Cottrell several years ago. The Cottrell Pump as it is known is illustrated in Fig. 5.

By applying heat to the bottom of the tube containing the pump, boiling is promoted, the vapour lifts doses of fluid and vapour up the tube, spilling them out so that they impinge on the walls of the thermometer, to be successful the boiling must be vigorous. If provision is made to condense the vapour and return the condensate to the boiler, the process becomes cyclic. An adaptation of this system in general use is shown in Fig. 6. It is immediately apparent that it is messy. Using the experience

gained with the heater described in the previous paper, and a little common sense, an attempt was made to clear up the mess. The result of this labor is illustrated in Fig. 7.

A small heater was prepared using the method already described, except that 25 watts at 30 volts was adequate and made possible a corresponding decrease in length. The glass insulating jacket had a signi-

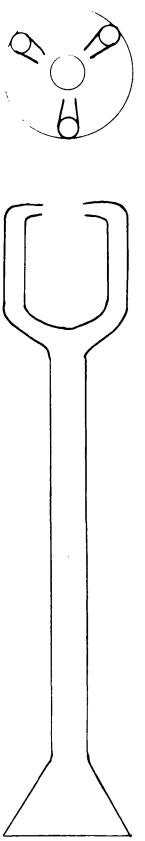

Figure 5

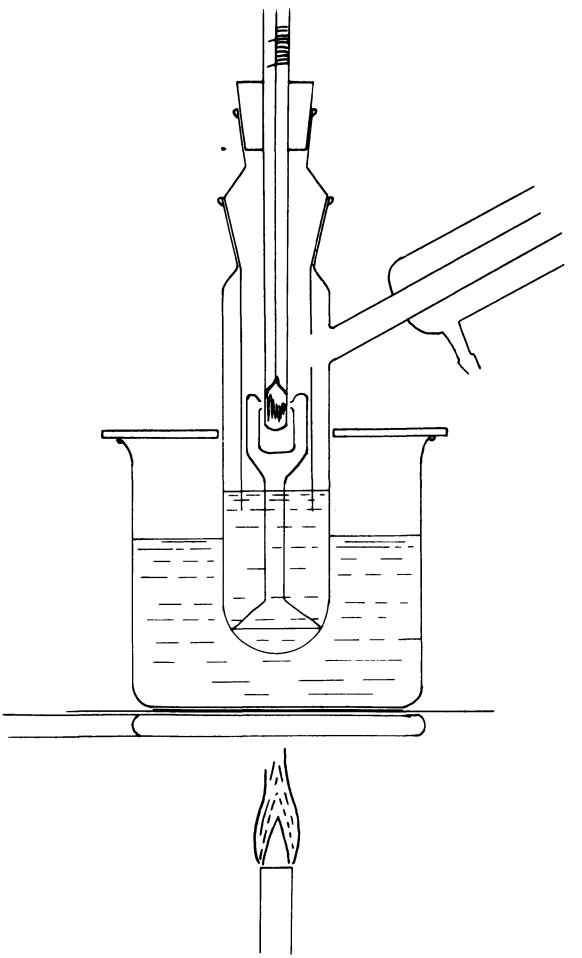

Figure 6

ficant effect in protecting the unit from draughts without interfering with a clear view of the interior. This jacket is sealed only at the top, the lower portion being tooled down to within 1 mm of the boiler tube, thus taking care of cracking caused by differential expansion. The interior

tube serves a dual purpose in that it guides the bulb of the Beckman thermometer so that the pump jets are preserved, and at the same time, reduces the possibility of cold condensate running down the bulb of the thermometer and causing errors. The provision of a standard taper joint on the top of the condenser permits the use of a drying tube in cases

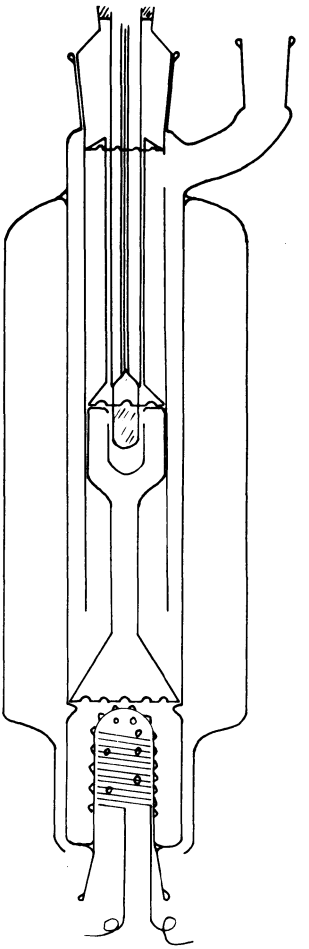

Figure 7

where hygroscopic fluids are being used. This is important as the absorption of atmospheric moisture would significantly effect the accuracy of the experiment.

Once again I would like to acknowledge the assistance of N. N. Holder.

SUBJECT C.

PRESSURE INJECTION OF LIQUID SAMPLES FOR KINETIC VAPOUR PHASE STUDIES

J. L. A. French and K. Bondrup Nielson

Utilisation of the procedures outlined by W. A. Guillroy[5] were mentioned in a previous publication.[6] In order to simplify the working procedure the modification referred to herein has been adopted.

Basically the study is the effect of heat on Di-Teriary-Butyl-Peroxide which is introduced into a reactor at 165°C in the presence of Nitrogen, the aim being to introduce sufficient D-T-B-P to achieve the vapour of the material at 20°C — 80 mms. At the same time sufficient N_2 must be

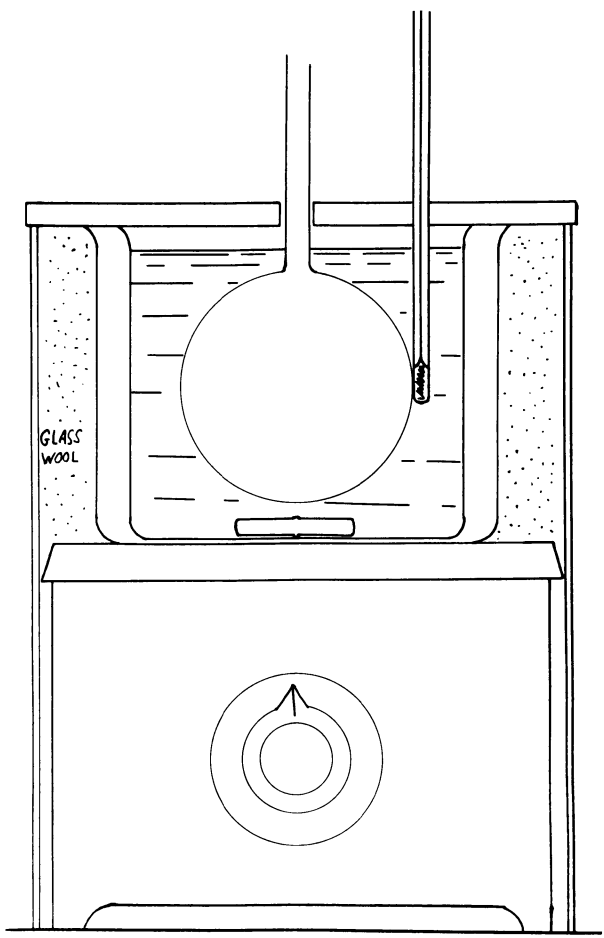

Figure 8

added so that the total pressure of the system at starting point is 400 mms. These reactions are based on time/temperature functions so that it is highly desirable to introduce the materials in the shortest possible time, otherwise it is difficult to decide when things got started. In order to clear away some of the fog, I will start by describing the reactor on which the whole thing is based. The unit is shown in Fig. 8.

It is necessary that the 1 liter flask be maintained at a temperature in the region 165°C with a variation over a three hour period of no more than 0.1°C. We have found the most practical way to do this is to contain the flask within two stainless steel beakers which in turn are supported on a hot plate equipped with a magnetic stirrer. The whole unit is boxed in with glass-wool insulation. Sufficient silicone to cover the flask is introduced into the inner beaker. A thermometer is positioned to read the average temperature.

In any system where pressure changes are measured and a large temperature difference exists, it is important that those parts of the system at room temperature be kept at minimum volume. A neglect of this requirement will cause gross errors to be introduced into the results.

Now to the solution of the problem. First, there is the question of the N_2 ballast gas, allowing 80 mms of pressure for the D-T-B-P, approximately 320 mms of N_2 is needed — dead easy, all that is required is a reservoir of N_2 with a capacity of twice the reactor, the slight excess in pressure being of no significance as confirmed by our studies. Now to the question of the liquid part, the problem is solved by the device shown in Fig. 9.

The construction of most of this unit is self-evident; therefore, I will concentrate only on the important points which are that the O-ring of the valve should be made of viton, and that the pressure exerted by the spring used to close the ball valve be adjusted so that it is minimal. Otherwise, the flushing action of the system will be hampered.

The operating technique is as follows:

The reactor is evacuated by a mechanical pump to a pressure of less than 10^{-1} mms, provision being made to trap vapours left over from a previous run. While this is going on, the ballast flask is filled with pure N_2 on a separate system so that the pressure is 800 mms. A predetermined volume of fluid, decided upon by its particular vapour, is pipetted into the reservoir of the injector.

A stopwatch is made ready and the tap on the N_2 flask is slowly opened. N_2 flows out of the flask via the injector reservoir, flushing out the air in the reservoir, and escaping through the ball valve. As the pressure in the ballast flask falls to normal, flow will cease, and the ball valve will close. At this point, open the valve of the injector rapidly. The fact that the reactor is evacuated and the ballast flask is full will result in the fluid being driven violently into the hot reactor. N_2 will continue to flow in mixing with the vapourising fluid until the pressure in the system has reached equilibrium, which will be approximately 400 mms. At the moment the valve is opened, the stopwatch is started; and, when there is a pause in the pressure rise in the reactor, the injector valve is closed, and a reading of the pressure taken, and the experiment is under way.

Total time for the introduction of the components is no more than 10 seconds, there are only two valves to play with; and, therefore, there are less spoiled runs.

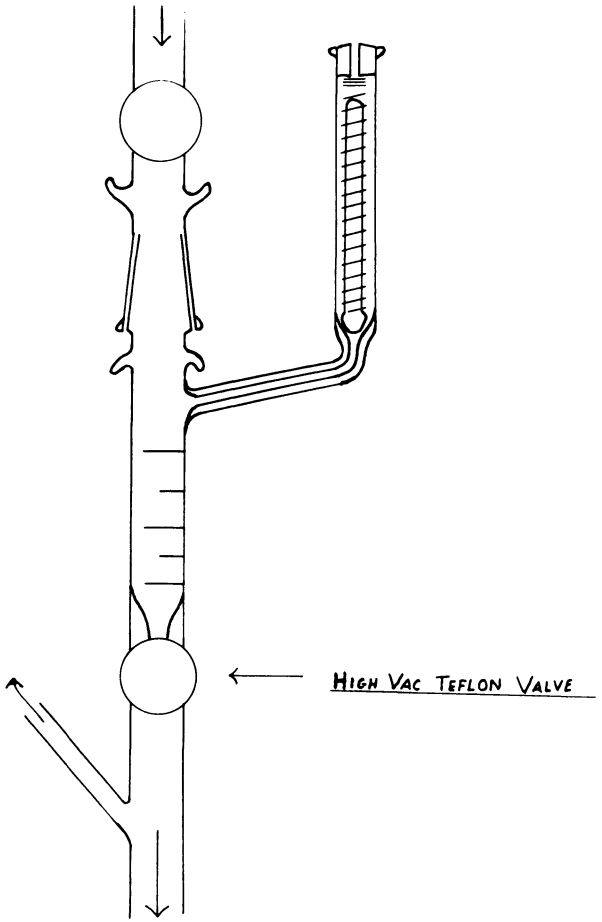

Figure 9

In conclusion, I hope that the foregoing material will illustrate how simple a matter it is to up date some of the antiquated monstrosities which clutter up many teaching labs to the torment of student and teacher alike.

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LOW EXPANSION CERAMICS FROM DEVITRIFIED GLASSES

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ABSTRACT

$Li_2O.Al_2O_3.SiO_2$ ceramics formed of mineral or synthetic petalite and spodumene have low expansion with some compositions showing negative expansion. Those compositions having essentially 0.0/°C coefficient of expansion in the range (5-35°C) have application as structural members of optical instruments and as surface plates, straight edges, gauge blocks and other devices requiring volume stability. Compositions of mineral base are known to yield product of suitably low expansion. Compositions based on devitrified glasses as starting materials for ceramic forming have given product of more consistent and desirable properties.

Typical properties of general interest are:

Coefficient of Thermal Expansion (5-35°C)	0.2 x 10^{-7}/°C
Modulus of Rupture	12,000 psi
Modulus of Elasticity	10 x 10^6 psi
Porosity (apparent)	less than 1%
Bulk Density	2.20 g/cc

INTRODUCTION

A great number of applications are known for ceramic materials capable of resisting rapid temperature changes. The properties that determine the ability of a ceramic to withstand rapid temperature change are thermal expansion, elasticity, strength, and thermal diffusivity. These properties are also of interest where dimensionally stable, rigid, and strong articles are desired such as surface plates, optical benches, parts of measuring devices, etc.

Our experience has shown that ceramic bodies with properties suited to thermal shock resistance and dimensional stability can be made from mixtures of natural or synthetic petalite and crystallized glasses. While the properties of these bodies are generally good, the chemical and mineralogical variation in the petalites have caused severe problems in applications such as optical tooling, surface plates, and similar items.

We have found that the use of crystallized glasses as starting raw material permits the manufacture of product with a thermal expansion coefficient in the room temperature range of 0.0 ± 1 x 10^{-7}/°C. We have arbitrarily assigned 5°-35°C as this temperature range. With extreme emphasis on compositions and process control, we can make product with a coefficient of thermal expansion (RT) from 1 to 5 x 10^{-8}/°C.

PROCESS

Ceramic articles with very low thermal expansion can be made from mineral petalite and lithia-aluminosilicate glass cullet starting materials. Any process that forms product from finely divided powders (essentially −325 Tyler mesh) can be used. Our product mix has been such that we prefer the slip-cast approach. The slips are prepared by wet ball milling. Sized mill feed and de-ionized water are charged to the ball mill. The water is about 20% of the dry weight of the mill feed. No binders or deflocculants are used. The slip is self-deflocculating. The green and dry castings have adequate strength for handling and some green machining.

The slips are cast into plaster of Paris molds. Solid-cast and drain-cast articles are made. Techniques common to ceramic casting are appropriate.

The green cast article is dried in standard drying ovens. This is usually accomplished on a 24-hour schedule but may be modified to suit the needs of the particular piece.

Firing is usually accomplished in a gas-fired kiln of conventional design. The schedule normally calls for a 24-hour heating to about 1250°C. This too, may require modification to meet individual piece demands.

For the most part, these ceramic articles formed from petalite and glass cullet have a coefficient of thermal expansion within the range $0.0 \pm 2 \times 10^{-7}/°C$ (5-35°C). It has not been, however, practically possible to consistently manufacture product with a coefficient of thermal expansion of $0.0 \pm 1 \times 10^{-7}/°C$ (5-35°C).

We have found that we can consistently make product with coefficient of thermal expansion $0.0 \pm 1 \times 10^{-7}/°C$ (5-35°C) when our starting materials are all glass cullet. The properties reported here were obtained with cullets having compositions listed in Table 2.

LITERATURE

Three naturally occurring minerals in the Li_2O-Al_2O_3-SiO_2 system are eucryptite, spodumene, and petalite. Eucryptite exhibits a negative expansion and has been reported[1] to have an expansion coefficient of $-90 \times 10^{-7}/°C$ from 25° to 650°C. Spodumene and petalite in both the natural and synthetic mineral states are reported to have very low expansion coefficients.

Hummel[2] determined the thermal expansion of samples of naturally occurring spodumene and petalite that had been fired to different temperatures. With spodumene, he found that the expansion was reduced after firing to 1000°C and higher because of its conversion to the β form. With petalite, it was found that dissociation into β spodumene and a siliceous glass occurred around 1000°C with expansion similar to cordierite ($20 \times 10^{-7}/°C$, 0° - 1000°C). When fired at 1000°C for 1 hour, petalite had a thermal expansion less than cordierite and was apparently undissociated. Firing at 1100°C reduced this expansion to about that of fused silica

TABLE 1

Natural minerals in the Li_2O-Al_2O_3-SiO_2 System

Eucryptite — Li_2O-Al_2O_3-$2SiO_2$

Spodumene — Li_2O-$Al_2O_3$4SiO_2

Petalite — Li_2O-Al_2O_3-$8SiO_2$

TABLE 2

	CULLET A	CULLET B
SiO_2	70-74%	68-72%
Al_2O_3	22-24	17-19
Li_2O	4-6	2-4
TiO_2		4-6
MgO		2-4
ZnO		0-2
Other Oxides	0-2	0-2

(5.6×10^{-7}/°C, 0° - 300°C) with additional heat treatment reducing the expansion still further.

Smoke[3] found that petalite has a negative thermal expansion. The heating curve that he determined had a minimum at approximately 420°C of −0.011% expansion, returning to its original length at 730°C. Smoke also determined the thermal expansion of a body prepared from natural spodumene. It showed negative expansion to 200°C, recovered its original length at 400°C with the expansion coefficient then positive.

Bulavin[4] and his associates found that the size distribution of the particles to be sintered influenced the phase composition of the material and, therefore, the thermal expansion and strength of the resultant ceramic. They obtained the greatest static bending strength and a negative coefficient of expansion with a starting mix of predominantly 10-30 μ particles.

Each of the cullets can be in the form of sized glass particles or in the crystallized state as a result of a preliminary heat treatment. The use of predominantly glass cullet for mill feed results in the sintered article having virtually zero apparent porosity. If the mill feed is all

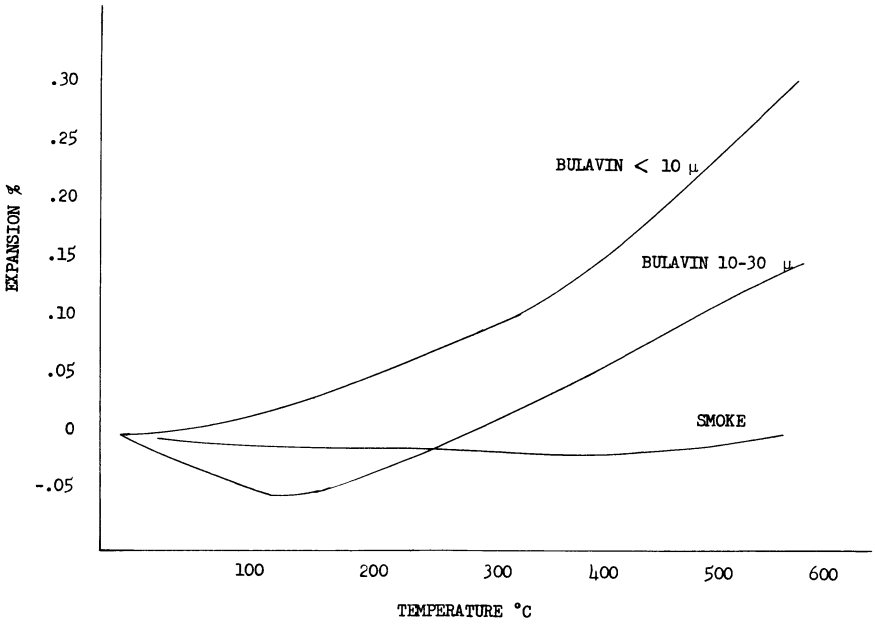

Figure 1
THERMAL EXPANSION PETALITE-BASED CERAMICS

devitrified cullet, the resulting sintered article will have some open porosity.

Useful articles can be formed by any of the conventional techniques that employ powders. Slip casting, isostatic pressing, impact pressing and extrusion techniques are satisfactory. Drying of the formed article is dictated by the forming method and article configuration. Drying practices common to the ceramic industry are satisfactory.

After drying, the articles are fired to 1250° - 1270°C on a schedule that includes one-half hour holds at 1050° and 1180°C and a two-hour hold at peak temperature. Heating and cooling rates of 50-100°C/hr have been found to be satisfactory.

PRODUCT

Code 9456 PYROCERAM® Brand material is a dense, fine-grained ceramic. The mineral phases are β spodumene and rutile with a small amount of glassy phase present.

This particular material was designed to have very low thermal expansion in the room temperature (5-35°C) region. As can be seen from Fig. 2, this very low expansion was achieved by selecting a composition having a minimum in the expansion curve near 0°C.

Other typical properties of interest are:

Modulus of Rupture	12,000 psi
Modulus of Elasticity	10×10^6 psi
Porosity (apparent)	Less than 1%
Bulk Density	2.20 g/cc
Thermal Diffusivity at 25°C cm^2/sec	13×10^{-3}

The properties that make this material ideal for volume-stable applications such as surface plates, optical benches, gauge blocks, etc., also make it resistant to thermal shock. There have been a number of applications where thermal shock resistance has been useful. This material should not be used in hot, reducing environments. A high-expansion glaze develops that effectively destroys the thermal shock resistance of the body.

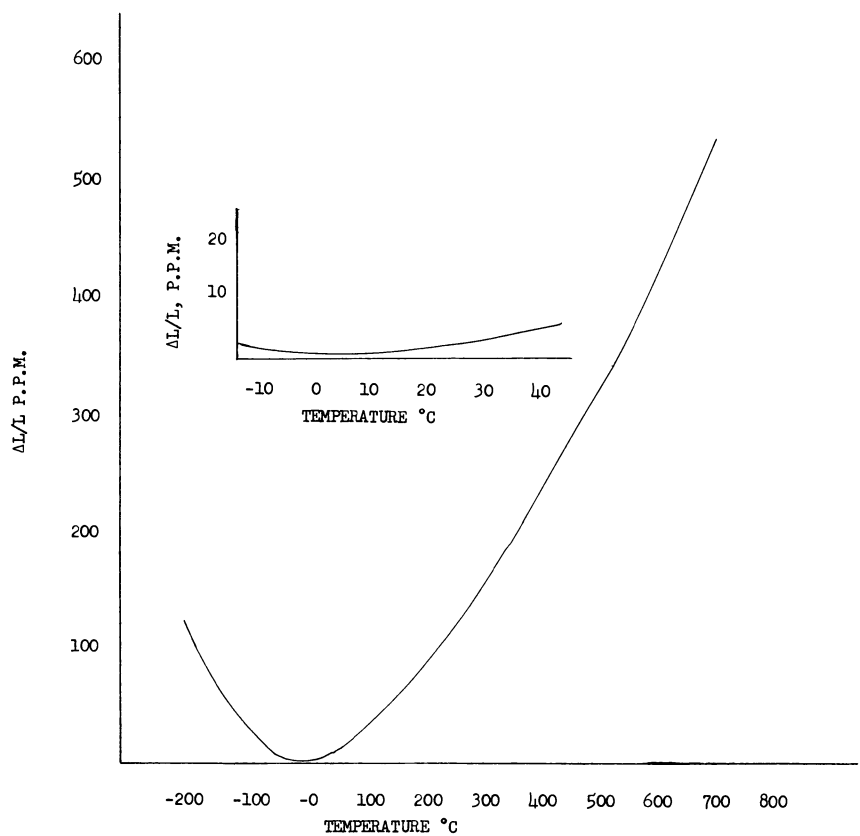

Figure 2
THERMAL EXPANSION CODE 9456

SUMMARY

Ceramic articles formed of mineral or synthetic petalite and spodumene have low expansion with some compositions showing negative expansion. Process thermal history and size distribution of the raw materials influence the phase composition and, therefore, the thermal expansion of each composition.

Conventional ceramic forming techniques that employ powders can be used to form generally satisfactory ceramic articles from petalite and glass cullet. Compositions based on crystallized glasses have given product of more consistent and desirable properties.

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FIELD ASSISTED GLASS SEALING

G. WALLIS, J. J. DORSEY AND D. I. POMERANTZ
P. R. Mallory & Co. Inc.

I. DESCRIPTION OF SEALING METHOD.

In a variety of different materials, hermetic glass-metal seals can be formed by placing a flat piece of glass on a flat piece of metal, heating to a temperature near the annealing point of the glass, and applying a DC potential across the glass-metal assembly. In most instances, the glass should be biased negatively with respect to the metal. If the voltage is applied for about one minute, it is found that a large number of glass-metal systems form strong, hermetic seals.

Since the bonding temperature is well below both the softening point of the glass and the melting point of the metal, both materials remain solid throughout the process. As a result, virtually no distortion of the glass takes place during the process. No fluxes or other intermediate phases are involved so that the seals are as clean as conventional fusion seals.

II. PROCESS PARAMETERS.

The most important factors involved in the bonding process are: thermal expansion match of the two materials, the surface flatness and smoothness, the bonding temperature, the bonding time, and the applied potential. Since the process is very new, its exact limitations are under intensive investigation. However, it is evident that most of the parameters are not critical.

A. THERMAL MATCH.

It is necessary that the glass and metal have a reasonable match of their coefficients of expansion. The exact requirements are dependent upon the material involved. For example, pyrex has been bonded to Kovar® with an approximately 50% mismatch. In analogy with the housekeeper seal, no matching requirements exist for foils or films.

B. SURFACE CONDITIONS.

The materials should have relatively flat and smooth surfaces. A convenient criterion is the following. If the glass is placed on the metal, the parts should be sufficiently close so that interference fringes are generated. Furthermore, with the glass lightly pushed against the metal, no more than 4 or 5 interference fringes should be visible over a linear distance of one inch. The preferred surface smoothness is of the order of one microinch. Unpolished surfaces in the roughness range 4 to 10 microinches have been sealed but in general these seals were found to be neither as strong nor as consistently hermetic as the seals between smoother surfaces.

C. TEMPERATURE.

To date, all glass-metal systems that were found to be sealable by this method, could be sealed at the annealing temperature of the glass. However, in several cases seals could be made at temperatures that were

about 150°C below the annealing points and 400 to 500°C below the softening points of the respective glasses. Sealing can of course also be performed at temperatures above the annealing point.

D. TIME.

Typically a sealing time of 1-10 minutes is adequate. Within limits, time can be traded for temperature. For example, a flat piece of silicon can be bonded to Pyrex® glass in approximately one minute at 350°C; and in several seconds at 550°C. Hence the technique can produce rapid seals at as much as 500°C below the softening point of glass.

E. VOLTAGE.

The electrostatic force between the materials is related to the voltage but that relationship is not simple. The recommended voltage for bonding depends on the characteristics of the glass, the smoothness of the surface, and the bonding temperature. Bonding is usually done around 1,000 volts but 100 volts have been adequate under favorable conditions. The upper limit of voltage is imposed by the requirement to suppress sparking in the air or dielectric breakdown in the glass which may damage the parts.

F. ATMOSPHERE.

Most work has been done in room atmosphere except when it has been desirable to suppress oxidation. Bonding can be accomplished, with some systems, in nitrogen, oxygen, hydrogen, argon and in vacuum.

III. MATERIALS.

Silicon, germanium, gallium arsenide, tantalum, Carpenter® 49, Niromet® 44 and Kovar are some of the metals and semiconductors that have been bonded to commercially available matching glasses. In addition, successful seals have been made to a number of materials which do not match commercial glasses provided the materials were in the form of films and foils. Examples are — iron, nickel, chrome, Nichrome,® boron, aluminum and magnesium.

The process has been applied to a large number of glasses including several borosilicates, soda-lime glasses, alumino silicate glasses and to some composites such as fiberoptics. Recent experiments with chemically strengthened and with tempered glasses were of particular interest in that they suggest that the strengthened glasses require less rigorous matching with regard to thermal expansion than do non-strengthened glasses. In addition, seals have been made to fused quartz, glazed alumina and to some glass-based ceramics such as CerVIT.®

IV. THEORY.

It must first be recognized that when the two materials are placed on top of each other, they normally touch at only a few points even if their surfaces are optically polished. Over much of their overlapping area they are separated by a thin gap which gives rise to easily observed light interference fringes. Before any bonding can take place, the surfaces must be brought into intimate physical contact. This is accomplished by an electrostatic attraction produced by the application of the DC potential.

