Proceedings

THE EIGHTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1963

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

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THE EIGHTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

Sponsored by

THE AMERICAN SCIENTIFIC
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JUNE 5, 6, 7, 1963

THE AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY
309 Georgetown Avenue
Gwinhurst, Wilmington, Delaware 19809

FOREWORD

Again, at this 8th Symposium and Exposition 1963, the calibre of the papers presented during the "Technical Sessions" and contained in these "Proceedings," were most appropriate, well delivered and well received.

For their contribution to the success of this phase of the meeting, and on behalf of The American Scientific Glassblowers Society and the Symposium and Exposition Committee, I want to officially thank the authors. Their papers are herein recorded for posterity and made available for those of our members unable to attend.

The theme or feature of this 8th Symposium, "Trends in High Temperatures," although referred to or part of many of the technical papers, was dramatically and practically demonstrated in the "Work Shop Sessions."

These Sessions were very well attended and were one of the "high" points of the Symposium.

"High Temperatures" as required for working VYCOR or Quartz glass was cleverly demonstrated on the glassworking lathe as was the "sealing in" of fritted or sintered discs and the fabrication of Glass-to-Metal seals, and the hand tooling of various types of blanks for ground glass joints. All these demonstrations were like a magnet, drawing even the most experienced glassblowers to watch someone else perform.

The Exposition again contained many new and varied pieces of mechanical equipment for the scientific glassblower to blow, cut, seal, drill, grind, bend or anneal, and I am confident that most everyone that strolled thru the exposition area found some item of interest to him and/or his employer.

However, as I look at these modern and quite necessary mechanical aids for the fabrication of modern glass apparatus, I can not help but think of the artist of yesteryear, who with the simplest of tools, but with a pair of nimble and skilled hands, guided by a keen and competent mind, could accomplish so much. I am thinking of the "Glass Flowers" in Harvard's Peabody Museum, which this author visits whenever in the vicinity of Boston and who considers them the 8th Wonder of the World.

Our Society is indebted to John A. Glover and his Committee for the direction of this 8th Symposium and to George A. Sites, Chairman Publications Committee, for assembling the technical papers, editing and printing of these Proceedings.

J. ALLEN ALEXANDER
President and Founder

CONTENTS

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LET'S EXPAND OUR HORIZONS

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The continued expansion of scientific investigation is leading many industries into independent research. These organizations recognize the need for many facilities and services necessary to their task. Depending on the size of the research department several or all of these aids may be provided.

The glass shop is generally a sign of a most complete research facility since small needs for glassware can be provided by commercial concerns either in standard equipment or apparatus of special design. When no glass shop is available on the premises, the research scientist may often attempt such projects himself or find ways to circumvent its use by resorting to "inferior" materials such as metals or plastics. Eventually, however, as an organization grows, its needs for glassware also increase and soon the economic feasibility of having a glassblower on the staff is demonstrated. A small corner in the basement is set aside and with hiring of a glassblower, the glass shop is established.

With the advent of the glass shop, the final link often is available in the chain from the initial idea of a research team to its realization in terms of the possibility of actually putting the idea to the test in an experimental way. At this point we also note a strange phenomenon begin to emrge. As the glassblower comes to be recognized as the one final link in the chain, it comes to be taken for granted that he also is the final and ultimate resource for whatever problem is in need of solution. Regardless of what you want to know, ask the glassblower, he will have an answer. Your question doesn't have to deal even vaguely with glass, for the glassblower is supposedly a veritable encyclopedia of little known information.

It's nice to be able to help under these conditions and often help is possible, if the glassblower has consciously tried to keep abreast of scientific development along the general lines of the industry in which he is employed. If a breakdown in the chain of research occurs due to the inadequacy of the glassblower, some remedy should be found to correct the situation. The reasons for this breakdown may be varied but the solutions are easy, once the specific fault is recognized. By enlarging our experiences and familiarizing ourselves more fully with the professional helps available, we can expand our horizons to a great degree.

Let's not overlook our heritage. Glassblowers have struggled in the past with many problems as we do today. Many of the techniques we employ have been handed down for generations and are common knowledge to us. However, the past has much more to offer in experiences, techniques, and apparatus design than we would generally conceive. Instead of inventing the wheel all over again at much time and cost, we can often save ourselves a great deal of trouble and pain simply by searching through the literature for the answer someone else may have provided to a similar problem. Whenever a new problem comes up in which we cannot put our finger on an immediate solution, I would suggest a trip to the library. A

few minutes may be well spent, if our source material yields only so much as a sense of the direction in which we could proceed. Examples of such use of reference material are numerous, therefore I will cite only one.

Our spectroscopy laboratory was in need of a high speed mercury pump to maintain an extremely high order of vacuum in an evaporation chamber where bursts of gas were expected. Searching through the literature we found reference to the pump described by Bull and Klemperer[1] and shown in Fig. 1. We built the pump exactly as described and then noted its operation. This pump has a rated speed of 90 liters/second at 10^{-5} mm and 20 liters/second at 3×10^{-6} mm. In operation it performs up to its rating. However, it has a drawback, as is indicated in the diagram. It has a tendency to throw a great deal of mercury vapor which must be trapped out. The authors succeeded in trapping it by the novel trap shown. This provides a metal shield *S* in contact with the liquid nitrogen reservoir and a deflector *D*, above. Mercury molecules emerging from the pump impinge either directly on the metal shield or by deflection off the cone above. Pumping speed through this trap is high.

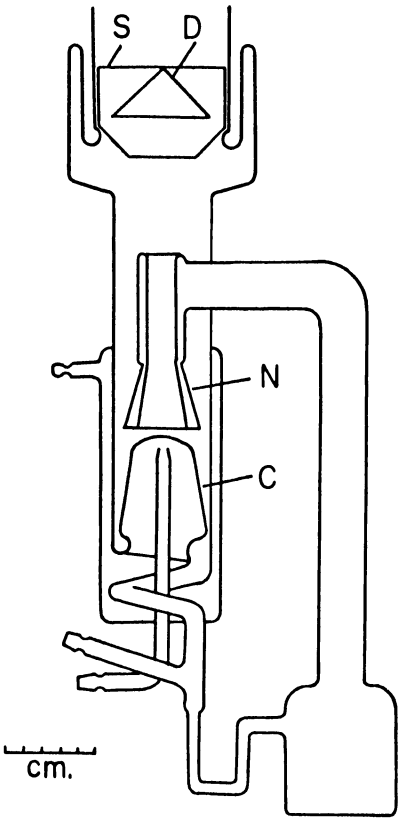


Figure 1
Bull and Klemperer High Speed Pump.

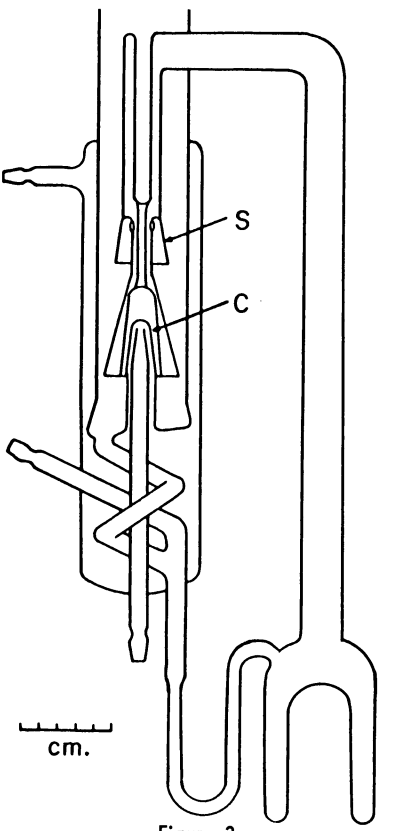


Figure 2
Haak-Vratny Annular Jet Pump.

While we did not employ this trap, we obtained similar results using a standard triple-wall dewar. The amount of mercury thrown out permits the pump to be used for only about eight hours before the level in the boiler falls too low for safe operation. On warming of the trap, however, the condensed mercury liquifies and falls back into the pump, making it usable for another short pumping run. This pump is currently used for hot pumping of dewars, where such short run operation is permissible. A second less important drawback of the pump is the high loss of liquid nitrogen caused by the large amount of mercury vapor striking the reservoir sides.

While at first it would seem that this pump is not a satisfactory solution to our problem in the spectroscopy laboratory, evaluation of the design produced ideas which led to an ultimate modification which overcomes its weak points.

The strength of the pump lies in its divergent annular jet design. This type of jet is capable of high pumping speeds since it is pumping through a large annular orifice. However, lack of proper cooling of the hollow cone of mercury vapor produced by the jet was the offender. As you will note, the jet is produced in a tubular divergent nozzle *N*. Mercury vapor is cooled adequately on the outer walls, but can escape over the cone shaped cold finger insert *C*. Some means to stop this path of escape was necessary.

Redesigning of the pump proceeded in two stages. A pump was built with the cold finger extending well into the nozzle and the top of the nozzle was sealed off. This produced better results so far as mercury loss was concerned, however, the ultimate vacuum of about 10^{-6} mm was not as good as we would have liked.

The final solution was achieved in the pump as shown in Fig. 2.[2] The long cold finger *C* is employed as before, but in addition another stage *S* is employed. This was motivated by the good quality of vacuum produced by the single stage. Such a backing pressure supplied to the stage above permits similar pumping speeds to be maintained while lowering the ultimate pressure to better than 10^{-7} mm. Actual design of the additional stage was accomplished by making up a pump with a large ground joint on top to permit access to the jets. These were made of glass supported by stainless steel tubes and could be adjusted individually as to size and position. By making a number of pumping runs and testing pump speed as well as ultimate vacuum, the optimum size and position of the upper jet were determined.

In use, a 40 liter vacuum line was exhausted to 2×10^{-6} mm in one hour. For the spectroscopy laboratory, it maintained almost constant pressure even though large bursts of gas were known to be evolved. Reference to the past had led us to solution of our problem.

Not every problem can be solved by reference to previous work, however. While it is said that there is nothing new under the sun, that everything has its basis in something done earlier, nevertheless at times we are confronted with new ideas, new concepts, or new designs which depart so far from the traditional that we find it hard to accept them as more than a novelty. As an example, we might think of the completely func-

tional approach brought to automobile design by the makers of the Volkswagon. It is taking a good deal of time to change our tradition-bound idea regarding so radical a departure as this "beetle" represents. However, I am sure most will agree that it doesn't appear nearly as queer to us now as it did when we first saw it. We can and are being conditioned to accept it as a bona fide automobile. Small, it is true, but not really in the novelty class any longer.

Our approach to most things new has been conditioned by caution. We are not ready to give up the tried and true for some unknown quantity and it is well that this is the case. Our homes and our shops would be in constant chaos, if we threw out everything old and brought in every new product as it appeared on the market. Of course, some of these products will prove to be worthwhile and after someone else has put them to the test we may purchase them ourselves.

In this light, let us take a look at the glassblowing burner which I designed some years ago and which is meeting with continually growing acceptance among the glassblowing fraternity. Initial sales of this burner were extremely limited and even nation-wide advertising among scientific people produced few additional sales. Gradually, however, and mostly by word of mouth recommendations, sales are snowballing to the point where demand and supply are finding it difficult to come out even. All this in respect to a burner, which even I still consider to be most radical in design.

Looking at Fig. 3A a partial cutaway view of the burner itself shows the outside configuration which is unique in itself. Traditionally burners should be heavy for proper stability. They are not easily shifted around. If you have a compulsion to move a burner around, use the hand torch.

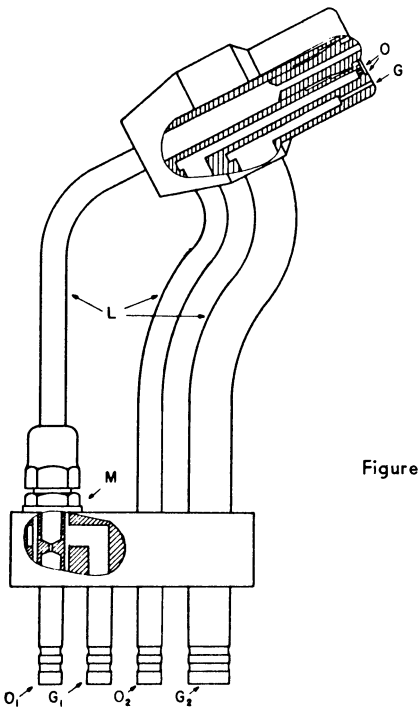
My underlying thought in designing this burner was to provide as functional and all around useful a unit as could be conceived. The previous concept of a separate burner for little flames, a large one for big work, others which would operate with hydrogen, modification kits to work with bottle gas—all of these had to be combined into one unit, and still be easy to operate. It seemed like a big order. Still, it wasn't quite like starting from scratch. There were several combination burner units on the market. These, in their operation, indicated to me a number of faults or weak points, which I should try to avoid. The advantages which these burners boasted should be retained in my unit.

The first concern was to provide a wide range of flame size, while operating from ordinary city gas pressures. Operation from low pressures would make the burner salable to many small laboratories where a gas booster would seem to be an unnecessary luxury. The only obvious answer was to consider surface combustion for the large flame and to provide a separate concentric small fire. For more easy control of the small fire, it was decided to employ premixed gas and oxygen to supply it. Oxygen and gas for the small fire are introduced at O_1 and G_1. The large fire is supplied through O_2 and G_2.

In actually putting the various considerations together, first thoughts were concerned with providing the function rather than producing a beautiful work of art. As the parts were sketched out, however, it appeared

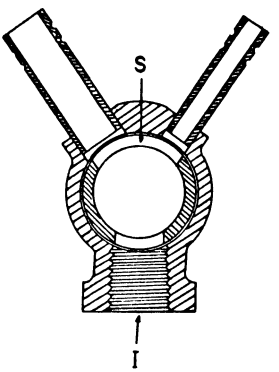
that the unit would not be too awkward to the eye if care would be taken in shaping supply lines and the head configuration. The supply lines *L*, were bent as shown in easy curves to provide a convenient hand-hold on the unit. The open design also allows cooler operation. The supply lines are almost never too hot to handle.

Construction of a working model produced a few changes. Theoretical considerations in the mixer had to be thrown out the window and trial and error produced the extremely hot fire now available. Most of our work with quartz and vycor up to 25 mm. O.D. is handled by this burner without resort to hydrogen. In addition, the critical determination of mixer hole sizes by the trial and error method, going one drill size at a time. produced a single mixer *M*, which gives optimum performance with every gas, from straight manufactured gas through natural gas, bottle gas acetylene and hydrogen. No modification of the burner is necessary when changing gas supplies.



A. Haak Model E Glassblowing Burner;

Figure 3



B. Control valve.

An important change was also introduced at a later date to overcome the tendency of the large fire to be noisy. This is a characteristic of surface combustion fires when gas and oxygen velocities are pushed too far. In this burner the oxygen is supplied to the large fire through small holes at *O*. Gas, which previously flowed unrestricted through the annular ring at *G*, is now channeled out in a similar jet fashion as the oxygen by means of a corrugated metal strip. Flame noise is considerably reduced.

Stability of the burner would have seemed to be a problem, inasmuch as so little weight has been allowed. In actual use, however, attaching the hoses to the bottom and providing a suitable cast aluminum base has lowered the center of gravity to such a point as to make it completely stable and yet light weight enough to pick up and perform certain operations with better results than a hand torch might produce.

While the burner itself is radical enough in design, its control is even more so. The idea of four valves to supply the two gas and two oxygen lines did not appeal to me, particularly since turning them off in the wrong sequence could produce a large flashback. A single valve to supply both gas lines and another to supply both oxygen lines in proper sequence and correct volume and pressure was needed. No commercial valve could meet the requirements and when the application for a patent[3] on the burner and valve was made, it became evident that none had ever been made. The valve, as finally produced, had a cross section through the center as shown in Fig. 3B. The opening in the core bridging across the two outlets *S* is in reality a slot which would not be evident from the section view. It will be noted as the core is rotated within the body it can connect the inlet *I* with the small outlet in any proportion and add on the large outlet in any proportion to the small outlet without reducing the size of supply to the small outlet. A stop on the valve is provided to prevent going past the point shown in the figure. Two identical valves are used to supply the gas and oxygen to the burner.

While these valves could be mounted and operated by hand, a further innovation was employed in supplying foot pedals to control them. Actually foot pedals are not new, but have been employed in various ways to control burners. With full control of the burner by the pedals, however, the hands are left completely free to manipulate the glass. For students this is an immeasurable help and professionals find the saving in time to be considerable. It takes only two or three days to become completely familiar with the operation of the pedals.

At this point, if you have not previously come into contact with this burner, you will probably have some serious reservations concerning your own advisability to purchase one. All I can say is—give it a try and it will convince you, as it has so many others. Although it is a completely radical departure from the old into the new, it has proved itself competent to the requirements set up as the ideal.

The particular point in this elaborate discussion is not so much to increase sales for me as to point out the great need in all of our dealings to retain an open mind to any new development if it can be of possible help to us. With all the helps from the past and the continuing investigations into new techniques, new glasses, new metals and adhesives, we should adopt a policy that most demands put to us can be met in one way or another. Unfortunately, it has been my experience that a number of glassblowers are not willing to accept this principle. Many times and from various localities I have received requests from former students at the university for items of apparatus which their own glassblowing staff should have been able to fabricate, but would not attempt. This is a situation, which I feel should not exist. Granted that some time will have to be

given to developing a technique, which I had opportunity to perfect. It may take an additional measure of patience for some to do this, but I feel that if we are to serve in our capacities to the best of our ability we must be willing to apply ourselves to the task. It is evident that glassblowers, who have spoken to previous symposiums, have universally all held this same position.

We should all resolve here and now that if demand requires new techniques of us, we shall develop them. If new materials will make a piece of apparatus better, we will use them. If a totally new concept of what we can accomplish is required, we cannot and will not remain blind to any possible avenue of approach to the problem. New research demands will continue to be made and we cannot allow our outlook to be inhibited in any way. We must continue to grow in all phases of our responsibilities.

To this end we should also be ready and willing to share our experiences with others in our chosen field. Our own *Fusion* magazine is begging for articles of this nature. As it has helped us in the past, it should continue to provide us with more and better articles to help broaden our vision.

With helps such as these, with a willingness to accept help from our predecessors, with a readiness to step out into the new and untried, we will in the end upgrade the glassblowing profession to ourselves, personally, and to those whom we serve. Gentlemen: Let's Expand our Horizons!

REFERENCES

1. C. S. Bull and O. Klemperer, *J. Sci. Instr.* **20**, 179 (1943).
2. W. H. Haak and F. Vratny, *Rev. Sci. Instr.* **30**, 296-297 (1959).
3. W. H. Haak, U. S. Patent No. 2, 598,787.

THE IMPACT OF AN ADVANCING SCIENCE ON THE GLASSMAKER

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I. INTRODUCTION

All of us are aware that we are living in an era of exploding technology. Hardly a day goes by without some announcement of a new development in missiles, space technology, computers, electronic marvels, nuclear energy or some other exotic area. In all of this, there is a great emphasis on materials or material combinations. Many of these materials are either new or are used in a hitherto unheard of way.

The impetus for technological advancement comes from two sources. One is the research and development area of the materials supplier, who wishes to market his new discovery. The other is the pressure of potential customers for a new material to satisfy advanced technological requirements.

The glassmaker has been an active participant in this technological explosion from several standpoints. First, he is continually trying to improve control of dimensional tolerances, such as wall thickness and distribution, surface finish, etc. Second, he is steadily improving glass quality, as well as reducing variations in chemical composition of the glass which in turn controls various properties of the glass. Third, he has been active in the introduction of new glass compositions or related materials and the extension of the useful range of these materials to satisfy new and varied requirements.

Today I would like to discuss with you some of the areas of technology in which the glassmaker has played an important part in this era of exploding technology.

II. GLASS FOR HIGH TEMPERATURE

The original high temperature glasses were the borosilicates which were developed in the early part of this century and found wide acceptance for use in laboratory ware and baking ware. Although these glasses required a very high melting temperature, the annealing temperature was quite low, in the neighborhood of 550°C. As a result, aluminosilicate compositions were introduced about 25-30 years ago, particularly for use in combustion tubes, or cooking ware for use on top of a stove. Their higher annealing temperatures, over 700°C., have permitted the use of tempered aluminosilicate glasses in such heat resistant applications as the windshield of the experimental X15 rocket plane.

The next breakthrough from the standpoint of temperature resistance was the development of extremely high silica glasses by the Hood-Nordberg process. Products of these reconstructed glasses, more generally known under the trademark of VYCOR, have annealing points above 1000°C. This, plus the extremely low thermal expansion has made these glasses particularly suitable where a high resistance to thermal shock is required as well as the ability to withstand a high operating temperature.

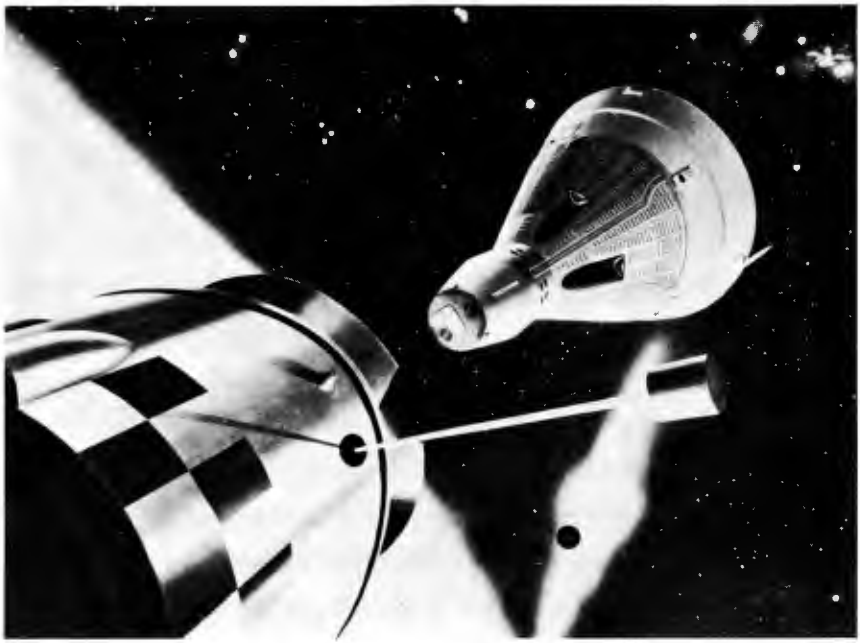

Figure 1

Windows will be of prime importance when astronauts maneuver Gemini to hook up with another vehicle while in orbit. Each window will consist of three separate, flat, parallel panels of high temperature, high strength glasses, proved out in Mercury and X-15 flights.

Unfortunately because of the low expansion, it is difficult if not impossible to seal these glasses directly to metal and a graded seal must be used.

Recently a new aluminosilicate glass, Corning Code 1715, has been introduced which seals directly to tungsten. This glass has an annealing point above 850°C. and should be useful in some high temperature electron tube applications. In order to successfully melt the glass, it is necessary to use temperatures near 1800°C. These temperatures are readily obtained in melting units by using oxygen instead of air for burning the gaseous fuel.

Pure silica glass has always been very attractive from the standpoint of its high annealing temperature and low thermal expansion. It has been found extremely difficult to obtain a homogeneous silica glass free from bubbles by direct melting of quartz crystals. However, silica glass can be made in a different manner by hydrolyzing silicon chloride vapor in a gas-oxygen flame and depositing it on a heated support. This type of fused silica, Code 7940, is extremely pure and homogeneous. It has recently found applications in space exploration, such as the outer windows of the Gemini space craft and in the 36 inch diameter telescope mirror used in Project Stratoscope II.

The need for high thermal shock resistance coupled with certain specified electrical requirements and resistance to atmosphere erosion led to the development of a glass-ceramic material which is finding use as the radome of certain guided missiles. Glass-ceramics, you may recall, while not true glasses in their final form are melted as glasses and converted to ceramic materials by a subsequent heating process. These materials are finding increasing use in space requirements, heat exchangers, such as the Cercor material, and even more prosaic uses such as frying pans and small stove units.

Figure 2

Blank for 36" Fused Silica mirror shown before the giant piece was precision ground and polished for Project Stratoscope II. It served as primary reflective piece in a 36" telescope carried aloft by an unmanned ballon for outer space photography. The blank measured 37" in diameter, was 5½" thick and weighed 450 pounds.

What does the future hold? This is difficult to say. Certainly the requirements for heat resistant materials in both space and industrial applications are going to keep advancing to higher and higher temperatures. New methods of producing higher temperatures are now beyond the stage of laboratory curiosities. These temperatures obtained by using plasma jets, image arc furnaces, solar furnaces and the like, now permit the melting of highly refractory oxide glasses containing high concentra-

tions of such oxides as silica, alumina, zirconia, etc. Some of these glasses will find a role in future technology.

III. GLASS FOR ELECTRONICS

The versatility of glass composition is found more in the electronic applications of glass than perhaps any other area. Alkali-lime glasses are used in lamp bulbs, fluorescent tubes, radio tube envelopes and the like where cost is the primary consideration. Alkali-lead glasses are used where high electrical resistivity and a long working range are desirable. Many different glasses are used in the television picture tube industry. For instance, a color television bulb consists of four separate glasses, a faceplate which will not darken under electron bombardment, a funnel which has a high absorption coefficient for X-rays, a neck of a different

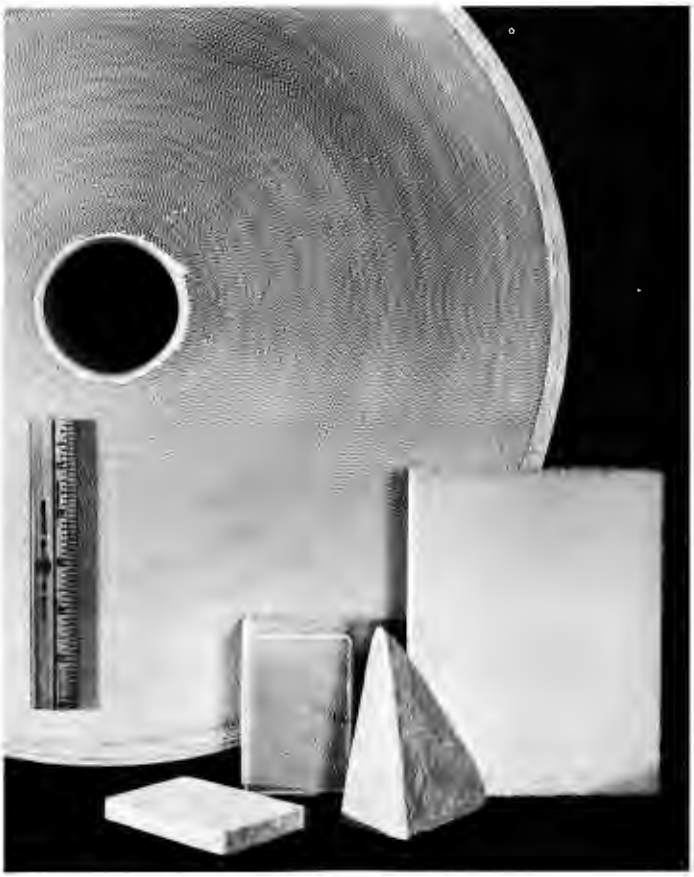

Figure 3

Cercor—A thin-walled cellular ceramic material which is finding use in heat exchangers and infrared burners.

composition and high resistivity which allows a graded seal between the funnel and the standard Code 0120 used for the stem. In addition, the faceplate and the funnel are held together by a solder glass.