In an ideal insulator extremely high voltages would be required to produce significant electrostatic forces. However, at typical process temperatures most glasses behave not as insulators but rather as electrolytes. Upon application of the DC voltage, a thin glass layer facing the positive electrode becomes polarized, i.e. it becomes depleted of charge carriers and acquires such a high resistance that virtually all of the applied voltage drops across the polarized layer. As a result, moderate voltages can produce extremely high electrostatic fields in the thin glass region which in turn gives rise to similarly high fields in the gap between the glass and metal. The electrostatic attraction between the materials is produced by the high fields.

The high electric fields at the glass-metal interface persist even after the surfaces have been brought into intimate physical contact. Under their influence, oxygen ions in the glass apparently can drift towards the metal and promote oxidation.

Whether actual bond formation takes place subsequent to the contacting of the surfaces depends primarily on the temperature and on the amount of time that the surfaces were held in contact. At the annealing temperature bonds usually form almost instantaneously upon contacting. It seems probable that electrochemical reactions such as the above mentioned oxidation may facilitate the formation of a strong bond.

V. SEAL PROPERTIES.

The strength of the seals has been investigated in greatest detail for the system Kovar-7052 glass. Under tensile stress it was found that 80% of the seals broke in the range 1500-3000 psi with failure occurring in the glass.

For all glass-metal systems that have been investigated so far it has been feasible to make hermetic seals as determined by helium leak detection. The test assures that any possible leak is less than about 5×10^{-10} cc He/sec.

Thermal cycling and thermal shock tests were performed on fiberoptics face plates of 1″ diameter that had been sealed to flanges of Niromet® 44. The thermal cycling consisted of five cycles of 125°C to −25°C. In no case did the cycling produce any adverse effects. In a destructive thermal shock test, seals were rapidly transferred from hot to cold water. The temperature difference between the water baths was increased in 10°C steps until a seal cracked or started to leak. Most seals cracked when the differential was between 70 and 80°C. The distribution of failures was similar to what is obtained for conventional seals of similar geometry.

Some work has been done on the effect on the strength of Kovar seals of a voltage reversal at elevated temperature. No substantial differences in strength were detected. In another set of experiments no change in seal strength was found when Kovar-7052 seals, made at 500°C, were heated to 750°C for 30 minutes.

In the application of this sealing technique to practical situations it must be kept in mind that electrostatic seals differ from conventional seals in some important respects, such as the re-entrance angles, or the surface structure of the glass near a seal. As a result it cannot be expected that

designs which optimize the properties of conventional seals are necessarily also the most suitable for electrostatic seals. As an example, it is found that electrostatic seals tend to be more sensitive to the stresses produced by the flexing of the metal parts than are conventional seals. Therefore, seals must be designed such that the possibility of undue flexing is eliminated.

VI. APPLICATIONS.

Probably the most interesting aspects of the process are the relatively low sealing temperature and the short sealing time. As a result it is possible to make seals in which the glass is virtually free of distortion. A straightforward application taking advantage of this feature is the sealing of glass windows to metal flanges. Typically, the window is 7052 glass and the flange is made of matching Kovar. No outgassing or preoxidation of the Kovar is required. The seal, made at 500°C with 1000 volts is hermetic and shows no perceptible distortion.

In another application a fused quartz window has been butt-sealed to a quartz tube in the following manner. First, a thin silicon film is deposited on the polished end of the quartz tube. The window is then sealed to the silicon film at about 900°C with a voltage of 1500 volts. Though the silicon has of course a much larger coefficient of expansion than the fused quartz, it is sufficiently thin so that no serious stresses are introduced.

The sealing technique may find applications in the hermetic encapsulation of semiconductor and other electronic components. This application is attractive because the sealing temperature is sufficiently low so that the characteristics of the devices are not affected. As an example, a flatpack containing a light sensitive electronic component was provided with a hermetic glass lid in the following manner. The faces of the ceramic wall of the flatpack were lapped flat and polished. They were then metallized with evaporated aluminum, and the window was sealed to the film at 450°C with about 800V. Many electro-optical devices, such as image intensifiers, and vidicon tubes require precisely spaced glass and metal components to be sealed hermetically without the loss of dimensional tolerances. It has been demonstrated that the sealing process can produce high tolerance seals at relatively low sealing temperatures. If desired, all seals can be made simultaneously. Another advantage of the process in this application is that it does not contaminate the components with foreign materials. Though we have stressed glass to metal seals, with some glasses the technique is also applicable to glass to glass sealing. Possible applications are in the lamination of glasses, and in the sealing to each other of two or more optical lenses.

The above examples illustrate that the sealing method permits the maintenance of extremely tight dimensional and optical tolerances during the formation of clean, hermetic and bakable seals. Undoubtedly, many other applications will be identified as the process becomes more generally known.

AN ALUMINUM FOIL OVEN

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In the field of scientific research the glassblower holds a very important position. Much of the research done today requires the skills of the glassblower to help bring the scientist's ideas to reality.

One of the outstanding and, I believe, the most important piece of equipment that the glassblower works on, is the vacuum system. At the General Electric Research and Development Center we use vacuum equipment for a large part of our experimental work and we call upon our glassblowers' knowledge often to help solve many of our problems, and I assure you we have our share of problems to solve.

We have worked on the mass spectrometer, the triggered vacuum gap and the vacuum switch and all of these devices require a high vacuum for successful operation. By high vacuum I mean pressures in the order of 10^{-7} Torr and below.

In order to obtain a high vacuum in this range, all of the parts must be clean. Care must be taken during fabrication and assembly of the vacuum tube to avoid contamination with oil, soldering fluxes, dirt and dust and contact with the hands.

The assembled tube is attached to a vacuum system and a bakeout of the entire system is then required. All glass and metal parts exposed to the vacuum must be baked out thoroughly to remove residual gases, unwanted residue and water vapor. Glassblowers are unusually adept at providing an ample supply of water vapor in a vacuum system.

There are many types of bakeout ovens. Most of them are satisfactory but somewhat difficult to handle. At our laboratory until the development of the aluminum foil oven, most ovens made were bulky boxes of sheet metal with hollow walls two inches thick filled with insulation such as rock wool or fiberglass. These ovens are expensive and time consuming to build. Sometimes two men were required to lift and place these ovens in position on a vacuum system. Occasionally, when a man was working alone a small hoist would be used to raise and lower it so he would not crack the glassware while putting the oven in place and these are not especially large ovens.

The aluminum foil oven, which I developed, overcomes some of these drawbacks because of its light weight. In this type of oven, the walls are a sandwich of Fiberfrax insulation and aluminum foil.

In Figure 1 you can see a cross section of the wall construction. The fiberfrax is in the center and the aluminum foil on each side. Fiberfrax is the trade name for a ceramic wool material pressed into sheets. It is put out by the Carborundum Co. of Niagara Falls, New York. The material we used is $\frac{1}{8}$" thick and comes in rolls 2 ft. wide and 40 ft. long. As can be seen in the diagram, on the left side of the figure, the Fiberfrax is

cut to size for the sides and top of the oven. An inch or so is added to the dimensions for stapling purposes. The aluminum foil, the ordinary household variety works just fine, is placed on each side of the cut pieces and attached by a couple of rows of staples. The sides are then joined at the ends and the top is placed in position and stapled. Sometimes it is desirable to leave the top off until the location of the heating elements have been determined.

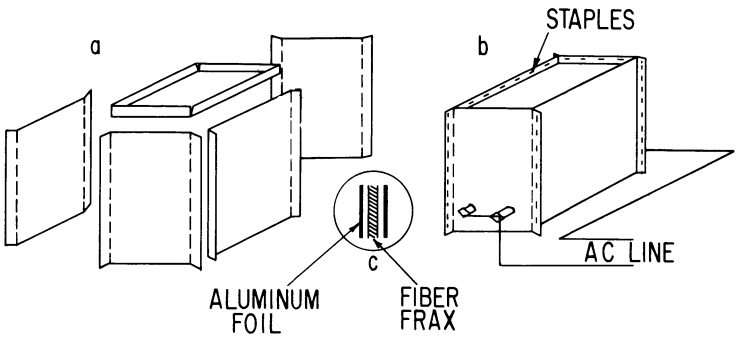

Figure 1

The heating elements are quartz infra red tubes made by the General Electric Company. They come in several lengths but the 19 inch size has been suitable for most of our ovens. They are $\frac{3}{8}$ inch in diameter and have pig-tail connections on each end.

The oven is placed in position on the vacuum system and holes are punched in the walls of the oven to allow the tubes to slip through to the opposite side. The quartz heating tubes run quite hot and should not be positioned too close to any glassware. The pig-tails projecting out on each side allow for electrical connections. They should be insulated with a fiberglass sleeving over each end to prevent personal contact with the electrical circuits while working around the oven.

The number of heating elements to use depends on the temperature required and the size of the oven. The 19 inch elements are rated at 1600 watts at 230 volts, but we normally operate at 115 volts, thereby cutting the power input by a factor of four.

Figure 2 shows a graph of a typical oven which has a volume of slightly over 3000 cu. inches. Two heating elements are used. The power input is controlled by a 115 volt variac and the resultant inside oven temperature and outside wall surface temperature is plotted vs. input power. As one can see for an oven temperature of 400°C a total of 1400 watts input power to the lamps is required. This could be done with a single lamp because of the 1600 watt rating, but using more lamps at reduced power produces a more uniform heat distribution. The oven in this case had the two heating elements located near the bottom and at 400°C the temperature gradient within the oven was 0.5°C/inch decreasing in the vertical direction, that is further from the heating lamps.

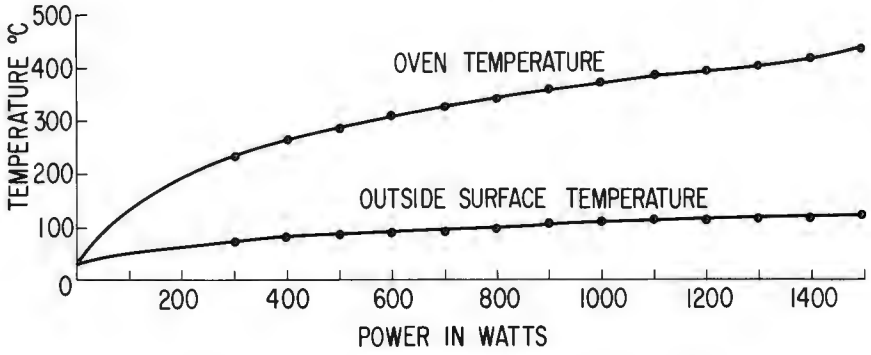

Figure 2

An unusual feature of this oven is that despite the 100°C outside wall surface temperature, very little heat radiation is felt from it. If you hold your hand within an inch of the walls while the oven is in operation, there is very little sensation of heat. This is an advantage when working in close quarters near the oven.

During a normal vacuum system bakeout, we generally use a pyrometer to control the heating elements to maintain the proper oven temperature.

Despite their light weight and fragile appearance, these ovens are unusually serviceable. I have seen some at our laboratory that have been in use for over a year and are still in excellent usable condition.

Figure 3

There are some that have been made in such large sizes that they require reinforcing. There are several ways to do this. One way as shown in Figure 3, is to make a skeleton of stainless steel rods over which the oven is placed. This method gives very good support and makes a neat job.

Also thin aluminum sheets can be used as in Figure 4 to make a shell in which the aluminum foil oven is attached. This method was used in

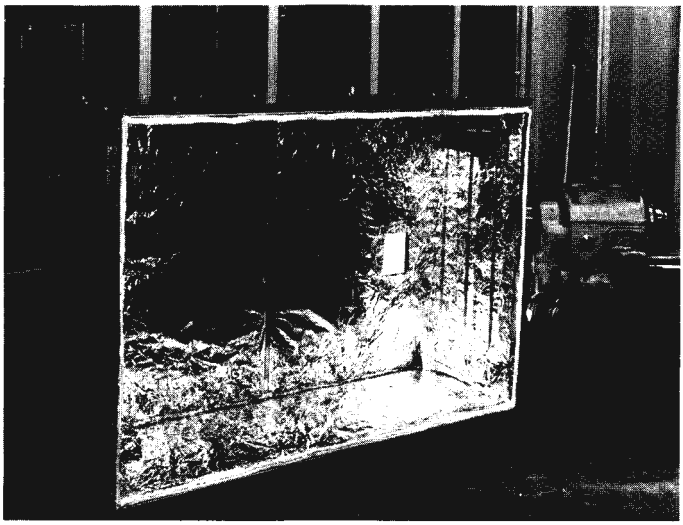

Figure 4

a permanent installation. The 19″ heating elements were not long enough for the size of this oven so the builder devised heat shields for the ends of the lamps. These shielded the ends of the quartz lamps from the internal heat of the oven and made them available for electrical connections. The front of this oven is a hinged door, which is not shown in the figure.

I find that these reinforcing procedures are not ordinarily needed unless the oven dimensions are over three feet in length or a more durable external surface is needed.

Figure 5 shows one of the ovens in use for baking out a mass spectrometer system. The diffusion pump is visible below the table. The oven is covering the mass spectrometer. The volume of this oven is about 5500 cu. in. and three heating elements running at 115 volts bring the temperature to 325°C.

There is one more way (Figure 6) that I would like to show you in which this oven structure has been used. This was part of an experiment and not just for baking out purposes.

The experiment required that three different temperatures be maintained in different parts of the experimental apparatus. This was done as

Figure 5

shown in this slide. Three ovens each with its own calrod heating element were maintained at different temperatures. The lower one at 200°C, the upper one at 500°C and the larger one was at 300°C.

If you need a bakeout oven that you can build yourself in a short time, which will operate in the temperature range of 400°C or more and is very economical to build, you might find this oven useful in your work.

Figure 6

FUSED QUARTZ
ITS CHEMICAL CONSTITUTION, REACTIVITY, DEVITRIFICATION AND CLEANING PROCEDURES

N. G. GRAFTON
General Electric Co.
Willoughby Quartz Division

My paper this morning will outline the technical constitution of various types of fused quartz, and reasons for quality control of raw materials and processing to maintain low levels of impurities. Slides will show the rate of attack of Silica Glass or Fused Quartz by Alkalies and other reagents as a function of time and temperature. These same factors, time and temperature, have dramatic effects on sag, indicating greater resistance to deformation by higher temperature materials. Contamination effect, handling and proper cleaning for long life expectancy will also be discussed.

Fundamentally, fused quartz is a glass. That is to say, it has no crystalline structure. This distinguishes it from quartz crystal, whether the natural variety found in the ground or the synthetically produced material. In quartz crystal all of the atoms are arranged in a definite pattern, whereas in the fused quartz the atoms have an irregular pattern.

Fused Quartz is not only a glass, but is a glass composed of essentially only silica or silicon dioxide to use the chemist's term. Practically all other glasses are made up of mixtures of silica and various other oxides, such as calcium, alumina, sodium and boron oxides. These other oxides profoundly effect the properties, making the glass unsuitable as a substitute for fused quartz in the myriad of applications where the unique properties of fused quartz are essential. Because of this, our efforts are continually toward higher and higher purity in our finished products.

We report the impurity levels of our materials in the oxide rather than the element. The first two figures (1 and 2) will show the conversion factors for the Element to Oxide and Oxide to Element.

CONVERSION FACTORS ELEMENT TO OXIDE

Fe	x 1.4298	=	Fe_2O_3
Ti	x 1.6681	=	TiO_2
Al	x 1.8899	=	Al_2O_3
Ca	x 1.3992	=	CaO
Mg	x 1.6579	=	MgO
K	x 1.2046	=	K_2O
Na	x 1.3479	=	Na_2O
Li	x 2.1527	=	Li_2O
Zr	x 1.3508	=	ZrO_2

EXAMPLE

Given: 10ppm Mg; find: MgO

10 x 1.6579 = 16.6 ppm MgO

Figure 1

CONV FACTORS OXIDE TO ELEMENT

Fe_2	x 0.69940	=	Fe
TiO_2	x 0.59950	=	Ti
Al_2O_3	x 0.52913	=	Al
CaO	x 0.71469	=	Ca
MgO	x 0.60317	=	Mg
K_2O	x 0.83013	=	K
Na_2O	x 0.74191	=	Na
Li_2O	x 0.46452	=	Li
ZrO_2	x 0.74030	=	Zr

EXAMPLE

Given: 10ppm Li_2O; find: Li

10 x 0.46452 = 4.6ppm Li

Figure 2

CHEMICAL ANALYSIS

For: Tubing Grades: 124, 204, 232
Fabricated Ware: Clear
Opaque Ware: 510
Quartz Fiber products (excluding binders)

Impurity	Avg.
Al_2O_3	50
B	0.5
CaO	7
Fe_2O_3	5
Li_2O	<1
MgO	2
K_2O	4
Na_2O	4
TiO_2	2
ZrO_2	<1

Figure 3

CHEMICAL ANALYSIS

For: Optical Grade: Type 151 Fused Silica

Impurity	Avg.
Al_2O_3	10
B	—
CaO	4
Fe_2O_3	6
Li_2O	0.2
MgO	3
K_2O	2
Na_2O	2
TiO_2	1
ZrO_2	—

Figure 4

Copies of these conversion tables are available, plus other technical data discussed today.

For many years we depended upon a raw material source from Brazil in the form of quartz crystals in varying sizes. Today, after much research, we use domestic sources entirely, so that foreign imports of raw material for most of our product line is no longer required. This includes clear tubing and rod as well as some types of solid stock from which plates and discs are produced. Many steps in the raw material processing is required to manufacture a consistent product that is very low in impurities. So much care is now taken that the domestic source produces higher purity fused quartz than the former imported crystals. Illustrations are shown in the next two figures. (3 and 4)

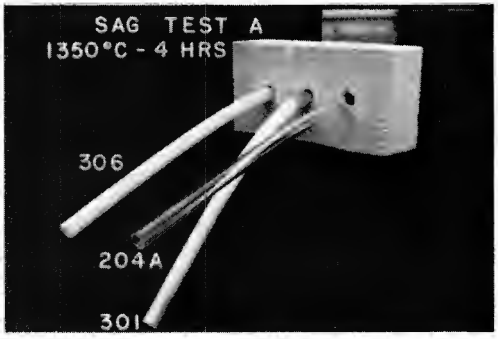

Figure 5

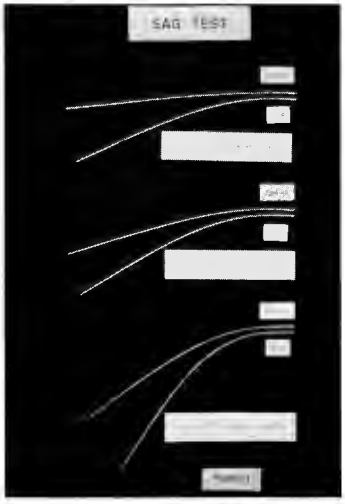

Figure 6

An illustration of the dependence of softening point on purity is shown in the next figure. (5) The rate of sag is almost completely dependent upon the purity of the product and clearly shows Type 204 to sag far less at 1350°C for 4 hours than Type 301.

The next figure (6) also shows a sag test at three different temperatures. Note that 204 A was the original name of our new purer material, but since these tests were made the new standard is known as 204. A change of approximately 100 ppm in impurity level has had a measurable effect on the sagging properties. No direct comparison of softening point has been made because of the difficulty in measuring at such a high temperature. The softening point is about 1670°C — though as the illustration shows, the older, less pure material clearly softens first.

The high softening temperature makes fused quartz very useful in industry, but certainly makes your job more difficult. It means using higher temperature flames since it must be worked in the range of 1850°C-1950°C, contrasted to temperatures of 1000°C-1200°C for other glasses.

Another feature of fused quartz is that it has the lowest expansion of any commercially available material. The advantage to industry is a material having minimum dimensional change with respect to temperature changes. Examples of this are optical flats for gauging purposes and optical windows and lenses used at high temperatures, where the optical path would be seriously distorted by change in dimensions.

Because of this low expansion, much lower stresses are developed due to temperature differences. In other words, it is much more resistant to thermal shock. Despite its low thermal expansion, it should not be assumed that fused quartz does not require annealing. Contact with metal chunks for instance should be avoided when working the material and large pieces should be flame annealed after forming. An annealing schedule we generally use is to bring the annealing oven temperature up to 1140°C and hold for five minutes. Then allow the temperature to drop at the rate of 3 degrees centigrade per minute to 1050°C. Oven can then be turned off and cooling can begin at a rapid rate.

Reactivity by Alkalies and other selected reagents can be seen by the next illustration. (7)

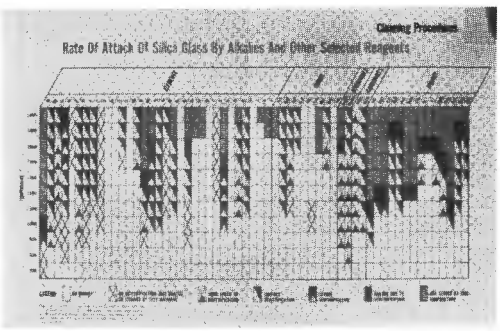

Figure 7

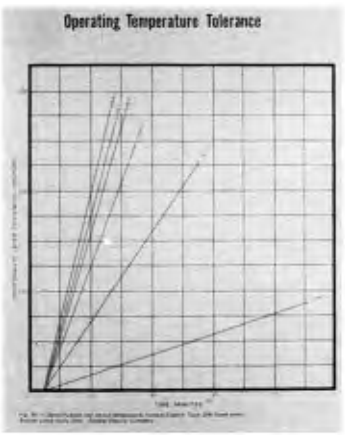

Figure 8

Any contamination, and particularly alkalies, will hasten devitrification. Where fused quartz material is to be used at elevated temperatures, particularly in the neighborhood of 1000°C and above, it is extremely important that the surface of the material be free of any contamination if accelerated devitrification is to be prevented. Quartz will devitrify at these temperatures, over a period of time in any case. Therefore, it is important that the material be clean before it is raised in temperature. Generally a solution of hydrofluoric acid of approximately 10% concentration at room temperature is used to clean the material. This acid is used primarily because it is one of the few solvents for silica. Water is then used for the rinse. Five minutes in the acid is usually sufficient to properly clean the surface and is short enough to prevent etching. Use clean cotton gloves to handle the quartz as it is important that tubing and other quartz be free of fingerprints, oils, etc., before it is acid washed. Alcohol or acetone will remove fingerprints.

Figures 8, 9, and 10 show:

1. Devitrification rate vs. temperature. (8)
2. Devitrification shown on a piece of quartz resulting from improper handling. (9)

Figure 9

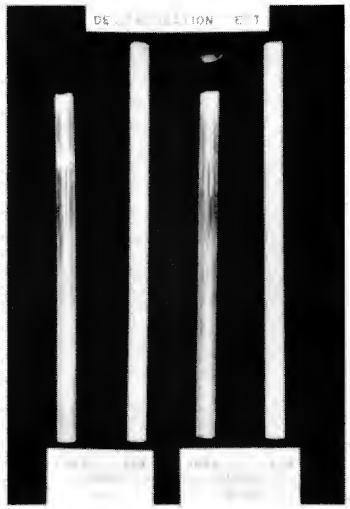

Figure 10

3. Devitrification test showing former clear tubing and present material. (10)

Sometimes when fused quartz is being blown or shaped in a flame you will notice a white film deposit on the cooler parts adjacent to the section being worked. This is not to be confused with the previously discussed devitrification, which it may resemble. The deposit results from the vaporization of the quartz and the condensing of the vapor on the cooler surface. (11)

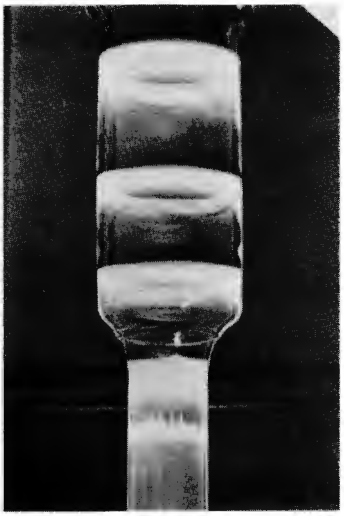

Figure 11

Heavy deposits can be prevented by preheating the material before working and by keeping material hot beyond the working area. Heavy vapor can only be removed by the flame chasing method, while light deposits can be removed by the above acid cleaning method. Most vapor is caused by an improper gas mixture. The best mixture to limit vapor is one which maximizes the volume of oxygen in relation to the volume of hydrogen while maintaining a working temperature. All burners do not mix alike so that adjustments must be made to obtain the optimum mixture.

There are many types of fused quartz, each having a unique purpose. We have recently added two new types called 124 and 125.

Type 124 is a solid stock, low in cost, and very high purity. It has uniform stress and has good transmission, especially in the infra-red region, since it has no water band. The main applications are Boats and Jigs, Slice Racks and parts for other apparatus in the Semiconductor industry.

Type 125 has a lower bubble content than Type 124 and the long established Type 101. It has good transmission in both the ultra violet and infrared. The purity is relatively good and it has a low stress level. Applications would include windows, lenses, domes, plates, discs, solar cell covers, optical flats and infrared windows.

I certainly appreciate the opportunity to be with you today, and you may be certain our organization will cooperate in every way to supply both technical information and the quality products you require.

ASSEMBLY TECHNIQUES FOR THE LIPPMANN ELECTROCAPILLAROMETER

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The Lippmann Electrocapillarometer is as much of a problem to make as it is to pronounce. The question that comes to mind is, "What is it used for?" In recent years, an energetic study of the physical chemical behaviour of mercury spheres acting as electrodes, in systems designed to utilize the principles of electro-chemical analysis, have and are being made by several workers. These tiny mercury spheres are formed by one mechanism or another and are surrounded by a chemical solution.

The requirements for the study of the behaviour of this mercury sphere are complex in that the unit requires a thermally controlled environment, distortion free observation, facilities for changing solution, electro-orientation, etc.

It is the burden of the glassblower to combine all these requirements into a comparatively small piece of glassware which offers an interesting challenge to the constructor. The main body of this paper is devoted to my own methods of satisfying the technical demands of this instrument.

The requirements of this cell consisted of:

–Thermostating jacket on the cell and bulb of electrode

–Double evacuated, optically flat windows to allow undistorted viewing of the capillary and to prevent fogging of the window at temperatures below 15°C

–Compact cell so the height of mercury between the capillary tip and the centre of the bulb is 30-35 cms. at most and this variable by 5-10 cms.

–Gas bubbler to deareate the solution and to mix the solution for rapid temperature equilibrium

–Five joints in the top for:

(1) Mercury bulb electrode
(2) Platinum wire electrode (to apply voltage)
(3) Reference electrode
(4) Thermometer
(5) Gas bubbler to seal the cell but will allow gas to escape when necessary.

–Ring seal joint for ease of mounting the cell on the nitrogen pressure line.

This cell is designed for experimental accuracy and it's compactness gives it the further advantage of being easy to handle and mount or move, and it can be cleaned quickly and easily.

CONSTRUCTION

I shall discuss herein only the main body of the cell. The problems of building this apparently simple cell lay in the compactness of the unit and in the application necessary to unite the second outer optical window with the interior optical window.

The two windows were ground to fit a piece of 48 mm. O. D. tubing (Fig. 1). They were sealed individually into separate pieces of tubing with the aid of a vertical lathe. This was done by supporting the window with a 25 mm. carbon rod which is drilled through the centre and has a piece of glass tubing wedged therein. A blow hose was attached to either end to allow for simultaneous blowing to create a slight curvature. The side arm used to evacuate the space between the two windows was sealed to the second sleeve prior to the window. The second window was sealed immediately above the side arm. After annealing, the first window was cut off squarely about 5 mm. below the seal and the second one with the side arm, about 20 mm. below the side arm. The extra length on the second sleeve prevents excess heat from melting the side arm when it is sealed to the outer portion of the jacket. A piece of 10 mm. rod was attached to the sleeves to act as a handle.