Many borosilicate glasses are used for electrical purposes. The first commercial lead-borosilicate, which was originally used for battery jars, baking dishes, and the like (Code 7720), is still being used to seal heat resistant borosilicates such as Code 7740 to tungsten. The development of Kovar metal in the early 1930's resulted in a new group of borosilicate glasses with expansions designed to match the new metal. These borosilicates were fairly difficult to melt and consequently had some quality problems. A higher expansion Kovar sealing glass, (Code 7056), was subsequently developed which could be melted satisfactorily in an optical quality melting unit. This glass has found widespread application in faceplates of various pickup and cathode ray tubes. In addition, this glass is free of halide, the level being held to trace amounts by routine control analysis. Therefore, the glass may be used in certain applications where halide evolution during bakeout or electron bombardment would interfere with the cathode response.

For application where high energy electrons are involved or for use in installations where high gamma radiation might be present, certain protected glasses have been developed which do not discolor under this radiation.

The need for a high dielectric constant coupled with a low loss factor and good workability led to the development of a special mixed alkali-lead glass, (Code 8871), for use in glass capacitors. The degree of precision which the glass composition is controlled and the care in manufacture of the individual capacitor has resulted in a reliability factor which allows these capacitors to be used in the most sophisticated of the guided missiles.

Glasses have also been used for resistors. The deposition of tin oxide films on low alkali or alkali-free aluminosilicate glasses has permitted the development of precision resistors. Two types of glasses are manufactured by Corning for this purpose. One is a lime aluminosilicate (Code 1723) which finds particular use in tubing or cane resistors, the second is a barium-aluminosilicate (Code 7059) which is available in sheet form and has found use in flat resistors and as a substrate for microelectronic circuitry.

The need to assemble various parts of an electronic tube without resorting to the high temperatures necessary for flame or electric sealing resulted in the development of what are known as solder glasses. These glasses will soften at a relatively low temperature, around 350-400°C., and allow satisfactory seals to be made at this temperature. Some of these glasses have the additional quality of devitrifying during the sealing process to a glass-ceramic type material of exceedingly high strength. In general, these glasses may be classified as lead borates.

Most of the applications involving electrical resistivity specifications require either a maximum or a minimum resistivity. Very seldom is it necessary to maintain a volume resistivity within a specified range. An exception to this statement is the image-orthicon target. In an image-

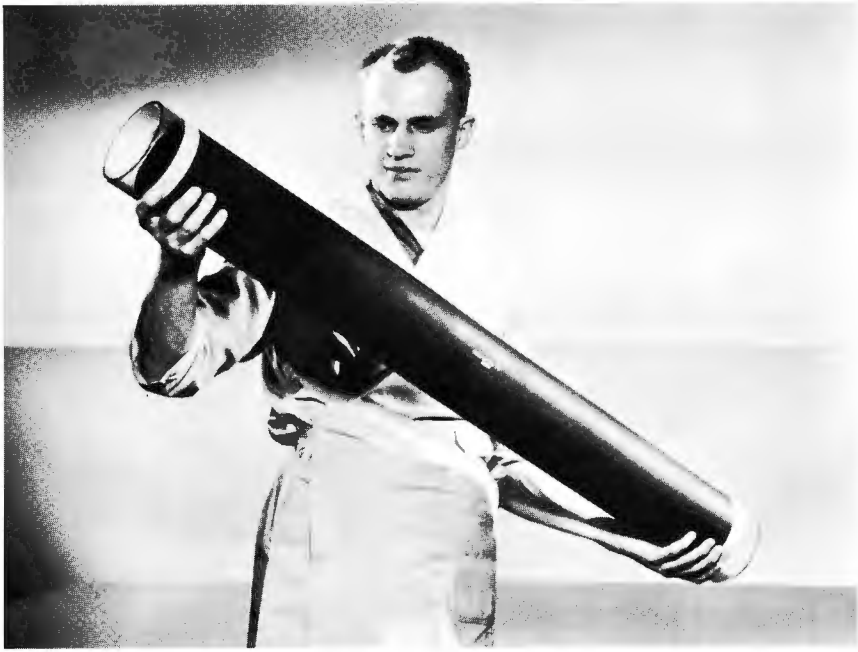

Figure 4

Resistors, usually regarded in terms of inches, were made in lengths of four feet for communications equipment in the world-wide Project Mercury tracking network. The massive resistors, as big around as telephone poles, are made of glass.

orthicon tube a charge pattern is built up on one surface of a glass target membrane by electrons from the photocathode. This charge pattern is then read by another electron beam from the backside. Each spot on the target is read about thirty times a second. Thus, the volume resistivity must be low enough for the charge pattern to be neutralized in 1/30 of a second and yet must be high enough for adequate resolution. In addition, if the resistivity is too high the charge pattern will not dissipate, resulting in a sticking image. The resistivity range for a satisfactory glass target is in the neighborhood of 10×10^{11} ohm-centimeters at room temperature. Here again close control of composition and melting procedures is needed to maintain this narrow resistivity range.

This concept of getting electrical information from one side of a glass surface to the other has recently been solved using a glass-to-metal sealing technique. In this technique many wires, as many as 250,000 in a square inch, have been sealed in a regular array. This technique is called Multilead by Corning. (Figure 5) These matrices are vacuum tight and can be sealed into a cathode ray tube. One of the applications of this process is in the printing of magazine address labels using an electrostatic printing tube with a Multilead matrix. A sophistication of this technique is miniature glass wires which are made from aluminosilicate

glass microcane that is only .002" in diameter. Each cane is coated with an electrically conducting film and covered with a transparent insulation. These microcane or glass wire arrays are useful in electroluminescent x-y display panels. These panels are made by sandwiching a phosphor between a layer of parallel metal conductors on the x-axis and an array of glass wires parallel to the y-axis. A spot of light appears where current in the conductors intersects on the grid. This type of device can be used in navigational or tactical plotting boards to display direction and speed of moving objects.

What does the future hold for glasses with electrical purposes? Let us consider the volume resistivity of glass. The resistivity of all common glasses is ionic in type. That is, there is actually a transport of material during electrolysis. In other words, under application of a direct current potential there is a gradual depletion of ions with a subsequent rise in the resistivity. In the last several years there have been more and more references in the literature to glasses in which the conductivity is not ionic, but is electronic; that is, the conductivity mechanism is based on the transfer of electrons. If practical glasses showing electronic conductivity could be made, there would be no problem of ion depletion or change in resistivity under an applied direct current potential. This would open up areas in which glass could be used as a true conductor and not as a resistor or insulator.

IV. GLASS FOR OPTICS

The first systematic research on the effect of various oxides on the physical and optical properties of glass was carried out as a result of pressure from an advancing science and technology. I am referring to the work of Abbe and Schott who widened the range of optical glasses in order to eliminate the dichroic effects of a secondary spectrum in microscope and other lens elements. At the time they started their work only six chemical elements; silicon, potassium, sodium, lead, calcium, and oxygen were used to any extent in glass. The optical properties of glasses made up of these six elements are such that as the refractive index increases so does the dispersion and it was impossible to make a color-free lens system. Abbe and Schott introduced 28 new elements into the glass technologist's repertoire, with the result that now there were high index glasses with low dispersion as well as low index glasses with a high dispersion.

However, the work of Abbe and Schott was not sufficient for the most sophisticated of the optical instruments. There was still a need for even higher index glasses coupled with a low dispersion. A big step in this direction was made in the 1930's when Dr. Morey introduced the concept of rare earth glasses, which was further refined by the work done at Eastman Kodak. This work extended that originally started by Abbe and Schott. These glasses never became large volume glasses because of the cost and difficulty in obtaining the various oxides in a sufficiently pure form. Since the war, with the development of various separation techniques and the decreasing costs of such oxides as lanthanum, thorium, niobium, etc., these glasses are increasing in use. Recent composition work done in Germany has extended the range of optical glasses even farther than that designed by Morey and Eastman Kodak.

In addition to the glass composition work, the glass manufacturer has been active in the development of new optical devices. One of the newest of these techniques is that of fiber optics. This is a refinement of the old principle of transporting light through a glass or plastic rod, with which I am sure all of you are familiar. By using glass fibers for rods which have a relatively high refractive index and coating these fibers with another glass of extremely low refractive index a light pipe is produced. If these fibers are drawn down to a small diameter, in the neighborhood of 10 microns, and bundled together, optical or light information may be transmitted from one place to another. An example of this is a fiberscope which may be used to examine the interior of the human body, interior of a motor, or reactions going on in a radioactive atmosphere. It consists of a bundle of fibers which may be in the neighborhood of five to twenty feet long. This bundle is quite flexible but obviously requires a high degree of transmission in the glass.

Figure 5
Multilead bulb for electrostatic printing tube. Inset shows detail of wire array.

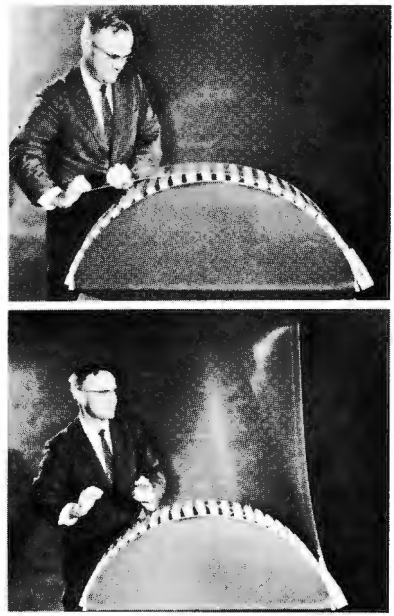

Figure 6
Piece of chemically strengthened glass is bent over 20-inch radius and then released. This glass has been flexed repeatedly over short radius arcs without failure. Corning calls the new basic strengthening method Chemcor.

Another type of application for fiber optics is in the faceplate of a cathode ray tube where it is desired to transmit information of high resolution from the inside of the cathode ray tube to the outside without losing this resolution. This is particularly of importance in photographing

various cathode ray tube displays. In cathode ray tube applications, problems confronting the glass technologists are many. First of all, the cathode ray tube envelope must be vacuum tight, which will require a vacuum tight fiber optic plate. This means that the net coefficient of expansion of a plug must be somewhere near that of the envelope itself. It also means that during the drawing of the fibers and subsequent fusing of them into a bundle or plate, no trapped air or other foreign material can be allowed. In addition in certain applications one must be very careful not to include in the glass composition lead or other easily reducible oxides which might be reduced during photocathode deposition thus turning the entire plate black. It is in this application that the new rare earth glasses are finding more and more use.

One of the most exciting new areas of optical technology is that of the laser. Suggested applications for this device have run the gamut from disintegrating ray guns to long range space communications.

The word "laser" is an acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation. It is a device for generating coherent light, that is, lightwaves of a single frequency that vary in a regular sinosoidal pattern similar to radio waves. Much of the research in lasers has been conducted on crystalline materials such as chromium doped ruby or gaseous materials such as the helium-neon laser. Glass is also of great interest in laser technology since it has been found that glasses containing the rare earth elements, in particular neodymium, have the proper fluorescent response to make satisfactory lasers. Glass offers many advantages because it lends itself to fabrication of a wide range of shapes and sizes. Single crystals such as rubies can be grown in only one shape and in relatively small sizes. The use of gas for laser material results in a large bulky apparatus. The entire field of laser technology is yet to come into focus, but projections indicate that this will be a multimillion dollar market in the next five years or so. Certainly the glass industry will have a definite place in this technology.

IV. GLASS FOR STRENGTH

One of the longstanding goals of the glassmaker has been a method of improving the practical strength limit of glass. While the theoretical intrinsic strength of glass may be as high as three million pounds per square inch, the useful strength has always been a small fraction of this value due to flaws induced by surface scratches or cracks. Since glass breaks only from tension, never from compression, the classical method of improving strength is chill tempering, capable of inducing compressive stresses up to 20,000 psi.

In chill tempering, a glass object is cooled rapidly from a temperature just below its softening point. Since the inner portion cools more slowly than the surface, it continues to contract after the surface is essentially rigid, thereby developing surface compressive stresses with compensating tensile stresses in the interior. This process is limited to relatively thick pieces and simple shapes because of heat flow problems.

During 1962, a new basic method for strengthening glass was announced by Corning Glass Works. This process is called Chemcor. It

embraces several different chemical strengthening techniques coupled with special glass compositions.

Two of the many techniques were described at the VI International Congress on Glass in Washington during July 1962. These two methods of chemical tempering both involve the formation of transparent polycrystalline layers within the surface of glasses of appropriate composition. Flexural strengths as high as #100,000 psi have been realized in the laboratory for certain compositions. The crystallized skin, which is grown at high temperatures, has a negative expansion and thus expands when it cools. The shrinking of the internal glass induces an extremely high compression of the skin, resulting in the high strength.

One of these methods employs surface nucleated crystallization of a lithia-alumina-silicate glass. The other, more complex, begins with a soda-alumina-titania-silica glass, replaces the sodium ions in the surface with lithium ions by immersion in a molten lithium salt bath and ends with titania nucleated crystallization of eucryptite at the surface of the glass.

Because of the high strength, the chemically strengthened glasses may be bent repeatedly into relatively short arcs without failure. This strength quality also makes possible the fabrication of lighter weight articles without sacrificing strength.

It must be emphasized that the Chemcor method of strengthening glass applies only to a finished article. Chemcor treated glass cannot be lampworked without losing its unusual strength characteristics.

VI. CONCLUSION

What I have tried to point out today in a very superficial manner is that the glassmaker has been an important participant in our present age of exploding technology. By inference, I have also mentioned some of the reasons for the many glass compositions which are commercially available. It also can be readily seen that if a suitable glass composition or material is not presently commercially available, the glassmaker can oftentimes suggest one from his background of experimental work. If not, it may be possible that he can develop a new glass or material to effect a technological breakthrough.

FRITTED GLASS FILTERS

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The increasing use of fritted filters by laboratories doing special research, particularly organics, will require that the glassblower be able to fabricate the necessary apparatus. The purpose of this paper is to provide the glassblower with a background in the structure, processing and testing of fritted discs. This background will be used to explain the purpose of the recommended sealing procedures.

A fritted filter, generally in the form of a disc, is produced by sintering ground glass to form a rigid porous piece of glass. The glass is the same high durability borosilicate glass used in KIMAX brand laboratory ware.

The glass is ground or crushed and separated into size fractions using commercial equipment. Each fraction will have a size range depending upon the shape of the particle and the method of separation. Figure 1 illustrates a fraction produced by screening glass.

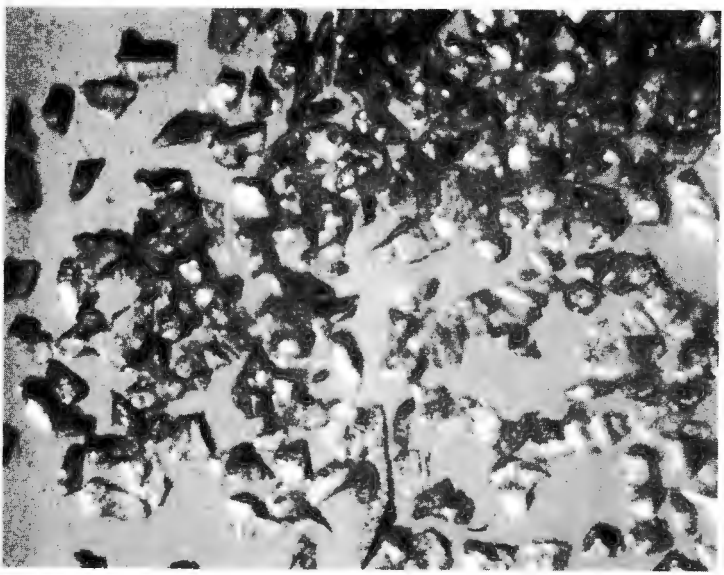

Figure 1
Screened Ground Glass 30X Magnification

Various means are used to produce the desired shape of filter.

The ground glass can be placed in a mold and fired. Normally a metal mold with a parting agent is used. Carbon molds are also satisfactory for limited use.

Ground glass can also be formed into filter shapes by dry pressing as used in the ceramic industry. The ground glass is mixed with an organic binder and granulated into a free flowing powder that is pressed in a die to the desired shape. The pressed part is heated in a "Burn Out" cycle to remove the binder, followed by the sintering cycle.[1]

Fine grade filters can also be formed into the desired shape by using a slurry and slip castings. The green ware is then dried and any binder burned out before sintering.[2]

Sintering temperatures range from the softening point (825°C.) to 1000°C. The time and temperature are varied with the process being used and the particle size being sintered; the coarser grades normally require more temperature or time.

As the filter is being sintered, shrinkage takes place in varying amounts, depending upon the size of the ground glass, and to a lesser degree, on the process. The shrinkage is important and will be more fully discussed later in this paper.

Commercial filters are classified into various grades by their "maximum pore diameter". This is natural, of course, but let's examine "maximum pore diameter" in a little more detail. Since none of the pores is round, pore diameter is based on the test method and is defined as follows:

"(a) Maximum pore diameter is the diameter in microns of a capillary of circular cross-section which is equivalent (with respect to characteristics related to surface tension effects) to the largest pore in the filter under consideration."[3]

"NOTE 1—It is recognized that the maximum pore diameter as defined herein does not necessarily indicate the physical dimensions of the largest pore in the filter, and furthermore, that the pores are highly irregular in shape. Because of this irregularity in shape and other phenomena characteristic of filtration, a filter may be expected to retain all particles larger than the maximum pore diameter as defined and determined by this method, and will generally retain particles which are much smaller than the determined diameter."[3]

The filter is tested by thoroughly wetting the filter with a suitable liquid and applying air pressure until the first bubble of air passes through the filter. The "Maximum Pore Diameter" can then be calculated from the surface tension and the applied pressure.

Now let us return to the matter of shrinkage. As illustrated in Figure 1, the ground glass contains sharp edges and points. When the glass softens, surface tension tends to round all sharp angles. Assuming no fusing, this would allow for immediate closer packing.

Fusing or tacking of the glass particles prevents the particles from becoming perfect spheres. This is shown in Figure 2. The fusing can be considered the same as two drops of water which touch, retain their identity for a moment, and suddenly merge into a single drop. The same process in glass is much slower due to the greater viscosity. This process is continued in completely or sintered components until entrapped air limits further shrinkage. Firing of filters stops long before this point is reached.

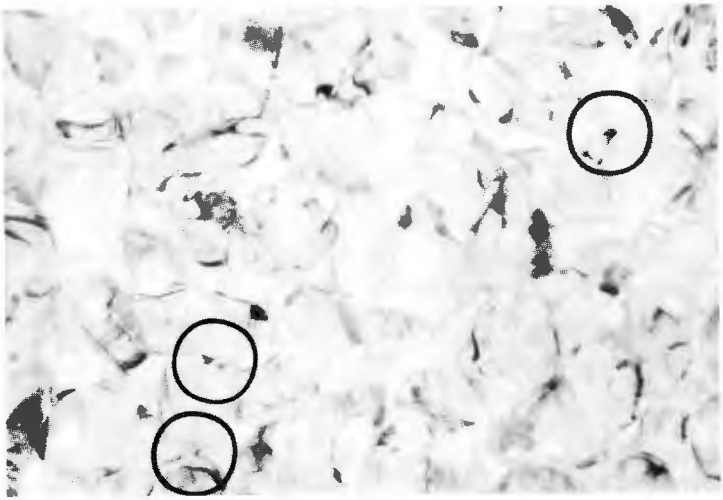

Figure 2
Filter Detail Showing Fusing

Consider next the drop of water which touches a much larger puddle. The small drop moves toward and is absorbed by the larger body. The amount of motion is related to the size of the particles concerned.

Relate this to the process of sealing a filter, composed of many small particles, to a solid piece of glass.

In an uncontrolled seal, the edge particle is torn between the attraction of the particles to which it is sintered and the solid mass of glass to which it has come in contact. The stronger attraction of the solid mass pulls the edge particles away from the filter creating pores larger than specification.

The easiest way to overcome this problem is to paddle the solid glass into the filter, reducing or closing the pores at the extreme edge. For the most efficient assembly, it is recommended that the seal be limited to paddling into as few edge particles as possible; little more than a mechanical seal.

The same principle holds when glazing the edge of a filter disc prior to making a glass to glass seal. Always reduce the size of the filter, filling the pores with the glazed portion.

Holes may be drilled in filter discs with the careful use of an ordinary drill press. A wet filter is less apt to crack. Before sealing, the filter should be cleaned with hydrochloric acid to remove any metal traces.

REFERENCES

1. Manual, *Technical Data Kimble Glasses,* Owens-Illinois Glass Company, June, 1962.
2. Kocatopcu, Sahap S., Massachusetts Institute of Technology, Cambridge, Mass.; "Different Methods of Slip Casting", *American Ceramic Society Bulletin,* Vol. 25, No. 2 (1946).
3. American Society for Test Materials, ASTM Designation E 128-57T, "Tentative Method of Test for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use", *Book of ASTM Standards, Part 5,* (1957).

GLASS LATHE CHUCKS AND ALIGNMENT OF GLASS LATHES

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PART I

GLASS LATHE CHUCKS

The first type of accuracy desired in a glass lathe is accuracy in the chucks themselves. This is easily checked by chucking a straight tube and then while the lathe is running, sighting across the top of this tube. With a good eye even an error of a few thousandths will be visible. The tube in this test may run true for its whole length or on the other hand it may have any type of eccentricity. Frequently, the tube is quite true close to the jaws but out of true farther away. This can mean either that the chuck jaws are only gripping firmly at one end or that while the grip is good it is not parallel with the chuck body.

Figure 1

Figure 2 →

The most accurate type of chuck is probably the Collet in which a wooden cylinder, usually redwood, is bored on the lathe on which it is to be used. Figure 1 shows the parts of a large one, the wooden block at the right being bored and its upper end slit into six segments. This is the Collet. It fits into the casing shown and is held in by the retaining ring. The assembly is shown in Figure 2. Tightening the knurled retaining ring squeezes the segments together and causes them to grip the glass tube. The arrangement has, besides its accuracy, the advantage of being relatively air tight and thus a blowing arrangement can be permanently attached to the lathe spindle. The great disadvantage is the small range of tubing size handled by any one Collet, and of course, the very destructible nature of the Collet material.

*Deceased. This paper was prepared for presentation at the Eighth Symposium but, due to Mr. Nieman's sudden passing, was not read. It is being included in its entirety in these "Proceedings", and as a two-part article in the August and November 1963 issues of FUSION.

Figure 3 →

Figure 4

The Scroll chuck is a close second in precision. It is the most accurate type of three-jaw chuck, the type that is used on metal-working lathes. For a glass lathe, certain modifications are necessary such as a large through hole and operation by means of a handwheel instead of a key. Figure 3 shows such a chuck assembled and Figure 4, the parts composing it. The Scroll is the spiral screw cut in the face of the circular plate at the right in Figure 4. The back ends of the jaws carry a series of teeth which engage with the Scroll. As the handwheel is turned, all three jaws are pushed in at an equal rate. After assembly the chuck is mounted on a Lathe and the jaws internally ground. It is not important at what size of opening this grinding is carried out because since the Scroll moves all the jaws equally, accuracy at one size means accuracy at all sizes. This, of course, within the limitations of machine practice. Such a chuck has a very wide range of size accommodation. Further, this can be increased to any desired extent and adapted to fit various shaped work pieces by designing special shaped jaws to substitute for the usual ones. This type of chuck is a feature of Heathway Lathes. It is not only valuable in ordinary work but especially so where a high degree of accuracy is required such as is frequently the case for glass to metal seals.

In a third type chuck the jaws swing about pivots and are controlled by the rotation of a sleeve or cam plate; this in turn accomplished by turning a knob on the back of the chuck. The jaws are internally ground after assembly of the chuck. This is the type of chuck used on Bethlehem-made lathes. It has advantages in quick action from fully open to closed,

← Figure 5

Figure 6 →

positive locking without the use of separate wrench or key and slimness of design. Figure 5 shows a chuck of heavy design opening to five and a quarter inches through spindle and by the use of extension bars Figure 6 holding anything to eighteen inches in diameter. Figure 7 shows one of smaller design. This smaller chuck is now available with an adaptor for various model Littons & Heathways. A chuck of this type adapts itself readily by the use of the proper attachment to so-called "production" operation. A handle is arranged on the lathe bed to operate the chuck to a small extent without stopping the lathe. Thus, if a quantity of tubes of the same size, any size within the chuck range, are to be worked on, one tube is firmly gripped in the chuck, the glassworking operations on it carried out, the handle on the lathe bed depressed, thereby loosening the chuck hold, the finished tube removed, a new one inserted and firmly gripped by operation of the handle, all without stopping the lathe. Figure 8 shows how a tube is inserted, the blurring of the parts of the chuck is due to the fact that the lathe is running. In this particular case, the lathe is also provided with a blowing attachment so that when a glass tube of any size is inserted, connection is automatically made with a blow hose in the rear.

The Sun and Planet chuck is a common type for holding large flasks and similar objects down to reasonably small tubing. Such a chuck is shown in Figure 9. The arms have a wide swing in opening from practically zero to their maximum. They are usually covered with asbestos to

Figure 7 ←

Figure 8 →

Figure 9 ↓

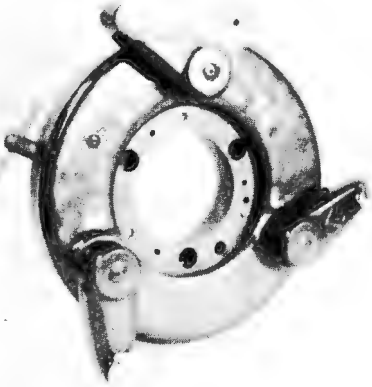

Figure 10 ↓

give them a better grip and because they are as a rule not intended for great accuracy. In fact, this quality is very difficult to obtain in any high degree because each arm is controlled for its full swing by a small gear which makes only part of a revolution. The operating elements are shown in Figure 10. The rotation of the worm is by separate key and it in turn causes the rotation of the large ring gear. The rotation of the latter causes rotation of the three small gears, one on each of the shafts of the swinging arms. Since each of the small gears is rotated the same amount, each of the arms moves through the same arc.