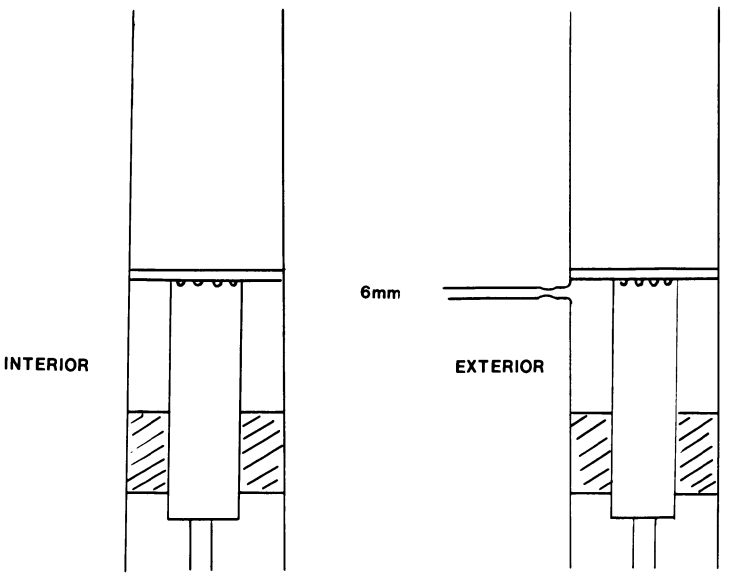

Figure 1

The inner and outer parts of the jacket were then partially prepared. A dome with a diameter of 48 mm. was blown (Fig. 2) on the inner jacket which is a piece of 75 mm. O. D. tubing. The end is then rounded 30 mm. from the edge of the dome and joined to a piece of 12 mm. O. D. tubing. After annealing, the dome was cut off so that it was perfectly flat with an outside diameter of 48 mm.

The exterior jacket of 110 mm. O. D. tubing, was prepared on the same basis as the internal jacket; rounding off the bottom end and attaching a piece of 20 mm. O. D. tubing.

The O-Ring, size 102/75, was cut off as short as possible and flared (Fig. 3). This occurs where the wall thickness of the tubing changes. It is supported by a glass holder and asbestos paper packing.

Now that the basic preparations have been made, it is time for the fun and games of putting all these bits and pieces together to the specification of the designer.

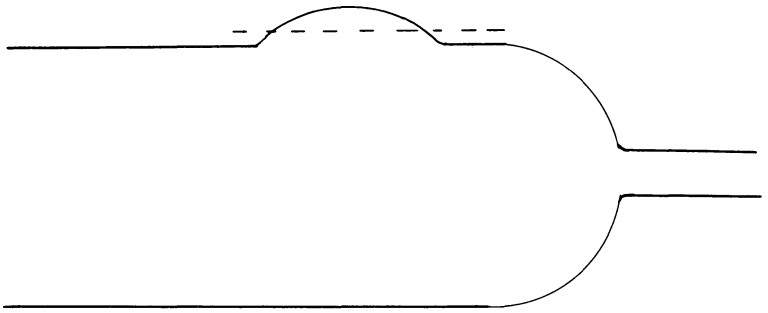

Figure 2

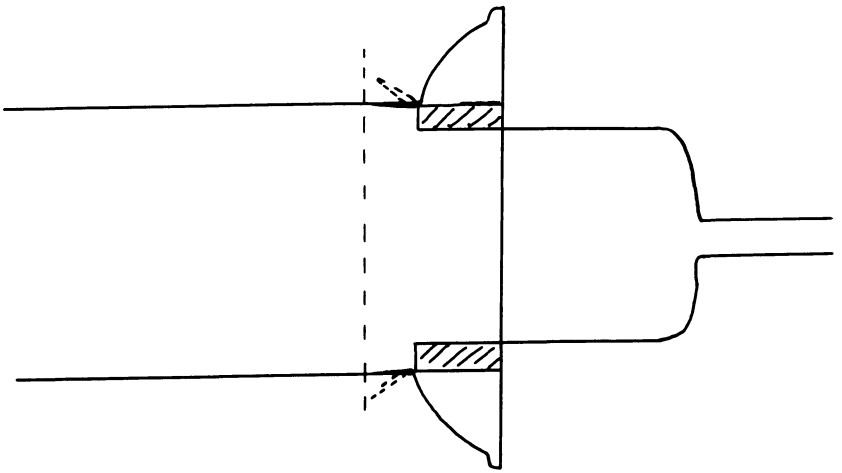

Figure 3

The first step in uniting these pieces was one of the easier steps for me. This was the joining of the internal window to the internal part of the jacket (Fig. 4). The opening of the jacket and the window seal had been prepared to fit perfectly. Both the window and the jacket were prewarmed and the rough edges glazed. When both pieces had been warmed thoroughly, the window was carefully tacked on and set straight, and the handle was removed. Then, using a fine flame, and working around it a

bit at a time, it was sealed in. After annealing, the excess tubing above the window was cut at the point where it would be centred and also meet the level of the outer jacket. It was necessary at this stage to cut the jacket the correct length allowing for the flare that would have to be made for the ring seal with the O-Ring.

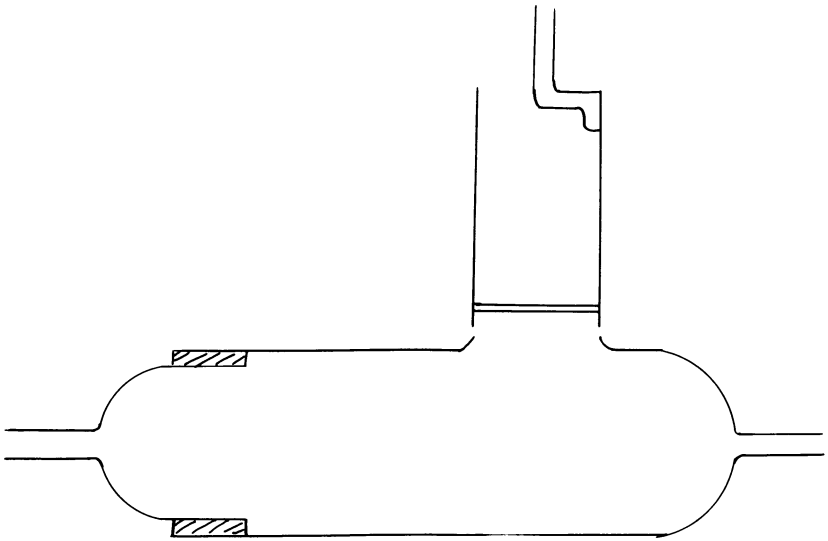

Figure 4

The next stage was to seal on the outer window and I can assure you, that if it is a challenge you want, try the peculiarities of this seal sometime. As in the preparation of the first seal, the window and the jacket were prewarmed and of course, kept warm during the operation. Initially, the outer edges of the curved cut off dome were folded down onto the extension of the first window seal (Fig. 5) ensuring that the outside edge was not distorted and that the top was kept flat. The next step was to seal on the second window and as you can see from the illustration, this presents a two-fold problem. The only place in which any blowing can be done is through the vacuum arm, but the distance between the level of the jacket and the arm is so short, that either direct or reflected heat could cause it to bend or collapse. A rather distorted blowing arrangement which had been prepared earlier solved the problem. The window was sealed on similarly to the first and annealed. The excess tubing was then cut off about 2-3 mm. from the window.

The ring seal at the bottom end was then completed (Fig. 6). This first necessitated the removal of the exterior tube so that the inner tube could be elongated, and then the replacing of the exterior tube. The ring seal was completed and the water inlet attached above the ring seal.

At this stage I was doing a great deal of worrying because the last major step had yet to be tackled, and when I realized how little room I had to work in, and that there was no room for mistakes, I shuddered.

The distance between the centre of the windows and the O-Ring seal was to be 10.3 cm. Gritting my teeth, worrying, and sweating a lot (as a substitution for blaspheme, being unlady like) I prepared; myself, and the cell.

For the protection of the windows, and for the stress factor that the cell would experience under the heat of the large ring seal, it was wrapped in asbestos tape except for the exposed sealing area, and mounted in the lathe. The cell was then warmed up slowly and thoroughly. The excess tubing was flame cut with an allowance of 13 mm. between the inner and

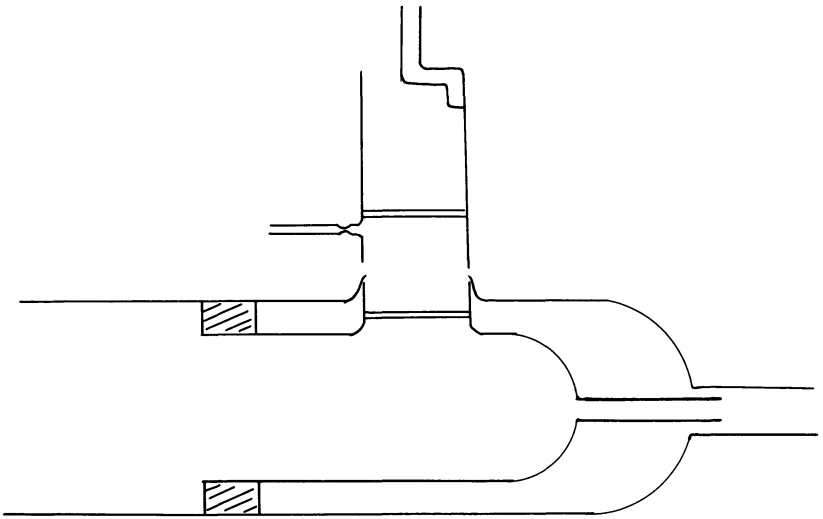

Figure 5

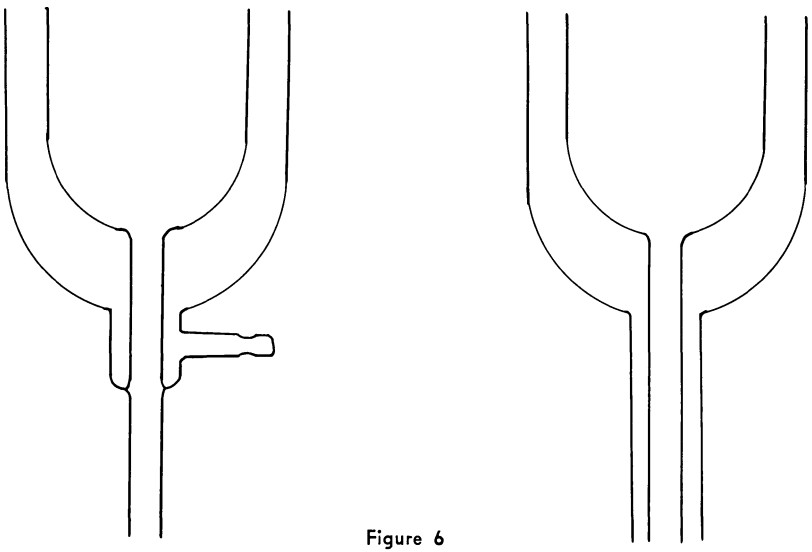

Figure 6

outer jacket (Fig. 7). The inner jacket was flared, but not all the way. The idea was to join the O-Ring to the exterior jacket and then bring it down onto the inner jacket to form the ring seal (Fig. 8). This was done and the shoulder was blown into a curve. The water outlet was added and it was again annealed.

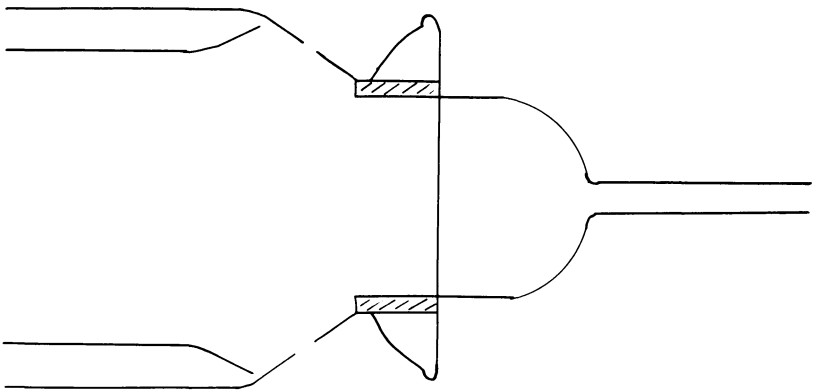

Figure 7

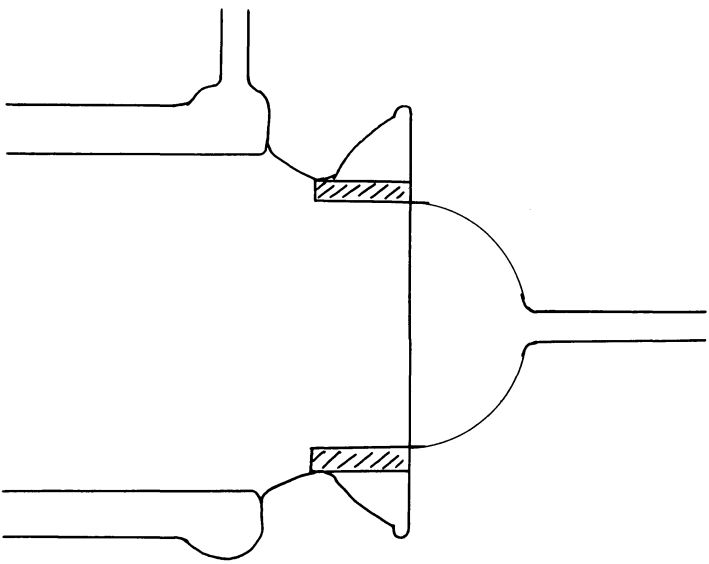

Figure 8

All that remained now was to add a small sintered disc and two teflon stopcocks to the bottom end (Fig. 9). They had been left off so as not to get in the way in earlier stages. The space between the windows was evacuated and the main body of the cell was completed (Fig. 10).

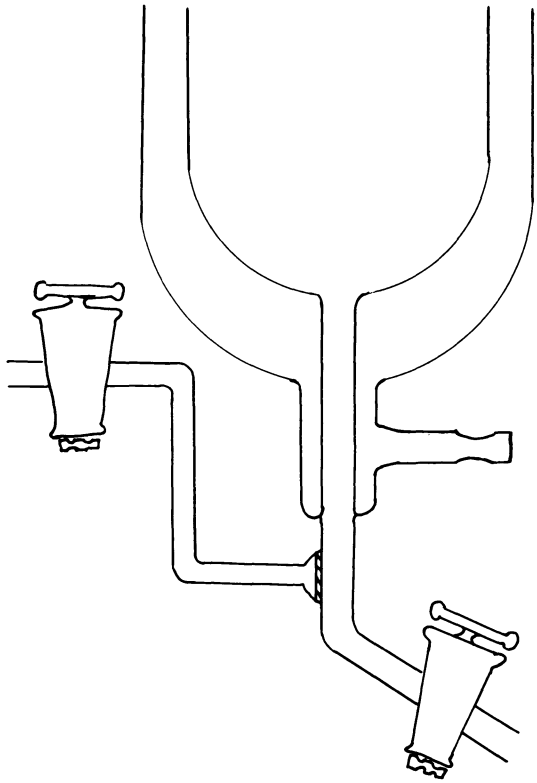

Figure 9

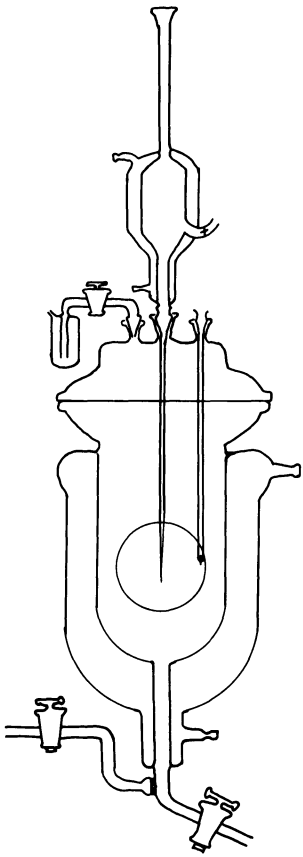

Figure 10

CONCLUSIONS

My first conclusion upon completing this cell was "What a relief!" From the viewpoint of the glassblower, I can assure you that it is a most challenging and satisfying piece of equipment to make. The scientist has been concerned with compactness both for accuracy and easy handling. This cell meets his requirements.

At this time I would like to thank Mr. Ed Herman for preparing for me a brief discussing the use of the cell, but foremost to Mr. John French who advised me and assisted me in the struggle.

INTENSE HELIUM LIGHT SOURCES FOR OPTICAL PUMPING EXPERIMENTS

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ABSTRACT

The use of intense helium light sources is a basic requirement for achieving high degrees of nuclear polarization in optically pumped He^3. This paper describes the construction and performance of several types of light sources which not only satisfy the above requirement but also combine compactness with ease of operation. The technique used in the making of reliable graded seals for introducing heavy metal electrodes through the glass of the discharge tube is given in detail. Maximum light intensities achieved as well as difficulties arising from the sputtering of the electrode metal during operation are also discussed.

INTRODUCTION

The production of nuclear oriented He^3 gas samples at low pressure by optical pumping was first achieved by Colegrove *et al* [1]. Briefly when a He^3 absorption cell located in a magnetic field and containing atoms in their lowest 2^3S_1 metastable state is illuminated along the field with circularly polarized 1.08μ light from a He^4 discharge, the metastable atom population acquire a net magnetic moment. The absorption of angular momentum of the light by the metastable atoms is possible because of the near coincidence of the $2^3S_1 \rightarrow 2^3P_2$ transition in He^4 with the 2^3S_1, $F = \frac{3}{2} \rightarrow 2^3P_0$ transition in He^3. The level scheme of He^3 and the spectra of both He^3 and He^4 are shown in Fig. 1. Typically 1% of the light is absorbed when the He^3 cell is filled to a pressure of 1 mmHg. The angular momentum absorbed by a metastable atom is partially acquired by the nucleus (spin $I = \frac{1}{2}$) through hyperfine coupling. The resulting nuclear polarization of the metastable population is then transferred to the nuclei of ground state atoms through metastability exchange collisions of the type

$$He^3 + He^{3*} \rightarrow He^{3*} + He^3$$

in which the nuclear spin state of the incoming metastable (He^{3*}) and emerging ground state atom remains unaltered. When the pumping radiation is strictly parallel to the direction of the magnetic field the maximum nuclear polarization attainable increases with the light intensity. This paper describes the construction and characteristics of intense helium light sources capable of producing nuclear polarizations of 20% in He^3 gas samples at low pressures. Higher polarizations should be attainable if the light beam collected from the source can be made parallel to the magnetic field.

Since only a small fraction of the 1.08μ radiation from a He^4 discharge is absorbed by He^3 the light must exhibit low self-absorption in the region

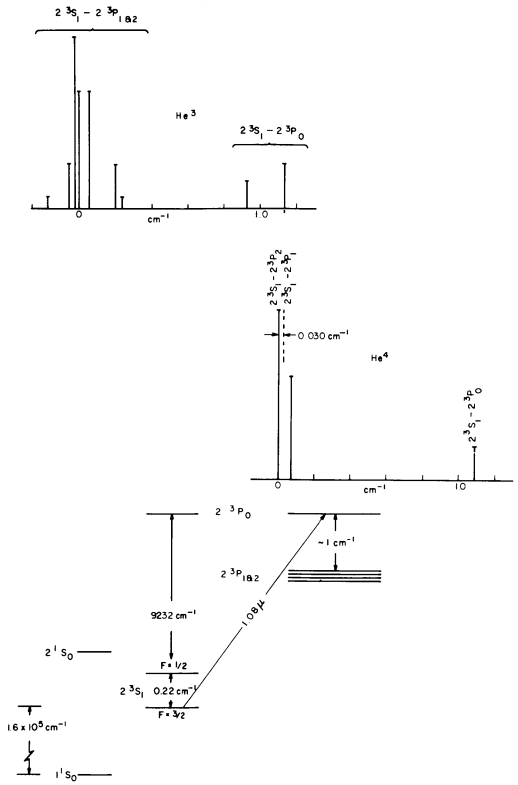

Figure 1

Top: 1.08μ line structure in He^3 and He^4 as calculated by Fred *et al.* [2]. The relative positions of the two spectra are drawn correctly to show the isotope shift measured in our laboratory.
Bottom: Energy levels of He^3 (not drawn to scale).

of the pumping radiation. The nature of the experiments to be undertaken with the light sources further requires that the lamp be both compact and capable of being operated a considerable distance away from the power supply. It was decided that these requirements could best be met if the lamp were excited with radio frequency of about 160 MHz.

DETAILS OF CONSTRUCTION

(I) General

The final version of the first successfully operated light source is shown in Figs. 2 and 3. The main body of the lamp is made up of a 24 mm O.D. quartz discharge tube provided with a narrow constriction in the middle. This constriction is slightly offset from the remainder of the tube to satisfy optical requirements, and the discharge produced in it generates

light with a minimum of self-absorption. The constriction is prepared separately by inserting part of a 100 mm x 20 mm x 1 mm forming tool (made of stainless steel coated with aquadag) into the softened end of a short length of 14 mm O.D. quartz tubing while it is held in a glassblower's lathe. The constricted area of the tubing is then cut to the desired length and the ends are trimmed and shaped to fit the discharge tube. The end section of each electrode, subjected to intense electron and ion bombardment during operation, consists of a molybdenum cap tightly screwed into a threaded stainless steel collar welded on to the end of a 4 mm diameter tungsten rod. The latter is introduced through one end of the discharge tube by means of a graded glass to tungsten seal. Because of the high thermal conductivity of tungsten, adequate cooling of the electrodes is ensured by soldering 39 mm x 6.4 mm water-cooled brass discs on to the nickel- and copper-electroplated external ends of the tungsten rods. The quartz cooling jacket fitted around and fused to the central section of the discharge tube is provided with a hemispherical protuberance of 20.5 mm radius located directly in front of the constriction. This protuberance is prepared separately by blowing fused quartz into a graphite mould and cutting off the blown hemisphere at its equator. Both the chosen diameter of the protuberance and the separation of 9 mm between its centre of curvature and the front side of the constriction are selected to achieve a workable compromise between maximum light collection efficiency and low beam divergence during operation when the cooling jacket is filled with water. It is usually attached to the cooling jacket by means of an epoxy cement (e.g. Lepage's "Two Ton" epoxy) after the electrodes are sealed to the discharge tube.

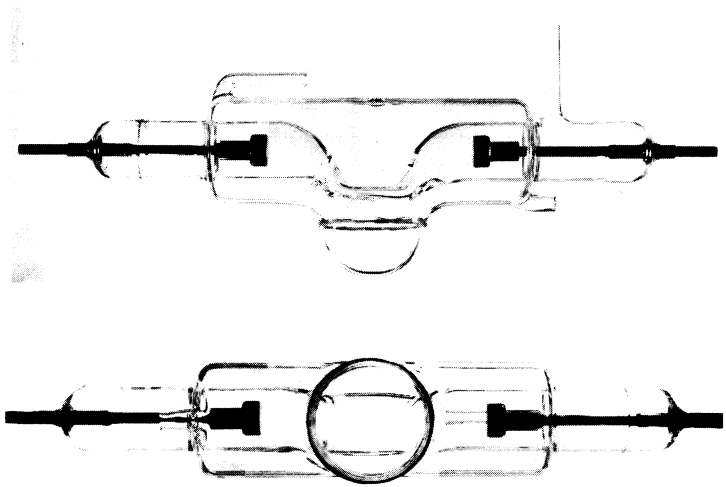

Figure 2
Side and bottom views of the first successfully operated light source.

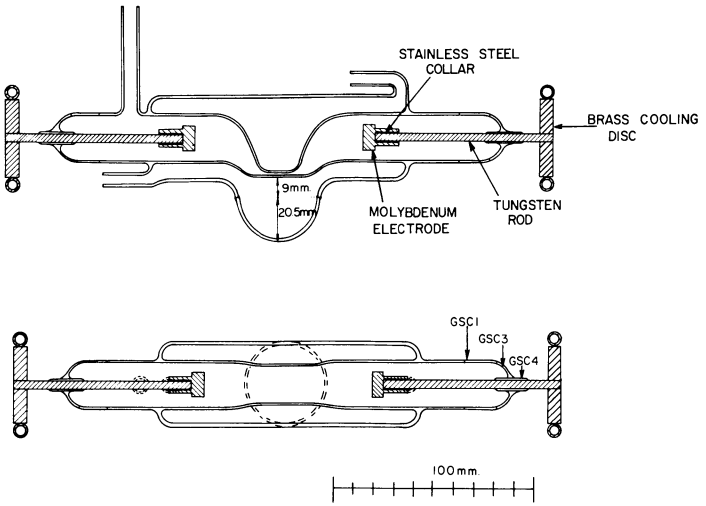

Figure 3
Details of the light source shown in fig. 2.

(II) Tungsten to Quartz Graded Seals

Great difficulty was encountered in the making of durable glass to metal seals for introducing the heavy tungsten electrodes through the quartz. Conventional methods of preparation were found inapplicable because of the relatively large diameter of the tungsten rods used. However, satisfactory results were obtained with the following procedure. The tungsten rod is first electro-cleaned and polished by being made the anode in an electrolytic cell. The electrolyte is a 15% solution of sodium hydroxide. Either a carbon tube, or a short length of nickel strip wound into a helix and placed around the tungsten rod, can be used as the cathode. After rinsing in distilled water and drying a 1″ length of close-fitting ½ mm wall thickness tubing, drawn from a GSC4 glass rod, is slipped over the tungsten rod while it is held in a glassblower's lathe. The clearance between the glass and the tungsten rod should not be more than about 0.001″. The heating and fusing of the glass on to the metal rod is then carried out with an oxyhydrogen flame. The melting must occur continuously and progressively from one end of the glass tube to the other in order to avoid the trapping of air bubbles between the tungsten and glass surfaces. The presence of such bubbles usually results in mechanically weak seals. A bead of GSC4 glass is then wound and sealed to the already fused glass sleeve near its centre and its edge immediately fused to a previously prepared end section of the discharge tube. The latter end section consists of a short length of GSC3 glass tubing tooled out to fit the GSC4 bead and connected to fused silica tubing via a short ring of grading GSC1 glass. An electrode already fused to the graded glass seal is shown in Fig. 4. The completed electrode is then electropolished in a concentrated solution of sulphuric acid, and sealed to the quartz body of

the discharge tube already wrapped with the cooling jacket. The external ends of the tungsten rods of the otherwise completed lamp are then electroplated, first with a strike of nickel, and then with about 0.005″ of copper, and the brass cooling discs are then soldered on to them.

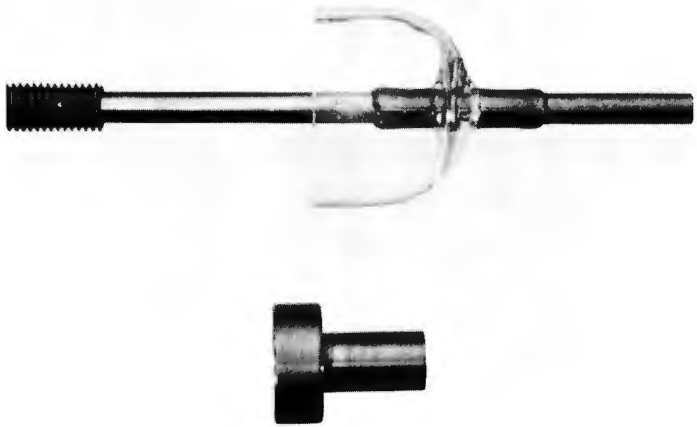

Figure 4

View of an electrode with a complete quartz to tungsten graded seal. The end cap is screwed into the stainless steel collar. The latter is welded to the tungsten rod.

LAMP EXCITATION

Because high stability of light output was not a primary consideration, no effort was made toward the designing of a well-regulated radio-frequency exciting source. A diagram of the oscillator circuit is shown in Fig. 5. The transmission line used between the oscillator and the lamp is a 50 ohm flexible coaxial cable RG214/U. The wide tuning range of the pi-network and its enclosure in a separate aluminium shielding box provided with coaxial feedthrough connections allow for its insertion anywhere in the transmission line connecting the power source and the lamp. The actual length of transmission line used between the matching unit and the lamp is obviously dictated by power loss considerations because of the relatively high VSWR set-up there. In practice lengths larger than about 2 metres are undesirable. The lamp is also fitted inside an aluminium container as is shown in Fig. 6 and power is fed to it through a standard RF female coaxial input connector. This lamp box has proven to be an adequate high-frequency shield since the RF leakage through such openings as the light output and gas and water inlet ports have proven to be quite tolerable even at high operating power levels. The length and apex angle of the conical lens holder screwed into the light exit port is determined by beam handling considerations.

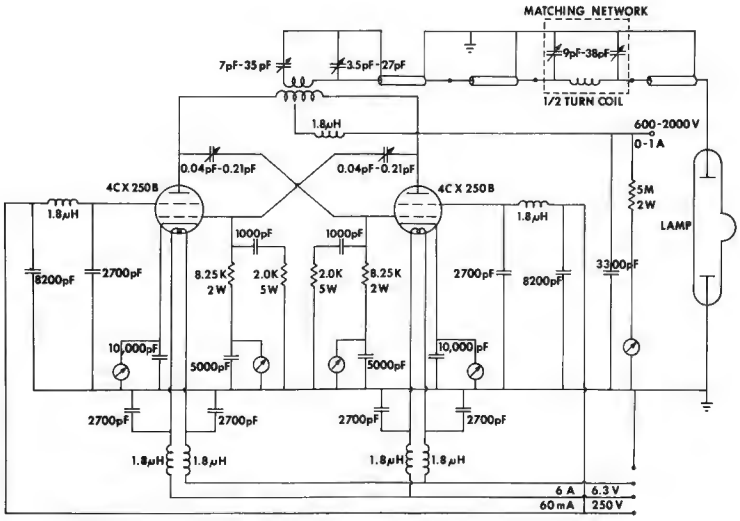

Figure 5
Circuit diagram of the 160 MHz oscillator with the auxiliary matching pi-network.

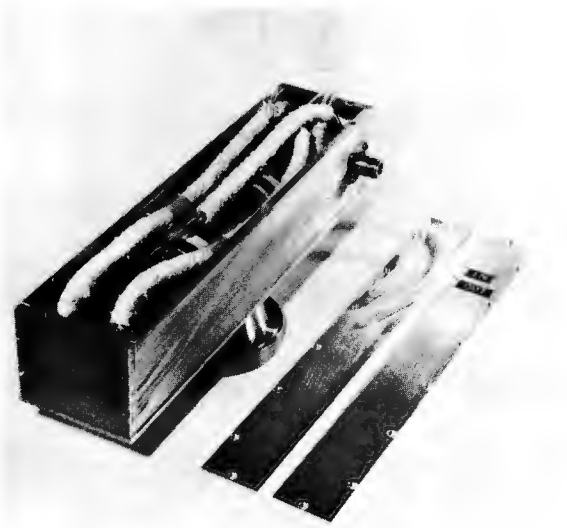

Figure 6
View of the lamp mounted inside the aluminium shielding case. The conical protuberance at the bottom carries the beam handling optics. The cooling fluid flows from the lamp outer jacket to the electrode cooling discs through plastic tubing wound with asbestos string.

PERFORMANCE

I) Emission Lineshape

We shall designate the three transitions 2^3P_0 - 2^3S_1, 2^3P_1 - 2^3S_1 and 2^3P_2 - 2^3S_1 responsible for the 1.08μ radiation of He^4 by D_0, D_1 and D_2 respectively. Theoretically and experimentally the relative strengths of the D_0, D_1 and D_2 transitions are 1:3:5 respectively. D_0 and D_2 are separated by 1.070 cm^{-1} while D_1 and D_2 are only 0.079 cm^{-1} apart [2], and will sometimes be referred to together as D_3. The lineshape of the infrared light emitted by the lamp was determined by means of a pressure scanning Fabry-Perot interferometer with a 0.691 cm spacer and a resolving limit of approximately 0.023 cm^{-1} in the wavelength region of interest. A typical spectral trace is shown in Fig. 7(a). Note that the D_3 and D_0 components shown there belong to two successive orders of interference. For the sake of comparison Fig. 7(b) shows the lineshape of the light emitted by a microwave excited discharge in helium gas at 3 mmHg contained in a cylindrical vessel of 1 cm diameter. The much lower self-absorption of the

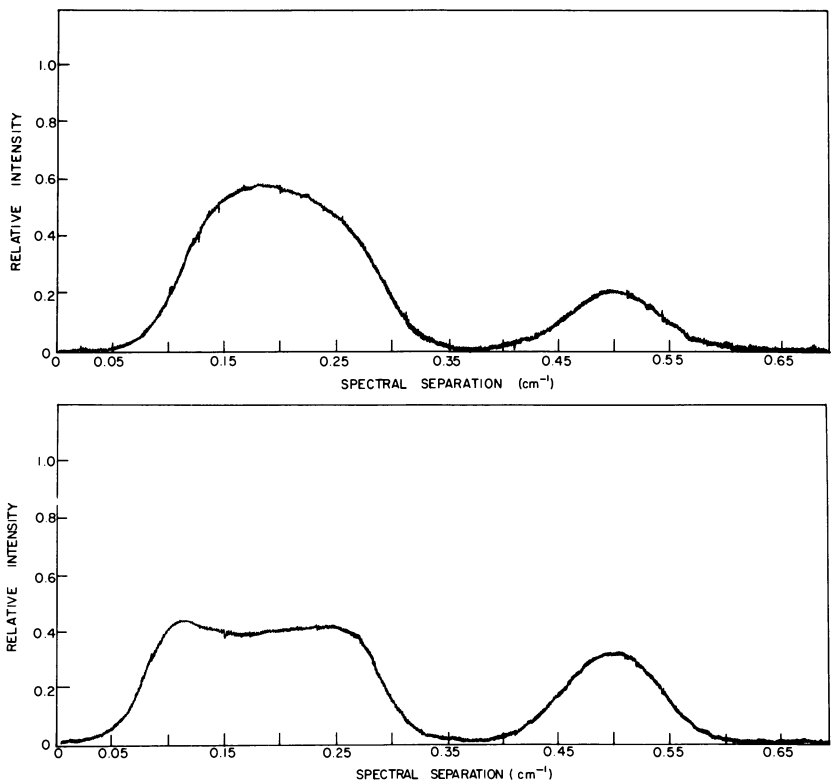

Figure 7

Spectra of the 1.08μ line obtained from (a) the lamp under investigation and (b) a microwave excited discharge contained in a cylindrical vessel of 1 cm diameter and viewed radially. The D_3 and D_0 components belong to two successive orders of interference.

light emitted by the 160 MHz lamp in the region of the pumping radiation is obvious.

(II) INTENSITY

Typical variations of the 1.08μ light intensity with both source power output and lamp gas pressure are shown in Fig. 8. A small displacement of these curves towards the 2.2 mmHg characteristic curve has been observed after only a few hours of intermittent operation. Optimum performance is usually obtained at a gas pressure of between 3 and 4 mmHg and an operating power level of 500 to 600 watts. Exceeding this power level limit results in intolerably high electrode sputtering rates with little increase in light intensity. When maximum absolute light intensity is desired an adequate cooling liquid must be used. Water has strong absorption bands in the near infrared and the water in the cooling jacket absorbs 38% of the 1.08μ helium light emitted by the constriction. Freon 113 ($CCl_2F.CClF_2$, boiling point 47.6°C) supplied by Du Pont of Canada, Limited, has been found suitable for cooling purposes but should only be used whenever light intensity fluctuations resulting from the formation of bubbles near the front surface of the constriction can be tolerated.

The measured total intensity of the 1.08μ light emitted by the lamp is 100 mwatts or 5.42 x 10^{17} photons/sec. The measured effective emitting area of 11.44 cm^2 of the constriction yields a photon flux of 4.7 x 10^{16} photons/sec/cm^2. If the cross-section for the interaction of a 1.08μ photon with a helium atom is assumed to be given by $2\pi\lambda^2$ (1.87 x 10^{-9} cm^2) and

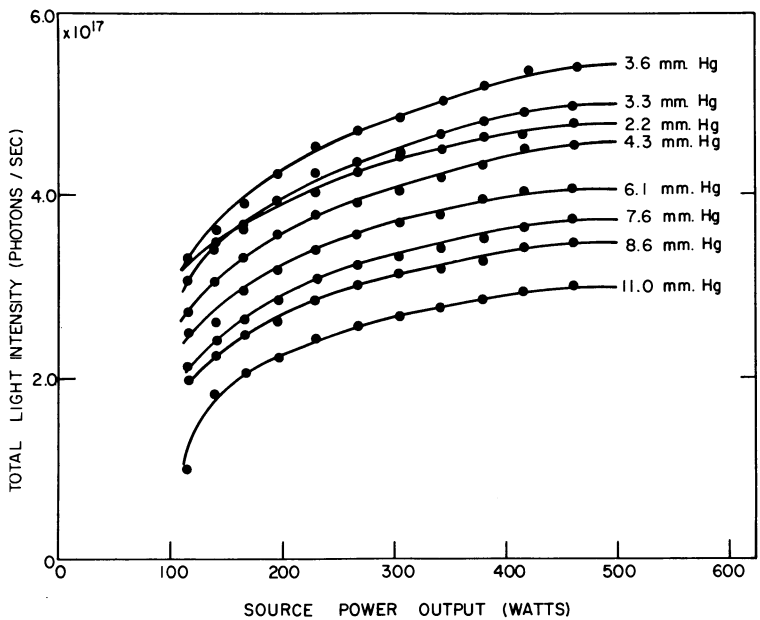

Figure 8

Typical dependence of the total intensity of the 1.08μ line on the RF power and the gas pressure.

at STP/min at 550 W operation. All light sources built with molybdenum electrode end caps have had useful lifetimes of over 400 hours. In all cases the molybdenum showed little sign of desintegration even after this total of operating time, although the ends of the discharge tube were heavily coated with a layer of sputtered metal. It is found that stoving the molybdenum in a hydrogen atmosphere at 1000°C prior to use considerably reduces the initial discharge cleaning time of the electrodes and the lamp.

Because of a variety of factors such as:

(I) the slow deposition of a semi-transparent molybdenum film on the walls of the constriction

(II) both unregulated flow and the formation of small bubbles at the walls of the discharge tube in the cooling fluid and

(III) lack of regulation of the power supply of the exciting source, it is difficult to achieve either a short or long run stability of better than 0.1% in the intensity of the emitted light. A voltage regulator placed in series with the exciter power supply only prevents large line voltage fluctuations from affecting the intensity level.

SECOND LAMP DESIGN

In an attempt to allow for both better cooling of the electrodes and greater mechanical strength of the graded glass to metal seals the original lamp design was revised to include modifications in the electrode structure. This is shown in Fig. 9. The molybdenum electrodes are re-entrant and cup-shaped, 25.4 mm length x 12.5 mm diameter, with the outside edge of the cup directly sealed to glass. A 3.17 mm copper pipe mounted coaxially with a 6.35 mm copper tube, which is screwed into the body of the electrode, make up the cooling system. Water flows in via the smaller tube and out into the gap between the two pipes after having come in contact with the electrode. "Woodhill" aluminium paste is usually used in the threaded section of the electrodes to stop water leaks that may develop there. Before fusing to the glass the electrode is thoroughly degreased, and electrolytically polished in a concentrated solution of sulphuric acid and then stoved in a hydrogen atmosphere at 1000°C. A quartz to Corning No. 7052 graded glass tube 17 mm O.D. consisting successively of 7940, GSC1, GSC3, GSC4, 7740, 7070, 7750 and 7052 glass is prepared with the 7052 glass end carefully tooled out to make a good fit to the electrode. The electrode is heated with an oxyhydrogen flame to a temperature slightly higher than the melting point of 7052 glass and quickly fused to the end of the graded glass tube in a conventional way while both are held in a glassblower's lathe. The sealing is carried out with an argon gas jet continuously blowing on the inside of the graded glass tube. The presence of a partial argon atmosphere prevents the build-up of too thick a molybdenum oxide layer on the surface of the electrode. Such layers usually lead to an unreliable glass-metal bond. The partial argon atmosphere further eliminates the evolution of molybdenum oxide fumes which may otherwise condense as hard-to-remove films on the inside of the graded glass tube. After cooling down to room temperature, the sealed electrode is immersed into a 50% by volume "chlorox" solution to etch off the outside

the ratio of the Doppler to natural halfwidth is correctly estimated at 1530 from the spectral trace, the maximum number of atoms contributing to the emitted radiation is approximately 1.35×10^{11}. Since approximately 40% of the light is self-absorbed, this implies that an atom emits about 6.7×10^6 photons/sec., or is excited to one of the 2^3P levels every 1.5×10^{-7} seconds. As the measured lifetime of this excited state is 10^{-7} seconds [3,4] it appears that an atom spends almost as much time in its emitting state as it does outside of it and hence that the lamp is operating very close to maximum efficiency.

ELECTRODE SPUTTERING, LAMP STABILITY AND LIFETIME

The lifetime of the lamp is essentially determined by the amount of electrode metal sputtered away during operation and collected both on the discharge tube walls and in the constriction. Most of the sputtered metal comes from the end caps of the electrodes since they make up the parts subjected to the most intense ion and electron bombardment. Furthermore it appears that the sputtered metal layers deposited onto the glass walls trap helium atoms and are responsible at least in part for the "clean-up" of the gas. This is strongly suggested by the following observations:

(I) A high sputtering rate results in a correspondingly high helium "clean-up" rate; this is particularly observable when the gas pressure drops to 1.5 mmHg or below and the "clean-up" rate suddenly increases several-fold, i.e. by a factor of 5 or more, over its values at the higher pressures. The explanation seems to be that at lower pressures the ions bombard the electrode surfaces much more energetically, since they make fewer collisions with other gas atoms, and are thereby more effective in causing sputtering.

(II) The "clean-up" is only little affected by the ever increasing surface area of the metal layer deposited on the walls; since helium does not diffuse through metals [5] its removal by the embedding and subsequent diffusion of the atoms through the fused silica walls, of which a large section is water cooled, does not appear to dominate the "clean-up" process.

It is therefore imperative to select a metal of high sputtering resistance when making these end sections. Caps made of either magnesium, aluminium or stainless steel proved inadequate. In the case of stainless steel, the most resistant of the three metals, the end caps desintegrate after approximately 100 hours of operation, and removal of the sputtered metal from the narrow constriction is required nearly every 30 hours in order to prevent the blocking off of the light. On occasions the sputtered metal builds up in a thick enough layer on the graded glass ends of the discharge tube to cause cracking of the glass in the area of introduction of the tungsten rods. This is caused by the heavy stresses which may develop on the glass surface when both the metal layer and the glass expand differently under the heat produced by the discharge. With stainless steel end caps the helium "clean-up" rate varies from 0.03 to 0.17 cc at STP/min at an operating power level of 500 W.

Molybdenum caps are used in the final lamp design because they sputter relatively little. The gas "clean-up" rate ranges from 10^{-3} to 10^{-2} cc

oxide layer formed during heating. After thorough rinsing in water the electrode is again electro-polished as described, and the completed section is sealed to the discharge tube.

The operating characteristics of this lamp are not significantly different from those of the first light source described. This is expected since the main body of the discharge tube is unaltered from that of the original lamp design. Unfortunately the graded glass seal never withstood more than 130 hours of operation. Moreover the improved cooling of the electrodes did not lead to a gas "clean-up" rate lower than that which had previously been observed with the first lamp. The only advantage of this light source over the original one appears to be its relative compactness.

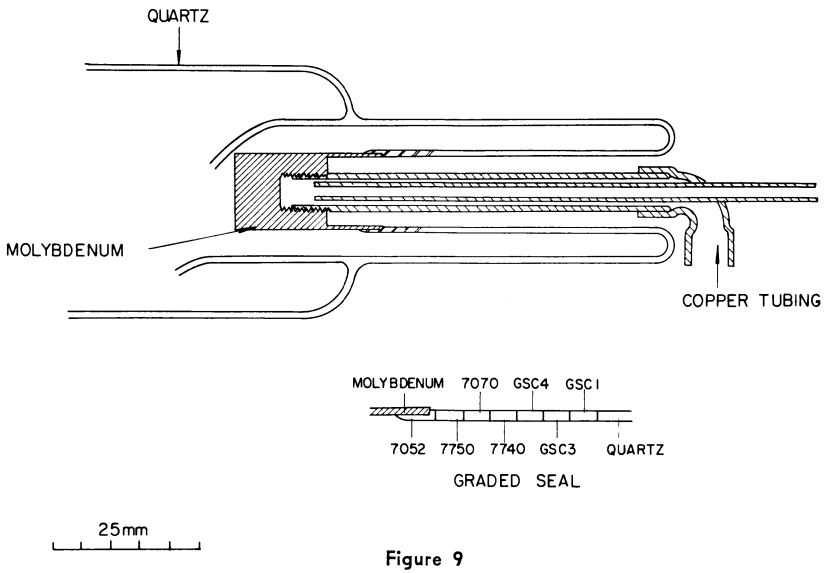

Figure 9

Cross-sectional view of a molybdenum re-entrant electrode used in the second version of the lamp.

THIRD LAMP DESIGN

In order to achieve a higher degree of compactness, a new design approach was taken. In this version the discharge tube is U-shaped as shown in Fig. 10. The electrodes are made out of either molybdenum or zirconium. The sealing on of the molybdenum electrodes is accomplished in the way previously described with the same arrangement of grading glasses. The fusing of zirconium to glass can be performed conventionally without the use of a partial atmosphere of an inert gas. The graded glass seal consists successively of 7940, GSC1, GSC3, GSC4, 7740, 3320 and either Kimble N51A or Jena G20 glass. The electrode must first be thoroughly degreased in any standard cleaning solution. The strongly bonded oxide layer on the metal is removed by first immersing the electrode into a silver soldering flux solution in an oven at 450°C and then polishing it

with emery paper. The completed electrode is electropolished in a 2:3 solution of hydrochloric acid and ethyl alcohol respectively and then sealed to the body of the discharge tube.

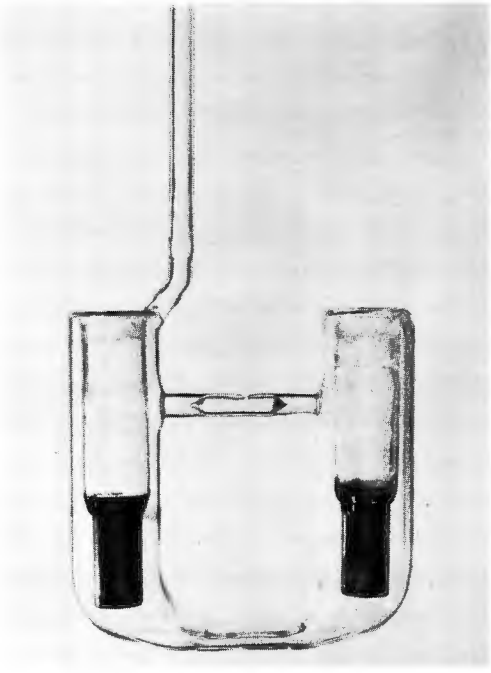

Figure 10
View of a U-lamp with zirconium re-entrant electrodes.

The lamp is usually operated when it is completely immersed in the cooling fluid as is shown in Fig. 11. The dimensions of the holding case shown are only typical. The lucite collecting lens is attached to the port at the bottom of the container with an ordinary epoxy cement (e.g. Lepage's Epoxy Cement). The separation between the constriction and the lens may easily be adjusted for optimum light collection. In order to ensure that the container be liquid tight, the coolant inlet and outlet feedthroughs are either cemented or soldered to the top removable lid. The latter carries the lamp support and rests on a rubber ring sunk into a rectangular groove at the top of the box. When the holding case is constructed out of a metal (e.g. brass) only electrically non-conducting liquids, such as Freon 113, may be used for cooling. As expected ordinary tap water, which is electrically conducting, is unsuitable for the purpose. When used it provides a low enough electrical resistance to ground that the lamp can be only weakly lit up. When the case is made out of an insulating material, and the light source operated at a reasonable power, it is found that the leakage conduction through the water between the elec-

trodes causes enough corrosion of the RF high voltage input lead to warrant its replacement after about 13 hours of operation. Furthermore, the dielectric container must itself be placed inside a metal shield to protect nearby electronics apparatus from stray R.F. pick-up. This not only makes for a difficult container construction, but also defeats the very goal of obtaining a compact light source. Tests carried out on the lamp showed that discharge heating of the re-entrant graded glass tubes is intense enough near the electrode junctions to melt part of the glass seals when the latter are uncooled. It therefore appears evident that the U-shaped lamp described above can be used successfully from our standpoint only when it is completely immersed in the coolant and when the latter is electrically non-conducting.

Zirconium electrodes perform in all respects much more satisfactorily than those made from molybdenum. They sputter visibly less than molybdenum, and the gas "clean-up" rate is correspondingly lower, approxi-

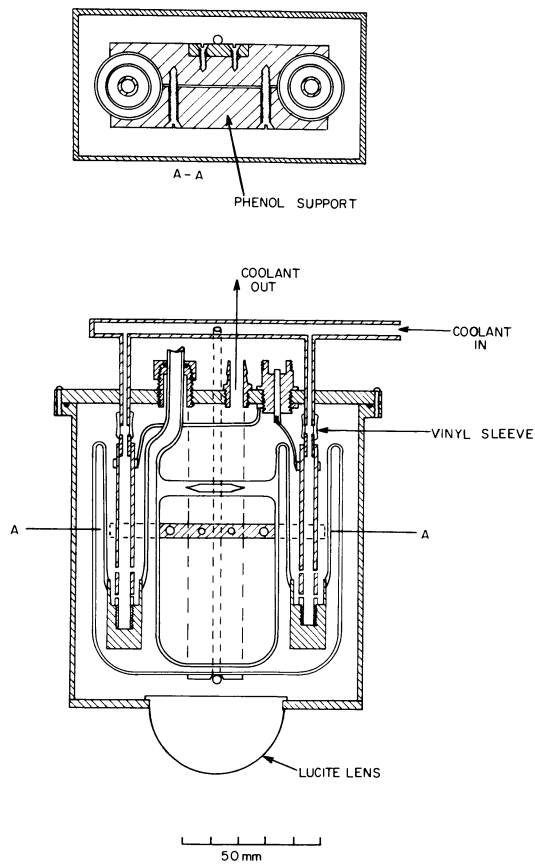

Figure 11

Cross-sectional top and side views of the U-lamp mounted inside the holding case. The dimensions of the container are only typical.

mately 10^{-4} cc at STP/min when the lamp is operated at 550 W. The dependence of the light intensity on the gas pressure and the input power, and the short and long run stability of the lamp, are essentially unchanged from those of the other light sources.

CONCLUSIONS

The construction and performance of three helium lamps have been described. These light sources are capable of generating intense 1.08μ light with low self-absorption. Linear lamps with tungsten rod electrodes provided with molybdenum end caps meet best the requirements of long useful life and ease of assembly and of operation. The use of re-entrant electrodes has proven successful from our standpoint only when the graded glass to metal seals are kept cool by direct contact with a liquid coolant. U-lamps are simpler in design, easier to construct and more compact than any of the other light sources described. However they require an intricate mounting arrangement and must be completely immersed in an electrically non-conducting liquid to operate satisfactorily.

The rate of electrode sputtering determines the useful lifetime of the lamps and appears to control the rate of helium "clean up". It is therefore important to select a metal of high sputtering resistance when making the electrode end caps. Metals such as molybdenum and zirconium have been found suitable for the purpose.

ACKNOWLEDGMENTS

We would like to thank Dr. A. D. May of the Physics Department of this university for suggesting the use of re-entrant electrodes in the last two lamp designs. We also wish to acknowledge the collaboration of Miss E. I. Dennig and Mr. A. K. C. Kiang in the construction of the required apparatus. This work was supported in part by a research grant from the National Research Council of Canada.

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GLASS TECHNIQUES FOR LASER FABRICATION

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Washington, D. C. 20390

Various methods are used for producing vacuum tight seals using optically flat windows for gas laser studies.

The use of epoxy has the advantage of convenience and it disturbs the window a minimum during sealing if proper care is taken. However, it is not recommended for use at temperatures much above 100°C. This temperature limitation precludes certain applications and also precludes high-temperature tube bakeout which is important in controlling gas purity for diagnostic studies of the laser plasma and for assuring very long tube life.

Another type of seal in use is a "cold seal". In this process the window is optically contacted to a polished tube end and then brought to a temperature near annealing where a molecular bonding occurs. This bonding occurs faster if a partial vacuum is used or a small oxy-hydrogen flame is used on the outer edges. Such a seal is somewhat lacking in mechanical strength and requires extreme care to keep the windows from failing due to cleaning or the sudden release of vacuum.

As a solution to the above mentioned disadvantages several techniques have been developed for completely fusing the quartz windows, maintaining optical flatness, and allowing high temperature bakeouts in excess of 500°C to control gas purity for diagnostic studies of the laser plasma. These tubes have actually been raised to 500°C while lasing at 6328 Å with no decrease in output power.

The windows are made from 3/8" high purity quartz 2" in diameter shaped to a 1½"step for holding on one side and tapered out to the 2" diameter on the other face. The window is then fitted into a 2" diameter bell which has a 45° recess taper. This allows a minimum volume of glass flow during sealing and also provides a smooth enough contact to prevent the torch flame from driving any silica vapor into the bell interior where it might deposit on the inside face of the window. Prevention of such silica deposits is the crucial requirement to seal windows without deterioring the optical quality. (1 and 2)

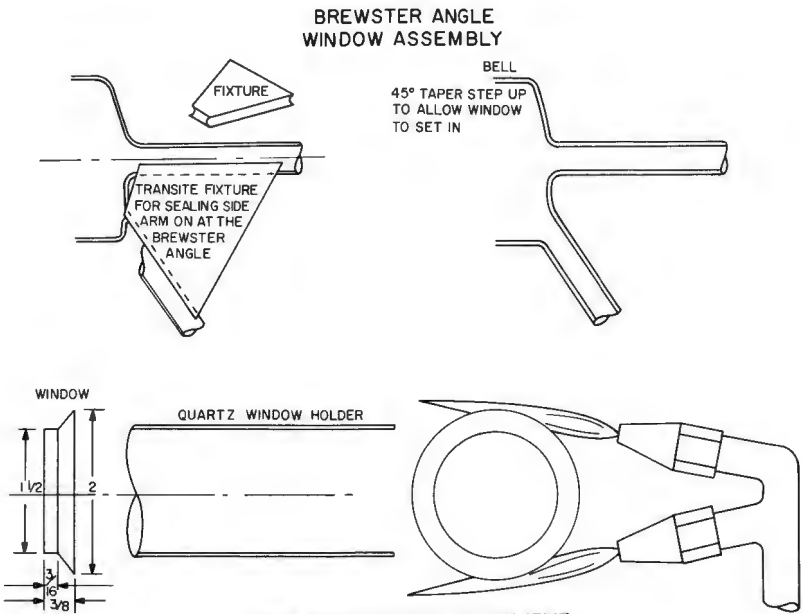
The bells are prepared with two ports, an axial one for use in sealing the window and the one set at the Brewster angle. Upon cooling after sealing the window flatness will deteriorate to 2 or 3 rings, but after annealing at 1000°C for 1 hour the windows will recover their original flatness of $\lambda/10$. I wouldn't advise annealing the cold seal windows. Of the 4 I have checked unannealed the flatness at the center was approximately λ 1/4 convex. I annealed the same 4 windows and they went concave to approximately 4 rings.

The other technique is to cut the Brewster angle on your tube which makes the face eliptical, shape your window to this face feathering the edges toward the center of the windows which are 1/8" thick. A spring loaded piece of pure graphite shaped to the window keeps the window and

tube face in optical contact. The feathered edges are then sealed, care being taken to keep the flame from pointing toward the center of window. After annealing approximately ½ of the window remains λ ¼ or better.