A chuck that is lately coming into extended use is the Vacuum chuck, two different types of which are shown in Figure 11. In one there is an internal cone lined with tightly wound asbestos, and in the other three concentric rubber rings. A connection to a small vacuum pump is made through a swivel arrangement at the far end of the spindle. A turn of a valve is sufficient to cause a very firm grip on a flask or other round-bottom object. The absence of jaws makes a neater and perhaps safer arrangement, and the fact that it can be operated while the lathe is running is frequently an advantage.

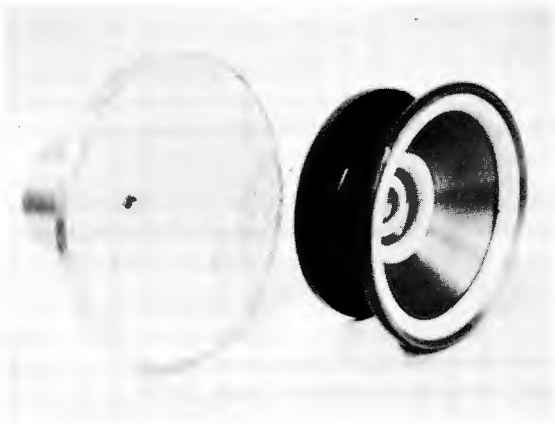

Figure 11

Figure 12

As a last example of a chuck, Figure 12 is presented. This is simply a Jacobs chuck such as is used on any drill press fastened to an adaptor to be attached to a glass lathe spindle. No key is required since hand tightening is sufficient. It is good for very small work.

GLASS LATHE CHUCKS AND ALIGNMENT OF GLASS LATHES

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PART II ALIGNMENT OF GLASS LATHES

The accuracy of alignment of a lathe has nothing to do with the accuracy or inaccuracy of chucks. It is a function only of the way the spindle bearings are set in relation to the lathe bed and to each other. A given spindle can be considered to revolve around an imaginary line, the axis of rotation, which passes through the center of the spindle and extends as far endwise as we care to imagine it. This line for a given chuck must be parallel with the lathe bed. For example, if viewed from the side it must not point upward nor downward. To make it correct in this respect a tilting adjustment is required. That is, the parts that support the spindle bearings must be capable of being tilted upward or downward as the case may require. The means for making such adjustment may be an actual screw adjustment or it may simply consist of shimming or scraping parts at the factory at the time of manufacture. In any case this can be designated as the first tilting adjustment, and is required on both headstock and tailstock spindles. A second tilting adjustment is now required because although the axes of rotation of both spindles may be level and parallel to the bed in a front view, when viewed from the top they may point off to one side or the other. Each spindle therefore must have a second tilting adjustment in a sideways direction. Or, expressed more technically, each spindle must have two tilting adjustments; one about a horizontal axis which is at right angles to the axis of rotation, and a second about a vertical axis.

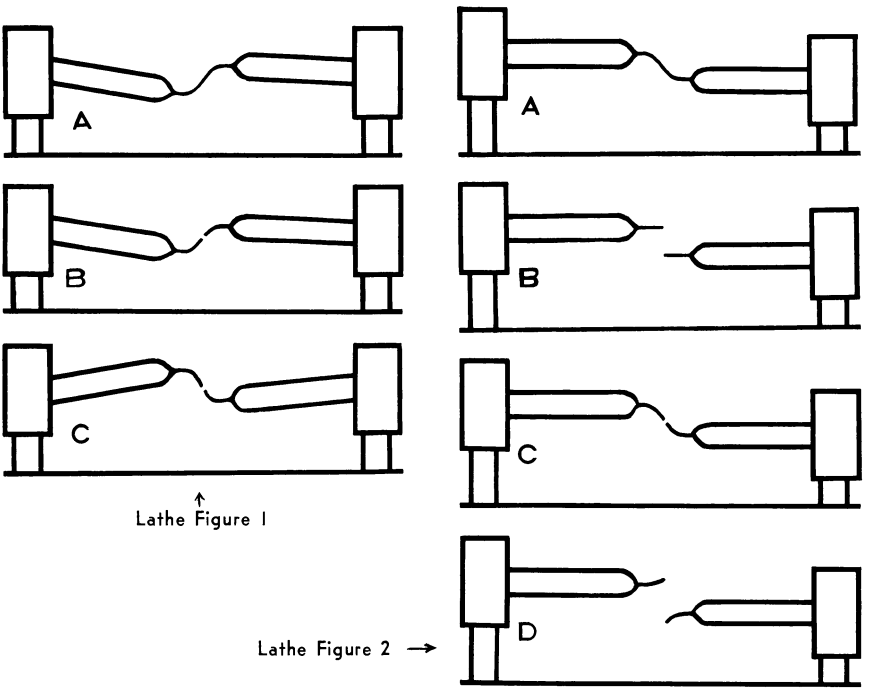
However expressed it is clear that there must be two tilting adjustments for each spindle—a total of four. By manipulating these, the axes of rotation of the two chucks can be made perfectly parallel with the lathe bed, which means also with each other. Unfortunately this is not enough. The spindle axes, although parallel, may be at different levels or viewed from the top one may be more forward than the other. Two other adjustments are therefore necessary since the axes of rotation of the spindles must coincide, that is, the axis of one spindle must be the same line as that of the other. The adjustments need be on only one of the spindles since the requirement is merely to bring the two together, and therefore either spindle can do the accommodating. The type of adjustment here required is not tilting as with the previous ones, but what might be called shifting, that is parallel movements, one permitting up and down shift, the other sideways shift.

These six adjustments, two tilting on each spindle and two shifting on one of the spindles are all of them necessary and they are enough to completely satisfy the problem.

A test frequently relied on to check alignment consists in clamping a tube in the two chucks, heating, and drawing the middle section out to

small diameter. After cooling, it is cut apart in the center with a knife scratch. Figure 1 shows this test carried out with two chucks with their axes in alignment but with the chucks themselves badly out of true. The drawn-out middle section is under no stress when cold and when cut the ends will stay exactly together in every position of rotation of the lathe as shown in the bottom two views.

The point to be brought out here is that the inaccuracy of the chucks themselves does not in any way affect the test. It is only the alignment of the axes that can affect the results.



Lathe Figure 1

Lathe Figure 2 →

Figure 2 is a case of misalignment. In this case the axes of rotation are parallel but do not coincide, the one on the left being higher than that on the right. The chucks themselves here and in the following cases are shown as holding the tubing centrally and at right angles to the chuck bodies, but they might be out of true without in any way altering the discussion. When the tube is first placed in the chucks and clamped tight, it is under stress because the chucks are not in line but this disappears when the central portion is heated and drawn out as in Figure 2a. The tube may now be cooled in two ways: 1) while the lathe is running; 2) with it at rest. In the former case, the thin portion will be equally stressed in all directions while cooling and when cut apart, the halves of the reduced portion will relieve the stress by straightening out parallel with the sections of the main tube but offset by the amount the chucks are shifted out of line. This is shown in Figure 2b. The error is shown so

greatly exaggerated in these drawings that it is hard to imagine the tube being springy enough to act as here described but, of course, actually the displacements are very small.

If the lathe is stopped after the middle section is drawn out and cooling then allowed to take place, there will be no stresses developed. When cut apart the reduced sections will be curved (2c), and when the lathe is turned a half of a revolution the ends will be far apart (2d).

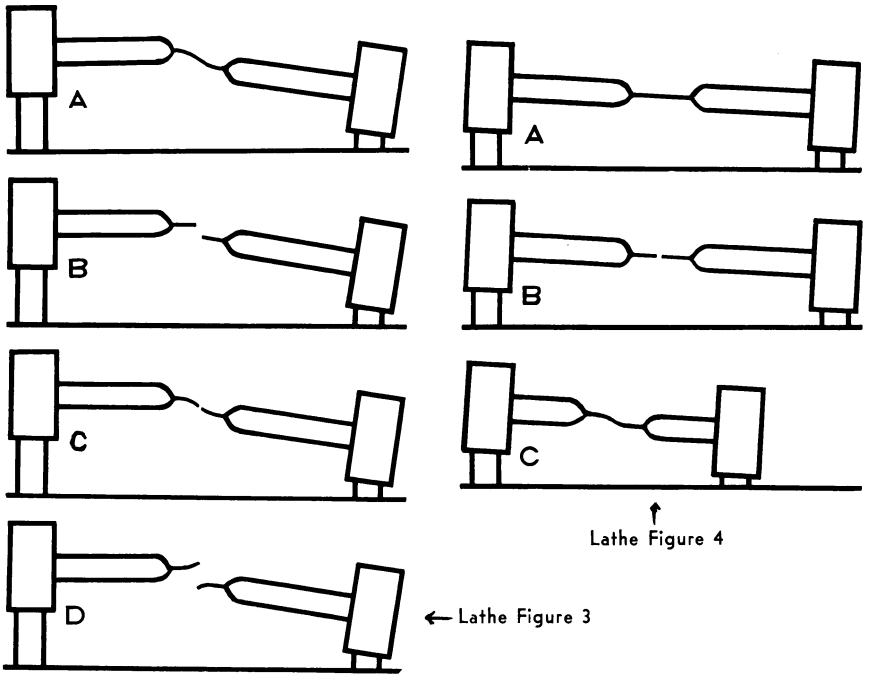
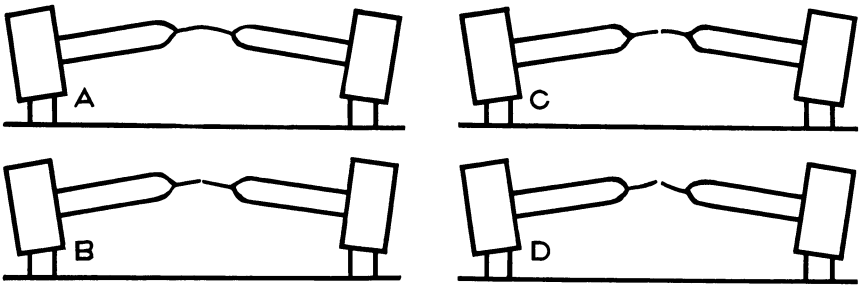


Figure 3 shows a condition where the chucks are not only at different levels, but also one of them is tilted. Exactly the same remarks apply as in the previous case.

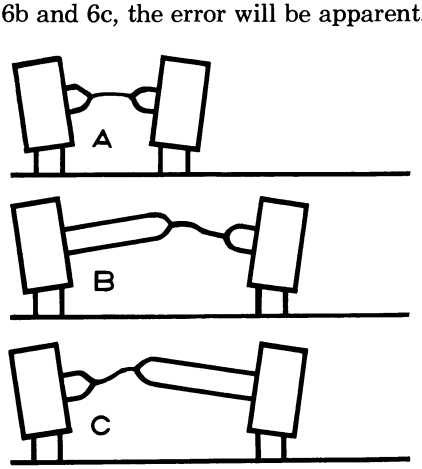
From these examples, it would appear that the test is a reliable one. Certainly it can be said that if the lathe is in alignment, the test will show no error. The converse, however, is not true. If the test shows no error, it is not proof that the lathe is in aligment. Figure 4 is an example of this. Here both chucks are tilted but still have their axes in line. The tube will be under no stress when clamped in the chucks. No stress will develop when the middle section is drawn out and cooled, whether the lathe is running or stopped while cooling. After cutting, the ends will remain together and the test will apparently show that the lathe is in perfect alignment—4b. If, however, the distance between the chucks is altered and the test repeated as in 4c, the error will show up.

If the chuck axes are not in line but meet at a point midway between the chucks (Figure 5), the error may not be apparent. 5b shows the result

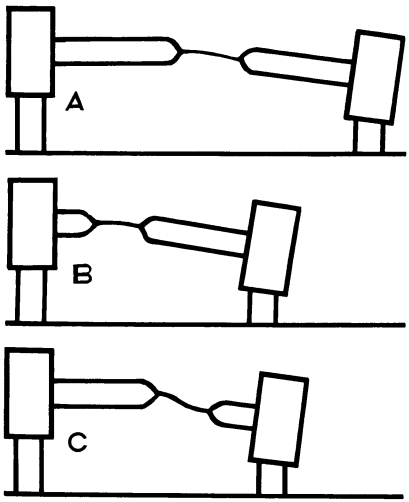


Lathe Figure 5

when cooling is carried out with the lathe running and 5c and 5d when cooling with lathe stopped. The ends of the tube remain opposite. In Figure 6a, the test is shown as carried out with the same chucks but close together. Again the error fails to show. If, however, the test is repeated with the drawn out section closer to one end than the other as shown at 6b and 6c, the error will be apparent.



Lathe Figure 6

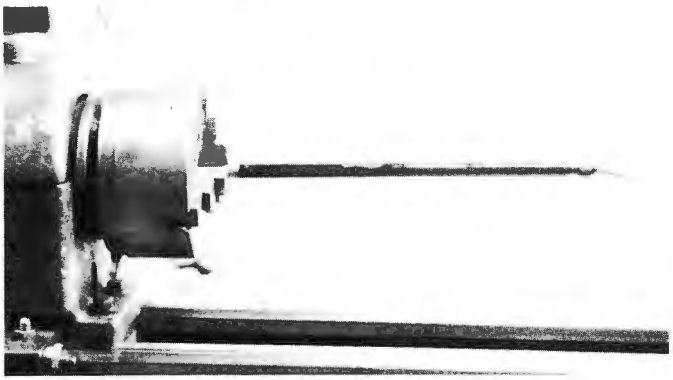


Lathe Figure 7

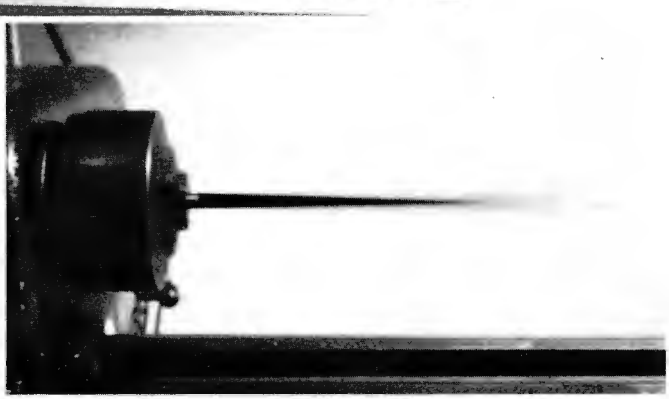
The test might even be perfect when carried out at the center and at one end but be way out when carried out at the other end. In Figure 7, the left-hand chuck axis is parallel with the bed while the right-hand one is both tilted and shifted below the axis of the first. It happens that the axes intersect in the middle, so that as shown in 7a the test would show no error. Neither would it do so if the tube in the chuck which is parallel to the bed were shortened as in 7b. If the tube in the inclined chuck is shortened (or lengthened) however, as in 7c, the error will immediately show up.

The crude examples just given are intended to point out the type of considerations that enter into lathe line-up as a prelude to an orderly development. The axis of rotation of a spindle or any revolving body for

that matter can be immediately located at any point along its line by the use of a Center-Finder (sometimes called a Wiggler), a standard tool at any hardware store. It is simply a bar of any convenient size and length carrying a ball and socket joint at its extremity. To this is attached a fine needle point an inch or two long which can therefore be swivelled in any direction in relation to the bar.



Lathe Figure 8

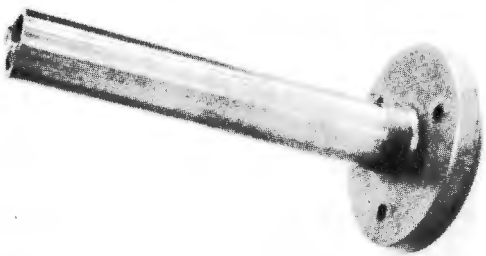


Lathe Figure 9

For aligning a glass lathe the bar which may be straight or crooked, is seized in any type of chuck, good or bad, and the lathe started. The needle point is then centered by holding a stiff object against the extreme end. Some slight practice will make this easy. Now during rotation the point of the needle remains stationary and truly represents a point on the axis of rotation of the spindle itself. Figure 8 shows a center-finder in a machine chuck which is obviously not holding the bar true. The lathe was run and the needle point centered as described so that it now makes an angle as shown with the bar. Figure 9 shows the lathe running and brings out the sharp location of the needle point on the axis of rotation. As a matter of fact, by the use of a lens or low-power microscope focused on the point any desired degree of accuracy can be obtained with almost no trouble.

In lathe adjustment two center-finders are used, one held in a chuck on each spindle. The points of each are trued with the lathe running and

then brought close together for comparison. Two observations are made—one on how close the points are to the same level, the other how close they are when viewed from the top. Such observations should be made under three conditions: (1) when the finders are both as close to the chucks as possible, (2) when the headstock finder is close in and the tailstock finder extended and (3) when the headstock finder is extended and the tailstock finder close in. There is a fourth possibility, that is, when both are extended. This test, however, is unnecessary since it can readily be shown geometrically that if a lathe checks out correctly in the first three conditions it is bound to do so in this fourth one. If, instead of using center-finders checks are made by the method of drawing out and cutting glass tubing, this should be done in the three positions mentioned above.



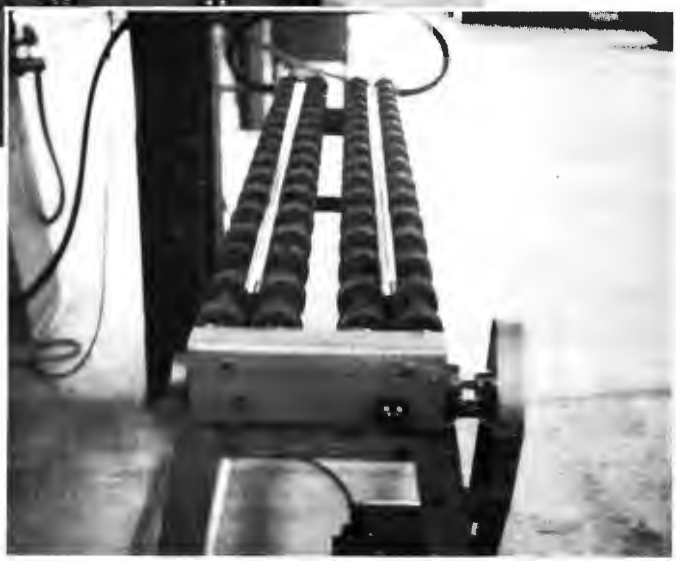
Lathe Figure 10

A reliable method of checking alignment used principally during manufacture is to provide a mandrel with an adaptor to fit it to the spindle nose, the whole unit machined to high precision. One of these is shown in Figure 10. In use a pair are employed, one on the headstock spindle nose and the other on the tailstock. A special carriage slides along the lathe bed and carries an indicator. This is moved along both the front and top of both bars. In the manufacture of Heathways, a two-thousandth error only is permitted.

Overlooking the details of how adjustments can be made on any particular lathe, the general principles of aligning can be readily expressed. Assume we have a lathe in which both head and tail spindles can be tilted up and down and sideways and the head spindle can in addition be shifted up and down and sideways. With the two finders close to the chucks, the head spindle is shifted to agree with that in the tailstock. The headstock finder is then extended and its spindle tilted to agree with that in the tailstock. The headstock finder is then brought in close, the tailstock finder extended and the two brought into agreement by tilting the tailstock spindle. The whole series of steps is then repeated and if adjustments are required, repeated a second and possibly a third time. When no adjustments are found necessary in any of the tests, the lathe is in alignment.

Formerly, and in many uses at the present time, accuracy is not too important. An inaccurate chuck, for example, can be compensated for by wrapping asbestos on the jaws or around the tube and knocking it until it runs true at the end; or by gripping firmly and truing the end by

Lathe Figure 11



Lathe Figure 12

heating close to the chuck. The demands, however, are becoming more strenuous and are likely to be even more so in the future, which emphasizes the necessity not only for accuracy in the lathe but in the tubing as well. As it comes from the manufacturer the smaller sizes are, of course, not straight; neither are they free from stresses that may cause curvature during working. The remedy is the tube straightener which is becoming a very general tool. This consists of a pair of parallel shafts with rows of graphite or stainless rollers along their length, all very accurately aligned. The tubing rests in the groove between the rollers. These are rotated slowly by a motor and a gas-air flame plays on the tubing from below. Figure 11 shows such a device. The tubing on the left has been purposely kinked to show in the photograph. After five minutes treatment the result is as shown in Figure 12. With such a simple cure at hand it scarcely pays to fool at all with tubing as received.

A DEVICE FOR FABRICATING COILS OF GLASS CAPILLARY TUBING

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In the early 1950's a technique[1] of separating volatile organic materials was developed. This technique, called gas chromatography, is simple, easily understood and applied, and highly informative. It has become the most powerful and widely used tool in the analysis of organic materials. Therefore, gas chromatography itself has been intensively studied, and has been unusual among analytical methods in receiving the closest theoretical scrutiny from its inception.

In its original form, gas chromatography used, as the means of separating volatile organic materials, tubes of 3-4 mm inner diameter (ID) and 1-30 meters length, packed with a solvent-covered powder. As the result of a theoretical study, Marcel Golay[2] suggested that the powder-packed tube with the solvent on the powder be replaced by an unpacked capillary tube with the solvent on the wall of the tube. The capillary tube was quickly added to the arsenal of gas chromatographic tools and itself in turn received further study and development. Most materials capable of being formed into long capillary tubes have been used for this purpose in gas chromatography. One such material is glass.

Glass is transparent and is workable in the average laboratory. The quality of the solvent film on the capillary wall can thus be observed. Also, the diameter of the capillary can be easily changed; any desired length produced within wide limits; and other relevant experimental ideas which may occur to the experimenter can be quickly put to test. In order more easily to exploit the potential of these characteristics, D. H. Desty[3] and his colleagues about 1958 developed an arrangement for making several-hundred-foot-lengths of coiled glass capillary tubing. In 1961, Mr. Desty worked for several months in the laboratories of Sinclair Research. As a result of and during his stay, the device reported here was developed from his original model.[3] One other similar device has been reported.[4]

DESCRIPTION

Mounted on a common U-shaped steel backbone are feed rollers, the furnace, pulling rollers, and a bender for the capillary tubing. The coil of tubing emerging from the bender is taken up on a rotating rod at right angles to the U.

The feed rollers consist of two sets of opposing, spring-loaded, brass cylinders. The drive cylinder in each set is two inches in diameter, and is driven synchronously at 1/6 revolution per minute, and is opposed by a similar, spring-loaded, idler cylinder. Two 1-r.p.m. Hurst synchronous motors, rated at 40 oz.-in. each, drive each drive-cylinder through a 1:6 gear reducer. One set of rollers is about two inches below the other. In each set, the cylinder farther from the U can be pulled back to admit the glass tube to be fed to the furnace. Each cylinder nearer the U bears two windings of ordinary friction tape serving as a traction pad for the glass

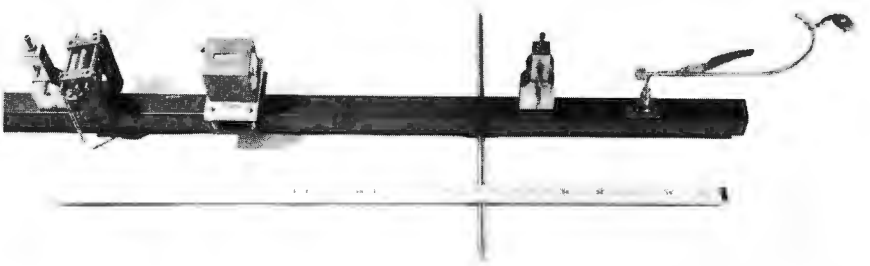

Figure 1
Apparatus for pulling glass capillary tubing.

tube. Stationary lateral guides above and below the feed rollers keep the glass tube from wandering across the friction tape. The glass enters the furnace approximately 7 inches below the lower feed rollers.

The furnace is roughly cubic, approximately 2½ inches high, 2 inches wide, and 2 inches deep. The top, bottom, and back of the furnace are

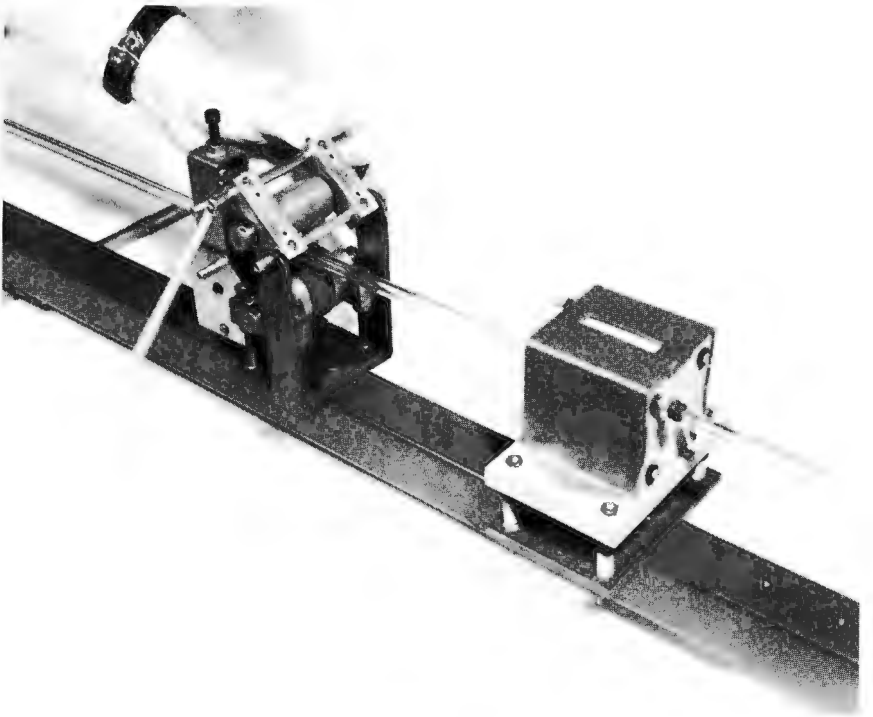

Figure 2
The glass tubing is inserted before drawing.

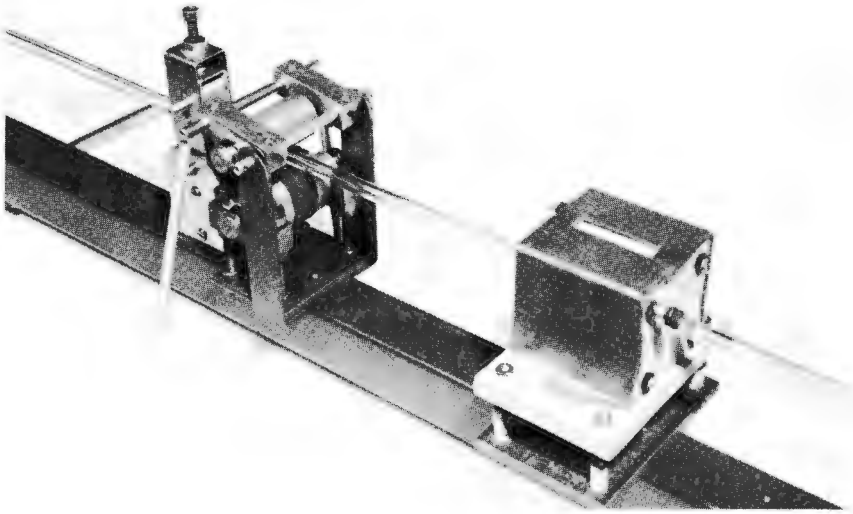

Figure 3
The undrawn tubing is ready for heating.