Initially, the output from a laser is reflected back on itself by a return mirror M, as shown. (Fig. 3) This establishes a laser reference axis. Alignment is quick and simple because of the brightness of the visible laser beam (about 1 mW at 6328Å).

The two halves of the laser tube T are then inserted such that the axis of each half coincides with the laser beam reference axis. For a tube bore



LASER REFLECTION ALIGNMENT

Figure 1

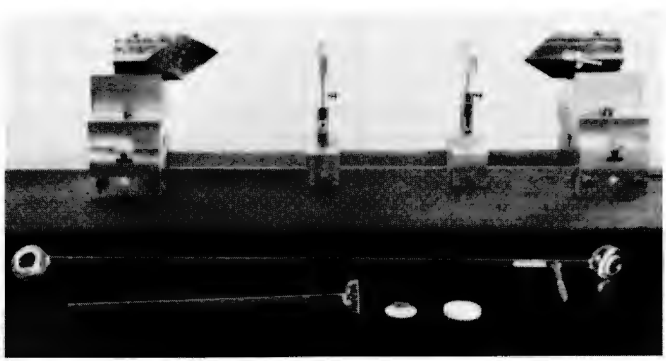


Figure 2

only slightly larger than the laser beam diameter this is moderately difficult. The brightness of the laser beam shows up any internal reflections clearly. (4)

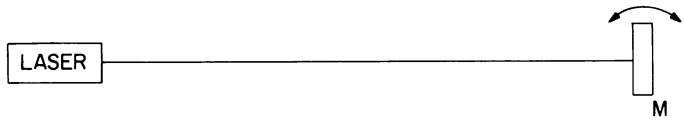


Figure 3

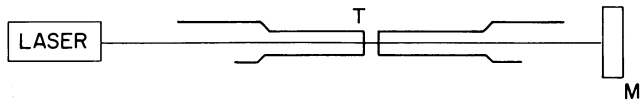


Figure 4

The laser windows w_1 and w_2 can now be held in place temporarily with tape. The reflections R_1 and R_2 from the outside surface of the windows converge toward a common region. (Reflections from the inside surfaces of the windows diverge and are not used.) These reflections are easily seen on a white card. (They should never be viewed directly, of course.) The reflections R_1 and R_2 will in general be skew lines in space and consequently will not meet at a common point. The situation is as indicated in case A. or C. As the card is moved toward or away from the tube, the reflections will approach each other to within a minimum distance dependent upon the relative skew of R_1 and R_2. (5)

By rotating one tube half about the tube/laser common axis, case B can be attained, in which R_1 and R_2 meet at a common point. When this occurs, both window normals are coplanar. The two tube halves can then be sealed. (6)

This method does not guarantee the accuracy of the Brewster angle, which must be measured separately. It does assure minimum skew and alignment of the two halves of the laser tube.

The latest in the gas laser field appears to be a CO laser with liquid nitrogen cooling. Not much information is available about these tubes but from a safety viewpoint extreme care must be exercised. Several explosions have occurred from an accumulation of an unknown gas or gases that have been condensed. The color of this gas is blue and we are told that when you see this, look out.

To build a 6 ft. CO laser is not too easy without proper lathes and annealing oven. I built 2, using 1″ O.D. for the lasing wall surrounded by a 2″ O.D. tube for the liquid nitrogen cooling with a 3″ O.D. tube for the vacuum wall. This tube had 3 electrodes sealed through these walls including the filling tube brought through the center of the tube. After a thorough annealing in my 6′ deep electric oven I pretested the tube for liquid nitrogen cooling. Both times the tube fractured at the ringseal of the filling tube.

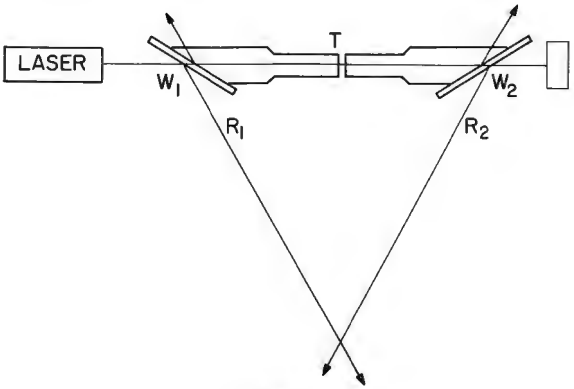


Figure 5

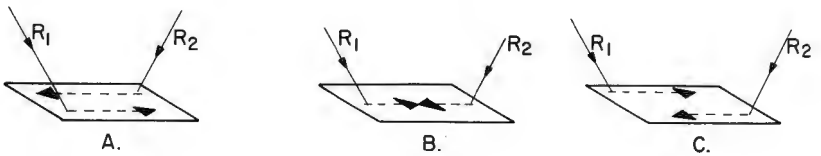


Figure 6

The only way I know of eliminating this fracture, that is due to the vertical contraction of the glass seal would be to use a metal bellows.

After learning of the two explosions I thought of other means to build a safer tube and arrived at a very simple design and it is 75% as efficient as a vacuum wall jacket would be.

I made the equivalent of a 6′ condenser with female joints at each end for filling. I then cast a ½″ thick plastic coat (Eccofoam) around this jacket. Over this plastic I then added a layer of glass tape. This insulation eliminated the vacuum wall, is 75% as efficient, plus giving the operator a good safety shield in case of an explosion. (7 and 8)

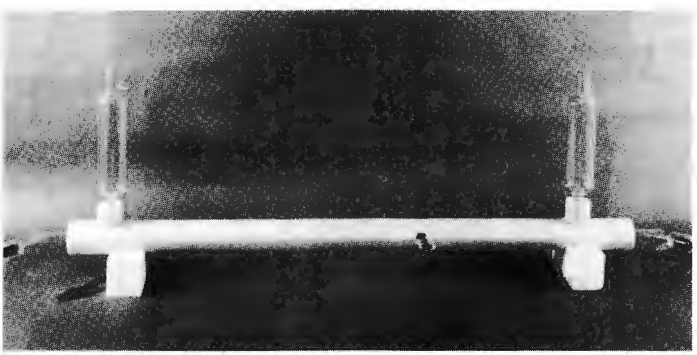


Figure 7

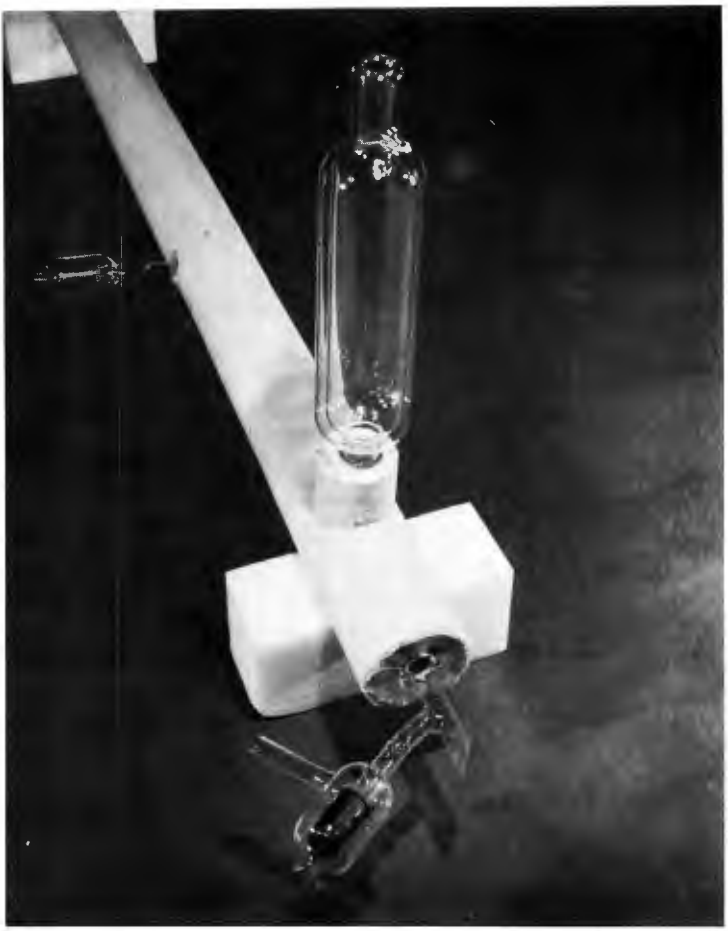


Figure 8

STRESS-STRAIN MEASUREMENTS IN GLASS

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Hot glass cooled without special heat-treatment is usually in an unequally strained condition which increases the probability of breakage.

Annealing is a process of controlled rate cooling by flame or furnace treatment to remove or reduce inherent strain-stress pattern and therefore decrease the danger of breakage.

Optical glass and joint seals of and with a variety of different glasses and metals and ceramics require fine annealing and controlled stressing to obtain reproducible optimum results in glass.

DETECTION AND MEASUREMENT OF STRAIN

Strain in glass is detected by its effect on polarized light, an effect which is similar to that of a birefringing crystal. Brewster discovered in 1813, that a glass plate under load behaved as a uniaxial negative crystal, in which the direction of application of the load was the optic axis; and that the birefringence as measured by the path difference between the two plane polarized light waves formed on traversing the strained block, was proportional to the strain. The birefringence thus serves as a direct measure of the strain, but the relation between stress and strain, *the stress-optical coefficient* depends on the composition of the glass.

Numerous polariscopes for the detection and measurement of strain have been designed, described and are in use today. For accurate quantitative measurement of strain, either a Babinet compensator or the more sensitive bi-quartz wedge described by Wright,[1] should be used.

Translucent or semi opaque glasses can be examined by a method devised by Littleton,[2] used by Mendenhall,[3] Ingersol,[3] and Johnson[3] in which either infrared or ultraviolet radiation is used.

The quantity measured is an optical path difference for the light waves, vibrating parallel with and normal to the axis, for the total length of path, L.

For unit length of path the birefringence $\overset{n}{E} - \overset{n}{w} = \triangle\ n/L$. This difference is usually expressed in millimicrons ($m\mu$) $= 10^{-6}$ mm.

In optical glass a birefringence of 5 $m\mu$/cm path-length is accepted as satisfactory annealing. (12.5 $m\mu$/1″) path length.

Plate glass should not exceed 50 $m\mu$/cm path length.

Chemical glassware according to their thermal and mechanical requirement should be located between these two standards.

Twyman[4] proposed that the limit of allowable stress in commercial glass be 1/20 the breaking stress which corresponds to about 100 $m\mu$/cm path length. When it is desired to express the strain in terms of stress units, a knowledge of the stress optical coefficient is necessary.

For most glasses a load of 1 Kg/cm^2 = 14 lbs/1 sq. in. produces a birefringence of about 3×10^{-7} cm. A strain of 30 $m\mu$/cm corresponds to $30 \times 10^{-7}/3 \times 10^{-7} = 10$Kg/cm^2 or about 140 psi.

To demonstrate compressive and tension stress and their relation to load and thermal history the following examples will be shown.

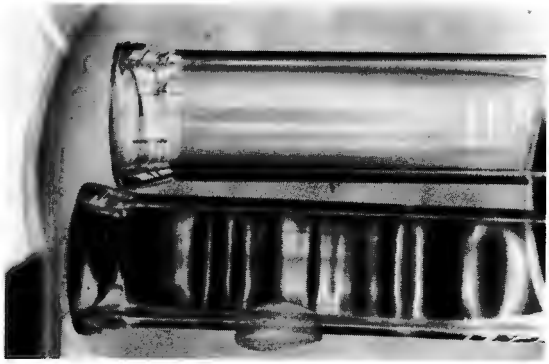

Figure A

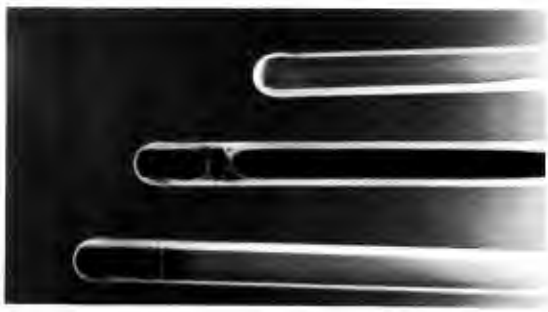

Figure B

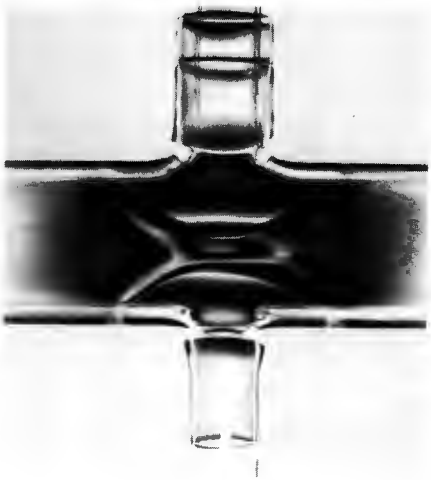

Figure C

Figure D

Figure E

The first five figures were photographed through a polarimeter with half wave plate fully crossed to show isoclines.

For purposes of better color contrast however, only pictures taken through the polariscope were used. You will recognize these samples when you use these and others as taken through the polariscope.

A — Short sections of glass pipe

B — Three rounded glass rods (half inch dia.)

C — Glass pipe with side seals

D — Annealed and unannealed Kovar to pyrex seals

E — Ehrlenmeyer flask with half inch rod sealed to bottom

Too many figures would have been involved had we attempted to make pictures of every setting required when the polarimeter was used.

FIGURE COMMENTS

Stress-strain interpretation on glass in polarized light with slight residual transmission in the 4300 angstrom range. The instruments used were a glass polariscope with mounted quarterwave plate in the ocular and a polarimeter with half wave plate fully crossed.

Figure 1

Glass tubing under two point bending load (see thumbs). The bottom half is under compression (blue) and the top half under tension (yellow-white). The tension is greatest in the center upper half as shown by light intensity, width of strain field and coloring. The glass is borosilicate exp. 33 x 10^{-7}°C. Estimated stress: stress optical coefficient 3 x 10^{-7} per 1000 g/cm² a strain of 30 mμ/cm corresponds to 30 x 10^{-7}/3 x 10^{-7} = 10 Kg cm² or about 140 PSI.

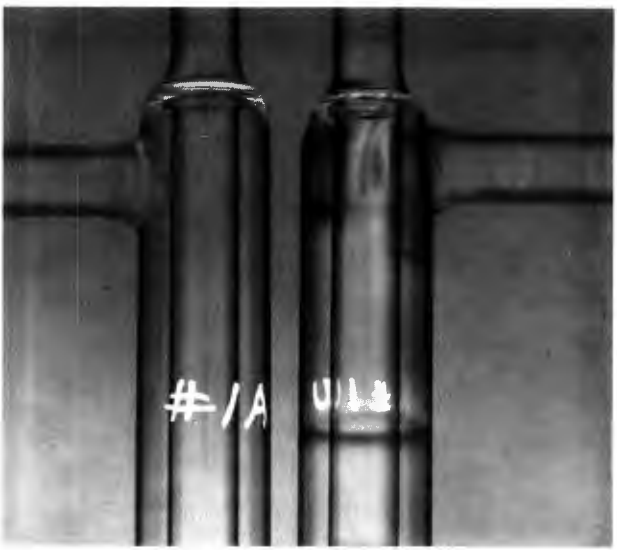

Figure 2

Tubular joints for traps or condensers: annealed trap shows residual stress in end seal of less than 3 mμ (slight yellow color). Unannealed trap shows strong yellow fringe approx. 30 mμ plus stress bands on T tube connection and stress bands 2" below joints with blue and yellow demarcation, indicating localized heating without proper thermal gradient or stress relief, approx. 10 mμ.

Figure 3

Variety of joints showing parallel samples in the annealed and unannealed state. T joints showing tension stress in ringband at junction (yellow). Compression stress in center of tube (blue) and increase in tension stress opposite the joint in the wall (intensity in the yellow-white) approx. 15 mμ. Seals on either side of the annealed T joint. one set is soft glass; the other hard. The lower two are annealed and the upper two unannealed. The soft glass shows intense yellow and blue band approx. 25 mμ. The hard glass has brighter blue and less intense yellow approx. 12 mμ.

Figure 4

Upper two tubular joints of soda lime glass. Top unannealed joint with slight yellow blue bands approx. 15 mμ. The bottom three are borosilicate glass rounded end tubes. Hand annealed furnace annealed and unannealed. The ring or band stress is approx. 12 mμ. In judging colors, allowance has to be made for the thickness of the glass as the pathlength of light and its birefringence shift, is a product of retardation X length.

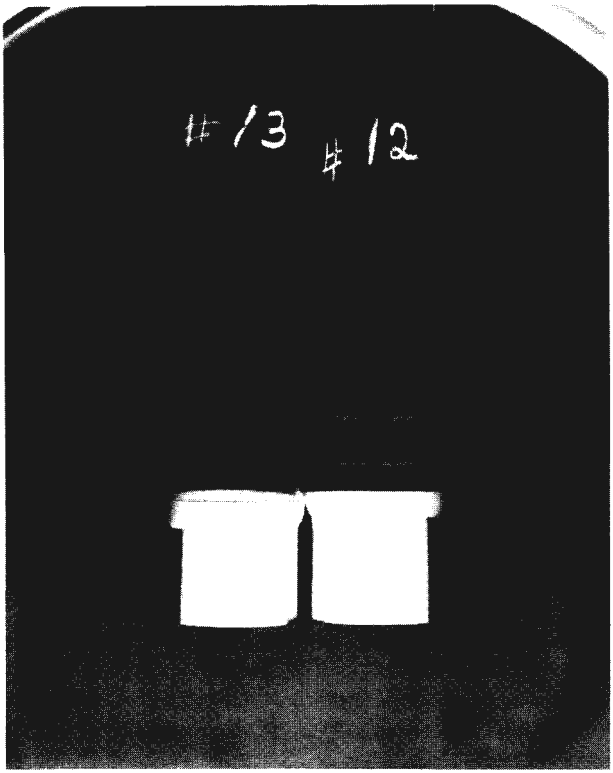

Figure 5

These are commercially available seals from different manufacturers. They are standard 1½" graded seals consisting of Kovar metal, joined to 7052 glass to 3320 glass to 7740 glass tubing. A slight difference in manufacturing technique as one Kovar tube is lined on the inside as well as the outside with glass (no yellow fringe). The other tube has no glass inside but shows a slight yellow fringe of approx. 7 mμ. The normal strain in the glass joints decreases progressively towards the 7740 glass due to the smaller thermal contraction factor, but residual values are in the range of 15-25 mμ which are safe in this case because of thickness of wall and right distribution.

→

Figure 6

Two inch Kovar to pyrex seals. #14 annealed and #15 unannealed. In #14 Kovar to 7052 shows no birefringence but residual strain between 7052 and 3320 approx. 15 mμ and approx. 18 mμ between 3320 and 7740. #15 shows strain from 10-15 mμ between Kovar and 7052; 20 mμ between 7052 and 3320; 25 mμ between 3320 and 7740 and residual band in the 7740 of approx. 12 mμ.

Figure 7

This is commercial glass pipe with which nearly everyone is familiar. Piece #11A shows no strain while the unannealed sample shows distinct bands from 30-10 mμ making special allowances for thickness and direction. The unannealed sample of course contains the tempering strains induced by the manufacturer.

Figure 8

Three rods with rounded ends (½" dia.) (1) fully annealed (2) end rounded on rod as received from manufacturer and (3) preannealed rod with subsequent rounding approx. strain 15 mμ compression. Commercially available qtz to pyx graded seal show perfectly acceptable band stresses of approx. 25 mμ. Tubular bend shows no appreciable strain (25 mm tubing) slight band stresses of 5-8 mμ at pulldown occurred only because the tubing was pulled to a point before making the bend for this picture.

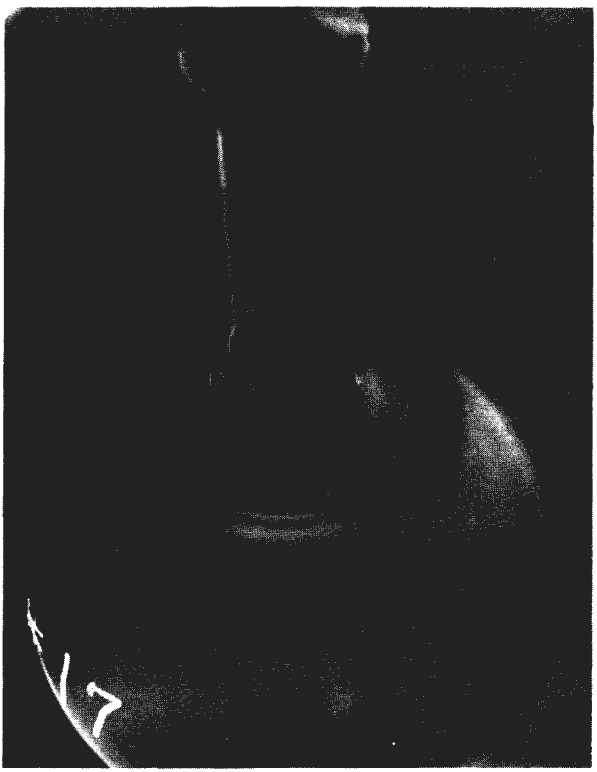

Figure 10

This is a 500 ml RB flask with a 22 mm dia. length of tubing sealed to the bottom. The colors at the end of the tubing are caused by tape that was used to hold the flask in place for the picture. The residual strain of 35 mμ is typical for section ring displacement with isometric (Maltese cross bysection) plus slight residual strain in tubing of 5-15 mμ. Because of the fairly thin wall of glass in this slide and the next slide, the strain shown is probably the most extreme of any of the samples shown.

←

Figure 9

This again is glass pipe which had been preannealed. The glass to metal seal and the 1/8" tungsten lead through on the opposite side were attached using a glass lathe in an attempt to produce some nice even strain patterns for this picture. No annealing whatsoever was done. A similar, longer piece than this was made for some experimental apparatus but it was properly annealed for obvious reasons. The ringstrain in the smaller tubing is approx. 25-35 mμ. Localized T joint strain in thick wall joint of 35-45 mμ, and center trapezoidal pattern of only 27 mμ (thickness corr.) Because of the thickness and the double wall, the strain is apparently not quite as bad as it looks.

Figure 11

This sample shows a ½" rod sealed to the bottom of a 1000 ml Ehrlenmeyer flask. Again this is the same as a piece of special apparatus that was made. This also was done in a lathe. This shows a Maltese cross pattern (isoclines) with multicolor strain pattern ranging from 40 mμ in the contact area to 15 mμ at the edges. Naturally the original piece was properly annealed in a furnace but this sample had no annealing.

Figure 12

This is a picture of an item which I am sure is very familiar to everyone. Tempered safety glasses which have been case hardened on both surfaces by airject blast. They are in full compression on both outside surfaces with approx. 100 mμ of compression. Note the stress and thermal flow pattern in the frame especially the bridge and hinge attachments.
These slides are representative of typical stress/strain pattern and should aid in the interpretation of fabrication techniques and shortcomings.

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NEW GROUP OF DEMOUNTABLE TUBE AND WINDOW SEALS FOR VACUUM OPERATION

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The subject matter of this paper, to which the program refers has evolved from a much broader concept, which is that of the utilization of interchangeable threads on scientific glassware.

This development is quite in keeping with the theme of the meeting and with the history of glass. Viewing in retrospect, the art of glassblowing has been changing to a science for several decades, in a very natural sequence. In the earlier days, which extend into the "thirties", much of the glass called "apparatus" was conceived and built by the scientist. This is a very unprofitable situation, so that, wherever practical, a skilled lampworker was employed. Thus the small lampshops originated, rendering a service to laboratories having occasional need for their skills.

It is apparent that the key to economic success for small lampshops is short time delivery (within one week's time) of specialty items. Delivery is also the key to success for larger lampshops; but this, *they* accomplish by maintaining stocks of specialized equipment which has been more or less standardized over the years. Standardization according to function and size has helped the scientist immeasurably, and further standardization will be absolutely essential to keep abreast of the accelerating pace of the scientific community.

Numerous organizations are engaged in this effort. Two of the most comprehensive efforts are those of the International Organization for Standardization (ISO) which is attempting to standardize all the major categories of laboratory glassware, even beakers, and in which the U. S .A. is represented by the U. S. A. Standards Institute with Scientific Apparatus Makers of America (SAMA) participation, while the second is Federal Procurement together with N.B.S. and SAMA. A vital third force is A.S.T.M. particularly in analytical equipment. Other important influences are the A.C.S. Microchemical group and the Commercial Standards assistance group of the U. S. Department of Commerce.

Literally hundreds of items are being standardized, enough that scientists will have almost immediate availability of basic tools on a world wide basis.

This is simply the result of economic force. Science has discovered that a higher rate of achievement is possible from disciplined team effort, the old story that "Two heads are better than one". — It also means that the cost of keeping technical men idle has increased. One large company has estimated that it costs well over $200 per day to keep one technical man idle, and they are willing to pay a large premium for special glassware in order to get it within 48 hrs. As a matter of fact, one of the larger

present-day lampshops established itself by providing this "emergency" service. Another company is willing to guarantee $50,000 per year in purchases to obtain 7-10 day delivery. The emphasis is on delivery, with very little sacrifice of quality.

In such an atmosphere, the innovative glassblower must have a more thorough knowledge of the sciences than has been heretofore required, but perhaps an even more important factor in innovation is a thorough knowledge of the attributes of the apparatus available; translated as "what works and what doesn't, and under what conditions, and why."

This is a field in which we concern ourselves quite extensively, because through it many of our products are improved and others originate. Our purposes, generally speaking, are somewhat different from yours although they often prove mutually beneficial. Our quest is for innovations having wide spread application, or for super specials which are within our capability. To illustrate, some of the former which we have invented or developed are the spherical joint, the fiber filter, precision tubing in which we improved accuracy to broaden the market; we were the first to produce interchangeable syringes, for instance, and the first to extend this to the clear-unground barrel, also Trubore stirrers, Teflon®[1] clad joints and stopcocks, reinforced Teflon stirrer shafts, and Instatherm,®[2] a practical and convenient method of applying heat by fusing the element to the glass surface. The Mini-lab system also must be considered an outstanding contribution, developed in a three way cooperative program. Its success is attested by the alacrity with which it was adopted. The wide mouth resin reaction kettle is another such item. All of these resulted from a need for a better, or non-existent product.

You will pardon me I am sure if I seem to be bragging; but we are proud of the acceptance of the contributions we have made, and rightly so. They have not been hap-hazard happen-stances, but have resulted from planned programs to produce better products, and part of a policy to increase profits to us and benefits to the consumer through progress. We now have another product which I know is of interest to some of you . . . Threaded glass joints and couplings.

Now we do not claim to be the originators of glass threading, we merely claim originality in certain aspects which eventually will be evident.

Some years ago we received a request for a stopcock which would be tight enough to allow shipping radioactive gases, and shortly afterward, another request for a high pressure/vacuum container and connectors. Readily available items proved unsatisfactory.

Now sometimes we have to be hit with an earthquake before we realize the potential of a product, but in this case it was laid out before us. All we had to do was solve the problem. If you will permit me I will take you on a tour through the research and development.

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[1] Trademark of E. I. du Pont

[2] Trademark of Ace Glass, Inc.

First we built a word prototype of the product with the following attributes:

1. Pressure tight to over 200 lb/in^2
2. Vacuum tight, with a low intrinsic leak rate, at least sufficient to maintain an internal pressure of 10 to 100 microns for three to four days in the case of the radioactive gases, even lower rates for high and hard vacuum use (hard vacuum generally is considered to begin at a pressure of 10^{-7} Torr and continue into outer space limits.)
3. Bakeable to at least 200°C.
4. Easily assembled and disassembled.
5. Chemically inert — non-contaminating.
6. Capable of being annealed.
7. Interchangeable parts.
8. Break resistant construction.
9. Minimum size.
10. Easily operated — (stopcock).
11. Reasonable cost.

A cursory consideration of these ruled out ground joints and stopcocks employing grease. Plastic sealed members, such as with our Plastic Coating, were not considered reliable enough at high pressures.

The pressure consideration forced us in the direction of O-ring seals, which when properly designed are capable of retaining high pressure and high vacuum; but as we soon discovered, special o-rings are required for a vacuum lower than 10^{-5} Torr. Viton®, properly compounded, has the least vapor pressure, is inert, and self-lubricating, and is satisfactory to 10^{-7} without baking. An initial pressure of about 5×10^{-6} can be reduced to 1×10^{-7} by pumping for about 48 hrs. When baking out, it is extremely important not to exceed 470°F. Baking at 450°F. for 4 hrs. will usually suffice.

The requisite chemical inertness suggested Teflon, but it is known to be somewhat porous, not particularly good for a high vacuum system. However, a survey of other materials still left something to be desired, so we returned to take a second look at Teflon. A specially processed high density material turned out to be satisfactory, bringing with it a bonus in better machining properties with the increase in cost.

We felt at this point that we had the nucleus of a better product. We could go into the hard vacuum range with moderate baking, and we had high pressure capability with minimum contamination, but the format had yet to be resolved. We could use a standard stopcock plug and place the O-rings in annular wells around the bore openings applying customary tail tension to regulate O-ring compression, a real advantage if the gases should cause O-ring swelling. Alternatively we could use a valve stem structure, a type of which was already on the market, and use a more or less fixed compression ratio.

We made a survey of types already available, analyzing each one, and decided on the valve stem type. Now we needed glass threads, but our capability was not commensurate with cost.

Should we have internal or external threads, and what size? External threads were readily made by blow moulding or grinding, and inexpensive; but they were vulnerable to impact, continuously exposed to dust; also, the ground threads, although more precise, had low shear strength.Using an external glass thread poses other difficulties; it increases the cost of the handle, and in machining it is difficult to clean up a thread in a blind hole. Moreover, we wanted to take advantage of the natural lubricity of Teflon to provide a smooth working thread. Teflon has still another advantage, it will cold flow to make a precise thread fit with almost zero back-lash, enabling the operator to make minor adjustments in position without hunting, To further this purpose a reference dot could be incorporated in the handle and a linear scale, referenced to O-ring position, added to the barrel. But Teflon is too slippery for a handle, and its cost/performance aspect weighted the decision in favor of an internal glass thread coacting with a threaded Teflon plug.

All we needed now, was an inexpensive way to make internal glass threads, but we didn't have the method. I don't know whether any of you have tried making glass threads; there are three basic methods, shrinking, wiping and tooling, and each one has attendant difficulties.

With shrinking, the thread surface must be precisely uniform or it will not unscrew. Longitudinal contraction also can cause enough binding to prevent withdrawal of the form. The mandrel can be unscrewed before the glass sets, but there is the constant and actual danger of distorting the threads.

Square, or Acme, threads are easier to work with than the tapered machine threads because the glass does not fully run into the deep square corners and the outside of the form can be centerless ground to the required precision; however, it pinches quite readily unless a metal with a low coefficient of expansion is employed, even when the form is slightly tapered.

Wiping is not suited to hand operation, it can be done with a paddle on a lathe.

Our object was to develop a fast hand tooling method because we are oriented in this direction. Hand tools have been around since about 1860, and are surprisingly close to the present day models in overall design. We found a rounded thread preferable to the others for tooling. We stayed to standard machine thread pitch and adjusted the dimensions to a Class 2 fit with the plastic, thus assuring interchangeability with machine made parts.

As you may have seen, it is possible for a solid Teflon stem to push the end out of the seat if standard wall weight is employed, because hundreds of pounds can develop into thousands of pounds per sq. in. thrust. So, in addition to providing a heavy walled seat for compensation, some of the thrust can be absorbed by reducing the Teflon stem diameters

somewhere near the seat. The thrust then causes a reflex stem compression. If this section is made optimum in size it will also distort sufficiently to take care of slight misalignment of the seat.

Another slight thing to be considered is the clearance between stem and body. The stem must be sufficiently small to prevent its touching the wall when the stopcock is baked out. The maximum temperature for o-ring bake out is ideally 450°F. so this value plus a safety factor is the upper design limit.

At this point we not only have a good hard vacuum valve but a thread which can be used for a variety of purposes, one of which is a vacuum manifold to which instrumentation can be connected easily. (Fig. 1)

Pipeline systems can be constructed using chemical piping (Parts are now available in Corning pipe dimensions. Couplings are available in Kel-F® and Teflon). (Fig. 2)

Figure 1

Figure 2

® Trademark of 3M

The couplings are sealed at one or both ends of the threads by o-rings and there is sufficient flexibility to accomodate considerable misalignment, yet the joint is rigid enough for long runs without support.

In the laboratory apparatus field numerous adaptations already have proven value. "High pressure" reaction tubes etc. (leak tight at 200 lb./sq. in. and over); Chromatographic column systems; interchangeable burettes; low pressure slip joints with o-ring seals for thermometers, stirrers, impingers, electrodes and similar pieces.

Figure 3

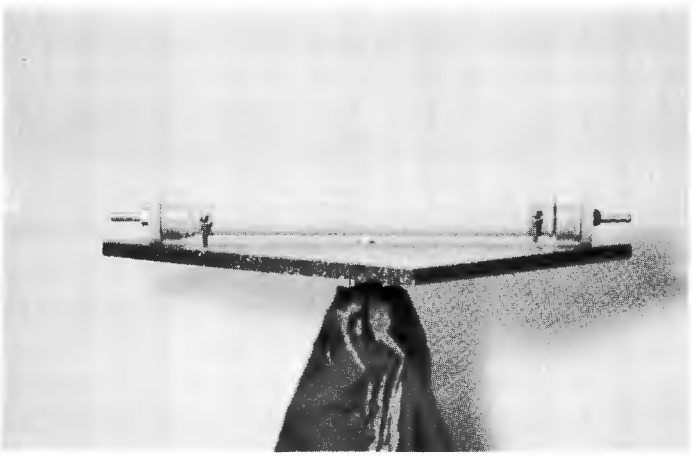

Figure 4

Figure 5

Another very recent application is construction of absorption cells with interchangeable optical flats which are o-ring sealed using a threaded bushing. (Fig. 3) One laboratory uses a laser beam to align the cells quickly and accurately. This also makes it possible to monitor refractive index in a dynamic system without super-expensive in-line equipment. This is a structure offering enormous time saving advantages in cell construction, while admitting the use of end materials which before were largely impractical.

Water cooled resistors are now being used in laser circuits at 50 amps 230 volts. (Fig. 4) We do not know how much higher we can go in voltage because we have no testing means for such power.

We have named this the T joint which symbolizes "Threaded Coupling." It is presently available in four medium wall tubing sizes, ½", ⅝", 1" and 2" I.D. although the 2" is only available on special order. Figure 5 shows it applied to a flask, impinger and cold trap for variable immersion, a jacketed chromatographic column (or condenser) and a distillation adapter, just a few of its applications.

We welcome all inquiries on its use, and appreciate the cooperation which we have received from glassblowers who have been using it. We especially want to recognize the critique of Mr. Jules Benbenick of R.C.A. who has been one of the innovators.

THE MECHANICAL AND CHEMICAL ASPECTS OF GLASS SEALING

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ABSTRACT

The completion of a successful glass-metal or glass-glass seal involves the appropriate mating of both the mechanical and the chemical properties of the components. This is generally accomplished by the glassblower calling on his arsenal of experience often without an understanding of the physical nature of the system. The basic nature of glass which gives rise to the term contraction coefficient and to the necessity for differential expansion tables will be discussed. The factors which influence the wetting of a metal by a glass and the resulting development of adherence will also be mentioned.

I. INTRODUCTION

Scientific glassware is one of the mainstays of any good materials research laboratory, and the glassblower is the recognized key link between the vast assemblage of glassware and the construction of the usually complex and highly functional glass research equipment. The glassblower is truly a skilled craftsman, but often he is content to view glass as the remarkable material it is without an appreciation of the associated science. True, the artisan can learn to work glass by referring to tables, recipes and standard procedures, but the coupling of this skill and experience with an understanding of the fundamental properties of glass can only produce a better glassblower. For example, an understanding of the causes of stress development in glass can greatly facilitate the analysis of failures which may result from slight and often overlooked variations in the standard operating procedure. But more important, with a scientific base, the glassblower can extend his knowledge and experience to cover new materials or to develop new processes. It is hoped that this report will provide an introduction to the scientific aspects of glass-glass and glass-metal sealing and will encourage the glassblower to inquire more deeply into the fundamental nature of his highly interesting material.

II. THE MECHANICAL ASPECTS OF SEALING

A. THE NATURE OF GLASS

The development of permanent stresses in glass seals is intimately associated with the structural changes which occur with temperature and to understand these stresses it is important to inquire into the nature of glass structure. First of all, is glass really unique? Are its properties sufficiently different from those of metals or crystalline ceramics to require a special treatment? The answer begins with a comparison of the

atomic arrangement of glasses and crystalline solids, particularly since glass is sometimes erroneously defined as a noncrystalline "solid."

In the rigorous sense of the word, a solid is not adequately defined as a rigid material but rather as a crystalline material. That is to say, a material whose atomic structure is ordered in that it may be defined at any point in space by the appropriate repetition of a small ordered group of atoms known as a unit cell. A glass, on the other hand, shows no longer range order. This is shown schematically in Figure 1 which compares in two dimensions (a) a crystalline array of silicon and oxygen with (b) an irregular array of the same elements in a vitreous state. In the latter case, one can visualize chains of the glass forming SiO_4^{-4} units of varying length. When other materials such as alkalies are added to this silica network, additional structural disruption and variable chain length formation takes place. This is shown schematically in Figure 2.

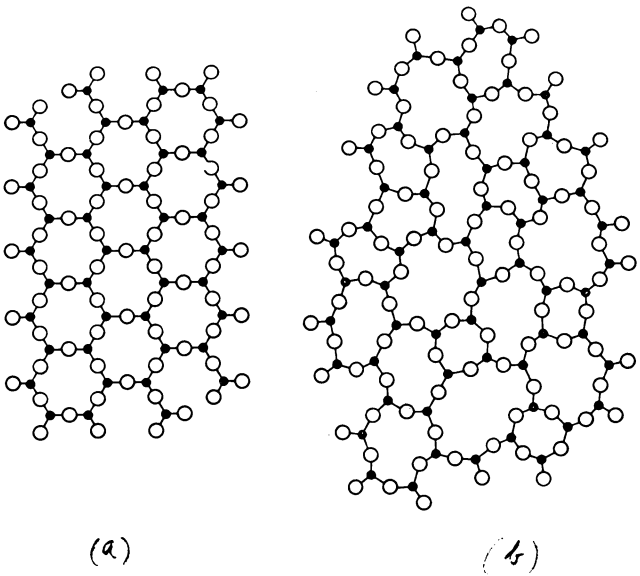

Figure 1
(a) Regular crystalline lattice and (b) corresponding irregular glassy network after W. H. Zachariasen[1] and B. E. Warren[2].

I have implied that glasses possess random chain-like structures, but this is hardly a sufficient definition. Other parameters, such as composition, and optical or thermal properties, also fail to be definitive. Common inorganic glass formers include in the oxide systems silicates, borates, and phosphates; in the non-oxide or chalcogenide systems, selenides and tellurides; and in the organic systems, such polymers as lucite and even rubber (if cooled to a low enough temperature). Optical properties range

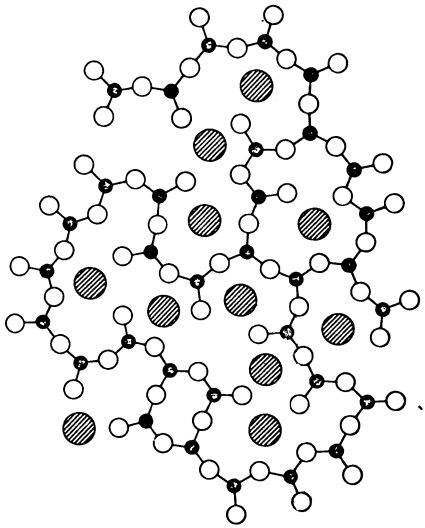

Figure 2
Schematic representation of a sodium silicate glass. After B. E. Warren[2].

from transparent to opaque. Thermal properties such as softening, annealing and strain points and expansion coefficients are highly variable from glass to glass. The one thermal property that unifies all of these compositions and serves as the basis for the definition of glass is viscosity. As defined by Morey[3]: "Glass is a material in a condition which is analogous to, and continuous with, the liquid state, but which, as the result of having been cooled from a fused condition, is characterized by so high a degree of viscosity as to be for all practical purposes rigid."

Morey's definition of glass is clarified by comparing, as in Figure 3, the expansion characteristics of the parent crystalline solid with those of the resultant glass. As the thermodynamically stable solid is heated it expands as a result of lattice vibration until it reaches its melting point and converts to the liquid state with an associated structural rearrangement and expansion. As one continues heating, the liquid will expand at a greater rate than the solid because of a combination of both a continuing increase in lattice vibrations and additional rearrangements in the liquid structure. If the material is capable of forming a glass the following will occur:

On cooling, the liquid will pass through the thermodynamic melting point without converting to the crystalline solid. The material now is a metastable or supercooled liquid. On cooling of the liquid, contraction will occur, as on heating, by both a change in lattice vibration *and* a structural reorganization. In a glass forming material, this structural change requires a rearrangement and redistribution of chain lengths to achieve a denser atomic configuration. This latter process in contrast to a contraction that is due to changes in lattice vibration involves viscous flow and the making and breaking of chemical bonds within the liquid.

The rate at which this process occurs decreases with an increase in viscosity or, in other words, the rate decreases as the temperature decreases.

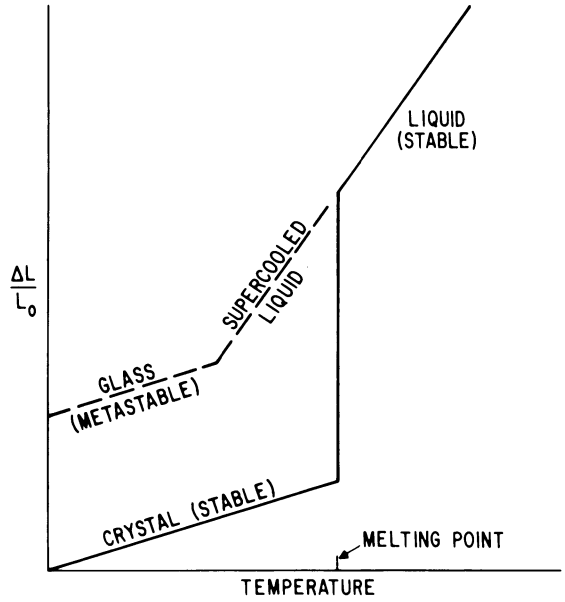

Figure 3

Relation between the thermodynamically stable crystalline and liquid states and the metastable states of the supercooled liquid and the glass.

On slow cooling, a temperature will be reached below which for all real time no additional change in the liquid structure can occur. This point is variously known as the glass transition or the fictive temperature and occurs at a viscosity of approximately 10^{14} poise. It is recognized by the abrupt change in slope of the theoretical expansion curve. Since this transition involves a rearrangement requiring viscous flow, it is also time dependent and, consequently, a faster cooling rate will result in a higher glass transition temperature. Below the glass transition temperature, t_g, the material — now a glass — continues to contract solely by the reduction in lattice vibration, and the liquid structure corresponding to the glass transition temperature is retained for all lower temperatures.

The details of a dilatometer curve of importance to the glassblower are shown in Figure 4. The strain, glass transition and annealing temperatures are designated, respectively, on the figure by the symbols t_s, t_g, and t_a. The viscosities associated with these temperatures for *all* glasses are, respectively, $10^{14.6}$, approximately 10^{14} and $10^{13.4}$ poise. The important features relative to sealing are: 1) above t_a the material is plastic and deforms in a short time to relieve any stresses which are imposed; 2)

below t_s the glass is rigid and cannot relieve stresses by internal flow; and 3) the glass "sets" with respect to the rigid material to which it is being sealed at a temperature generally between t_g and t_a.

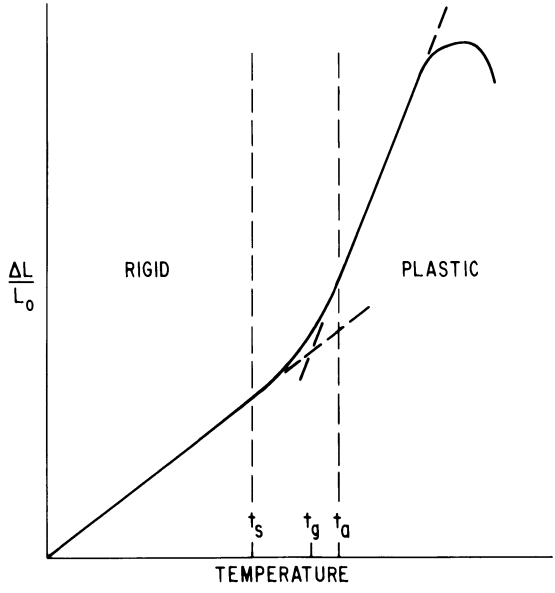

Figure 4

Schematic dilatometer curve for a glass showing the strain point, t_s, the glass transition point, t_g, and the annealing point, t_a, and the regions in which the material can be considered to be (1) plastic and (2) rigid.

After the glass sets no additional stress relief by internal flow can take place, and strains due to differential expansion of the two joined materials become permanent. Even though some stress relief can theoretically occur between t_a and t_g, this is seldom realized since the driving force for stress relief in this range, i.e., the strains developed by differential expansion, is generally small and the relief times are prohibitively long. For practical sealing operations, the set point can be taken as being t_a.

B. Relationship of Expansion Properties to Stress Development in Glass-glass and Glass-metal Seals.

The stresses which are encountered in forming a glass-to-glass or a glass-to-metal seal may be divided into two categories: transient stresses and permanent stresses.

1. *Transient Stresses*

Transient stresses result from the establishment of temperature gradients within a specimen because of sudden changes in the temperature

of the environment. Several material parameters affect the severity of a transient stress for a given heating and cooling schedule. The inherent strength of the material is of importance. Glass in this respect is poor, not due to a low theoretical strength which to the contrary is of the order of millions of psi,[4] but resulting rather from its susceptibility to internal and surface flaws which lower the practical strength to a value of several thousands of psi. High expansion coefficients can be disastrous. As you know, the low expansion coefficient of fused silica gives it its excellent thermal shock resistance. Thermal conductivity (or more properly, thermal diffusivity) is the measure of a material's ability to dissipate heat and eliminate thermal gradients. Once again glass is poor in this regard, particularly when compared to metals.

On the positive side, transient stresses are relieved with the elimination of the temperature gradient and can be avoided by controlled heating and cooling of the specimen. For this reason, transient stresses, even though they can be made severe enough to cause failure, are considered to be of secondary importance in the preparation of a seal.

2. *Permanent Stresses in a Glass of Uniform Composition.*

Permanent stresses are, as has already been implied, an inherent property of a particular glass-glass or glass-metal seal and *cannot* be relieved by the elimination of temperature gradients or other time dependent changes. The one possible exception is the development of permanent stresses in a glass of uniform composition by imposing non-uniform cooling rates on the system (not to be confused with the application of a thermal gradient alone) and dropping the temperature from above the annealing point to below the strain point. This produces a range of fictive or glass transition temperatures or, in other words, a range of glass structures each of which undergoes a different amount of total contraction. The development of stress in this system of uniform composition but variable structure is diagrammed in Figure 5. In this case, the permanent stresses *can* be removed by annealing which homogenizes the glass structure.

Figure 5 also illustrates the rule of thumb that the glass that cools last is in tension. To digress a moment, consider the advisability of the usual practice of flame annealing a piece of glassware before bringing it below the strain temperature. If this practice is not followed, the ware must be reheated (assuming it has survived the cooling process) to relieve the permanent stresses which are compressive on the outside surfaces and tensile on the inside surfaces. The thermal gradient on reheating causes both of these stresses to increase in magnitude, and the inner surface tensile stress may easily exceed the breaking strength of the glass.

More germane to this report, however, are the permanent stresses which arise from the joining of either dissimilar glasses or glasses and metals. The thermal diffusivity of the respective materials which is important to the development of transient stresses plays no role here. The significant parameters are Young's modulus, Poisson's ratio, the relative thicknesses of the two materials and the differential be-

tween the thermal expansion coefficients and also between the sealing temperature and the operating temperature.[5,6] For a detailed discussion of the development, the calculation and the measurement of permanent stresses in cylindrical glass-wire seals the reader is referred to the classic paper by Hull and Burger[7] or for a more general discussion to the book, *Technical Glasses,* by Volf.[8]

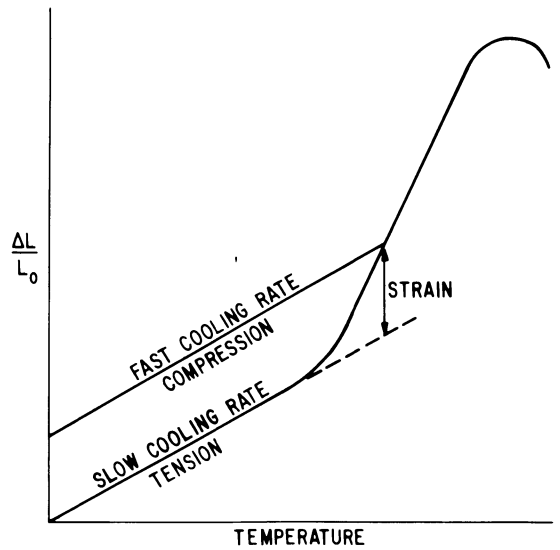

Figure 5

Schematic dilatometer curve detailing the development of stress in a glass of uniform composition due to non-uniform cooling rates.

For the most part, the expansion and contraction of metals and crystalline ceramic materials may be considered to be a linear function of temperature and defined by a single expansion coefficient (assuming that no phase transformations occur in the temperature interval under consideration). We have seen, however, that glass does not fit this generalization. Consequently, the effective contraction which occurs in the glass portion of a glass-metal seal is higher than that predicted by the reported linear expansion coefficient. The *entire contraction curve* from the *set point* to room temperature must, therefore, be considered in determining the resultant stress level. As a general rule of thumb, a seal combination is considered satisfactory if the expansion curves of the glass and the metal differ by no more than 150 ppm at the set point of the glass.

The basis for this latter rule of thumb is Hooke's law which relates the stress, σ, to the strain, ε, in a system through the Young's modulus, E, for the material by the expression:

$$\sigma = E\varepsilon \quad .$$

The strain in a seal at temperature, T, can be estimated from the expan-

sion coefficients and temperature differentials as $\varepsilon = (\alpha_1 - \alpha_2)\ (T_{\text{set point}} - T)$ where the α for the glass is the effective contraction coefficient from the set point and not the linear expansion coefficient. Taking for a glass, E to be approximately 10^7 psi and a conservative breaking stress to be 1500 psi, one calculates the maximum permissible strain to be 150 ppm. Differential expansion tables for standard materials are available,[9] but the glassblower must use his knowledge of material parameters to solve the problem of the non-standard case.

Figure 6 illustrates the production of a poor glass-metal seal when linear expansion coefficients are matched and the production of a good seal when effective contraction coefficients are matched. It should be mentioned at this point that even though the contraction curves for most metals can at best be matched to those of glasses only at the set point and room temperature, there are some notable exceptions. A few widely used alloys such as Kovar and Fernico have expansion curves which closely match the *total* contraction curve for several specific glasses at all temperatures and yield good, stress free seals.

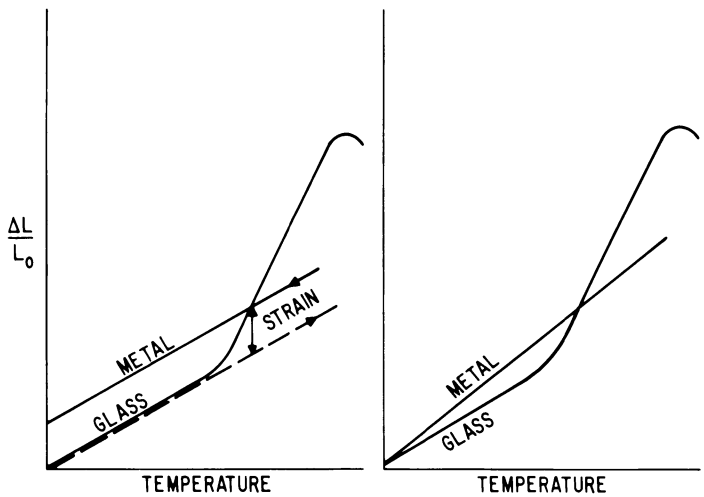

Figure 6

Comparison of the formation of (a) a poor seal and (b) a good seal by matching in case (a) linear coefficients of expansion and in case (b) contraction coefficients.

4. *The Classification of Seals According to the Level of Permanent Stress.*

The previous discussion has been concerned primarily with the production of seals with a low stress level by achieving a good thermal match between the materials to be joined. This, of course, is not the sole requirement for the completion of a good seal. In the case of a low stress seal, good chemical bonding must also be established between the joined materials. This is discussed in the next section for the case of both glass-glass and glass-metal seals.

Another mode of sealing is available in the glass-metal category which employs the development of compressive stresses in the glass through the use of a metal collar having a higher contraction coefficient than the glass. In these high-compression seals, mechanical bonding may be considered sufficient although the development of a good chemical bond is always desirable. Mathematical relationships have been developed for the calculation of the stress distributions in compression seals and are available in the literature.[5,6,7]

III. THE CHEMICAL ASPECTS OF SEALING

The formation of a chemical bond in a glass-glass or glass-metal seal is best defined as the development of first order attractive forces across the interface equivalent to the attractive forces between atoms in a single phase material. The formation of such a bond in a glass-glass seal is readily understood. Glasses are usually mutually soluble in one another and form a continuous metastable liquid structure of varying composition in the region of the join when sealed together. This is shown schematically as a smoothly varying concentration profile of SiO_2 in Figure 7a.

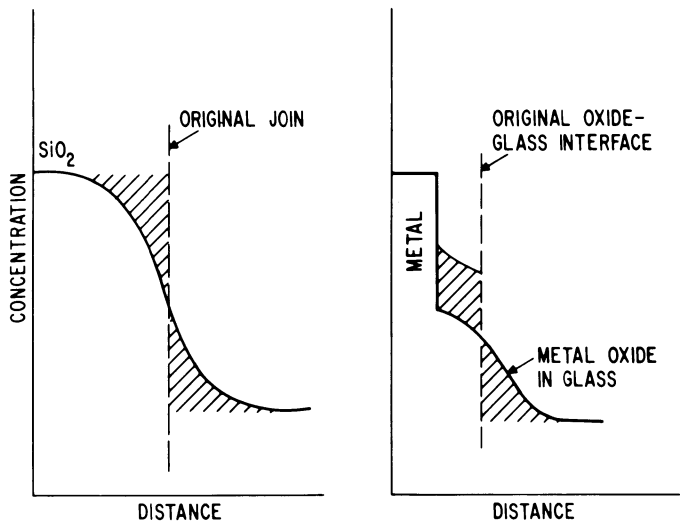

Figure 7

Schematic diagram of concentration profiles generally encountered in the production of (a) a glass-glass seal using glasses of different concentrations and (b) a glass-metal seal using an initially oxidized piece of metal. The crosshatched regions indicate material transferred by diffusion during the sealing operation.

The development of adherence between a glass and a metal is more complex and less completely understood. Both practical experience and scientific investigation have shown that wetting of the metal by the glass must occur before adherence can be developed.