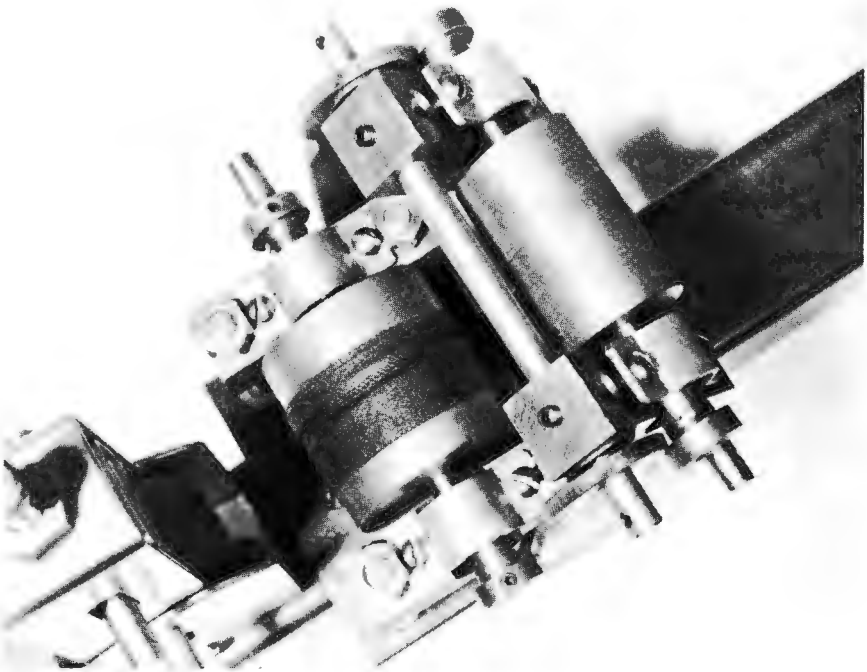

Figure 4
One brass feed roller is taped for traction.

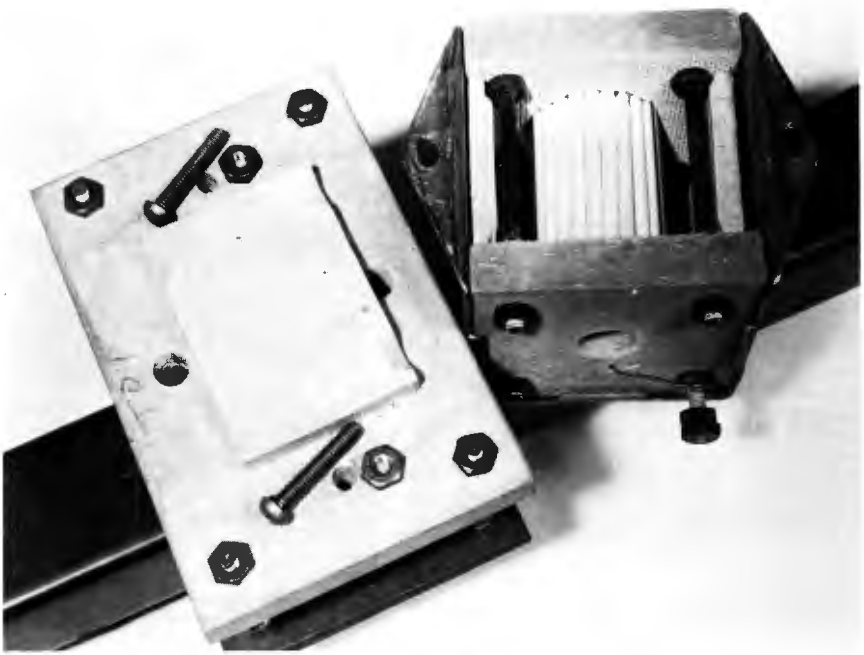

Figure 5
The furnace can be easily dismantled.

transite, $\frac{3}{8}$ inches thick. Various diameters of glass tubing are accommodated by adjustment of the spring-loaded furnace support. Holes $\frac{1}{2}$ inch in diameter in the top and bottom of the furnace allow the glass tube to pass completely through the furnace. With this arrangement, the glass tube to be drawn can be passed easily and quickly through the furnace, whether or not the furnace is hot. The glass can then be stopped, clamped by the feed rollers, and drawn manually by grasping the cool lower end of the tube. The tubing within the furnace is surrounded by a cylinder of white-hot radiators.

The radiators are pieces of ceramic tube, $1\frac{1}{2}$ inches long by $\frac{1}{8}$" in diameter, with two longitudinal passages in each piece. A long piece of Nichrome resistance wire, 24 gauge, 0.0201 inches in diameter, resistivity 1.609 ohms per foot, is passed through the holes in each tube section. The sections are then placed side by side to form a cylinder. The inside of the top and bottom of the furnace is scored with circular grooves to hold in place the cylinder formed from the individual heating tubes. The ends of the resistance wire go to terminals on the top of the furnace. A 20-ampere variable auto-transformer supplies power to the resistance wire. The capillary tubing drawn at about the middle of the furnace moves from the furnace toward the pulling rollers about 16 inches below.

The pulling rollers are identical to one set of feed rollers except for two items: both rollers are taped instead of just one; and Hurst synchron-

ous motors with 10 r.p.m. shaft rotational velocity are used. The capillary tubing is thus produced at approximately 300 feet per hour. (The torque on the pulling rollers is approximately 32 ounce-inches.) The glass capillary leaves the pulling rollers to enter a section of hot stainless steel tubing in which it is bent.

Just below the pulling rollers the capillary is touched by a siphoning tube. This tube deposits a minute flow of a heavy paraffinic lubricating oil* onto the capillary, which carries it into the bender.

The bender is a ten-inch piece of 18 gauge stainless steel tubing, ¼ inch outer diameter. The capillary first passes through a straight vertical section six inches long, then through a 120° arc of two inch radius. The whole bender is connected to the secondary of a large step-down transformer and acts as its own heater. Electrical contact with the bender is made by brazing heavy braided copper cables to each end of it. The emergent capillary tubing coil is taken up on a rotating rod, the axis of which is at right angles to the plane of the bender.

The take-up rod, ½-inch in diameter, rotates with a tangential velocity roughly equal to that of the emergent capillary. The rod is driven through a continuously variable speed changer so that the rotational velocity of the rod can be changed while the coil is being produced. Used with the take-up rod is a wooden board paralleling the rod, and a number of thin brass rods.

The board, 1 inch by 2 inches by 6 feet, is situated parallel to and just outside the coil, at its horizontal diameter. The board carries a row of horizontal holes spaced at one inch intervals. These holes receive and support the thin rods which project through the coil and divide it into ordered segments.

OPERATION

The glass tube to be drawn is inserted through the furnace and held there by the feed rollers. A milliliter or so of the lubricant is dropped into the tube bender. The furnace is turned on. In two or three minutes, the glass tube is drawn manually down to a capillary one or two milliliters in diameter. The thick lower end of the tube is then broken off; and the feed and pulling rollers, the bender, and the take-up rod drive turned on. The capillary is then led through the pulling rollers but not allowed to enter the bender. Several meters of capillary tubing are produced until the product seems satisfactorily uniform.

The uniform capillary tubing is then broken and the fresh end led into the bender, which is just short of glowing dull red. The lubricant siphon is put into contact with the entering tube. The emergent coil is led over the take-up rod. Rods are then inserted through the coil at the judgment of the operator to keep the product moving evenly out of the bender onto the rod. The speed of the take-up rod is also eventually varied to maintain even production.

The tube to be drawn is being used at about one inch per minute, so that a four-foot section is consumed every 48 minutes. If lengths of capillary tubing longer than 150-180 feet are desired, a new length is sealed to the length being used.

*Kaydol, Sonneborn Chemical Co.

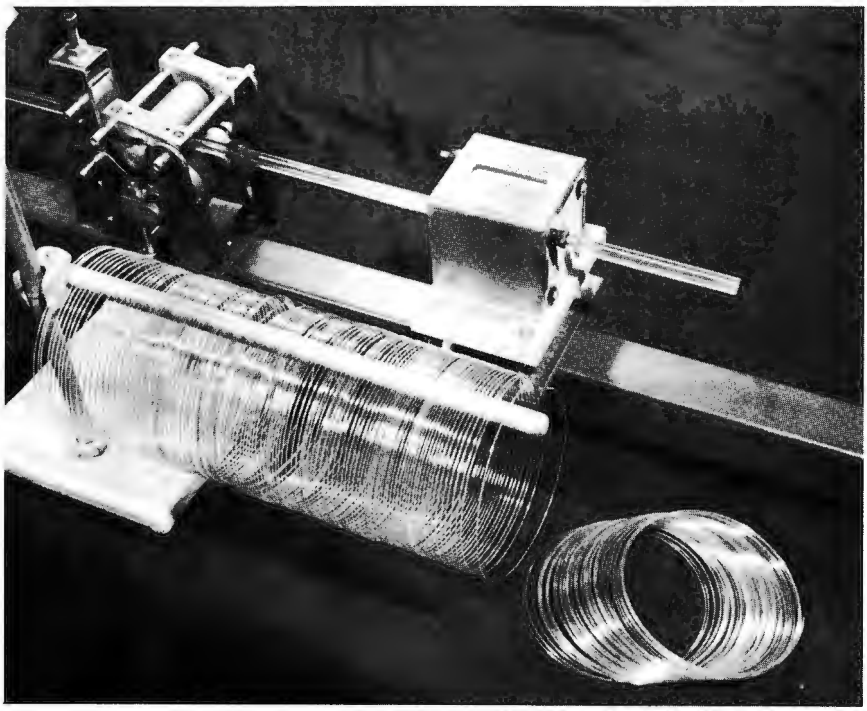

Figure 6
Two examples of coils of glass capillary tubing.

COMMENTS

A uniform inner diameter is desired in the capillary tubing. This is achieved if the feed rate, the pulling rate, the furnace temperature, and the feed glass composition and bore are uniform. Variations in glass composition and bore not only can be minimized by the use of precision tubing (3), but the drawing process itself reduces such variations by the drawing factor, 60, which is the ratio of pulling to feed roller rotational velocities. Also, the furnace has a relatively long time constant, operates in an air-conditioned room, and can be fed through a constant-voltage transformer. The furnace temperature is therefore not likely to change significantly. Further, the drawing factor and the initial bore establish the capillary bore over a wide range of furnace temperatures. Consequently, the main sources of nonuniformity in capillary inner-diameter are the feed rate and the pulling rate.

The feed rate in this apparatus is nominally established by the synchronous drive and the feed roll diameter. The original apparatus of Desty *et al*[3] incorporated rubber tires on the feed rolls. These tires would at times deflect under loading pressure and "store up" rubber which would eventually have to come forward under the glass tube, resulting in an uneven advance of the tube.[5] Kreyenbuhl[4] also used a rubber feed wheel,

but only the weight of the drive motor was on it; no difficulty in feed rate from this source was mentioned. In the present apparatus, the feed rollers are friction-taped brass, so that no material "storage" occurs. The outer brass roller is mounted on a spring-loaded arm which is pivoted an inch away from the roller axis; thus the roller can easily give way or take up any sharp variation in the tube diameter. Finally, two sets of feed rollers are used to prevent any such sharp variation in tubing diameter at one set of rollers from affecting the feed rate.

The pulling rollers are identical in design to the feed rolls, but no sharp variations in capillary tubing diameter are likely to occur, nor is any sizeable force needed to draw out the hot glass or to push it through the lubricated bender.

In sum, no difficulty has been experienced in obtaining uniform inner diameter. Our difficulties lie in getting and keeping the capillary moving smoothly through the bender, and in making lengths of capillary tubing greater than 150-200 feet.

The article of Desty[3] does not mention trouble with the bender, but that of Kreyenbuhl[4] does. The glass tends to fuse locally to the bender wall and therefore break, disrupting the operation. Our difficulties with this localized fusing of glass onto the inner surface of the bender have been greatly alleviated by the use of the lubricant carried into the bender on the surface of the capillary. This paraffinic lubricant resists cracking and coke formation which in time breaks the capillary.

The other difficulty has been in keeping the capillary emerging from the bender in such a way as not to break. A fairly satisfactory answer has been the combination of a variable speed on the take-off rod and spacing rods through the coil. Because of the interaction of the different arbitrary diameters of the puller rollers, the capillary, and the take-up rod, the rotational velocity of the take-up rod is never exactly correct. As a result, if the take-up rod is driven at a constant velocity, the tubing either emerges too rapidly for the coil already made, so that the emergent tubing bends; or too slowly, so that the coil tends to pull the tube out of the bender. If the speed mismatch is allowed to persist, the coil can react by convoluting on itself. However, a judicious occasional adjustment of take-up rod rotation speed plus the use of rods which impose order on the coil make for a relatively smooth process.

The production of lengths exceeding 200 feet involves either an initial length of tubing over four feet long—this is commercially available—or a joining of two lengths. Desty *et al*[3] joined the large tubes, Kreyenbuhl[4] the capillaries. We are able to join the large tubes without the use of internal air pressure by highly localized heating of the joint.

The end of the additional piece of the feed capillary tubing is manually centered on and aligned with the end of the slowly moving tubing already in place. The ends are warmed briefly, then the flame is made very small and quite hot; the inner cone of the small flame is perhaps one millimeter long, the outer, one centimeter. The joining surfaces are then heated uniformly, with occasional concentration to fuse the areas at the joint. Heating is intense but local and brief during fusing, so that the glass flows locally but does not pull away. Also, the rest of the glass does not flow

under the weight of the top section. A joint which cannot be detected visually can be made in about two minutes. Actually, such joints are not optimal for this purpose. The joint should be somewhat thinner than the rest of the glass to enable it to make a uniform, undetectable joint in the capillary tubing.

ACKNOWLEDGMENT

The interest and helpful assistance and suggestions of Mr. Calvin J. Bragg are herewith gratefully acknowledged.

BIBLIOGRAPHY

1. James, A. T., and Martin, A. J. P., *Biochem. J.* (Proc.) **48** VII (1951)
2. Golay, M. J. E., in *Gas Chromatography 1957,* Ed., Coates, Y. J., Noebels, H. J., and Fogerson, I. S., Academic Press, 1958. p. 1-11.
3. Desty, D. H., Haresnape, J. N., and Whyman, B. H. F., *Anal. Chem.* 32, 302 (1960)
4. Kreyenbuhl, A., *Bull. Soc. Chim. France,* 1960, 2125 (1960)
5. Desty, D. H., Private communication, 1961.

NEW TYPES OF GLASS ELECTRODES

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The history of glass electrodes dates back to 1875, in which year Lord Kelvin noticed that an E.M.F. was produced when two metal electrodes were separated by a glass plate. He reported that this E.M.F. was almost the same as that produced by dipping the same two electrodes into a liquid electrolyte. This remarkable phenomenon was confirmed by a laboratory assistant of von Helmholtz, named Giese, but it was not until the development of more sensitive current measuring devices that further study took place. In 1906, Cremer discovered that glass electrodes in bulb form had a remarkable sensitivity to changes in the acidity of the liquid into which they were dipped. Cremer's work also led to the study of electric potentials at phase boundaries of other materials than glass, thus leading to many important physiological discoveries. Further investigation by Heber and Klemensiewicz, and by Hughes, led to the development of glass electrodes of practical value in the measurement of the acidity of liquids. In 1930 McInnes and Dole made a thorough study of the relation between pH sensitivity, and glass composition in soda-lime glasses. They finally selected a glass composed of 72.2% SiO_2, 6.4% CaO, and 21.4% Na_2O. This glass became known in this country as Corning O15, and in Germany as Jena Schott 4073[3]. For many years, this was the most satisfactory glass for pH measurement. There are now other glasses, some with Lithium replacing the sodium of O15, which give better performance, and show less error. It is from these Lithium glasses that most commercial pH electrodes are now made. In Fig. 1 (a), (b), and (c), are shown some different types of glass pH electrodes, while in (d), and (e), two methods of producing thin windows for electrodes are illustrated.

Thus far, all work with glass electrodes was directed towards the measurement of pH values, and it may be of some value to define this symbol, "pH". In general, it is used to indicate the degree of acidity of a solution. In Samuel Johnson's dictionary of 1773, an acid was defined as "A substance composed of pointed particles, which affect the taste in a sharp and piercing manner." It is now recognized that these pointed particles are in fact Hydrogen ions, and that the concentration of these ions in a solution determines the acidic properties of that solution. The negative of the logarithm of the hydrogen-ion normality is what is known as the pH value. The pH scale is thus a series of numbers ranging from O to 14, with acidity greatest at O, a neutral solution being 7, while from 7 to 14 indicates increasing alkalinity.

A new phase in the development of glass electrodes opened in 1934 with the discovery announced by Lengyel and Blum, that the addition of aluminum oxide, or boron oxide, to sodium silicate glasses, would produce a glass sensitive to several cations other than hydrogen. Electrodes made from this type of glass were shown to be sensitive to ions of Na, K, Li, Ru, and Cs, the so-called "alkali" metals. It is interesting to note that this work was the direct result of investigations of the "alkaline error" of pH electrodes, which was found to be caused by slight amounts of

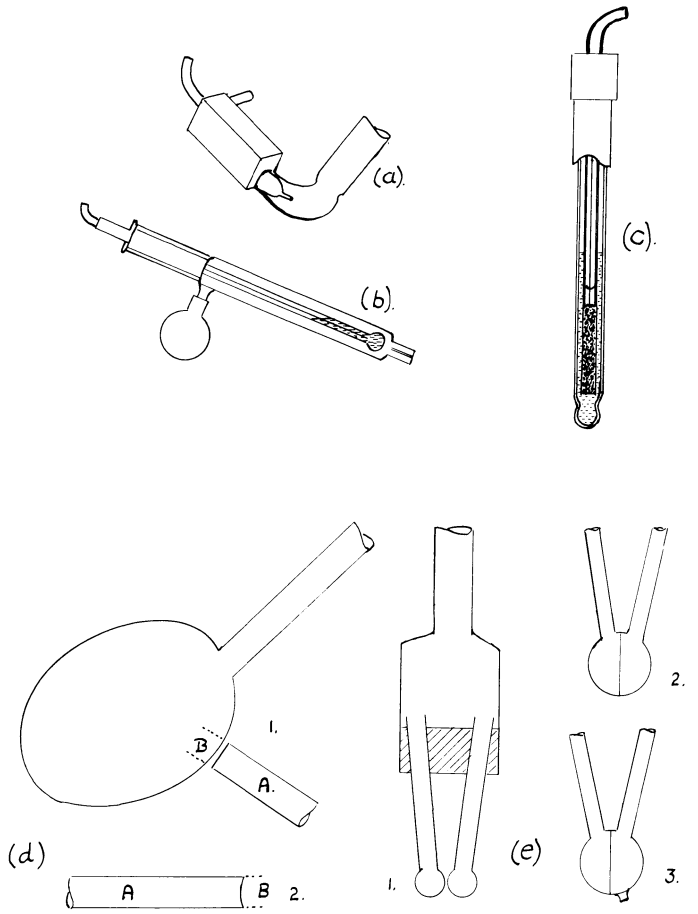

Figure 1

(a), (b), and (c), Some types of glass pH electrodes.
(d), and (e) Two methods of making thin window electrodes. In (a), 1. the end of tube A is heated, then touched to the thin bubble at B, resulting in a thin diaphragm being sealed to A. In (e), two small bulbs 1. are joined together and blown into the shape shown in 2. resulting in a thin diaphragm between the sections. A small opening, 3. is then blown in one side.

boron oxides, being present in the electrode glass. This whole phenomenon of cation specificity in glass is the subject of a thorough investigation still being pursued by Dr. George Eisenman and other workers. It is the starting point for a tremendous extension in the range and uses of glass electrodes.

It would be appropriate to mention here that Dr. Eisenman, currently at the University of Utah Medical School, is typical of a new type of medical research scientist, specializing in the application of modern techniques of physics and chemistry to clinical problems. He has become an authority on the theory of ionic transfer, involving abstruse modern

physics of a very high order. Recently, he has presented a paper to the Glass Congress, in Washington, in which valuable light is thrown on the structure of glass, as deduced from his work with ion-specific glasses. For the purpose of this paper, it is sufficient to refer to Fig. 2, which shows isosensitivity curves for Na and K, in glasses composed of Al, Si, and Na, oxides. It is from such data that Eisenman and his co-workers have formulated the composition of the most suitable glasses for the construction of electrodes.

For some time, medical research teams have been investigating the effects of the sodium and potassium content of blood on the metabolism. This has been shown to affect, for example, blood pressure, which in turn affects many other metabolic processes. Until recently, the analytical methods used, involved flame photometry, which meant that there was a certain delay between changes taking place, and these changes being registered on the equipment. With the advent of sodium and potassium sensitive glasses, it became possible to construct electrodes which would give immediate indication of any changes taking place. The first types of such electrodes constructed at the University of British Columbia by Dr. S. M. Friedman, were cannula-type electrodes designed to be inserted intra-venously. Other dip-type electrodes were constructed, and inserted directly into the blood-stream. These were succeeded by other types which allowed passage of blood through the actual electrode. This latter type was most successful, resulting in simultaneous readings being obtained of sodium content, potassium content, and blood pressure, showing clearly the interdependence of these values. Fig. 3 shows some of the results obtained, and Fig. 4 shows some of the electrodes used.

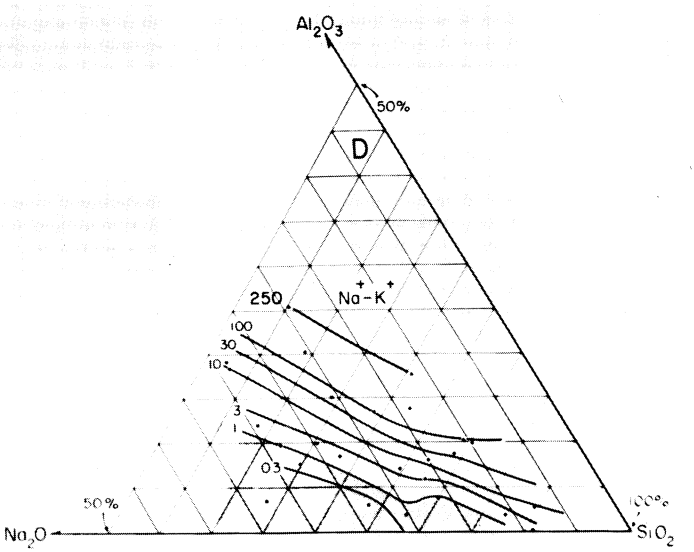

Figure 2
Isosensitivity curves for Na and K according to Eisenman.

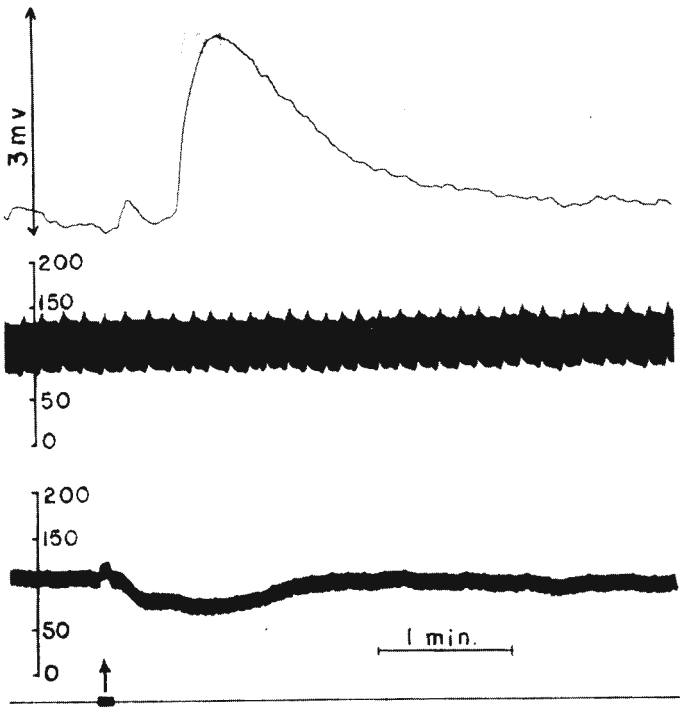

Figure 3

The measurement of sodium in the blood stream of a dog (upper trace), following the injection of NaCl into a femoral artery. Systemic blood pressure is shown in the middle trace, and femoral arterial pressure in the lower trace.

As shown in Fig. 4 these electrodes are simple tubes, some with a slight swelling in the center, some plain. Many variations of shape were tried, and those having a large swelling in the center were found to have a greater error due to "flow potential" than those with no swelling. In all cases, the center section of about 1 cm. was thinned down to about .01 mm. in wall thickness. These electrodes were of the type known as metal-connected, in which the sensitive glass is directly connected through a deposited layer of silver, on which is plated copper, and a wire is "plated in" to the copper coating. This system eliminates the need for KCl connection to the lead, and has the added advantage that the electrode is mechanically quite sturdy. Other electrodes were constructed of a simple dip type, and latterly, a mounting system was employed which allowed three different electrodes to be immersed in a blood flow which was kept to correct temperature by a heating bath as shown in Fig. 5.

The first cation sensitive electrodes used at U.B.C. were constructed from glass actually produced in the glass shop there. The furnace used for this purpose was a simple dental furnace of a type available from any dental supply house. It is merely a firebrick pot, 12 inches high, about

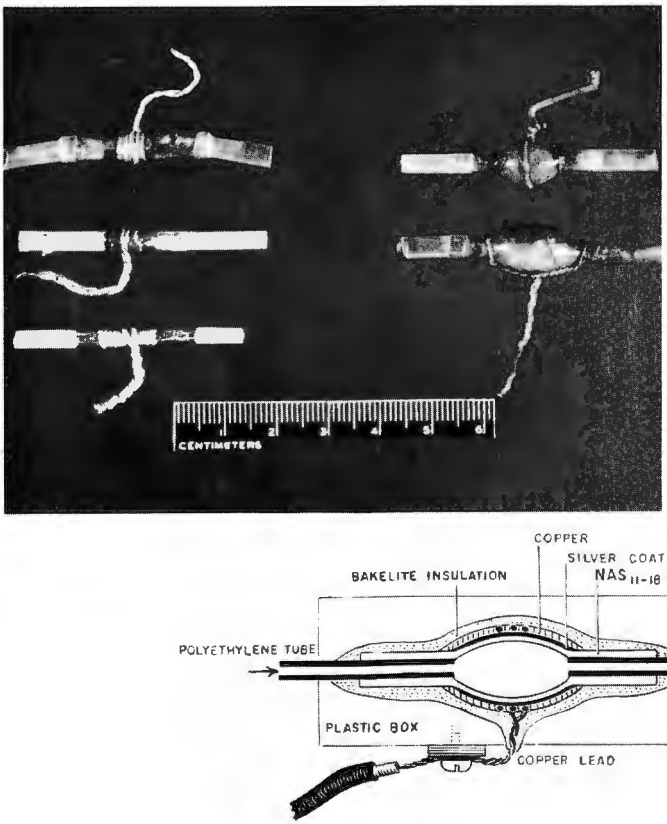

Figure 4

Metal connected, flow through type glass electrodes. The glass dimensions in the diagram are approximately 2 cm. in length, 0.5 cm. in diameter.

10 inches external diameter, and about 2 inches wall thickness. There is a firebrick lid, and a hole near the base at one side for the insertion of a simple gas-air blast burner. The temperature was measured by means of an optical pyrometer. Fireclay crucibles were used to contain the batch. Using this furnace, several of Eisenman's recommended glass compositions were melted, and the glass so produced was used in the manufacture of many of the electrodes mentioned above. Glass-making in this manner, though rather primitive, is very instructive. Many long-established principles of glassmaking were rediscovered, and some new, and hitherto untried additives were used, albeit unintentionally. For example, the first melt resulted in a devitrified and lumpy mass which proved impossible to work in the flame. This was remelted with the addition of a small amount of lime, and the resulting glass looked and worked much better. This same batch was then remelted in the furnace, but through a very familiar kind of accident, instead of being poured on to a carbon slab, the whole mass

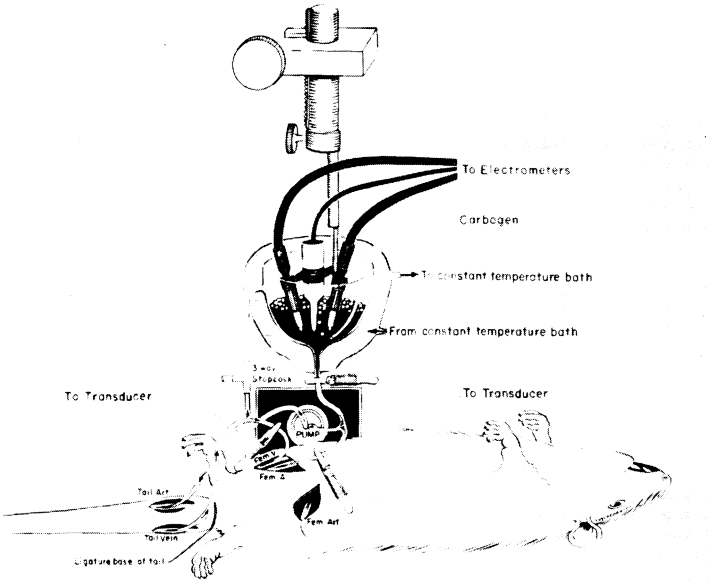

Figure 5
Three electrode assembly with constant temperature bath.

was dropped onto a polished asphalt tile floor. Once again, this batch was remelted, and the result was a very nice piece of pale green glass which worked very well in a very soft flame, using only gas, with no air or oxygen. It would appear, therefore, that the addition of a small portion of floor polish to a batch may perhaps improve the quality of the resulting glass. By a similarly odd chain of circumstances, this glass became known as Super Glass Mark 1. It produced electrodes with the remarkably good K to Na sensitivity ratio of about 10 to 1. Unfortunately, it was subject to ready attack by atmospheric moisture, and was not too stable in normal working conditions, so that eventually, we settled on a glass which was more stable, but had a K to Na ratio of only 5 to 1. Melts of sodium sensitive glass were attempted with varying success, but the high temperature needed for this type of glass caused difficulties with our somewhat primitive equipment. We were very glad when good friends at Corning produced this glass in experimental quantities of a good quality. Sodium sensitive glass works well, but is a hard glass which compares in working qualities with GSC 3, or GSC 4, to either of which it will seal.

Flameworking techniques with these glasses vary considerably with each type. However, in all cases it is desirable to limit the amount of working as much as possible. The composition of the glass, and hence its sensitivity, is altered by excessive flame working, especially in the small quantities and thin walls used for glass electrodes. The potassium sensitive glasses described above will devitrefy very rapidly in too hot a flame. However, if this should happen, it is often possible to clear the glass

again by using a very soft flame of gas only. It is convenient to make a torch for the final working of the electrode, from a point of glass tubing. In forming tubing from lumps of glass from the initial furnace melting, it is wise to preheat the lumps to close to melting point in a small furnace. It is also desirable to avoid as much as possible, the forming of bubbles in the sensitive section of the electrode, as, in addition to causing mechanical weakness, this can give rise to varying potentials in use. In dip type electrodes it is desirable to have a high resistance between the sensitive tip and the rest of the assembly. This is most conveniently accomplished by sealing the tip to a high resistance glass. Fortunately, in the case of the above K sensitive glasses, Corning No. 0010 is a very good match and seals readily to these glasses. As mentioned previously, both GSC 3 and GSC 4 will seal to the Na sensitive glasses. For the purpose of making dip type electrodes, it is better to use the harder of these, GSC 3, even though it is not quite such a good match as GSC 4.

A further use for cation specific glasses is found in the manufacture of micro electrodes designed to indicate the changes taking place at the surface of cells. Much clinical research is concerned with cellular functions, and ionic transfer is believed to be one of the mechanisms involved in such functions. In practice, micro electrodes have been constructed with the sensitive tip measuring less than one micron in diameter. Dr. Hinke of U.B.C. has constructed electrodes of 20 microns diameter, for use on single cells of crab muscle. Much of the construction of these electrodes is perforce done under a microscope, using micromanipulators to handle the glass, and a "micro-torch", consisting of a loop of nichrome wire, to supply the heat needed. Fig. 7 shows the construction of such a micro-electrode.

I am sure that all glassblowers are familiar with the situation where, after having laboriously explained that some particular process is impossible, one is confronted with the flat statement "But I've been doing it for the last three months." Such a situation occurred with Dr. Hinke's elec-

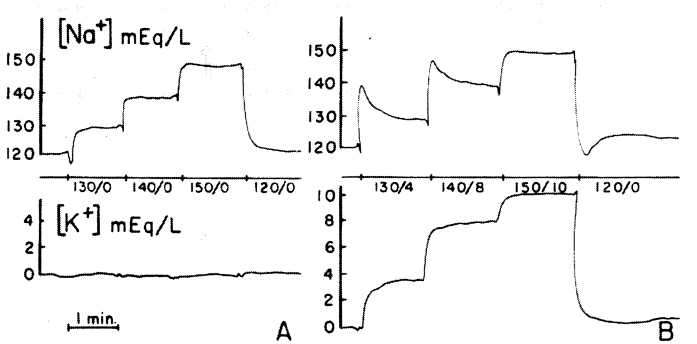

Figure 6

Simultaneous measurements of Na and K in blood, obtained with the assembly shown in Fig. 5. The output from the electrodes is fed directly into a computer which analyses the data, compensates automatically for the errors, and almost instantaneously plots the results as shown above.

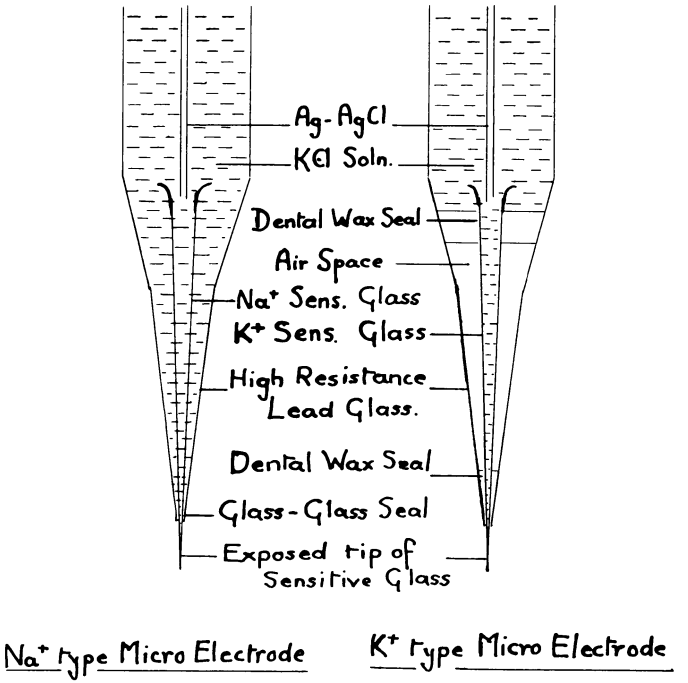

Figure 7
Types of Micro-electrodes by Hinke.

trodes. He spent some time doing research in England, where, as explained above, he required a high resistance glass for the stem of his Na sensitive micro electrodes. The glass he obtained was a soft lead glass, almost identical to Corning 0010. He proceeded to seal this to the hard tip of the electrode, making a tight seal, with no cracking. I had a very hard time convincing him that this was not a seal but merely a very close fit. However, this does illustrate the established fact that sometimes ignorance is the best tool for solving a difficult problem.

Among the many problems associated with the construction of micro electrodes, not the least is that of filling. It is necessary to fill the tip with KCl solution, and the problem is in sealing the tip after filling, or filling with the tip already sealed. In either case it is necessary, but difficult, to avoid bubbles in the sensitive tip. One method, laborious but successful, is to fill the electrode, (after the usual procedures such as boiling in alcohol, etc.), then seal the tip and work out the inevitable bubble by manipulating the micro-torch. Another method is to seal the tip, then endeavor to insert a nozzle to "squirt" solution right to the bottom of the tip. Vacuum filling is another possibility, and we are currently engaged in a combination of the "squirt" and vacuum methods.

It will be evident that we are only at the beginning of a great expansion in the uses of ion-specific glasses in many fields, and it is also evident

that glassblowers are going to be called on to perform their customary miracles. It is interesting, however, to contrast the short time which now elapses between discovery and exploitation, with the long periods which used to pass in previous times. For example, the technique of chromatography was first announced in 1906, but was not used by chemists until 1931. Again, Mendel's laws were unnoticed for thirty-four years. It is gratifying to see the speed which now attends development of new discoveries. There are already sodium sensitive electrodes commercially available, from such suppliers as Beckman, and E.I.L., and research is proceeding in this field in a steadily increasing number of places. The future will undoubtably bring a great increase in the number of types and uses of glass electrodes.

I am greatly indebted to Dr. Sydney M. Friedman, and Dr. J. A. M. Hinke, for their patient advice and for the kind provision of photographs and diagrams. I would also like to express my great appreciation of the help given by Mr. Peter Holborne of U.B.C., in the preparation of this paper.

BIBLIOGRAPHY

1. Cremer, M., *Z. Biol.* 29, 562, (1906).
2. Heber, F., Klemensiewicz, Z., *Physik. Chem.* 67. 385, (1909).
3. Hughes, W. S., *J. Am. Chem. Soc.* 44, 2860, (1922).
4. McInnes, D. A., Dole, M., *J. Am. Chem. Soc.* 52, 29, (1930).
5. Dole, M., "The Glass Electrode" Wiley, N. Y.
6. Ives, D. J. G., & Janz, G. J., (Editors) "Reference Electrodes." Academic Press, N. Y., 1961, Chapter 5, Bates, R. G., "The Glass Electrode."
7. Friedman, S. M., Jamieson, J. D., Hinke J. A. M., Friendman, C. L., *Proc. Soc. Exp. Biol. & Med.*, 1958, V. 99, 727, 730.
8. Friedman, S. M., and Friedman, C. L., *The Anat. Record,* V. 138, Oct. 1960.
9. Eisenman, G., Rudin, D. O., Casby, J. U., *Science,* Oct. 25, 1957, V. 126, 831-834.
10. Eisenman, G., *Biophys. Jnl.,* 1962, V. 12, No. 2.
11. Friedman, S. M., "Methods of Biochemical Analysis" V. 10. Wiley & Sons, N. Y.

THE USE OF ALUMINO-SILICATE GLASS IN MICROWAVE DEVICES

EDWARD M. DOYLE

In our field of microwave tubes a need for high temperature windows that could withstand the very high power output required in microwave devices was apparent. A standard window used in most microwave devices is one of the limiting factors that determines the maximum power that could be transmitted through a single waveguide or transmission line.

Most high-power devices are pulsed with a high ratio between peak and average power. The breakdown that usually occurs in devices with high power, high duty cycles and long pulse length, is associated with window failures.

An evaluation of various materials and techniques was conducted in order to prevent this common cause of failure in high power devices. This evaluation was divided into three phases:

Phase I — Material Evaluation

Phase II — Evaluation of New Sealing Techniques

Phase III — Final Testing

PHASE I — MATERIAL EVALUATION

This phase called for the evaluation of the possible window materials that could be used. The requirements for such a window were as follows:

a) Must withstand a bakeout temperature of 700°C.

b) Have the proper dielectric properties at 1 Mc and 20°C. which is the standard electrical level of testing the window.

c) Coefficient of expansion for sealing.

d) Ease of production and cost would also be considered as a requirement.

e) Evaluation of proper metal material for sealing purposes.

A number of materials, such as sapphire, quartz, mica, ceramic and alumino-silicate glass were evaluated to determine the feasibility of such a window. Electrically, the desirable microwave window properties can be divided into three general requirements; reflection, power loss and breakdown characteristics. Unfortunately, these properties cannot be considered separately. From the standpoint of reflection, microwave windows can be sub-divided into two general categories—iris type windows and half wavelength windows. Both types can exhibit relatively good impedance matches over a narrow frequency range. The iris or "thin window" type is superior to the half wavelength type from the standpoint of broad band matching—demanded by today's microwave tubes. In addition, the thin window type is less lossy by virtue of the decreased volume presented to the passing wave. However, until the advent of high temperature, low loss, glasses the ceramic half wavelength window was used as the output window because of its high temperature properties demanded by today's high quality tubes. The ceramic window has another property in addition to its loss which makes it undesirable at higher frequencies—the variation in dielectric constant from batch to batch .100 kmc and 2 kmc. both fall within the microwave frequency range. However, a plus or minus

.0001 tolerance on a half wavelength window represents a tolerance factor at 100 kmc of 50 times that at 2 kmc. This, coupled with the higher loss factor of a half wavelength window, plus the variation in dielectric constant, plus the practical fact that ceramic is opaque gives ceramic only one advantage at higher frequencies and powers—its high temperature properties. Although 7070 (Corning Glass) glass has many desirable properties, it also has two undesirable properties—its relatively low softening point plus its high rate of resistance—temperature change causing a "runaway condition" resulting in a melted window. 1723 glass (Corning Glass Co.) combines the desirable properties of #7070 (Corning Glass Co.) with a high temperature glass with excellent resistance-temperature properties.

Various methods for sealing of window material were looked into in order to determine the coefficient of the alumino-silicate glass. The following materials were investigated, Alloy #4, Kovar and various other steels along with molybdenum. It was decided due to the ease of handling, coefficient of expansion and non-magnetic qualities that molybdenum would meet the requirements.

PHASE II

Although the use of alumino-silicate glass and sealing to molybdenum is not new to the field of glass-to-metal seals, it is new as a microwave window. In the past alumino-silicate glass was used in connection with stems, capsules, etc., and the methods that were used to seal this glass would suit the requirements in connection with stems and capsules. However, the main method that was used which utilized a technique which caused reboiling which affected the electrical and mechanical properties of the glass was found not suitable in sealing for a microwave window. This therefore required the development of a new technique which would meet the following requirements:

a) Would not affect electrical or mechanical properties of the glass.
b) Ease to handle in production and also the cost factor was considered.
c) Would give leak type seal capable of withstanding 700°C. bake-out.
d) Would be leak tight.

Various methods were tried, however, two methods were selected. The most promising was Chromallizing* of the molybdenum which would allow the alumino-silicate glass to be sealed to the molybdenum by normal sealing techniques. This will be described in the latter part of this paper. The other method called for a plane upon the molybdenum surface during the glass-to-metal sealing operation on high purity argon atmosphere which is also described in the latter part of this paper. Either one of these methods meets the full requirements that were previously stated.

CHROMALLIZING* METHOD

This method calls for the molybdenum to be chromallized* which produces an impregnated chrome surface on the molybdenum. The chromallized* part goes through a thorough cleaning and firing operation to

*Chromallizing Corporation's method.

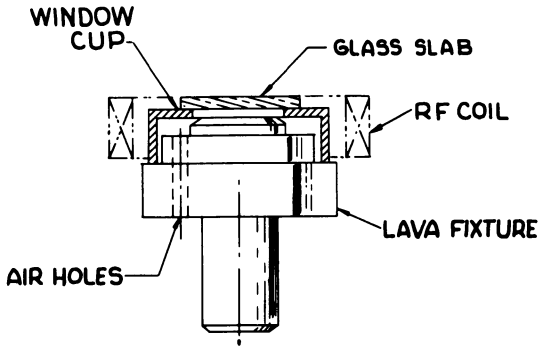

Figure 1

prepare the surface of the molybdenum for sealing. The alumino-silicate glass is also thoroughly prepared by cleaning and then placed onto the chromallized molybdenum window cup. It is then placed in a fixture for sealing as shown in Fig. 1. The disadvantage of this method of chromallizing* is the impregnated chrome oxide cannot be removed chemically. To remove chrome oxide outside of glass sealing area a mechanical method such as grinding or polishing must be used. This can set up stresses in the glass and is also very costly.

Method No. 2 calls for the raw molybdenum to be specially prepared by cleaning and firing. The molybdenum window cup is sealed directly to the glass without the aid of the chromallizing* process. This is accomplished by the use of an inert atmosphere such as Argon. There is quite a difference in the surface appearance between the molybdenum and the chromallized* molybdenum mentioned in the previous method.

The fixture with the molybdenum and the alumino-silicate glass assembly is next placed into the normal glass sealing equipment. However, as shown in Fig. 2 a bell jar is placed over the assembly and allows the inert atmosphere to enter. By the use of the inert atmosphere this prevents oxidation of the molybdenum surface prior to the sealing. Both atmosphere and inert gas firing methods are satisfactory. The latter method, besides being less expensive, has the main advantage of not having chromium on the surface which would interfere with the brazing of the window to the microwave body assembly.

PHASE III — ELECTRICAL, MECHANICAL & ENVIRONMENTAL TESTING

Once the material and technique was determined electrical, mechanical and environmental tests were conducted in order to determine whether it would meet all the necessary requirements for such a microwave window. The requirements for such are listed below:

a) electrical
b) mechanical

*Chromallizing Corporation's method.

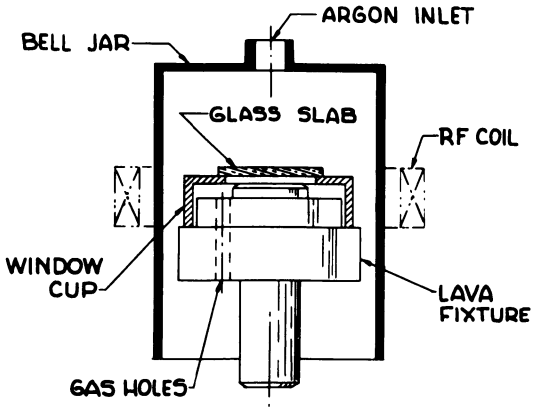

Figure 2

The part was baked at 700°C. and cooled at room temperature. Then it was lowered into a thermos of liquid nitrogen after part had reached room temperature. It was checked on a leak detector capable of detecting a leak in the order of $10 \times {}^{-10}$ leak rate and then checked on a Polariscope to determine the strain pattern.

In conclusion, either of the two methods used will meet all of the requirements. However, the method used in the argon is preferred primarily due to the ease in brazing of the assembly, and it is the least expensive of the two methods, and this must be considered in regard to production costs.

SEALING TO SILICA AND SIMILAR GLASSES

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INTRODUCTION

Modern technology is making increasing use of the unique thermal, optical and electrical properties of fused silica and other "hard," ultra low expansion glasses. Many of these uses call for hermetic or vacuum tight seals between such glasses and other materials. To be of greatest value, such seals must be able to serve up to temperatures of around 1000°C. since otherwise the full capabilities of these high temperature, low expansion glasses cannot be realized. Since in most cases, the material to which it is desired to join these glasses is of much higher expansion, the realization of these seals has presented a serious problem to which there is still no easy or universal solution. It is the purpose of this paper to examine the problems involved, to review briefly the sealing methods that have been used in the past, and to describe and illustrate some of the latest developments in this field.

PROPERTIES OF THE MATERIALS

The starting point in any consideration of sealing to a glass is, of course, the expansion and viscosity behavior of this glass.

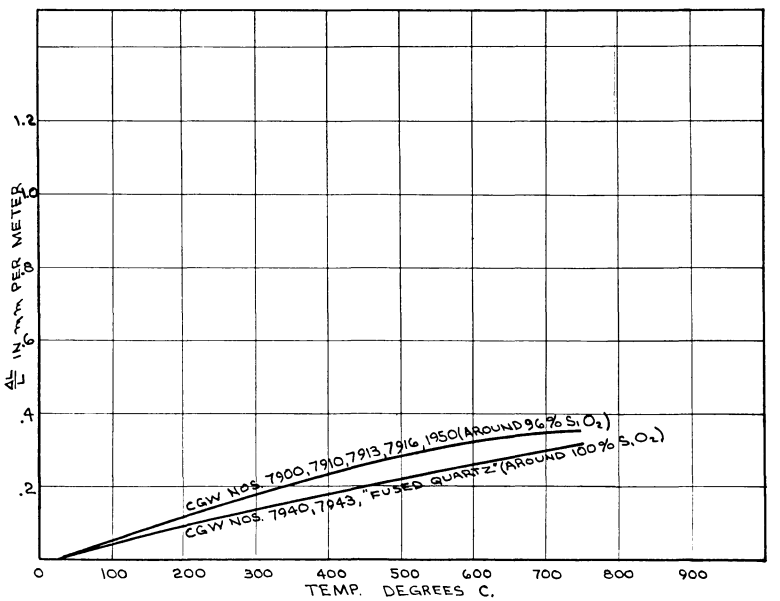

Figure 1
Expansion of Silica and Similar Glasses

Figure 1 shows the expansion curves for typical samples of the glasses we will be considering. These include commercial "fused quartz" and Corning Glass Works' Nos. 7940, 7943, 7900, 7910, 7913, 7916 and 1950. They fall into two groups, those that are more or less 100% silica and those that are around 96% silica. Within each group the expansions are nearly the same, so to avoid confusion they have been consolidated and only two curves are shown. The change of length per unit length (referred to 25°C.) is plotted vertically against temperature (in degrees centigrade) horizontally. In most cases, the measurements are those of the Research Laboratory at Corning. The expansions are so similar that for sealing purposes they all present about the same problem. The average expansion coefficients range from around 5 to 8 x 10^{-7}/°C.

In viscosity there is a somewhat greater spread as the figures in Table I indicate. Unlike the expansions, the viscosity results do not fall into two groups according to the silica content. This is because traces of impurities such as water and alkalis play a dominant role. The annealing point is taken as the temperature at which the viscosity is 10^{13} poises. The difficulties of obtaining viscosity data at high temperatures are formidable and in the case of the glasses we are dealing with it was necessary to estimate the sealing temperatures. An effort was made to select temperatures corresponding to the range from 10^{7} to 10^{4} poises. Obviously, these sealing temperatures are above the melting points of all but the most refractory metals.

Table I
Viscosity Values for Silica and Similar Glasses

Glass Number	*Annealing Point*	*Sealing Range (Est.)*
"Fused Quartz" (GE)	1140°C.	1700°-2100°C.
7943 (CGW)	1100°C.	1600°-2000°C.
7940 "	1075°C	1600°-2000°C.
7916 "	1100°C.	1600°-2000°C.
1950 "	1060°C.	1600°-2000°C.
7913 "	1025°C.	1550°-1950°C.
7910 "	910°C.	1500°-1900°C.
7900 "	910°C.	1500°-1900°C.

Let us turn now to the properties of the materials we may wish to join to these glasses. They are of course many and varied, but Fig. 2 gives the expansion curves of some likely prospects.

Of all the metals, only Invar comes close to an expansion match and unfortunately its low coefficient prevails only up to around 100°C. It is, therefore, of little value for our purpose since the seals, even if they could be made, would serve only at low temperatures. Similarly, the glasses which we usually desire to seal to are nearly all of much higher expansion than silica. Most glass equipment is made either from a boro-

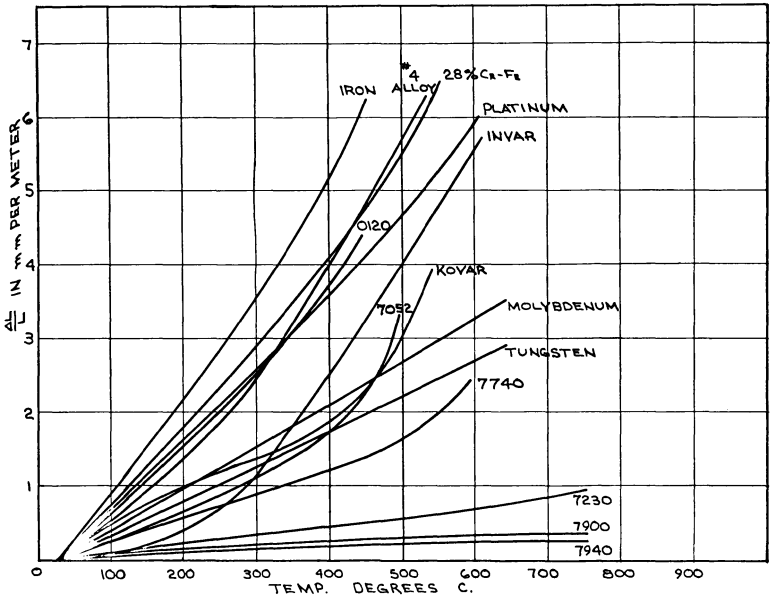

Figure 2
Expansions of Various Glasses and Metals

silicate glass having an expansion in the general range of CGW No. 7740 or from a lime or lead glass in the general range of CGW No. 0120.

Thus, practically all the materials of interest have such high expansion that a direct seal of the conventional type is impossible. In the case of most metals such a direct seal would be out of the question in any case due to the high sealing temperature needed. We are, therefore, usually forced to the introduction of intermediate materials.