Wetting is best described by reference to Figure 8 which shows the contact angle, θ, for a liquid droplet resting on a solid surface for both a wetting ($\theta < 90°$) and a nonwetting ($\theta > 90°$) condition. The vectors represent the surface tensions or the surface-free energies at the solid-liquid ($_s\gamma_l$), the solid-gas ($_s\gamma_g$) and the liquid-gas ($_l\gamma_g$) interfaces. These vectors represent the forces acting to minimize the area of the corresponding surface. The droplet configuration is the result of the equilibrium of these forces as given by Young's equation:

$$_s\gamma_g = {}_s\gamma_l + {}_l\gamma_g \cos\theta$$

The surface tension or surface-free energy of a material arises from the fact that the atoms at a free surface are not fully coordinated, and consequently tend to withdraw toward the bulk material in an attempt to satisfy their coordination demands. If a droplet of a material with a low surface tension (glass typically 300 to 600 ergs/cm^2) is placed on a material with a higher surface tension (metals typically 1000 to 1200 ergs/cm^2) mutual screening of the atoms at the solid-liquid interface generally occurs which results in a lowering of the surface-free energy of the metal and a contact angle of less than 90°. The degree of lowering of the contact angle depends on the degree of screening interaction of the materials at the solid-liquid interface.

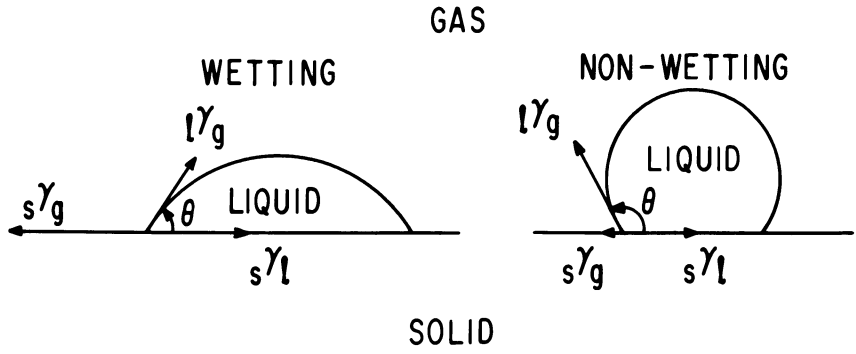

Figure 8

Configurations of liquid droplets on solid surfaces for wetting and non-wetting conditions. The surface tension forces and associated contact angles are shown for each case.

It has been shown in the case of molten glasses and solid metals that the wetting of the metal by the glass depends upon the glass composition, with the degree of wetting reaching a maximum value when the glass *becomes saturated* with the low valence oxide of the substrate metal.[10] These conditions have also been associated with improved adherence between the glass and the metal.[11] The exact quantitative relationship between bond strength and glass composition has not as yet been determined.

It is interesting to note at this point that there are only two practical ways of achieving a saturated glass composition at the glass-metal inter-

face: 1) formulation of a homogeneous glass of the appropriate composition and 2) establishment of a local composition at the interface due to the dissolution of the oxide of the substrate metal. Method (1) is often undesirable since it may result in the loss of required properties of the bulk glass such as chemical durability, thermal expansion, softening point, etc. Method (2) has the disadvantage of being a kinetic process which requires that the time-temperature relationships be carefully controlled.

Method (2) is the most commonly employed in the production of a glass-metal seal. The process of the dissolution of the oxide of the substrate metal is diffusion controlled and is well understood.[12] The main features of the concentration profile is illustrated in Figure 7b. As the oxide is dissolved by the glass, the saturation concentration is immediately established at the interface and is maintained only as long as undissolved oxide is present. The dissolved oxide becomes an integral part of the glass structure and moves away from the interface by diffusion giving rise to the profile illustrated in Figure 7b.

When the last bit of discrete oxide is dissolved, continuing diffusion begins to drop the substrate oxide concentration in the glass at the interface to values lower than the saturation concentration. The quality of the adherence also begins to drop. The most desirable situation is to dissolve all the discrete oxide and have the saturated glass composition contact the clean metal surface. If, however, the oxide adheres strongly to the base metal, as is the case for some chromium-iron alloys, the presence of a residual discrete oxide layer does not weaken the seal. In this case, the conditions for the formation of the seal are less critical.

IV. SUMMARY

The following important points relative to glass sealing procedures have been discussed:

1) Glass, because of its viscosity relationships, possesses the structure of a higher temperature liquid and is characterized by a glass transition point.

2) The time and temperature dependences of the viscosity give rise to stress development in single glasses of uniform composition.

3) The viscosity of the material and the existence of the glass transition temperature complicate the thermal matching of glasses with either metals or other glasses and give rise to the need for the term contraction coefficient.

4) Correct metal oxidation procedures are a prerequisite for the successful completion of a glass-metal seal.

The main purpose of this report has been to stimulate curiosity regarding the "why" rather than the "how" of glass sealing. In this respect, this report is only introductory and additional suggested reading is given in the references.[13]

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NEW INFORMATION ON GLASS FRACTURE

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1. INTRODUCTION

New ideas and discoveries of science do not pass immediately into the technologies of their respective fields. A period of consolidation is needed for the application of the new ideas for general use, and in some instances, to await a practical need for the use of the idea. In the case of glass technology we find that Griffith[1] first published his flaw theory of brittle fracture in 1920. Although the general theory was readily accepted, its full significance as applied to glass was not recognized for another 20 years or more. The effect of load duration on the breaking stress of glass was investigated by Grenet[2] in 1899, but his results were neglected for more than 30 years because of the elementary state of technology for the structural use of glass, and also because an imperfect understanding of the Griffith theory left technologists unprepared for concepts of stress fatigue in this material. Extensive investigation in this field during recent years has been somewhat restricted in its range so that our understanding of these phenomena is still imperfect.

At the present moment new advances are being made in a number of phases of the problem of glass fracture, and the results are in different stages of absorption into established technology of glass. The purpose of this discussion is to review several of these ideas and to indicate how they can be applied to some of the problems now being faced by glass technologists.

2. FRACTURE ANALYSIS FOR BREAKING STRESSES

Procedures for obtaining fracture information from the examination of the fragments and the surfaces exposed by the break are called fracture analysis. The general methods are applicable to any material, but they are particularly effective for glass because it is not altered by plastic deformation during fracture and because the fineness of the structure permits certain information to be recorded on the fracture surfaces in great detail. Some of the procedures, such as those used to determine direction of crack propagation, the location of the origin, and to a limited extent, the crack velocity, have already been established in glass technology. Other procedures, such as those for estimating breaking stresses are not yet in general use. These methods will be discussed briefly here.

A glass fracture originates in some weakening defect, usually some type of surface damage. During the fracture process, this defect develops into a crack which tends to propagate at an ever-increasing rate as it expands. The velocity attempts to build up to a critical value, of the order of one mile per second. When this condition is reached, the crack surface first takes on a roughened appearance, and with still further ex-

pansion, becomes hackled and fragmented. The flat surface, bounded by the roughened zone, is called the fracture mirror. The form of the mirror will vary depending upon conditions under which fracture occurs. Two photomicrographs, Figs. 1 and 2, illustrate the originating defect, the mirror, in various forms with its stippled boundary and hackles beyond.

Figure 1
Fracture mirror and flaw from impacted glass. Mirror width, 0.0052 inch (stress — 36,000 psi). Effective flaw depth, 0.00045 inch (stress — 33,000 psi).

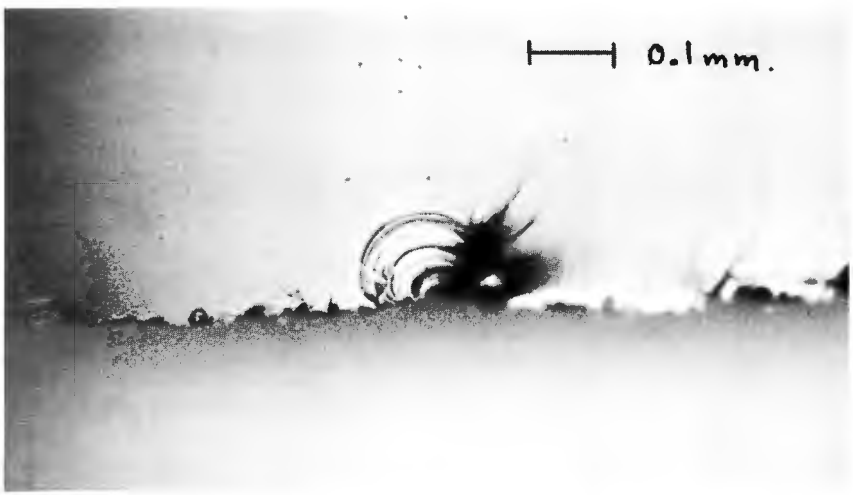

Figure 2
Fracture from grinding check in glass surface. Mirror width, 0.027 inch (stress — 15,500 psi).

Flaws and defects produce high stress concentrations and corresponding weakening in the general manner shown by Griffith.[1] When one of these flaws develops into a fracture, the profile of the flaw will appear, more or less definitely, on the surface exposed by the fracture crack. The patterns of these flaws are clearly visible in these photomicrographs. The weakening effect of the fracture flaw is related to its dimensions as they appear on these pictures, so that the dimensions can be utilized in some manner to determine this weakening, and from this, the breaking stress.[3]

The Griffith relation for the nominal stress in glass can be stated

$$\sigma_a \, h_e^{1/2} = m$$

or

$$\sigma_a = m/h_e^{1/2} \qquad (1)$$

where σ_a is the nominal stress

h_e is the effective flaw depth

m = is a quantity which is a function of the particular glass considered and upon the time duration of stress.

Dimensions of the fracture flaw, — width and depth —, can be

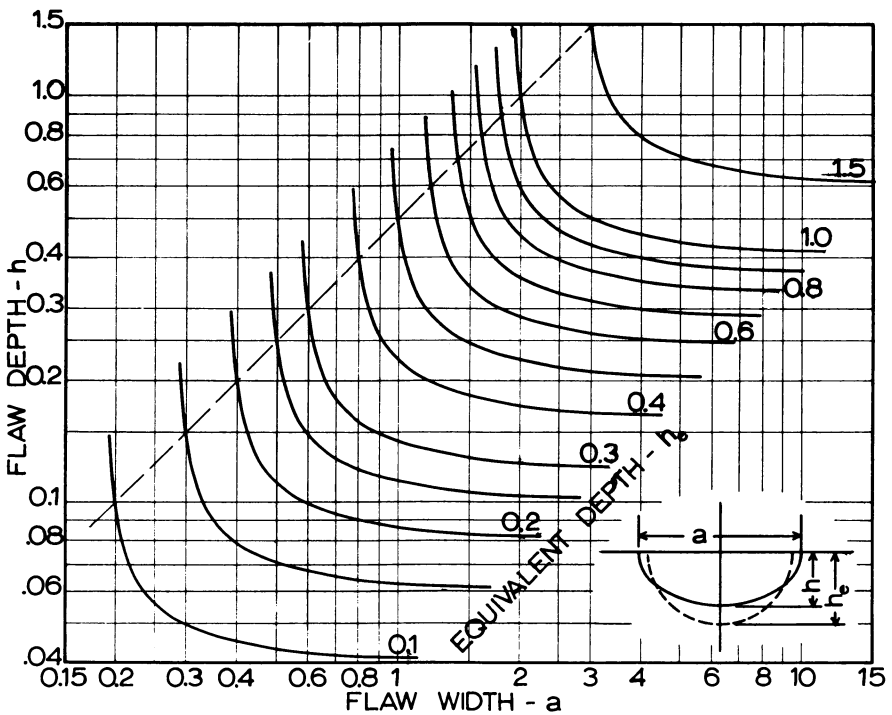

Figure 3
Curves for finding effective flaw depth, h_e, from length and depth of flaw.
Values are relative.

measured with a microscope. The effective flaw depth, h_e, can then be determined by introducing the measurements into the curves of Fig. 3, using any suitable multipliers (e.g. 10^{-3}). For a specific fracture flaw in a specific piece of glass the breaking stress may vary over a range of three to one depending upon the interval of time during which the stress is applied. The value of m will vary correspondingly. Figure 4 represents ranges of m for soda-lime glass as a function of stress duration. Having determined h_e and a suitable value of m, the breaking stress can be computed from equation (1). The value of m may vary appreciably for other glass compositions.

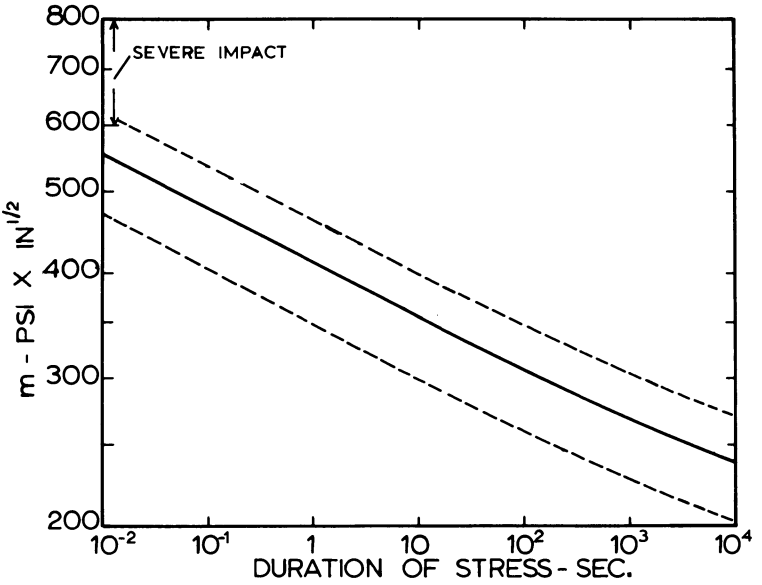

Figure 4
Mean value and probable limits for factor m shown as a function of stress time duration.

Under simplest conditions, the mirror, as bounded by the stippled zone, represents the fracture crack in a dynamic state, with the fracture velocity having just attained its critical value. The factor m now corresponds to a duration much less than any included in Fig. 4 so that if h_m is the effective depth of the crack for this dynamic condition, the normal breaking stress may now be expressed —

$$\sigma_a = 1870/h_m^{1/2} \qquad (2)$$

Although equation (2) is satisfactory for small, semicircular mirrors, it cannot be used in many cases, particularly for flexure breaks, because of the relaxation of stress in the fracture process which can distort the shape of the mirror so that the boundary is no longer semicircular. For this reason it is more satisfactory to substitute the mirror width, w,

along the original surface of the glass for h_m, and express the breaking stresses in graphical form for different types of specimens. This arrangement is shown in Fig. 5. The curves give satisfactory breaking stresses until relaxation at lower stress values causes them to deflect and flatten out. The mirror size is not affected by stress fatigue which may occur in the early stages of fracture.

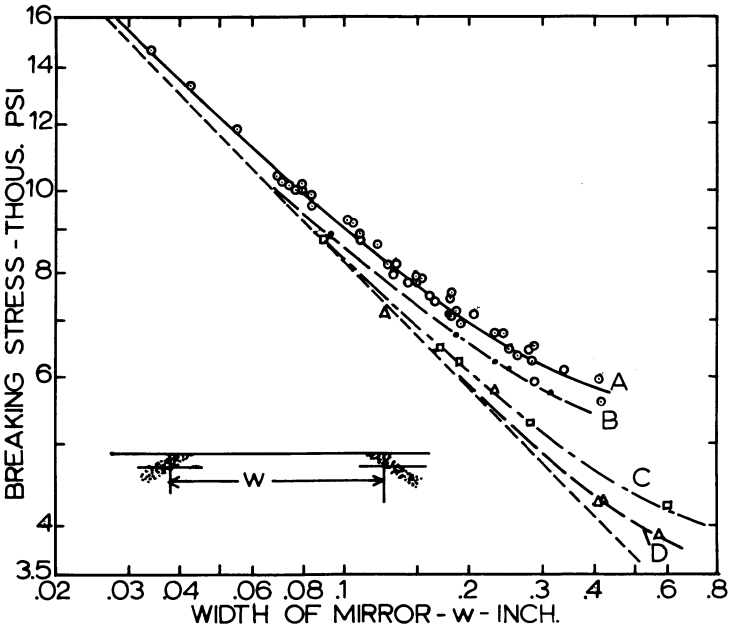

Figure 5

Breaking stress versus mirror width, w, for glass strips broken in flexure. Section dimensions in inches; A — 0.09 x 0.75; B — 0.09 x 1.25; C — 0.19 x 1.25; D — 0.22 x 1.25.

A third method for estimating breaking stresses makes use of the number of times the fracture crack divides as it passes through the section of the glass, or the number of fragments broken off during the process. In the case of a flat plate, this fragmentation can be expressed as the number of cracks radiating from the origin. Figure 6 is a photograph of 35 or more such cracks spreading from the origin at the center of one surface of a small square of sheet glass. Figure 7 includes data collected on similar squares of window glass, 0.09 inch thick, broken by impact. In order to obtain consistent results, only those cracks which passed completely through the section of the glass at a radius of $\frac{3}{8}$ inch from the origin were counted. Although the spread of the data is relatively wide (about $\pm$ 35%) the method can provide a rough approximation of the breaking stress.

Figure 6
Fracture pattern, glass plate broken by impact.

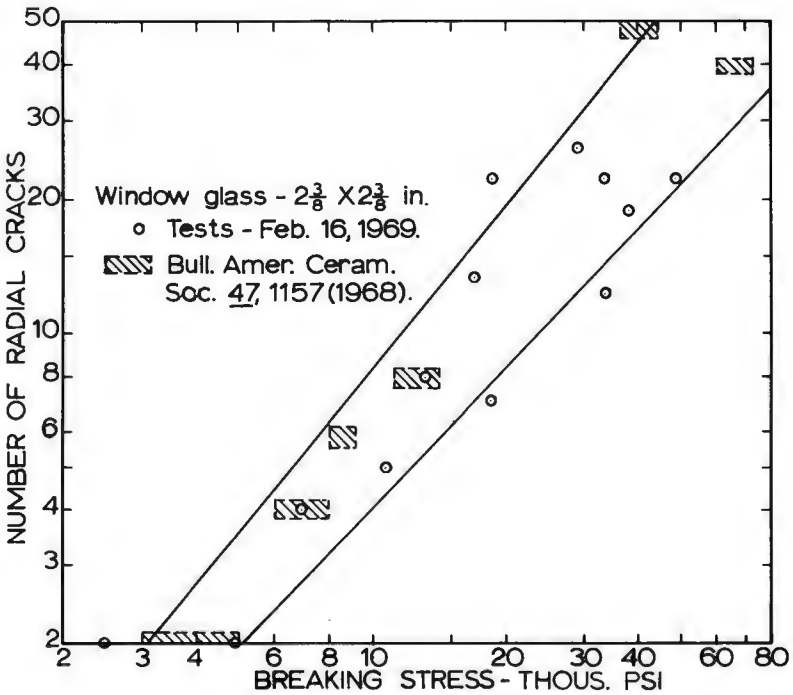

Figure 7
Breaking stress versus number of radial cracks around origin. Window glass broken by impact.

It may be noted that all three methods give stress values which include, not only the applied stress, but also any residual component which may be present.

3. FIELDS OF APPLICATION.

These three methods for estimating breaking stresses are not equally accurate, nor are they equally adaptable for all fractures.

The method of the fracture mirror is most frequently used. It is also the most accurate, provided that the breaking stress is not too low, where stress relaxation during fracture tends to vitiate the results. If calibration tests have been made on similar specimens of the same glass composition, the expected error should not exceed 5 percent, and with special precautions it may be reduced still lower. For many glass fractures, where available information is limited to the fragments collected after the event, an accurate breaking stress value can be determined with the mirror method. In making impact tests, or carrying on other tests where the determination of stress by other methods presents difficulties, this method can also be very useful. I have used this method regularly to check the accuracy of stress values computed from measured loads, because the adjustment of equipment used for this purpose can be critical. In some types of tests, stresses cannot be computed accurately from the applied loads. A breaking test in tension is a good example of this condition. Bending components which are not intended may increase the maximum stress in the section 50 percent above its nominal value. The actual breaking stress can be determined from measurements of the fracture mirror. As has already been mentioned, breaking stresses obtained from the mirror method are not influenced by stress fatigue.

The size of the fracture flaw represents the extent to which the glass has been weakened by its presence. A second weakening effect results from stress fatigue, so that the duration of the breaking stress must be taken into account. Results are not as accurate as those with the mirror method. Flaws of very small dimensions may present difficulties in making measurements. In addition, the region around the flaw may become spalled or damaged during the fracture process so that it becomes impracticable to determine the original dimensions of the flaw and the method loses much of its usefulness thereby. However, it becomes very useful under two circumstances. In the case of extremely large flaws, such as the fracture flaw of a bottle shown in Fig. 8, the mirror method loses its effectiveness, but the flaw method will give quite satisfactory results. A second application is found when it is desired to compare the strengths of glasses of different compositions. The breaking stresses are adjusted to a flaw of some standardized size by means of equation (1) so that these stress values represent the relative strengths of the glasses.

The third method, based on the degree of fragmentation around the origin, is used only for special conditions. When a bottle or plate is broken with a sharp blow, the entire region around the origin may be lost so that neither fracture flaw nor mirror is available for analysis. It may still be possible to estimate roughly the breaking stress from the number of

cracks radiating into the remaining body of the specimen. The method is also used in the manufacture of certain articles of tempered glass. Samples of the product are struck with a center punch using specified procedures. The number of fragments in the surrounding region is considered to be an indication of the magnitude of the residual stresses produced in the tempering operation, and consequently whether or not this operation was carried out properly.

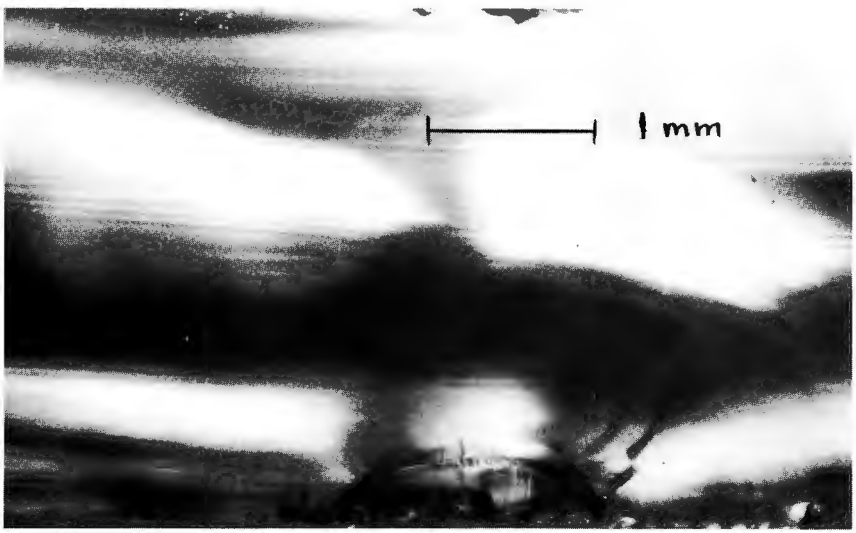

Figure 8
Fracture flaw at mold seam of bottle. Effective depth, 0.024 inch.
Breaking stress from impact, 4800 psi.

4. FRACTURE UNDER COMPRESSIVE FORCES.

The high strength of glass in compression provides definite advantages to this material if used for hollow structures to be subjected to high external pressures of deep ocean submergence. This possibility raises new needs for information regarding the fracture of glass under unusual conditions.

A typical application is a hollow sphere or hemisphere under external pressure. The compressive stresses in two principal stress axes, — meridional and hoop, — may be of the order of ten times the external fluid pressure. In the third, or radial axis, the compressive stress at the outer surface will equal the external fluid pressure, while at the inner surface, it will be zero. At ocean depths of 20,000 ft. the meridional and hoop stresses in a hollow sphere may be of the order of 85,000 psi in compression. When the vessel is composed of two hemispheres held together with some form of joint, these basic stress conditions will not be changed, but the presence of this joint will introduce highly localized stress com-

ponents across the interface at the discontinuity. As a consequence, the pressures which cause failure may be reduced greatly, so the joint becomes the critical feature of any structural design of a shell. The resulting limitations are not yet well understood.

Measurements of the uniaxial compressive strength of glass when pressed between two plattens were made by Winkelmann and Schott[4] before the beginning of the present century. These tests demonstrated that any differential movement across the interface as a result of pressure could reduce the apparent breaking stress greatly. Recent engineering tests on glass hemispheres have emphasized the importance of this differential movement, although means for eliminating the effect have not yet been worked out satisfactorily.

In his study of high-pressure, P. W. Bridgman[5,6] observed that the phenomena involved fracture, so that he devoted some effort to the fracture study of various materials, including glass. His results, although meager, constitute some of our most significant data on the effect of multiaxial stress conditions on fracture. As early as 1912 he had investigated his "pinching-off" effect, or the characteristic tensile failure produced when compressive forces are applied to the lateral surface of a cylinder, but not to its two ends. Years later he returned to this problem, using equipment which permitted variable stresses to be applied to the two ends as well, so that he could produce compression in all three axes. In these investigations he discovered that the rigidity of the material in direct contact with the glass had a pronounced influence on stress conditions which cause failure. A contacting fluid resulted in low breaking stresses in the third axis, but that when the glass was protected from this liquid by a sleeve of a more rigid material, such as lead or copper, the breaking stress was raised, even by a factor of 5 or 6. The few data of Bridgman and of several other investigators are included in Fig. 9. The horizontal axis represents the equal compressive stresses acting in two axes, which may be the lateral surface of a cylinder, while the vertical axis shows the stress applied to the two ends of the test piece.

Details of the individual tests are as follows:

SUPERPOSED TENSILE FORCES

A. No protective sheath. Pressure fluid in contact with glass.

B. Sheath of low-rigidity Neoprene

C. Lead sheath.

D. Copper sheath. Turned down to 0.005 inch thick at center.

SUPERPOSED COMPRESSIVE FORCES.

E. Specimen soldered in enclosing housing of lead (Point E', glass was undamaged).

G. Data of Cordell and Corll[7]. Lateral surfaces exposed to hydrocarbon fluid under high pressure.

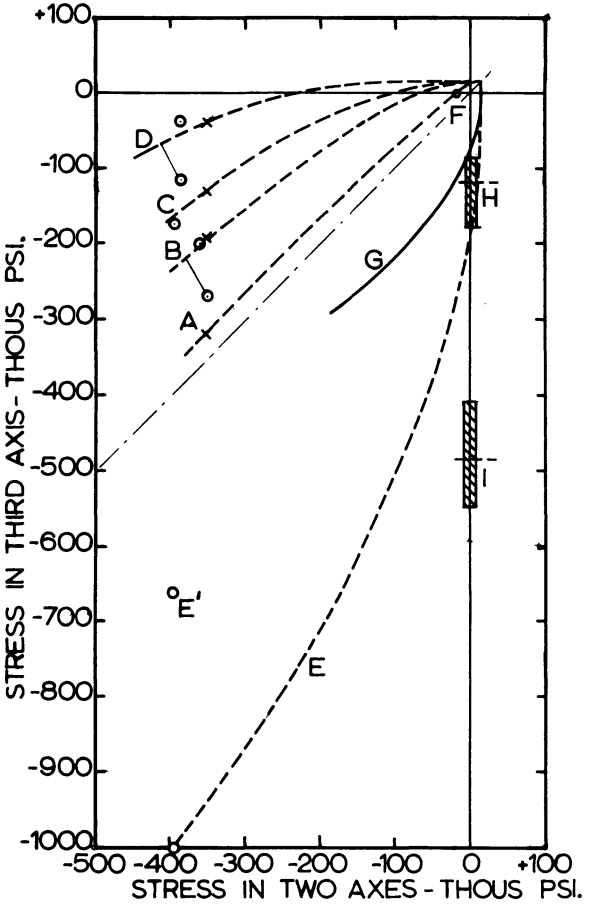

Figure 9

Breaking stresses of glass under triaxial stresses. Horizontal axis — equal stresses in two axes; vertical axis — stress in third axis. Effect of material in contact with glass; A, F, and G — fluid in contact; B — soft rubber in contact; C — lead metal in contact; D and E — copper in contact. H and I compression in single axis.