GRADED SEAL TECHNIQUES

The most obvious and no doubt the oldest approach to the problem consists in using intermediate glasses. Some of the glasses that have been used for this purpose together with their pertinent properties are listed in Table II. The first six glasses are useful in coming up to the range of tungsten and the conventional "hard" glasses. The last six are used to go from the "hard" to the "soft" glasses. So far as the writer is aware, no one offers a completed seal that goes all the way from silica to "soft" glass, but seals from silica to "hard" glass and from "hard" glass to "soft" glass are available.

Seals made by this method are, in general, rather expensive and not very satisfactory. They are necessarily highly stressed and therefore subject to excessive breakage. They occupy considerable space and impose temperature limitations. In most cases they do not offer an acceptable solution to the sealing problem and are mentioned here only for the sake of completeness.

A second approach to the problem which still utilizes intermediate glasses but in a somewhat more sophisticated manner is the Multiform Graded Seal. Here the glasses are powdered and blended, then pressed into cylindrical form. Such a seal suffers from some of the same drawbacks as the conventional step seal, but it has the advantage that it can be made to accurate dimensions and that it lends itself to low cost-high volume production. Such seals were used in quantity for a number of years in germicidal lamps to permit sealing Kovar leads into No. 7910 glass. However, these lamps now use a different type of seal to be described later. There is currently very little production of the Multiform Type Seals.

Table II
Properties of Intermediate Sealing Glasses

Glass Number	*Expansion*	*Annealing Point*	*Sealing Range (Est.)*
7230 (CGW)	14 x 10^{-7}/°C.	750°C.	1200°-1600°C.
GSC1 (GE)	13.9	..	.. ..
GSC3 (GE)	14.5	..	.. ..
7200 (CGW)	19	645°C.	1100°-1500°C.
7240 (CGW)	21	555°C.	900°-1300°C.
GSC4 (GE)	24.1	..	.. ..
7750 (CGW)	40 x 10^{-7}/°C.	473°C.	700°-1100°C.
7510 "	50	517°C.	700°-1000°C.
7520 "	60	571°C.	750°-1100°C.
7530 "	71	559°C.	725°-1000°C.
7550 "	79	548°C.	710°-1000°C.
7560 "	86	539°C.	700°-1000°C.

The first real innovation in the method of making graded seals was the introduction of the "impregnated type". In this seal[1] alkalis and other expansion raising materials are introduced into a low expansion porous glass (CGW No. 7930) in amounts that vary from point to point. In this manner we can produce a tube which has a gradual, continous change of expansion along its length. This eliminates the jumps between glasses and gives a much stronger more satisfactory seal. Unfortunately, the expansion cannot be pushed above about 35 x 10^{-7}/°C. by this technique, but luckily that brings us up to the important range of the common "hard" borosilicate glasses and tungsten. Graded seals of this type are available commercially in a variety of sizes. Figure 3 shows a sample along with samples of the other types previously mentioned.

Since tungsten is the lowest expansion metal that it is practical to use for leads, considerable effort has been expended in trying to devise the simplest and cheapest method of sealing it to silica and similar glasses.

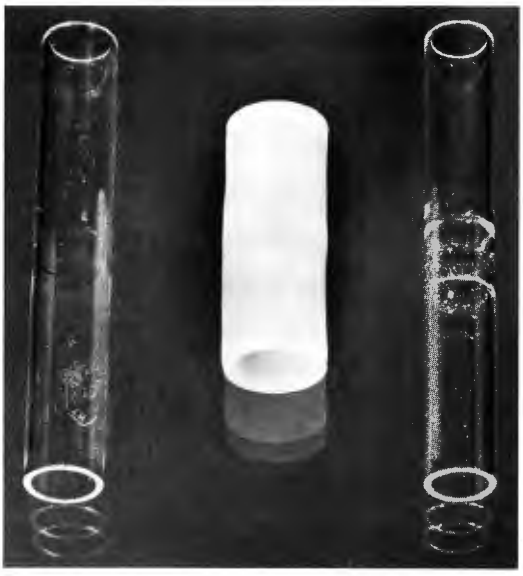

Figure 3
Various Type of Graded Seals

Left: New Type

Center: Multiform

Right: Step Type

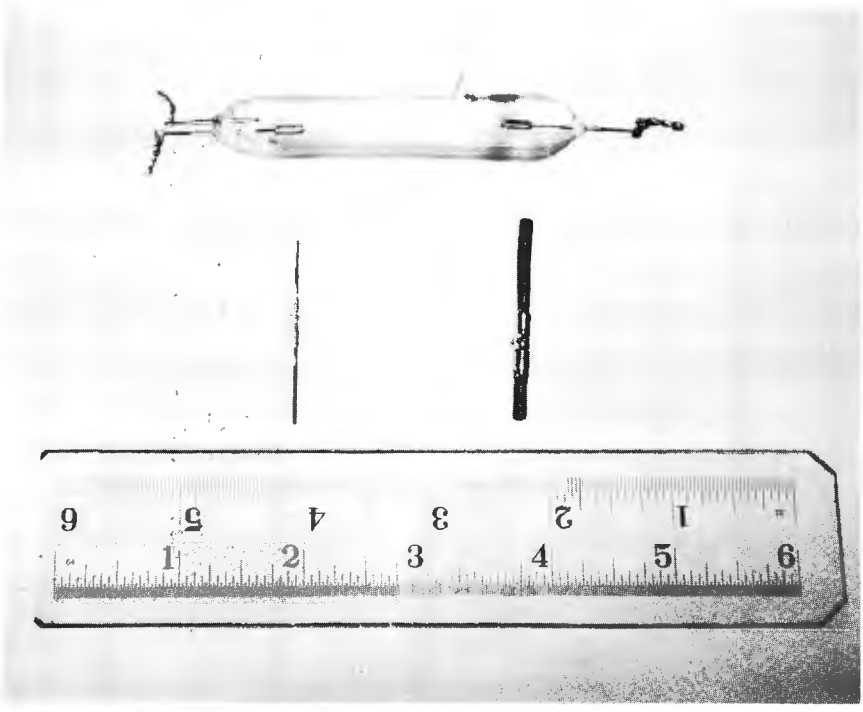

Figure 4
Seals of Tungsten to Silica

This work demonstrated that with the proper technique a seal could be achieved with a single intermediate glass, namely, CGW No. 7230 or GE No. GSC1. Since the expansion of these glasses is around 14 x 10^{-7}/°C. compared to around 45 x 10^{-7}/°C. for tungsten these seals are highly stressed and it is remarkable that they hold so well. A high fire polish and a favorable shape are essential. Also, the tungsten must be bright and shiny under the glass and the interface must be clean and smooth. Any spots of the usual amber oxide will lead to cracking of the seal. This technique was used successfully for some time in the commercial production of sun lamps and other mercury arcs. It has now been largely displaced by the molydenum foil seal to be described later. Figure 4 shows some tungsten leads beaded with the No. 7230 glass illustrating the preferred shape. A silica envelope provided with leads of this type is also shown.

THIN METAL TECHNIQUES

The electronic and lamp industries have for many years sealed glasses to metals of much higher expansion by using the so-called Houskeeper technique in which the metal is thinned to the point that it cannot exert a lethal stress on the glass. In trying to apply this principle to silica and similar glasses we are of course handicapped by their high sealing temperature which is so extreme that most metals would either melt or oxidize. In fact, to the writer's knowledge there is no metal that has been used successfully for a direct seal in air, although it would seem that iridium and rhodium should be possibilities. However, by going to a vacuum or a protective atmosphere, molybdenum has been quite successfully sealed by this thin metal technique.[2] The thickness of the moly should not exceed 0.0005 in. and the edges should preferably be feathered. This type of seal has been so successful commercially that it is now employed in practically all mercury vapor lamps that use silica or similar glasses. Figure 5 shows a seal of this type from a mercury arc lamp.

While platinum is not high enough melting to permit direct sealing by the Houskeeper technique, it is possible to seal silica to thin platinum ($<$2 mils) if one makes the joint with a softer, low expansion glass. The thin platinum can then in turn be joined to other metals by a brazing or welding technique. An example of this type of seal is the silica disc with platinum flange shown in Figure 6. The seal between the fused silica and the platinum may be made with CGW No. 7230 or GE No. GSC1. A suspension of the finely powdered glass in a suitable vehicle is sprayed onto the sealing area of the silica. This is then prefired at 1250°C. for about 20 minutes. The fired glaze should be a few mils thick. After cooling, the platinum washer is carefully placed on the disc and put under a load of around 2 lbs. per square inch. The assembly is next heated in a furnace for about 30 minutes at 1320° (or somewhat higher if this is possible without objectionable distortion of the article) and then allowed to cool in the furnace. Seals of this type will stand temperatures as high as 1000°C. in air and have been cycled up to ten times from –80°C. to +900°C. without failure. Figure 7 shows a 6-inch diameter silica window sealed to platinum by this technique. It is intended for mounting in the stainless steel housing that is shown. The housing is designed to support

the window mechanically since the platinum, while it provides a hermetic seal, has very little mechanical strength.

Figure 5
Molybdenum Foil Seal

Figure 6
Platinum Foil Seal

Figure 7
Platinum Foil Seal and Housing

SOLDER GLASS TECHNIQUES

Since fused silica and similar glasses are often used for optical windows and other precisely finished parts, we are sometimes faced with the problem of trying to seal such parts without distorting them. Similar problems with ordinary optical glasses have been solved by using a "solder glass sealing" technique in which the articles are joined by an intermediate glass that fuses and seals at a temperature at which the articles will not distort. Such "solder glass" should preferably match the expansion of the article.

Unfortunately, no "solder glasses", in the true sense of the term, have been found with expansions as low as fused silica. The closest approach is the No. 7230 glass previously mentioned. This can be sealed to silica and similar glasses provided that it is restricted to a thin layer (<5 mils). However, although its Softening Point is more than 500°C. below that of silica, the sealing temperature is still so high (around 1300°C.) that optical figuring would be appreciably distorted. The deformation is of course slight, and such seals are adequate as far as ordinary appearance is concerned.

Lower sealing temperatures may be realized by going to a higher expansion "solder glass." This of course means greater expansion mismatch,

and it can only be tolerated by keeping the "solder glass" layer extremely thin. One application of this technique is in the sealing of an absorption cell such as that shown in Figure 8. The faces are high transmission fused silica (CGW No. 7940) and the side walls are CGW No. 7900. The parts are sealed together using a special " solder glass" CGW No. X-750-ZY. A small amount of the glass is applied by spraying a suspension of a very fine powder. Since the expansion of the glass is around 60 x $10^{-7}/°C$. the thickness (in the finished seal) must be under one-half mil and the glass must not extend beyond the actual seal area at any point. The glass is applied to the spacer which is then prefired in a furnace for about 10 minutes at around 900°C. Upon cooling it is immediately assembled with the faces, put under a load of about 200 grams and fired for around 5 minutes at 1150°C. Following this the sealed assembly is removed from the furnace and allowed to cool in air.

METALIZING TECHNIQUES

While this paper is concerned mainly with seals that are accomplished by fusion of a glass, it should be mentioned that Bondley[3] at General Electric, Heil at Eitel-McCullough and others have joined silica glass to metals by metalizing techniques. In general these depend on deposition of an active metal such as titanium on the silica followed by

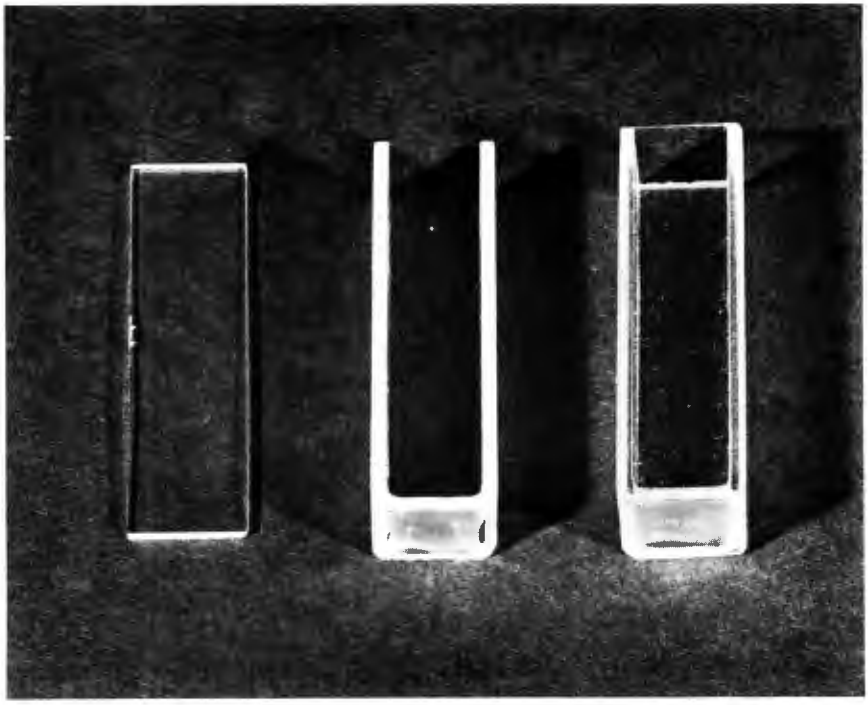

Figure 8
Absorption Cell Seal

bonding of this to a ductile (low yield point) metal such as gold or silver. All of these metals must of course be kept thin where they are in contact with the silica. They can be bonded to other metals provided a thin bridging section is retained. The writer has seen no definite statements on the maximum temperature at which such seals may be used but it would undoubtedly be limited by the oxidation and fusion of the metals employed.

REFERENCES

1. R. H. Dalton, U. S. Patent No. 2,336,227.
2. A. J. Meadowcraft, *et al,* British Patent No. 588,184.
   E. H. Nelson, *et al,* U.S. Patent No. 2,699,847.
3. J. R. Bondley, Proc. Int. Congress on Microwave Tubes, Munich, 1960, p. 598.

SPECIAL SELECTION AND HANDLING TECHNIQUES TO BE OBSERVED IN FABRICATION OF OPTICAL AND ULTRA HIGH PURITY QUARTZ GLASSES

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During the past several years, the Amersil Quartz Division of Engelhard Industries has made available several new and exotic grades of transparent fused quartz, each with properties that are unusual and distinctive and make these grades suitable for a number of special applications. I am sure that most of you are familiar with these grades under the trade names of Optical I, II, and III, Homosil, Ultrasil, Suprasil, and Infrasil. It is of course of paramount importance to first select that grade which most satisfactorily and economically meets the end requirement to which it would be put. Although available literature describing the unique properties of these grades will serve as a guide to selection, I will point out some of the outstanding advantages of the newer exotic grades as a preliminary guide in this discussion.

The more important intent of this discussion however, is to provide you with tips and useful information with respect to special handling and cleaning procedures which we find to be of vital importance particularly in these grades in order that they will retain their full value when fabricated into the equipment which you will be called upon to construct. You are of course fully familiar with the importance of using only clean material when working with any glass or quartz in order to avoid burned in stains and inclusions. When working with our exotic grades of quartz, this ordinary cleanliness becomes insufficient. These grades of quartz must be ultra clean. Micro particles of foreign contamination can reduce the desired qualities and result in inadequate performance of the end product.

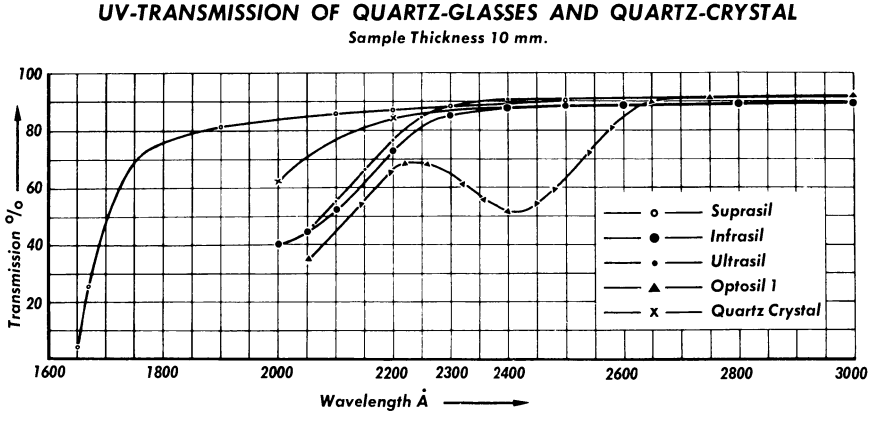

Figure 1

First and with respect to selection of the grade of quartz best suited to your requirement, it is noted that one of the most common uses to which quartz is put is to provide for adequate transmission of ultraviolet light. When considering ultraviolet transmission alone, it is obvious that Suprasil material is by far more efficient in the range below 2300 angstrom units than either quartz crystal or any of the other grades of fused quartz shown. Ultrasil and Infrasil Grades will perform with equivalent satisfaction down to 2300 angstroms but percentage transmission drops off rapidly after this point. All other grades to which we make reference exhibit an absorption band at 2400 angstroms, Fig. 1.

In selection of grades suitable for infrared transmission Infrasil will be found to provide most desirable qualities in that the OH absorption band at 2.72 microns as well as at 2400 angstroms are suppressed to the extent that the product is ideal for the entire spectro range. Infrasil provides these transmission characteristics in an Optical Grade suitable for the most exacting optical instruments. Our Homosil Grade, while it does not provide the transmission characteristics found in Ultrasil, Suprasil, or Infrasil Grades, does provide an exceptional homogeneity with regard to optical uniformity of the material in all directions and is similar to Ultrasil in this respect but at lower cost. Fig. 2

Suprasil is a very pure synthetic fused silica which is produced from chemical compounds under oxidizing conditions. As a result, Suprasil provides a quartz which is exceptionally resistant to discoloration from radiation bombardment. Fig. 3.

I would again point out that it is not the intent of this discussion to delve into the more complex qualifications of these various grades but

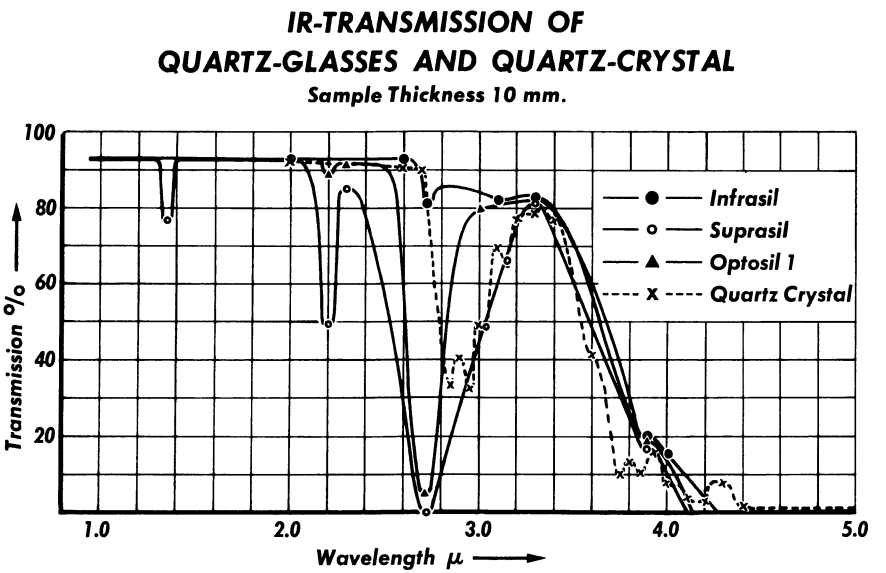

Figure 2

rather to discuss the preparation in handling techniques which will assure satisfactory function of the material in the apparatus which you will be called upon to construct.

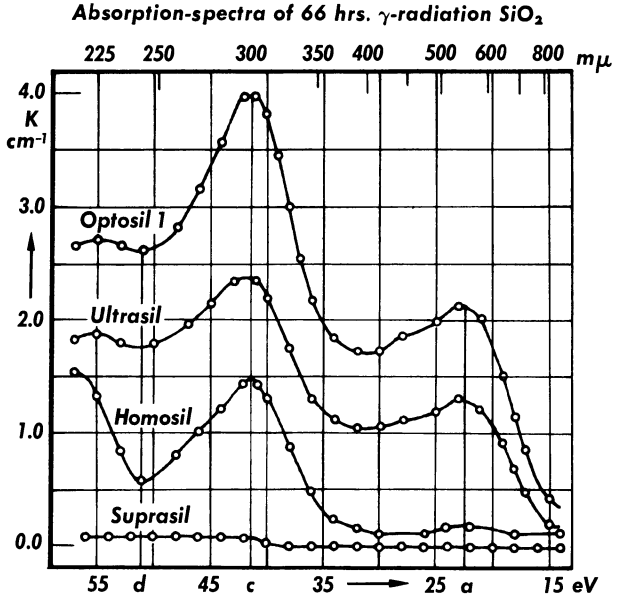

Figure 3

We would point out that it may first be desirable to examine a piece of quartz ingot to be used under polarized light for striae pattern and to orient the material so that striae will have the least effect on the function of the equipment. This of course would be a primary requirement in those instances where you may be cutting a disc, plate, or prism blank from a piece of ingot stock. This requirement would be particularly true when using Suprasil II or Infrasil II Grade material. This selection would not be a matter of critical importance in applications calling for the more perfectly homogenized grades of Homosil, Ultrasil, and Suprasil I. For those of you who would obtain ready cut blanks or polished pieces, this step of orienting the material would be unnecessary.

For most of you, the starting point for preparation of material in these optical grades will be with the cleaning procedures required. For the most part, the optical grades of quartz are supplied in ingot, plate, disc, and prism form. These may be rough cut or ground ready for fire polishing or ground and polished to the desired finish. Suprasil quartz is available in the form of tubing as is also Homosil. A good grade of OH free tubing is also available on special order for use in conjunction with Infrasil and for other applications where a water free tubing is desirable. For the most part standard grade tubing will be used in conjunction with the optical grade flat pieces such as is commonly the case in the construction of cell bodies. In any case, tubular sections which will be joined to

optical grade windows should undergo the same exacting cleaning procedures in preparation as does the exotic optical grade part.

In the preparation of tubular parts, the tubing should first be selected and preferably be free of capillary or air lines. For the removal of dust and oils from tubing, we recommend first a thorough washing, using readily available liquid detergent such as Joy, Lux Liquid, Mr. Clean, and others. Powdered or granular detergents or soaps are undesirable since they may leave fine particles or film particularly if they are not completely dissolved. After washing thorough rinsing is necessary. The first rinse may be running tap water provided of course that the available water supply is not excessively hard. This first rinse step should, under all circumstances, be a running water rinse with no recycling. Immediately on completion of the first rinse, the work should be finally rinsed with running distilled water or at least with distilled water which will be disposed of after each batch rinsed. Final cleaning and drying of the inside of tubular pieces can be very effectively accomplished with a Bethlehem tube cleaner.

On removal of the tubing from the rinse, it should not under any circumstances be handled with the bare hands, and we recommend that lint free paper toweling can be used most satisfactorily for picking up and handling the tubes. These towels should of course be thrown away and not reused and as a result such handling will prove more effective even than handling with gloves which cannot be so easily discarded. Disposable gloves should be used in all later handling of dried material. After rinsing, lay the material down on paper toweling if an intermittent period is necessary before final drying of the outside. Outside drying can be best accomplished by grasping the tube on one end with a paper towel and then wipe downward with the second towel disposing of the towels as often as necessary. At all times avoid handling with bare hands and the possibility of leaving fingerprints on the material.

We do not recommend the use of cloth towels for drying since they are not disposable and since laundering will leave an alkaline residue which will burn into the surface when fired.

The same procedure may be used for the cleaning and drying of small parts such as cell plates, short sections of tubing, and joints, however, we strongly recommend ultrasonic cleaning for such work. A fast procedure in ultrasonic cleaning is to use trichlorethylene which will remove dirt and oil deposits from handling. A most important step in this procedure is to be sure that all work holders used will not be subject to corrosion in trichlorethylene and thereby cause a worse contamination than may have existed originally. Work holders made of quartz such as pieces of quartz rod are ideal, and naturally, since we are in the business of selling quartz, we would be most happy if all work holders used were made of quartz. Seriously, glass, polyethylene, and other materials which are not affected by trichlorethylene are equally desirable as holders.

On completion of the trichlorethylene wash, the material should be immediately removed to a container of distilled water and again thoroughly rinsed ultrasonically and finally dried either with an air blower which can assure a flow of clean air or by the paper towel method. The

use of trichlorethylene is of course hazardous particularly in ultrasonic cleaning and should not be considered without an adequate exhaust system.

A second and slower but safer method of ultrasonic cleaning can be accomplished by using a liquid detergent put into running tap water. After this wash, the material should be thoroughly rinsed in running distilled water and then only placed in distilled water in the ultrasonic washer. This distilled water should of course not be reused for more than one batch of work. It is of course indicated that more than one ultrasonic machine should be available to provide for the steps required, however, the entire operation and changes from one procedure to another can be accomplished very satisfactorily with one machine where the work load makes it totally uneconomical to have more than one machine available. It is possible to accomplish several operations in an ultrasonic washer by putting small batches of work in separate stainless steel or polyethylene buckets with each containing a different solution. For example, the tank of the machine may contain a liquid detergent wash but distilled rinsing can be done by removing the parts and placing them in a small polyethylene bucket containing distilled water and then inserting the bucket into the wash water. The ultrasonic vibrations will be of course carried through into the separate container.

Discs and plates which are supplied with a ground and polished finish may very well contain waxes and grinding compound materials even though they are not visible to the naked eye. Such pieces may have been satisfactorily cleaned by ordinary methods after polishing, however, any polished surface still contains microscopic scratches into which these compounds may be deposited. The amount of this deposit is of course much greater in a commercial polished finish. Work which has been finished to a pitch polish would have finer micro scratches and contain a lesser amount of wax. Ultrasonic cleaning is indicated to provide the best method for removal of these imbedded contaminents and will usually prove sufficient if used in either of the two procedures proposed.

In some extreme cases, polishing waxes may not be completely and satisfactorily removed and the extent to which they are left may be detrimental to the end use to which the optical grade of quartz is put. It is unfortunate that all polishing waxes cannot be dissolved in a universal solvent and the composition of the polishing wax used in the optical shop may not be readily available. In these cases, some experimentation with various solvents may be required when the cleaning procedures become this critical. Acetone is probably the closest to a universal solvent in these instances, however, it is again important to recognize that Acetone presents a very serious fire hazard if used in any volume. We have frankly not yet developed sufficient nerve to attempt the use of Acetone in an ultrasonic washing machine. We make use of Acetone only in small quantity lots and with adequate ventilation. Oother solvents which may be employed would be boiling nitric acid or boiling aquaregia. In all such cases, thorough rinsing in running tap water and a second rinse in distilled water should be employed.

The use of hdrofluoric acid in 5 to 10 percent solution as a cleaning agent is generally only indicated for cleaning of old material which is to

be reworked and where it becomes necessary to etch the quartz in order to remove imbedded surface contamination. Such old work should first be washed with liquid detergents to remove oil so as to allow the hydrofluoric to work most effectively and very thorough rinsing preferably in running distilled water, is recommended following the use of hydrofluoric.