In all cases of fracture, the glass exhibited complete lack of ductility, and the basic fracture planes were smooth. Bridgman concluded that these fractures were aided by the material in contact with the glass, which forced itself into small surface checks and thus produced cleavage. When the glass is protected with a copper sheath the area enclosed by curves D and E represent freedom from fracture. When the liquid is in direct contact with the glass, the corresponding area is that enclosed by the Curves A and G. In the case of a hemisphere under external pressure, the interface at the joint corresponds to the sheathed surface of these tests with indeterminate characteristics.

The uniaxial stress data of Winkelmann and Schott are included in the shaded area marked H. More recent uniaxial data of Outwater and Gerry[8] are in the area marked I. Outwater used a specimen shaped like an hour glass to give high stresses in the necked-down section. In this manner they reached nominal stresses (load divided by glass section) of 547,000 psi.

Another method adopted by Ernsberger[9] gave values of concentrated stress under compression rather than technical strength. His method is based on an analysis originally proposed by Griffith[10] for stress concentrations produced in flaws of different orientations under biaxial stress conditions. In his specimens he produces a void in the form of an oblate spheroid (disk-shaped) oriented at an angle of approximately 45° to the axis of compressive stress. The maximum concentrated stress may be computed for two points roughly on the diameter of the spheroid. His data indicate local stress values for failure between 600,000 and 900,000 psi. The technical strength of a glass specimen would depend upon the geometrical form and size of any void or flaw in the glass, and also its orientation with respect to the axis of stress.

Small cracks of the type studied by Ernsberger have been actually observed in walls of glass hemispheres which had been subjected to high external pressures. In one instance, a hemisphere with a glass-metal interface was subjected to external pressures of the order of 10,000 psi. On inspection it was found that small cracks had developed in the glass near the joint as indicated in Fig. 10. Because of the theoretical importance of this type of crack, it was decided to investigate them in some detail. A small section was cut from the rim and its surfaces were polished for observation. The maximum height of the cracks above the interface was roughly 0.10 inch, and the orientation of the inclined part is the critical one as defined by Griffith. Careful scrutiny indicated that in addition to these inclined cracks there are many others which penetrate in a normal direction from the interface; in fact, only two or three percent of all the cracks develop into the inclined type. Observation of the interface of the glass shows that these small cracks originated at this surface. On counting them, it was found that there were roughly 5,000 to 6,000 of these cracks per square inch of interface.

This peculiar failure was diagnosed as the type studied by Bridgman. The cracks originated at the glass interface where the radial compressive stress is low and where some material, probably the pressure fluid, forced itself into existing flaws in this surface. Many small cracks propagated in this manner, but only a very small proportion of them were deflected into the critically inclined plane. Several obvious methods may be employed to prevent this type of failure in the interface region:

1. Elimination of small flaws on the glass interface before testing.
2. Prevention of fluids coming in contact with the interface.
3. Adding a radial component of compressive stress across the interface.

No failures of this type have been observed in any region removed appreciably from the interface so they are assumed to be associated with

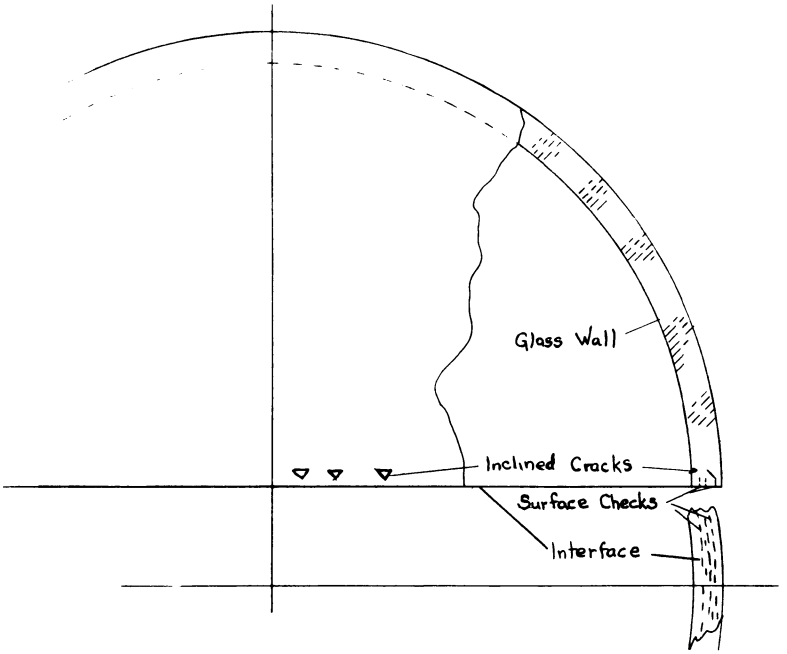

Figure 10
Glass hemispherical shell after being subjected to external pressure of 12,000 psi. Inclined cracks shown to originate from the interface (joint surface).

this surface. In order for these cracks to originate in other regions two conditions would have to be met; first, the originating flaw would have to be relatively large and in the form of a flat void; second, its inclination to the principal stresses would have to be relatively close to that of the critical angle. The probability of both conditions being met can be reduced to a very small value with proper manufacturing and inspection procedures.

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SOME EFFECTS OF THERMAL PROCESSES UPON THE STRUCTURE AND PROPERTIES OF GLASS

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ABSTRACT

The general effects of thermal processes as applied to the manufacture of glass products beginning with initial cooling from the molten state are reviewed. Of particular concern is the evaluation and control of thermal effects upon glass properties such as viscosity, density or thermal expansion; also involved are atomic and other structural considerations such as temporary stress (strain) conditions, annealing vs. tempering of glass articles, and general dimensional stability of the final product.

1. INTRODUCTION

We will review the "state of the art" of determining and evaluating the effects of thermal processes as applied to glass both as a material and a product. This will include general thermal effects upon certain glass properties and upon the associated dimensional and atomic structural considerations.

2. NATURE OF THE GLASSY STATE

Silicate type glasses have been described in terms of a "random network" of SiO_4 tetrahedra as schematically represented in Figure 1, wherein certain of the four oxygen atoms per tetrahedron are "non-bridging" or are not bonded closely to two silicon atoms. Such a *network* is due to the melting of *crystalline* SiO_2 in the presence of other compounds of metallic or other atoms, sometimes termed "network modifiers" which may be monovalent or bivalent (such as sodium or calcium in soda-lime glass) and which inhibit the orderly establishment of a crystalline structure; a network may also be the result of incorporating in the melt other "normally" *trivalent* atoms (such as boron or aluminum) which can also be "network formers" similar to the *tetravalent* silicon.

Glasses have also been described as "super-cooled liquids" and in terms of being visco-elastic materials, because at elevated temperatures they can flow as a viscous liquid while at lower temperatures they exhibit the elastic behavior of a solid with regard to proportionality of stress and strain. Figure 2 shows a typical graph of viscosity *vs.* temperature with certain terms indicated which are significant in glass manufacture.

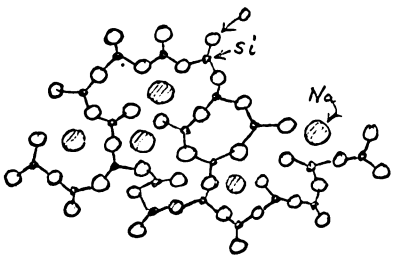
Such viscosity data have been represented empirically by the Fulcher[1] equation:

$$\log \zeta = -A + \frac{B}{T-To} \qquad (2\text{-}1)$$

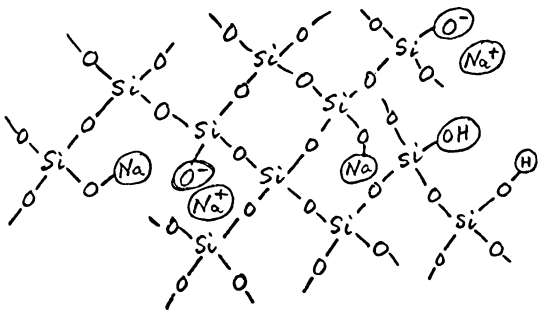
where ζ = viscosity at temperature T

A, B, To = constants

which is applicable only *within* the temperature range employed in the test, as limited further by the *conditions* of the test. The slope and relative position of the curves, as well as the constants of the Fulcher equation, depend upon the *method* of *test* and the *glass composition.* At lower temperatures the "viscosity" and other properties of glass often depend also upon the "*thermal history*" of the specimen being tested.



(a)



(b)

Figure 1

The random network of sodium silicate glass as schematically represented (a) in two dimensions and (b) with four oxygen atoms per silicon.

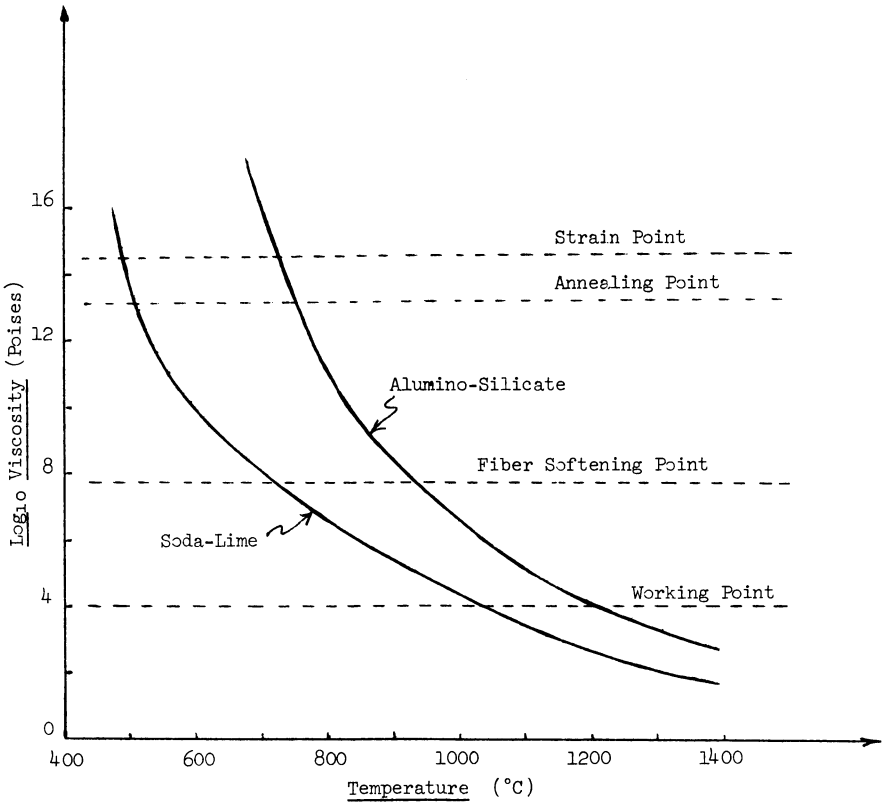


Figure 2
Typical Log Viscosity (poises) vs. Temperature (°C) Curves for Some Glasses.

3. TEST METHODS FOR GLASS PROPERTIES RELATED TO THERMAL PROCESSES

3.1 Viscosity Tests

High temperature viscosity (from 10^2 poises up to about 10^7 poises) generally has been obtained by use of a *rotating cylinder* viscometer[2]; in some instances a *"restrained sphere"* method[3] has also been used, with relatively good agreement. For lower temperatures, a constant-temperature *fiber elongation* method and an improved *beam-bending* method[4] have also given good agreement for the viscosity range from 10^8 to 10^{14} poises. Standard A.S.T.M. methods of test for the Fiber Softening Point[5] (F.S.P.) and for Annealing (A.P.) and Strain Points[6] (St.P.) of glass are based on *dynamic* fiber-elongation methods. By these methods the temperature of a fiber suspended vertically in a furnace is either raised at about 5°C per minute

through the fiber softening point or lowered at a similar rate through the annealing point while observing changes in the *rate* of *elongation.* For consistent and comparable results at temperatures where viscosity changes with time, it is important that the specimens have similar thermal histories; this is particularly true for the beam-bending method, where a specimen may be taken from a glass article which has been annealed, as contrasted with the A.S.T.M. fiber elongation tests, where the fibers have been "flame-drawn" from glass at temperatures well above the softening point and cooled rapidly to room temperature. Properly used, the A.S.T.M. tests have a precision of about ± 3°C for F.S.P. and A.P.

3.2 Density and Thermal Expansion or Contraction Tests

The densities or specific gravities of solids have been evaluated by various types of tests, including specific gravity balance and pycnometer methods. A comparison method termed "sink-float", utilizing calibrated liquid baths and reference standards, is under consideration for glass in A.S.T.M. Committee C-14 for use with glasses of density 2.0 and 3.0 grams per cubic centimeter. Properly used, this test has a precision of ± 0.0002 g/cc, or at least ± 0.01%.

The thermal expansions and contractions of glasses (and other materials over the range from about –195°C to 1000°C) are most frequently evaluated by vitreous silica (or alumina) dilatometer methods such as those given in A.S.T.M. Designation E228 recently prepared and revised by a task group under Committee E-1. (This method has been accepted by Committee C-14 as a replacement for C337-57, Average Linear Expansion of Glass from 0°C to 300°C, and is under consideration by E-1 and other committees to replace methods for other materials such as B95 for metals.) Properly used, this test has a precision of the order of ± 1% for the thermal contraction of glass from the annealing range to 25°C. As in the case of the empirical viscosity tests, the thermal history of the specimen can affect these measured properties.

3.3 Standard Test Methods and Reference Materials

Within the National Bureau of Standards, development of standard test methods and standard reference materials for use with standardized test methods was initiated some time ago. At present, the NBS Institute for Materials Research[7] has available seven types of viscosity reference glasses, useful for the A.S.T.M. viscosity methods, and is engaged in a program which may lead to standard reference glasses, metals and ceramics, which will be useful for thermal expansion and contraction methods as related to the seal characteristics of such materials. A.S.T.M. Committee F-1, Subcommittee VII is working in this area for the electronics industry; related activities have been the concern of groups such as the American Scientific Glassblowers Society[8] in their annual symposia for the past dozen years. Those engaged in such standardizing activities are increasingly

aware of the importance of specifying the thermal treatment of specimens in preparation for tests and the temperature-time conditions to be observed during such tests.

4. ASSOCIATED THERMAL PROCESSES AND GLASS PROPERTIES

4.1 Melting, Forming, Annealing and Tempering

When glass passes from melting temperatures (often in excess of 1200°C) through the working, softening, annealing and other empirical points during the process of forming, different properties of glass are influenced by not only the melting conditions, chemical composition, and the glass temperature, but also by the rate of cooling. Gases may be evolved from the liquid at higher temperatures or from the solid at lower temperatures by the processes of dissociation, diffusion, and desorption. Migration of ions and transfer of electrons make the glass electrically conductive at elevated temperatures; at lower temperatures and under suitable conditions of electrical field, ambient atmospheres, liquids or pressures, or exposure to radiation, ion migration (particularly of the smaller alkali ions) and electron transfer or other sub-atomic reactions can occur. Such phenomena are employed in the production of chemically strengthened, photosensitive, or other special forms of glass.

In cooling, the vitreous (non-crystalline) material passes through a transformation range as shown in Figure 3, extending from slightly above the annealing point to well below the strain point. Since cooling (or heating) inevitably sets up thermal gradients within the glass body, the rate and manner in which the solid random network is established in different regions of the glass body is affected by the cooling rate and the temperature. This fictive temperature may be defined as that temperature representing attainment of a stable atomic structure under a prescribed rate of heating or rate of cooling. The relative spacing of *network atoms* or ions in rapidly cooled glass is *greater* than it would have been if the glass had been cooled by small temperature decrements with intervening constant-temperature periods of time sufficiently protracted to allow the glass structure to adjust toward a stable condition known as equilibrium[9]. Temporary strains are also set up in different regions of the glass by thermal gradient; such strains can decay exponentially with time in the transformation range. Near the upper transformation temperature these strains can be relieved in seconds, at the annealing point in minutes, at the strain point in hours, and near the lower transformation temperature in days or weeks. As a result, when rapidly-cooled glass (quenched from temperatures above its softening point) reaches room temperature, its density is less than if the glass had cooled slowly, a difference which can amount to over 0.3%. The glass article has a compressive strain at or near any surfaces which were rapidly cooled, induced in part by an internal tension toward the center of cross-section where the glass cooled less rapidly, as shown in Figure 4.

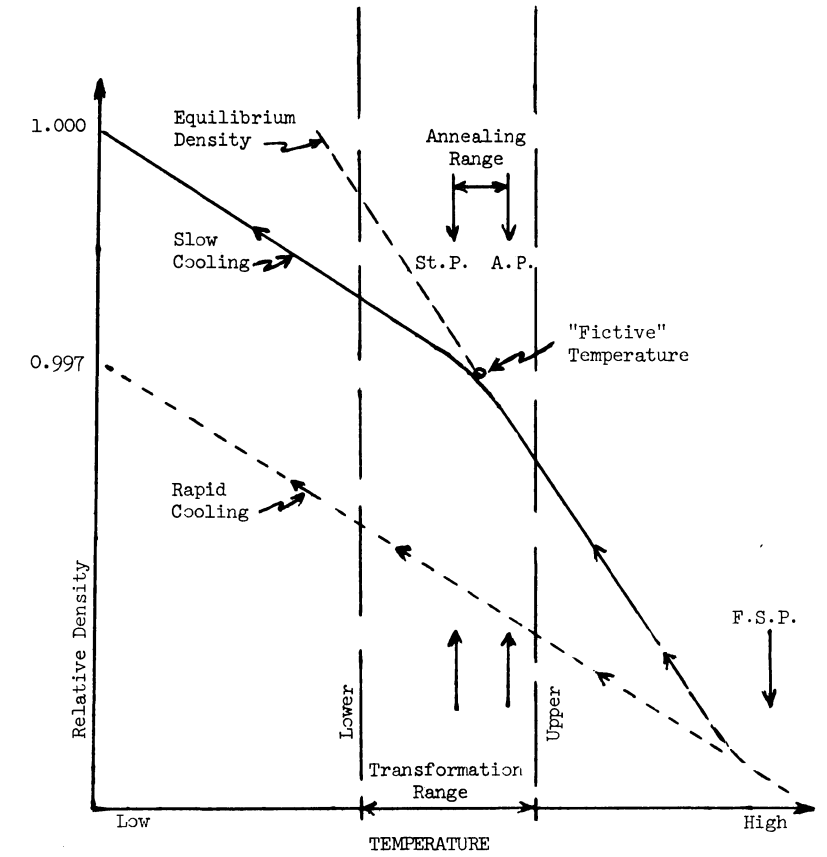


Figure 3
Relative Density of Glass vs. Temperature.

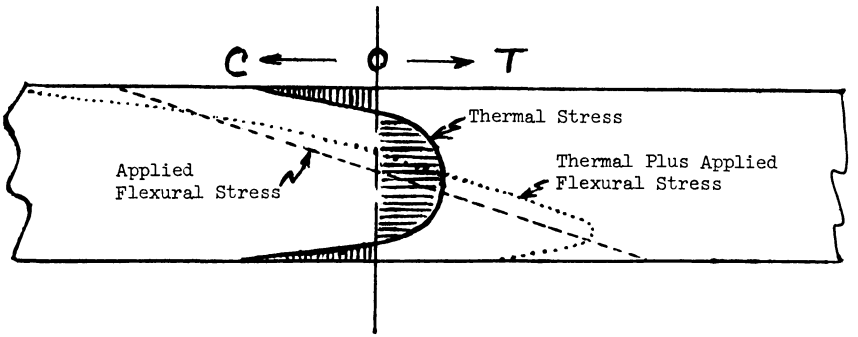


Figure 4
Stress Distribution in Flat Glass after Cooling Rapidly from Temperatures Near the Softening Point, Under Flexure at Room Temperature.

Such a glass article can be considered unannealed, strained, or stressed if the rapid cooling is improperly distributed or uncontrolled; the article may be termed thermally strengthened, tempered, or heat treated if the rapid cooling is well-distributed and controlled. The relative surface strain can approach 0.2% or about 2,000 parts per million (ppm), i.e. a compressive stress may exist of the order of more than 20,000 pounds per square inch (psi); the maximum internal tensile strain can be over 0.1% (1000 ppm), i.e. a tension of more than 10,000 psi. The article is considered undesirably stressed if during service it is subjected to additional thermal or mechanical stressing (flexure, pressure, or vacuum loading) so that brittle fracture occurs usually at or near a surface, originating at a stress-concentrating defect. (Fracture occurs under a tension stress, which under certain circumstances can be as low as 2000 psi.) Conversely, the article is considered thermally *strengthened* if the compressive stress is uniformly distributed and of sufficient degree at or near the surface so that externally imposed tension will not cause fracture. Unannealed glass articles are annealed as suggested by Figure 5 by raising their temperature to slightly above the annealing point for a matter of minutes, and cooling them through the annealing range (A.P. to St.P.) at a slow rate, determined largely by the thickness and shape of the article.

4.2 Heat Flow in Glass

Problems associated with the flow of heat energy through glass have

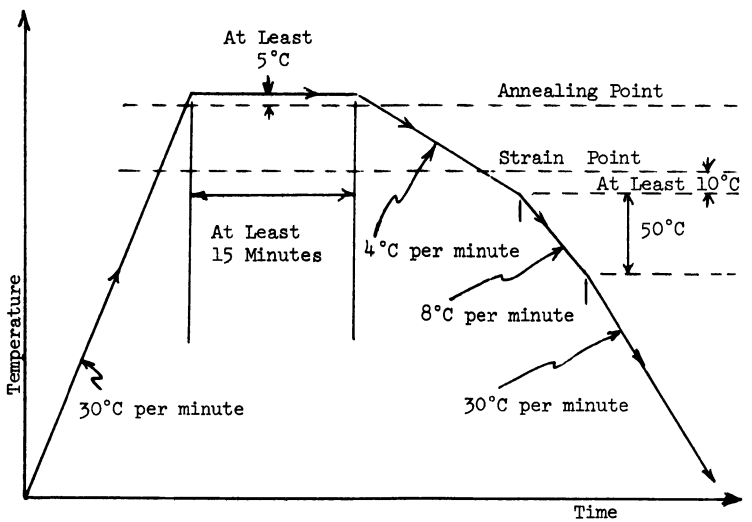


Figure 5
Typical Temperature-Time Schedule for Commercial Annealing of 1/4 Inch Thick Soda-Lime Glass.

been interpreted in terms of a "combination" physical property termed thermal diffusivity[10]:

$$K = k/\rho\ C_p \qquad (4\text{-}1)$$

where K is thermal diffusivity in unit area per unit time,
and k = thermal conductivity
ρ = density
C_p = true specific heat (at constant pressure)

The property of thermal conductivity increases with increasing temperature for glasses, but its measurement for *transparent* glasses is complicated by the effects of radiant transmission and absorption. The infrared absorption occurring in some glasses at 2.9 microns is associated with the presence of water, or rather OH^- groups[11].

Recent work[12] on the densification of glass by application of high pressure assigns the infra-red absorption at 9.05, 12.4 and 21.4 microns to Si-O bond *stretching*, Si *stretching*, and Si-O-Si *bending* frequencies. Such densification of silica glass from 2.20 to 2.60 g/cc caused shifts and/or broadening of absorption bands attributable to changes in bond angles or lengths within the network. Density decreases, as has been shown previously, with increasing temperature, as does the true specific heat, in such a manner that thermal diffusivity increases rapidly at temperatures above about 400°C.

5.0 DIMENSIONAL STABILITY

A thermal gradient is established within a glass cross-section within a few minutes after the surface is heated or cooled rapidly, so that a temperature difference ΔT exists between surfaces or between the center of cross-section and a surface determined by:

$$\Delta T = a^2R/8K \qquad (4\text{-}2)$$

wherein a is the cross-sectional thickness between two surfaces cooled at a constant rate R, and K is the thermal diffusivity. The thermal stress developed by the thermal gradient may be expressed by:

$$S = CE \propto \Delta T/(1-\gamma) \qquad (4\text{-}3)$$

where C is a dimensional restraint constant, determined by the shape, thickness, and "edge restraint" of the cross-section:

E = Young's Modulus
$\propto$ = coefficient of linear thermal expansion
and γ = Poisson's Ratio

Whether or not a stress is set up in the glass depends upon the temperature and viscosity of the glass. When viscosity measurements are attempted by the constant-temperature fiber elongation method, the value obtained during the test will either *increase* with time if the fiber is flame-drawn (and cooled rapidly to room temperature before returning it to test temperature) or *decrease* if the flame-drawn fiber is held a long time at temperatures below test. An *equilibrium viscosity* at infinite time is thereby approached.

Similar effects are observed, as reported by Tool[9], for thermal expansion and contraction data obtained on glass specimens which have been rapidly cooled from near the softening point, then heated and

cooled at constant rates with a peak hold temperature in the transformation range. This effect is shown in Fig. 6. Rapidly cooled glass on reheating will attempt to approach an equilibrium condition so that the *rate* of elongation with temperature rise diminishes and at peak temperature the specimen length will decrease toward equilibrium for that temperature. On cooling again it will depart from the equilibrium curve at a lower temperature depending upon the rate of cooling and to what degree its fictive temperature has been lowered. Upon going through another heating and cooling cycle, the specimen length will change in the direction of equilibrium, which yields a *decrease* in the *rate* of *elongation* before the equilibrium curve is crossed, and *increase* in this rate after crossing. The specimen may continue to elongate at peak temperature if the fictive temperature has been lowered and the peak temperature is high enough; or it may shorten at peak temperature if this is below the fictive temperature.

It may therefore be concluded that the final dimensions of a glass article, and the stability of those dimensions through subsequent temperature-time cycles within the transformation range, depend upon the effect of its *thermal history* following melting of the glass. Physical properties such as viscosity, density, and thermal expansion or contraction, as well as the degree of approach to an equilibrium glass structure are determined

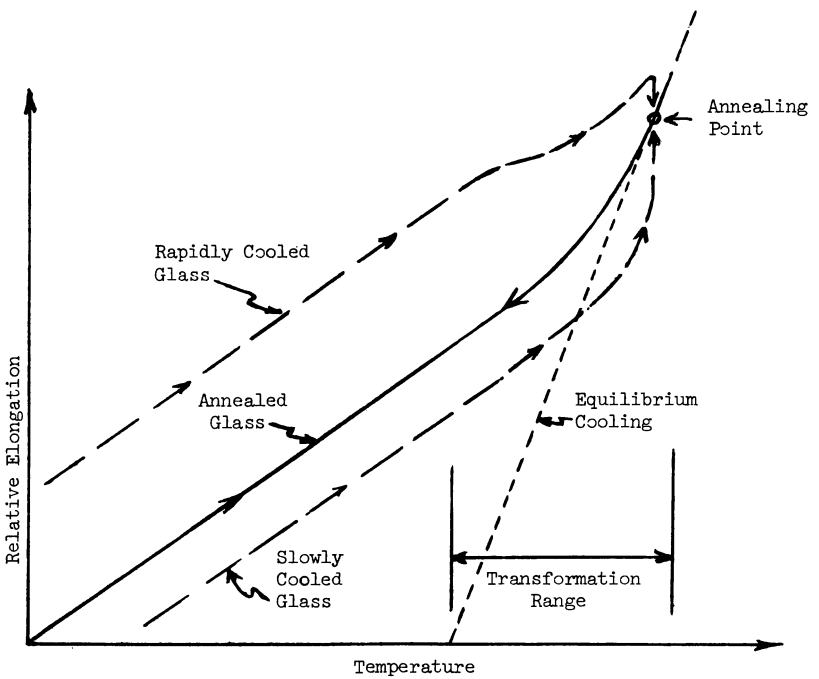


Figure 6
Thermal Expansion and Contraction of Unannealed vs. Annealed Glass.

by thermal history. The dimensions are also affected by a design or shape factor which determines whether different portions of the article are heated or cooled at different rates, or may arrive at final constant temperature at different times. Actual or true "dimensional stability" is difficult to attain because of the visco-elastic nature of glass.

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IN ATTENDANCE

The following are on record as having attended the Fourteenth Symposium on the Art of Glassblowing held at the Thruway Hyatt Motor Inn, Albany, New York, June 25, 26, 27, 1969. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

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