Following the washing and drying operation, and if the material is not to be flame worked immediately, it must be completely protected against any further possible contamination including airborne dust and dirt. We find the use of polyethylene bags or polyethylene sheet to be both practical and desirable for the protection of cleaned quartz parts. This material is readily available, inexpensive, and because of transparency permits visible selection without reopening the package. Alkaline free tissue paper of course may also be used. We would caution against any use of silicone impregnated materials. Lens or eyeglass tissues are excellent for the uses to which they are commonly put but are detrimental when used on optical grades of quartz particularly when it is intended to flame work the quartz. The wax film deposit can be burned in and deteriorate the desired optical qualities. Even in finally finished work such film deposits can effectively hinder the transmission characteristics of the quartz. It is also of course a good precaution to use plastic mats or the contamination free resilient matt material as a bench or table cover to protect against the possibility of chipping or scratching of edges and surfaces.

After cleaning, material should of course never be handled with bare hands. Disposable gloves are recommended. Work areas where the exotic grades of quartz will be fired should of course be meticulously clean but it is also desirable to isolate the bench at which exotic grades of quartz would be flame worked from other benches or lathes where foreign material may be in process. Glass tubing for example will discharge sufficient contaminating vapors when fired to permit a carry over and deposit of fluxes on the hot quartz surface. This also points out the importance of maintaining as long a section of quartz tubing as possible on the end of a graded seal to which Suprasil, Infrasil, or other exotic grade window may be attached. Excessive heating of the seal area can result in a similar deposit on the window area.

The use of filters in the gas lines supplying burners are highly important. Line slag of course must be prevented from coming through but it will be found that fine graphite particles are also present in most manufactured gas and oil picked up from compressor pumps will frequently contaminate the quartz surface. We find porous bronze filters to be quite satisfactory and would also recommend ceramic filters offered for this purpose.

An exceptionally good filter can be produced in your own shop by using a quartz bulb blown to about 3″ diameter and with inlet and outlet nipples 180 degrees apart. This bulb is then filled with fine grade quartz wool and then inserted in the gas line. This type of filter has worked very satisfactorily for requirements where extremely clean gas is required. The filter has the added advantage of permitting visible observation of the dirt particle buildup. The wool can then be removed and replaced. Obviously,

we are again delighted to sell quartz bulbs or provide quartz for making such bulbs since we are in the quartz business, however, there is no indication as to why a glass bulb might not serve equally satisfactory and would be simple to construct from scrap tubing in your own shop.

Very special precautions must be taken when sealing on windows or plates made of Homosil Grade, Ultrasil Grade, or Infrasil Grades of quartz. Reworking of Homosil or Ultrasil will distort the structure and reduce the valued optical properties of these grades. Reworking of Ultrasil and Infrasil Grades will also change the transmission characteristics of these materials and may reduce the percentage transmission to that of ordinary grades. For this reason, attaching windows made in these grades must be done with extreme care and with a pin point fire which will effect only the immediate area around the seal. Flame polishing of plates of these grades is not recommended. Suprasil Grade material on the other hand can be successfully reworked or reshaped by flame operations without effect on the transmission, however, striae could be developed in Suprasil I material unless handled with extreme care.

On completion of your working operations on apparatus including these optical grades of quartz, it is certainly desirable to protect all critical surfaces to the best degree possible and dust hoods or covers made of polyethylene or other materials should be fashioned to provide for permanent covers for all periods of time when the apparatus is not in use.

I would like to thank you for this opportunity of bringing these suggestions to you. We recognize that many other questions may present themselves to you when you return to your shops with respect to the handling techniques of these exotic grades of quartz. We shall be pleased to hear from you at any time that such questions arise and will endeavor to work with you in solving your specific problem.

CHARACTERISTICS OF FUSED QUARTZ AND TECHNIQUES FOR HANDLING THIS MATERIAL AND SOME RECENTLY DEVELOPED VARIETIES

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First let me express my appreciation for the opportunity of discussing with you some of the important properties of fused quartz along with some new developments in quartz. I will also describe a new and unique alumina material, Lucalox® ceramic.

The use of fused quartz has increased greatly over the last ten years. I'm sure that many of you in the room have had occasion to work with the material—a decidedly different situation than existed only a short time ago. From its rather limited use as arc tubes for mercury lamps early in the game, its unique characteristics of high melting point, low expansion and extreme purity have been put to work in applications ranging from semiconductor melting and immersion thermocouple tubes to fused quartz cloth. As a result of the increasing variety of demands on the material to perform in many different ways, our technology has had to keep pace in providing the type of quartz best suited to each job in quality and price.

Historically two types of the material have been available—that is clear fused quartz and opaque or translucent fused quartz—or as we call it—"satin surface". The basic difference between the two is that the clear is relatively free of air seams or bubbles, while the translucent is filled with tiny capillaries which make the material translucent or opaque. Also because of a difference in raw materials the clear is of higher purity. Roughly the clear material, which is higher priced of the two, is used for applications requiring either high purity, good transmission (visible or other) or a shape not readily manufactured in the translucent material. On the other hand the translucent is used where the refractory properties are paramount and the purity and transmission are less critical. Both materials are essentially 100% silica glass with total impurities of about 100 ppm for clear, and 800 ppm for translucent.

Type 206 (commercial grade) is a material having purity equivalent to that of the earlier 204 (*i.e.*, essentially the same as Brazilian crystal) and is characterized by the presences of a substantial number of relatively large air seams. This type has found wide application for use as tubing—that is non-fabricated shapes—and is doing many of the jobs that were previously satisfied by 204 and at considerably lower cost.

Clear (Type 204) and translucent (Type 301) materials have served us well in the past, and are still the preferred materials in a wide variety of uses. However, we recognized that some applications requiring the high purity of the clear did not need the transmission and relative freedom from air seams. As a result two new varieties have been developed which

permit certain jobs to be done more economically without sacrificing performance.

Type 302 is a semi-clear material which has many air seams, but purity equivalent to 204 and at a lower price. The material is available in tubing and in fabricated shapes such as crucibles.

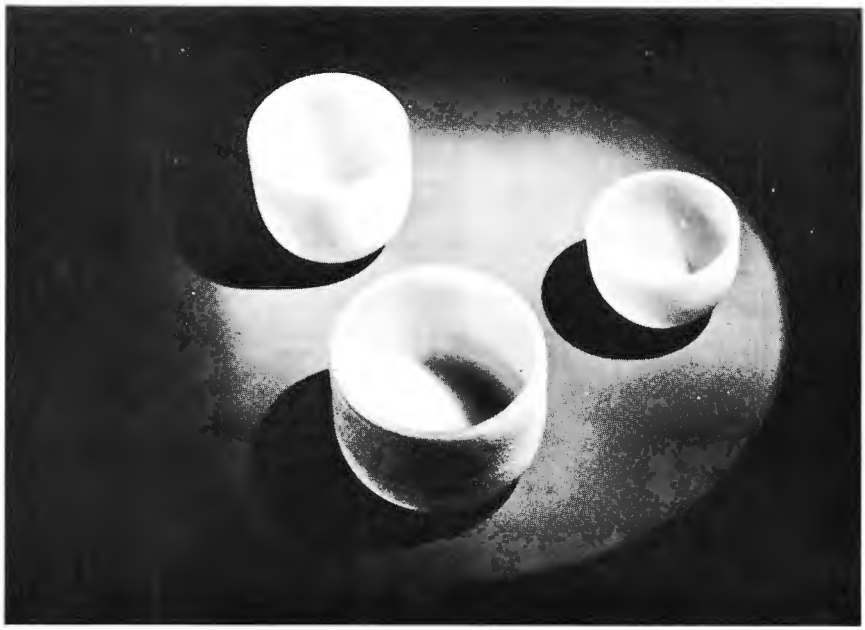

Figure 1

Type 510 is a material, generally referred to as opaque, characterized by very small bubbles. It also is of highest purity, and is available in crucibles (Figure 1) and limited tubing shapes.

A good example of the improvement prompted by new demands from the quartz users has been the attainment of higher purity materials for the semi-conductor industry. Purity, of course, is of primary importance in melting of silicon and germanium for transistor use. Since impurities of less than a part per million of some contaminants can greatly alter the characteristics of the product, there was great demand for a quartz of higher purity. The improvement that we made in the clear 204 quartz was essentially the reduction in alumina which was 150-200 ppm and boron which was 1-1.5 ppm. This is a significant improvement and has resulted in a material with greater resistance to devitrification and sagging as we shall see later. Figure 2 shows impurities in the improved material.

Let us now consider the factors which are important in determining the physical characteristics and idiosyncrasies of handling and processing these different varieties.

204 Quartz		
IMPURITY	Avg.	Max.
Fe_2O_3	7	9
TiO_2	9	12
Al_2O_3	47	61
CaO	17	23
MgO	0	0
K_2O	4	8
Na_2O	4	6
Li_2O	1	2
B	0.5	0.6
ZrO_2	3	5
P As	.08	

Figure 2

Generally, the physical characteristics of quartz are determined by its composition and not the presence or absence of voids. By that, I mean, that such things as softening point, total transmission, resistance to devitrification, expansion, and so forth, are dependent upon the inherent purity of the material. It is true that the "in-line" transmission is affected by the presence of voids in the material due to refraction, but the presence of any absorption band is strictly related to composition.

An illustration of the dependance of softening point on purity is shown in Figure 3. (Note that 204A was the original name of our new, purer material. Since this test was made, the purer material has become standard and is now 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 this 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. We would expect the sag and softening characteristics of Type 302 and Type 510 to be essentially the same as Type 204 since they are all of the same purity. The working of these materials may vary, however, because of the effect of voids in the material on heating rate and thermal conductivity.

The high softening temperature of fused quartz, of course, makes it a very useful material, particularly in this day of higher and higher temperature operations. But it does present a different situation to the glass worker, since fused quartz is worked in the range of 1850-1950°C. com-

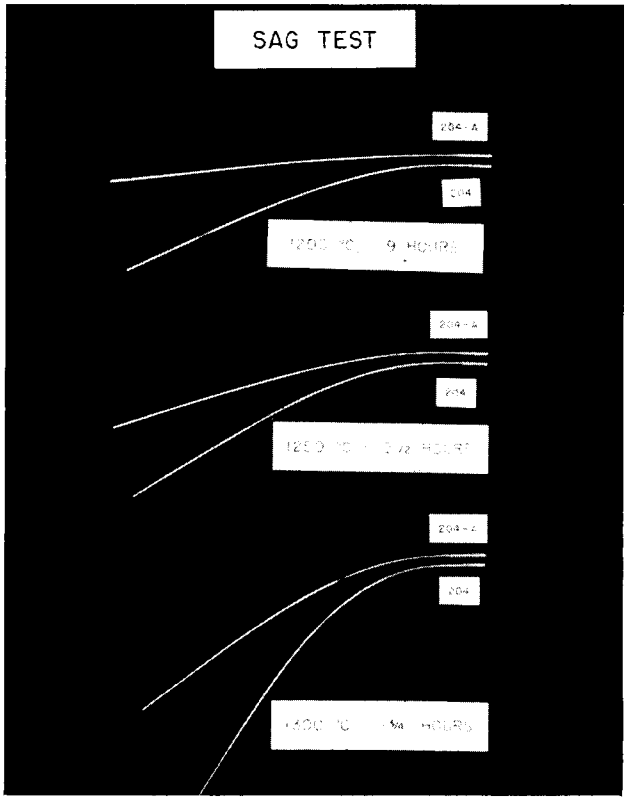

Figure 3

pared with temperatures of 1000-1200°C. for other glasses. Also it has a much narrower working range.

Another of the important characteristics of the material, and one of the most troublesome to those working with quartz at high temperatures, is devitrification or re-crystallization. Technically fused quartz is not the stable form of silica. Since the vitreous or glasseous state is really a super cooled liquid, the tendency is for the material to return to the crystalline state. As the temperature is increased this tendency becomes a practical problem because recrystallization occurs in relatively short times. Below about 900°C. the problem does not exist. Even at 1000°C. we are normally talking of perhaps days for devitrification to start and even then generally a problem arises only when it has proceeded sufficiently to mechanically damage the piece of quartz. At 1400°C. devitrification will begin in a matter of hours and will proceed rather rapidly in all fused quartz materials regardless of purity. However, the rate of devitrification is accelerated by the presence of most other materials either combined in the quartz or in contact with the material at the high temperatures. The new, purer Type 204 devitrifies at a slower rate and the same would hold for the

purer 306 vs. 301. Remember also that handling the material is of prime importance in avoiding acceleration of devitrification rate.

In the absence of a concentrated included impurity, devitrification proceeds from the surface into the body of the material, appearing first as a faint film on the surface. As devitrification progresses the material will become more and more opaque as it fills with small cracks. These observations can be made only after the material has cooled. They cannot be seen at high temperatures. The mechanical damage to the structure does not occur until the quartz has been cooled—past the region of 250°C. —where a change in crystal structure and dimensions occur—which result in the creation of tiny cracks or fissures.

Briefly I would mention some of the other characteristics, perhaps well known to you, which make fused quartz useful. Transmission, both in the ultra-violet and near infrared is higher than other glasses, and most other materials. Again the presence of impurities is determining in the existence of absorption bands. A good example of this can be shown by comparison of the infrared transmission of two grades of our material. Type 104 which contains water in the form of combined hydroxyl groups, exhibits an absorption band at 2.72 μ in the infrared. Type 106 does not. The difference in the materials is the "water content". This can be illustrated at various absorption bands along the scale. The purer the material the better its overall transmission, and this is particularly evident at the far U.V.

By the way, we have a material under development in which the U.V. transmission is considerably improved over both the 106 and 104. I might mention that these are solid shape materials available in the form of ingots, discs, plates and bars.

The low thermal of expansion of fused quartz is perhaps its most dramatic property. This useful property also creates some problems, such as the attaching of quartz to other materials, which normally have much higher expansions. You are familiar with the classic techniques using a graded seal to gradually increase the expansion in steps to match that of the desired material, and to minimize the stress created due to expansion differences. Also the ability to seal directly to very thin foils of metal such as moly and tungsten has been demonstrated and put to wide use.

Despite its low thermal expansion, it should not be assumed that fused quartz does not require annealing. As we shall see considerable stresses can rise in quartz, not only in combination with other materials such as a graded seal, but in the quartz itself as a result of high thermal gradients. And, of course, because of the high temperatures involved in using the material, these gradients can be higher than normally encountered.

Let us proceed then to discuss some of the handling and processing measures that can be taken to realize maximum benefit from the use of the material. We will consider the following problems:

1. Devitrification
2. Cleaning and Cutting
3. Annealing
4. Working

1. *Devitrification*: As I mentioned, devitrification will gradually occur over a period of time at high temperatures regardless of purity. However, the presence of contaminants accelerates this so that care should be taken to maintain cleanliness in handling and processing the material. For instance, clean cotton gloves or other protection from direct contact with the hands should be provided. The most graphic illustration of the effects of contamination on devitrification rate occurs when a finger print is left on the material. You have perhaps seen the perfect reproduction of the print as a devitrification spot on a piece of quartz. It is important to keep quartz clean and to avoid contact at high temperatures with other materials—particularly alkalies. Of course, this avoidance of contact is not always practical because the quartz is frequently being used to contain materials at high temperatures—and in many cases the material being processed is an alkali or other fast accelerator. In these cases devitrification occurs rather rapidly and the quartz tube or part ultimately fails mechanically due to cracking of the material. As was pointed out, the actual mechanical damage is increased as cooling down past 250°C. occurs. Life of the part can sometimes be extended by maintaining the temperature above this point and by avoiding cycling below 250°C.

Sometimes when fused quartz is being blown or shaped in a flame, you will notice a white film depositing on the cooler parts adjacent to the section being worked. This should not be confused with earlier devitrification, which it may resemble. The deposit results from the vaporization of the quartz and the condensing of the vapor on the cooler surface. The effect of a reducing atmosphere or flame greatly accelerates this—the mechanism being the reduction of the silica, the vaporization of the reduced form, the reoxidation and condensation.

2. *Cleaning and Cutting*: Because fused quartz is composed of silica alone it is very resistant to most acids and alkalies at room temperature. Hydrofluoric acid is the one acid that attacks fused quartz readily at room temperature, and, for this reason, we use it to clean quartz. Normally we use a concentration of 10% and water for approximately ten minutes, rinsing in distilled or deionized water. Of course, we are very much interested in avoiding etching of the material, which damages the appearance of quartz which will be sold. On the other hand, in many of your applications, particularly in the case of a repair of a partially devitrified tube—you are not concerned with etching, but want to be sure that the surface is free of impurities, including those which may be firmly attached. In this situation, faster cleaning actions can be realized by using higher concentrations and heating the solution.

The necessity of using hydrofluoric acid in cleaning of fused quartz gives rise to a potential hazard in handling the material. Hydrofluoric acid is dangerous and every precaution should be taken to avoid contact with the skin.

In the case of a grease deposit or oil from the skin (as a finger print) the material should first be cleaned with an organic solvent, such as alcohol or acetone, before washing with hydrofluoric acid.

Because of the hardess of quartz, as with most other glasses, cutting is performed with diamond or silicon carbide wheels. The cutting operation

may be wet or dry, and the choice is important depending on the material being processed. Tubing with air seams, such as translucent 301, commercial 206 and 302, should not be wet cut. Closed air seams are under vacuum before cutting and as they are opened by the cutting wheel, water is sucked into the seams. This would not be a serious problem if the water could be easily removed by baking, but cutting dust which is often sucked into the air seams traps the water. When this happens the tube when heated will either tend to spall as a result of pressure buildup, or, if heated to the working point, will cause excessive bubbling. Dry cutting has usually been done with a silicon carbide wheel because it was thought that the life of a diamond wheel would be seriously impaired by dry cutting. However, we have found that good life can be realized using a dry diamond wheel on a straight-through cutting of tubing up to about 30 mm diameter.

The same 6″ wheel with either .035″ or .025″ diamond thickness is used for both wet and dry cutting. The wheel is a resin bonded "man-made" diamond wheel. The thickness is determined by the tubing diameter—the larger tubing using the heavier diamond. For dry cutting the cross section of the tube should not exceed 30 mm in diameter, and 1.5 mm wall, or there will be excessive heat generated and the resin bond fills with powdered material and impedes cutting. The advantage of wet cutting is a finer finish of cut. However, the cut pieces must be washed immediately in HF after cutting to prevent drying of the residue on the tube. In dry cutting other cleaning procedures can be used, and, if acid washing desired, it may be delayed. And as was pointed out, dry cutting is the only practical method for certain varieties. These varieties which contain air seams may be washed after dry cutting, since at that point the seam is open to atmosphere and there is no danger of entrapment. However, the piece must be baked after washing to remove water.

Briefly let me mention the score and snap cut which may be used successfully on all types in the smaller diameter range. We use a Carboloy cutter—grade 799—5″ diameter—¼″ thick—ground to a 60 degree sharp edge—the tubing is rotated 360 degrees against this cutter and snapped. For hand cutting we use back cutters of 883 Carboloy.

For large diameter tubes of 50 mm or more, we continuously turn and score with a 6″ diamond wheel. When we have scored completely around the tube, the tube is then cut straight through. This avoids excessive chipping.

For translucent tubing, which normally has a heavier wall than clear tubing, carborundum wheels 10″ diameter and ⅛″ thick are used—following the same procedure.

3. *Annealing*: While stresses in quartz normally are quite low, the condition of thermal gradients created by working the material can sometimes be troublesome. Contact with metal chucks should be avoided, and large pieces should be flame annealed after forming. In the case of graded seals, furnace annealing of the high expansion component is recommended. For annealing of quartz alone, which is frequently important in the use of solid shape materials for optical applications, we recommend that the piece be furnace annealed at a temperature of 1140°C. for about five minutes, depending on size, followed by cooling at a rate of 3 degrees C°/min.

to 1050°C., and finally, furnace cooling at a rapid rate characteristic of the particlular furnace.

Relating to the actual forming of quartz, you will have the opportunity to observe the lathe demonstrations this afternoon. Let me just mention that oxy-hydrogen burners are used and generally graphite forming tools. In the case of working certain materials with air seams, butt joints are more readily accomplished by first clearing up a small section on the ends of the tubes before joining. This can be accomplished easily as the air seams will exhaust and close readily over a short section.

Another rather general problem is repair of partially devitrified tubes. To accomplish this the tube should first be soaked in concentrated hydrofluoric acid until it is fully etched. It is sometimes advisable to abrade the surface with a carborundum cloth before the acid treatment. This breaks up the surface and cleans off particles that are loose and also promotes the acid attack by creating an open surface. After rinsing and drying, the tube is heated in a glass working lathe using an oxy-hydrogen burner. For best results it is advisable to actually move the quartz, *i.e.*, work the tubing—starting at one end and proceeding for the length of the devitrified area. This will be demonstrated this afternoon.

Figure 4

Before closing I would like to take this opportunity to mention some of the newer and more exotic products that are finding use in some rather interesting applications. Quartz is now made in fiber materials such as yarn and roving. (Figure 4) The filament diameters of these materials are

about .0004". Quartz fiber is finding applications in the area of high temperature insulation of wire and is also used for space age structural components, such as radomes. These are made by impregnating the quartz fiber material with appropriate resins such as silicones. Recent advances in technology now permit us to supply fibers coated with binders that are compatible with some of the resins used. This eliminates the necessity of cleaning the binder—which is required for processing the material—by baking off. This cleaning procedure greatly reduces the strength of the fiber because of the handling and chemical damage which is involved. Since the purpose of using quartz fiber is the excellent strength, even at high temperatures, it is important that this not be lost due to excessive handling. Fiber strengths range to about 200,000 psi. The excellent dielectric and insulating properties of fused quartz are useful in any composite made from quartz fiber products.

To bridge the gap between fiber, which is extremely small diameter, and the more conventional quartz products—micro bore tubing and a full range of solid rod types has been developed. Tubing down to .001" I.D. x .0015" O.D., has been made. A particularly interesting use for this small diameter tubing is in its use for purifying helium. Helium has a substantially higher diffusion rate through quartz than most other gases except hydrogen. As a result by passing contaminated helium over a bank of very thin wall quartz tubes, the helium diffusing through the quartz can be collected in a highly purified condition. The increasing use of helium in nuclear and space applications makes the conservation and purity requirements of helium extremely critical. Small laboratory units have been built and the feasibility and design proven.

Lastly I would like to mention a new alumina material called LUCALOX*® ceramic. Lucalox is unique because of its lack of porosity and, therefore, attainment of ultimate density for an alumina ceramic. In fact Lucalox is essentially the same as sapphire, except that it is polycrystalline, rather than single crystal.

Because of this absence of pores, Lucalox exhibits unique light transmitting properties for a ceramic material. Our initial interest in Lucalox was for its use as a lamp envelope since its high melting point (2000°C.) and inertness to alkali vapor gave promise of development of a highly efficient vapor lamp; and such a lamp has been developed. Additionally Lucalox has properties of hardness and attainable finish (it will take an excellent polish) which make it a good candidate for a variety of wear applications. Also Lucalox has the excellent dielectric and electrical insulating properties of sapphire—and is characterized by an extremely low loss factor—.000025. Purer than other aluminas it shows excellent resistance to the highly corrosive alkali vapors—increasingly important in nuclear power applications.

Since the properties of Lucalox ceramic are so closely allied to those of sapphire, we expect many similar applications of the two materials. The ability to produce Lucalox in machined shapes, however, is a distinct advantage. (Figure 5) While in the green state prior to firing, Lucalox can be formed

*Registered trademark of General Electric Co.

Figure 5

PHYSICAL PROPERTIES

GENERAL

Constitution①	α-alumina
Purity①	99.9 per cent Al_2O_3
Structure①	polycrystalline
Density①②	3.98 gm/cm³
Porosity①	gas-tight, essentially zero;
Melting point①	2040°C.

MECHANICAL

Hardness, VPN scale②	1660-1930
Hardness, Rockwell "A" scale①	85
Transverse rupture strength in bending①②	45000 psi average
Poisson's ratio μ②	0.205
Young's modulus (E)①	56.1 x 10^6 psi
Rigidity modulus (G)②	23.3 x 10^6 psi
Bulk modulus (K)①	31.7 x 10^6 psi
Sonic shear velocity (C_s)①	6355 m/sec
Sonic compressional velocity (C_c)②	10417 m/sec

THERMAL

Figure 6

Coefficient of expansion①	see curve
Thermal conductivity①	see curve
Thermal shock resistance①	excellent

OPTICAL

LUCALOX ceramic is translucent rather than transparent. Scattering of transmitted light is caused by refraction at the polycrystalline interfaces and by crystalline birefringence.

Transmission, total and in-line②	see curve

ELECTRICAL

Dielectric strength①④	1700 volts/mil average
Volume resistivity①②	see curve
Dielectric constant (K)①③	9.9
Power factor (sin δ)①②	0.000025
Dissipation factor (tan δ)①⑤	0.000025
Loss factor (DK)②③	0.000248

①—General Electric Research Laboratory, Schenectady, N. Y.
②—General Electric Glass Technology Laboratory, Cleveland, O.
③—At 20°C., .02 in/min. loading rate.
④—At 20°C., .20 mil thickness.
⑤—At 20°C., 9720 megacycles.

into any machined configuration—much the same as conventional alumina ceramics. It can also be pressed or extruded.

Because of its high melting point and resistance to chemical attack, we foresee applications for Lucalox as melting containers. Platinum which melts at 1774°C. can be melted in a Lucalox ceramic crucible. Because of its high resistivity and low dielectric loss, even at high temperature, we anticipate a range of applications—including microwave windows, substrates, lead in insulator supports for electron tubes, and others. A particularly interesting possibility is in the use of Lucalox for circuit substrates. The ability to produce extremely fine surfaces combined with its high thermal conductivity and electrical properties are of real significance. Also its high temperature strength is of importance.

The properties of Lucalox ceramic are described in our catalog. (Figure 6) Standard sizes normally available from stock are listed.

Let me again express my thanks to you for this opportunity. I will be happy to answer any questions you might have.

HIGH-TEMPERATURE PHASE CHANGES IN GLASS

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ABSTRACT

Glass which has been defined as an undercooled liquid, will under certain conditions of elevated temperature start to crystallize and revert back to the solid state. In most glass fabrication processes this is an economic nuisance and efforts are made toward its avoidance. In others, it is deliberately cultivated to produce materials of even greater economic value than just plain glass. Several examples of the latter will be given.

The mechanism of phase change as determined by phase rule applications will be discussed and illustrated with a simple binary system. Other factors relating to phase change such as rate of crystal growth and nucleation time will also be discussed and methods of their determination described.

INTRODUCTION:

There is scarcely a glass maker or fabricator who has not encountered problems caused by phase changes in glass during its working at elevated temperatures. The means of the phase change might be direct devitrification, where the glass reverts to a crystalline form, or reduction as from a PbO in Pb in a soda-lead glass or solution as in corrosion. Where the latter result in a crystalline residue, it may also be described as devitrification.

Generally, the result of a phase change in glass is a semi-opaque product which has lost its gloss, is somewhat stringy in melting, and if the phase change were extensive, the glass might be completely unsuitable for its intended use. Although the ultimate product of complete devitrification is a solid crystalline mass, this rarely occurs in practice unless deliberately intended. What is more likely to occur is a sprinkling of fine crystals on the glass surface. The surface of glass is the usual site for devitrification because it acquires the suitable temperatures first and is the location of numerous nucleation centers.

Since the index of refraction of the imbedded crystals is usually different from its glassy surround, multiple internal reflections will be produced resulting in a cloudy to white appearance. In the case of the soda-lead glass, the result is a black surface film which is cosmetically and sometimes functionally objectionable.

For a long time, the defect of devitrification has been put to good use in an empirical fashion in the manufacture of opal glass. This was done by intentionally incorporating some sodium fluoride in the form of bone ash in the glass batch. The subsequent rapid devitrification that was induced in this fashion resulted in myriads of tiny crystals within the glass. Not only did this make the glass translucent and white but it also imparted a fiery opal glow when examined by transmitted light because of the scattering of the light by crystals which were sub wave-length in size.

RECENT USES OF PHASE CHANGES IN GLASS:

More recently a series of important technical glass products have been put on the market which derive their value from planned phase changes. Such glasses include devitrifiying solder glass, photosensitive glass, pyroceram, chemcor and vycor. It is the intention here to describe several glasses of this type and then to discuss some of the mechanisms and cause and effect relationships which make them possible.

DEVITRIFYING SOLDER GLASS:

Devitrifying solder glass arose from the need of multiple properties in a glass. First it was desired to have a glass with both a thermal expansivity matching that of regular commercial glass and a softening temperature well below that of commercial glass so that in the sealing or soldering operation, the latter would not distort. When such a composition was made up, namely the ordinary solder glass, it was found that in applications involving vacuum tubes, television plates, etc., such a glass was inadequate. In these applications a subsequent high temperature baking under vacuum was necessary. The combination of elevated temperature and pressure was more than what ordinary solder glass could withstand. By the addition of nucleating agents to the batch, a new product devitrifying solder glass was obtained. With this glass the low softening temperature remained virtually unchanged so that the required fusing could readily be made. By prolonging the heating for a period of about an hour, the fused glass was made to devitrify. Insofar as the melting point of the devitrified crystals is well above the softening point of the solder glass, such a tube could later be evacuated and baked out at temperatures which would have caused ordinary solder glass to flow out of the sealed joint.

PHOTOSENSITIVE GLASS:

This glass is made by putting photosensitive salts and thermal reducing agents in the glass. After exposure to ultraviolet light of sufficient intensity, colloidal gold, silver or copper particles are produced. These act as nucleation agents for crystallization which is induced by subjecting the exposed glass to a time-temperature soak in an oven.

In a modification of this process, glasses of different solubility are produced in the exposed and unexposed portions. So that by using a suitable template during exposure, intricate shapes can be made and etched out in a manner not possible by any other means.

PYROCERAM:

This product starts out as a glass batch with included nucleating agents. The composition of the batch is so adjusted that the crystallization products after devitrification will be hard, high melting, and corrosion resistant. It is manufactured in its vitreous state first. While it is still a glass, any defects can be seen through the wall. Additionally, the low softening temperature of the glass permits it to be fabricated into various shapes by an inexpensive molding or centrifugal casting operation.

After the glass has assumed its final form, it is devitrified in an oven to a crystalline condition. The result is a hard, impervious ceramic shape

that will withstand extreme temperatures or abrasion without damage.

VYCOR:

Perhaps one of the most unusual utilizations of phase changes in glass is the product of the Corning Company called VYCOR. In this glass, the phase change is not devitrification but rather the conversion of a glass into two glassy phases. Each of these phases is a glass but of different compositions. The two particular glasses so formed are immiscible, acting like an emulsion of oil and water.

As a glass, it is molded into the desired shape at conventional glass molding temperatures. It is then immersed in an acid solution. This removes one of the phases which is relatively soluble. The remaining phase is almost pure silica glass. After heating and compacting a glass which is over 96% SiO_2 is the result. Thus a product which approaches fused silica in all its properties can be produced without the difficulties and expenses associated with the working of quartz at high temperatures.

MECHANISM OF PHASE CHANGES:

In order to discuss the mechanisms of phase changes in glass, it is necessary to define its state. Despite its rigidity and elasticity at room temperatures, glass is considered to be an undercooled liquid. Confirmation of glass as an undercooled liquid is evidenced in many ways. These include X-ray diffraction, differential thermal analysis and the continuous nature of its physical properties when plotted against temperature.

The answer to what possible changes of state and compositions can occur when systems of liquids, solids, or gases, or combinations are heated or cooled was answered in 1874 by one of America's greater, if not better known scientists, Josiah Willard Gibbs of Yale University. In a paper entitled "Equilibrium of Heterogeneous Substances" he enunciated his famous phase rule.

The implications of this important work were not realized until well into the 20th Century, after interpretations by Roozeboom, Shreinmakers and others. Use was first made of the phase rule by geologists and mineralogists in systematic studies of earth mineral. To-date, thousands of phase equilibrium studies have been made and a rich literature is available on the subject.

The phase rule states that for a system in equilibrium, the number of phases plus the number of degrees of freedom (or variance) is equal to the number of components plus 2. It is usually represented as a mathematical equation as follows:

$$P + F = C + 2$$

Here "P" stands for the number of phases. A phase is defined as any portion or the entire portion of a system which is homogeneous, has a boundary, and can be mechanically separated from the other parts. The phase boundaries need not be contiguous. For example, in an oil-water emulsion, all the separate droplets of oil would constitute only 1 phase.

"F" represents the number of degrees of freedom or variance. It is the number of variable factors such as temperature, concentration of components and pressure which must be arbitrarily specified in order to per-

fectly define the condition of a system. For "F" = 0, the system is termed inivariant, for F = 1, univariant, for F = 2 bivariant, etc.

"C" is equal to the number of components. It stands for the smallest number of independently variable chemical constituents which are necessary and sufficient to specify the equilibrium of each stage. Ice, water, and steam represent 3 phases of the one component H_2O.

In systems of oxides which are of interest to the glassmakers, the vapor pressure is very low and is scarcely affected by large changes in temperature. In such systems, the one degree of freedom (the pressure variance) can be omitted. In this case, which is called a condensed system, the "P" will only apply to solid and liquid and the phase rule reduces to

$$P + F = C + 1$$

Let us see how this can be applied to a glass forming system. Figure 1 is a diagram of a 2 component or binary system consisting of a liquid phase and 2 solid phases (S_1 and S_2 with compositions corresponding to A and B). To keep the example uncomplicated, we will assume that no intermediate compounds, solid solutions or glass immiscibility occurs.

Since this is a binary system C = 2 and the condensed phase rule becomes P + F = 2 + 1 or P + F = 3. From this we can predict the number of phases (P) that will be in equilibrium if we are given the number of degrees of freedom (F) available. Or given the phases, we can calculate the variance.

For example, if we are given a condition where 3 phases are in equilibrium we have P = 3. Substituting this in the expression for the phase rule of a binary system, it becomes 3 + F = 3 or F = 0. This is the condition of invariance or no degrees of freedom and is represented at point C in Figure 1. Any slight change in any direction will cause one or more phases to disappear.

When 2 phases are present, or P = 2, the equation becomes 2 + F = 3 or F =1. This is the univariant condition and is realized on the liquidus curve which is the boundary where 2 phases are in equilibrium (liquid above the curve and solid + liquid below) and only one degree of freedom is left. That is the freedom to vary the temperature and composition but not independently so that if equilibrium is to be maintained any change in temperature constrains the composition to a specific value.

Similarly when only one phase is present, F becomes 2. This is illustrated in the liquid region above the liquidus curve where changes in both temperature and composition can be independently made without disturbing the equilibrium.

COURSE OF CRYSTALLIZATION:

The course of crystallization, the kind of crystal that is formed, and the composition of the phases, can be secured directly from the phase equilibrium diagram.

Starting in the liquid region and decreasing the temperature, a composition such as represented by J in Figure 1 will remain a liquid until the liquidus temperature of this composition is reached. Below this temperature it can separate into 2 phases, one a liquid phase of composition

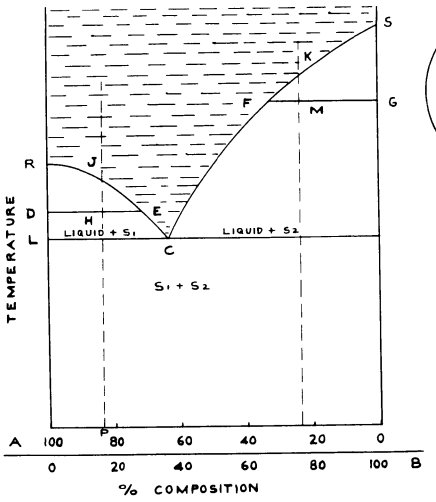

Figure 1

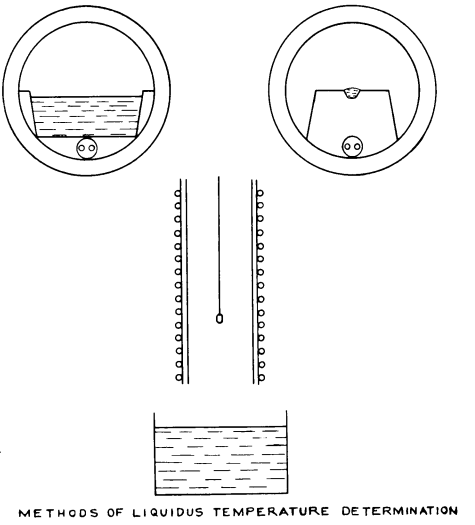

Figure 2

E and the other a solid phase of composition A. The composition of the liquid phase can be calculated exactly from the Lever Law. The composition of the solid will precisely conform to the composition corresponding to 100% component A.

The lever law gives the quantitative relationship between the phases. At point H for example, the relationship between the quantities and the compositions of the phases is given by the equation

$$\frac{\%\ \text{Solid}}{\%\ \text{Liquid}} = \frac{\text{HE}}{\text{DH}}$$

The temperature indicated at L is known as the solidus temperature. Under equilibrium conditions, no liquid can exist below this temperature. Any point in this region can only consist of a mixture of solid A and Solid B in the ratio given by the Lever Law.

RATE OF PHASE CHANGE:

Although the phase rule can predict what will happen under equilibrium conditions, it does not provide information on the rate of change or on what intermediate forms crystallize out. Such information can be secured by various quenching methods which "freeze" in the condition corresponding to a higher temperature state so that the sample can be examined under practical room temperature conditions. Several such methods are indicated in Figure 2.

In the classical "quench" method developed at the Geophysical Institute a small sample of the given composition in the crystalline form is wrapped in a platinum envelope and suspended by a fine wire in an electrical oven maintained at a particular constant high temperature value. After a period of time deemed sufficient to attain equilibrium (Varying

from a few minutes to several hours or even several months) an electric current is passed thru the wire which melts and causes the charge to drop immediately into a mercury bath. The sample is removed and examined with the Petrographic microscope. The continued presence of crystals indicate that the liquidus temperature has not been reached and the experiment is repeated with successively higher temperature until the value of the liquidus temperature has been determined.

In the Silverman method a larger sample contained in a platinum boat is placed in a thermal gradient furnace to attain equilibrium. It is then quickly removed, broken out of the boat and examined microscopically. The liquid-glass boundary position is correlated with the gradient oven temperature and the liquidus temperature interpolated.

In a method that the author helped develop, small cells are perforated in an inverted platinum boat. These cells hold a small mass of sample in intimate thermal contact with the platinum and the removal of the specimen holder from the gradient oven, more closely approaches the Geophysical method in the rapidity of quench. In both gradient methods the size of the crystals can be measured after any number of treatments and the rate of crystal growth thus established.

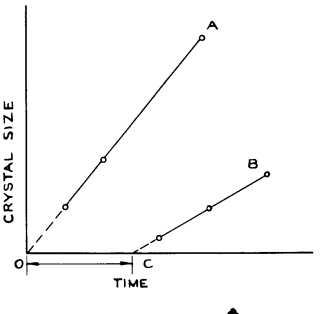

Figure 3

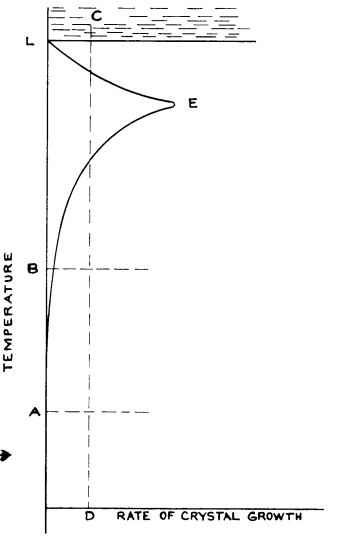

Figure 4

Figure 3 is a graph of crystal length versus time at the particular elevated temperature. The slopes of OA and CB indicate two different rates of growth. With OA, the commencement of growth is instantaneous. With OB, extrapolating the curve to the time axis indicates that growth only started at time C. In this case, a definite period of time for nucleation of the crystal was required before it could start to grow.

A typical curve for rate of crystal growth vs. temperature can be compiled from crystal length versus time data at various temperatures. Figure 4 is a curve of such data. Above L only the liquid phases can exist.

E, corresponds to the temperature where rate of growth is a maximum. B, represents the softening temperature of the glass and A the annealing range.

If devitrifying solder glass were heated starting at D, (Fig. 4), it would appear as a powder until B was reached. At about this temperature, it would soften and start to fuse so that the vitreous appearance would be very evident. As it is continued to be heated, it would enter the region of rapid crystal growth. Maintaining the temperature constant for a period of about one hour would cause the solder glass to devitrify into large interlocking crystals. Then if the temperature were lowered to room temperature the solid state would be frozen in "permanently". The rate of crystal growth is an important determining factor as to whether it is possible to make a glass

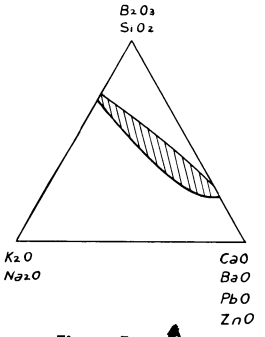

Figure 5

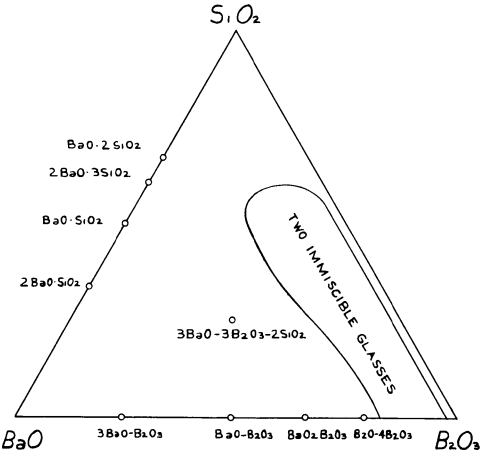

Figure 7

In figure 5, we have a schematic triaxial diagram in which the glass formers, fluxes and alkaline earths have all been summed up and represented at a different apex. The enclosed area on this diagram represents the range of compositions of most practical glasses today. The region of high silica imposes limitations on account of the high melting temperatures. The alkalie apex results in excessive hygroscopicity and the alkaline earth apex results in rapid devitrification.

Rates of crystal growth in glass forming and non-glass forming materials are represented in Figure 6. The tremendous rate of crystal growth in phosphorus and picric acid indicate why they cannot be made into glasses. Glass E1222 is just about on the borderline of what is required for glass formation in small melts, and glass E1105 is about the lower limit for practical glasses.

In some systems, phase change results in two immiscible liquids. In the case of the Vycor glass where one of the products was soluble and the other a high melting glass a very valuable product could be made as was indicated previously without having to resort to the very high temper-

RATES OF CRYSTAL GROWTH FOR GLASS FORMING AND NON-GLASS-FORMING MATERIALS

Material	*Maximum Rate of Crystal Growth*	*Temperature*
	μ/Min.	*°C.*
Glass E 1105	9.8	895
Glass E 1222[a] (devitrifies readily)	63.3	890
Picric acid[b] (non-glass-forming)	860,000	85
Phosphorus[c] (non-glass-forming)	60,000,000	[d]25

a. A low-dispersion, high-index experimental glass.

b. A. Bogojawlensky, *Z. physik. Chem.* 27, 585 (1898).

c. M. D. Gernez, *Compt. rend.* 95, 1278 (1882).

d. Not maximum.

Figure 6

ature necessary for forming silica. Other systems also have regions where the phase change results in immiscible liquids. An example of this is the B_2O_3-BaO-SiO_2 system in which the area of immiscibility is indicated on the triaxial diagram of Figure 7.

As the system becomes more complex, the mathematics and the experimental work become very involved. In some cases, four dimensional and higher representations are required to illustrate the system. However, there can be no doubt that increasing technological demands for glasses possessing diverse, extreme, and multiple properties will have to be met by completely new glass compositions and even diphase and polyphase materials. Nor can there be any doubt that the successful achievement of such materials can be greatly helped by phase rule application and rate of crystal growth measurements.

REFERENCES

1. J. W. Gibbs—*The Collected Works of J. W. Gibbs,* Vol. 1, Longmans Green and Co., 1928.
2. A. Findlay, A. N. Campbell and N. O. Smith—The Phase Rule and Its Applications—Dover Publications, Inc., 1951.
3. E. M. Levin, H. F. McMurdie, and F. P. Hall—Phase Diagrams for Ceramists, *A. Cer. Soc. Inc.,* 1956.
4. O. H. Grauer and E. H. Hamilton—*J. Res. Nat. Bur. Stand.* V44, May 1950.
5. W. B. Silverman—*J. A. Cer. Soc.* 22, 378, 1939.
6. S. M. Cox and P. L. Kirby—*Nature* 159 (4031) 162 (1947).

GLASS TECHNOLOGY AND NOVEL INFORMATION PRESENTATION DEVICES

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1. INTRODUCTION

Transmitting visual information between two points on the surface of our planet is nowadays a common practice. The explosive development of television after the second world war necessitated an equally fast development of presentation devices for the transmitted visual information. These presentation devices, television picture tubes, are now present in nearly every household.

A variance of the common TV picture tube, namely a device displaying an electrical signal in visual form, has found wide spread application in science and industry. Oscilloscope tubes are used in electronic research, production control, in nuclear science, for the presentation of high speed electrical signals, etc. While the number of TV picture tubes in use exceed by far the number of oscilloscope tubes, it is noteworthy that the latter is actually the father of the TV picture tube.

Tubes of the type discussed here have the task of translating a one-dimensional (time dependent) electrical signal into a three-dimensional (x-y and time dependent) visual display. Other devices pick up a three-dimensional signal carried by electromagnetic radiation and convert it into a three-dimensional amplified signal of similar or different wavelength. These devices are commonly called image intensifiers or image tubes. They find wide spread application in medicine, nondestructive testing, warfare, etc.

Other information presentation devices have the task of translating a time dependent electrical signal into a visually perceptive record. These "high speed printing tubes" are used for labeling, multiplication of printed information, etc.

During the last few years, a host of new developments have occurred in the field of information presentation devices. This new impetus may be traced to the everlasting desire of mankind to expand the scope of knowledge in science and to the necessity of achieving technological superiority in the present battle of minds commonly referred to as cold war.

In this paper, we shall outline some of the information presentation devices presently produced or in development. The envelope material forming the vacuum enclosure of these tubes will be discussed in detail. Sealing techniques, that is, joining parts of the vacuum enclosure together as well as making provisions for mounting internal tube parts onto the vacuum enclosure, will receive special attention.

Presentation devices of the type discussed here differ from earlier vacuum devices in that the vacuum enclosure, previously serving solely as a barrier against room air, is now expected to perform also as an active element of the tube, for example, as a part of the electron optical system. Developments in the field of fiber optics have enhanced the importance of sections of the tube envelope as integral parts of (light) optical systems external to the vacuum enclosure. The impact of these developments on glass technology shall be outlined.

2. SURVEY OF INFORMATION PRESENTATION DEVICES

It might not be superfluous to describe some selected information presentation devices to prepare the discussion of the glass technology required for a successful development and production of these types of tubes. It should be appreciated that the listing of such devices given below is not necessarily a complete one.

2.1 *Devices Converting a Time Dependent Electrical Signal into a Visual Display*

As mentioned already in the introduction, black and white as well as color television picture tubes belong into this category together with the oscilloscope tubes.

So-called monitor tubes, TV picture tubes of special design applied to the reproduction of special TV signals, namely industrial TV monitors, ground and air traffic control monitors, display tubes for medical and astronomical applications, etc., should be mentioned here. High resolution display tubes, flying spot scanners as used for TV movie transmission and character writing tubes, so-called alpha-numerical display devices for computor read-out, also belong to this category.

2.2 *Devices Converting a Time Dependent Electrical Signal into an x-y and Time Dependent Electrical Signal*

Tubes of this type are printing tubes; the input end is quite similar to a normal TV picture tube while the phosphor screen is replaced by an array of metal contacts reaching through the faceplate permitting to utilize the charge deposited internally by the scanning electron beam.

2.3 *Devices Converting an x-y and Time Dependent Electromagnetic Radiation into an x-y and Time Dependent Visible Display*

Vacuum image intensifier tubes, for short "image tubes", form this category. There are now image tubes available which are sensitive practically to the entire electromagnetic spectrum starting at the very high frequency end with radiation such as emitted by high energy accelerators (LINAC, betatron, radiation in the 20-40 MeV range), radio isotope (in the range of several hundreds of KeV to somewhat in excess of 1 MeV), medical X-rays, soft X-rays such as used for the specific tasks of non-destructive testing, very soft X-rays and extreme ultraviolet radiation such as emitted by the sun and picked up from an orbiting space platform, ultaviolet radiation applied to biological research, visible radiation, used in warfare and near infrared radiation applied in so-called active night viewing systems for warfare and specialized scientific research such as sensors for lasers, Raman spectra investigations, etc.

As a special type of image presentation device, an image tube for electronography should be listed. While photography is normally achieved by the photo-chemical reaction between electromagnetic radiation and the photographic emulsion, electrons impinging upon a photographic emulsion also blacken the grains, but with a much higher quantum yield than photons. Image tubes of this type find special application in astronomical research extending the range of telescopes far beyond the limits previously imposed. Several of the information presentation devices discussed here, are shown in Fig. 1.

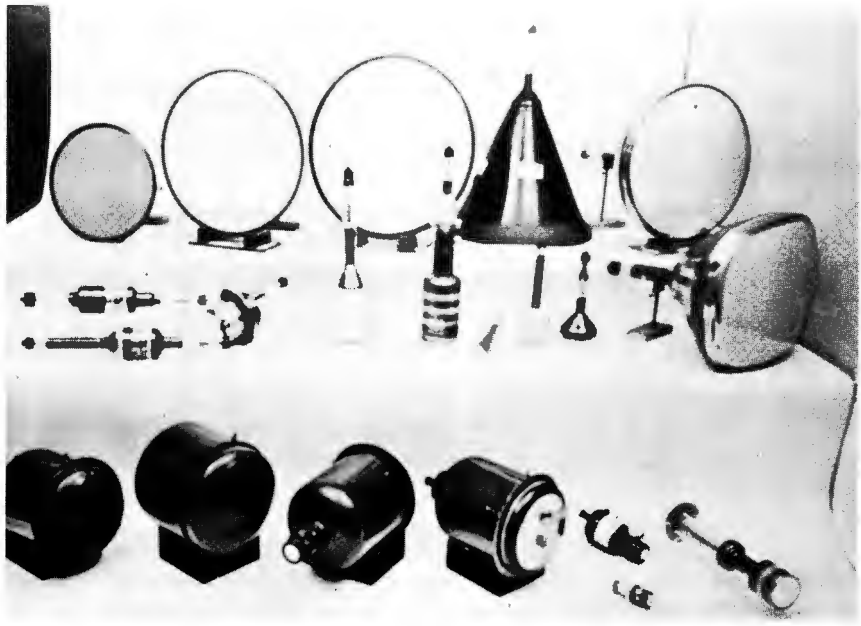

Figure 1
Examples of Information Presentation Devices

One will appreciate that the far flung application of image presentation devices and the almost daily occurrence of new uses for such devices necessitates an intense development effort directed not only towards device design but also, or possibly even mainly, concentrated on technological aspects.

In the next sections it will be attempted to discuss some of these developments.

3. VACUUM ENCLOSURE

3.1 *Requirements of the Vacuum Enclosure*

While information presentation devices may also be of the solid state type, possibly not requiring a vacuum tight envelope, the discussion here is restricted to the more common vacuum tubes.

The most important requirements to be fulfilled by the vacuum envelope are listed and discussed below:

a) *The tube envelope should serve as vacuum enclosure.*—It will be appreciated that all materials are in principle permeable to certain gases to a greater or lesser extent. The smaller the gas molecule the greater the rate of diffusion through the envelope material. Such a "diffusion" may follow physical laws or may occur by a chemical reaction. The helium diffusion through glass serves as example for the first mechanism while the well known permeability of kovar tubulations is based on chemical interaction.[1]

b) *The tube envelope should serve as carrier for electrical contacts.*—A presentation device may necessitate a multitude of electrical contacts. Electrical leakage between these contacts should be as low as possible. Equally, the external and internal potential distribution along the enclosure wall between two adjacent regions of different electrical potentials may have to obey certain laws. This point will be elaborated on later.

c) *The tube envelope should have an area for admittance as well as emission of energy.*—In the case of presentation devices utilizing a primary electrical signal, the admittance "window" of the envelope is simply an electrical contact. For image tubes, a window permeable to the information carrying input radiation is required.

The output window should in general be permeable to visible radiation or assume the form of a contact mosaic as in the case of printing tubes.

d.) *The tube envelope should be an integral and functional part of the internal tube structure.*—This requirement is in a certain sense a rather new one. While, for instance, the vacuum enclosure of a TV picture tube serves nearly no other purpose but to permit achieving a low internal pressure, the envelope of an image tube is used in many instances as part of the electron optical system. In principle, this new requirement means that tolerances previously frowned at in glass technology are now asked for by the electron optical designer. It may mean also that new physical and chemical requirements will have to be fulfilled.

e) *The tube envelope should be an integral part of an external light optical system.*—An image presentation device serves as a component of an image presentation system. Thus, a (light) optical system is generally used on the input and/or output of the image tube. If the input and output windows consist of "clear" glass, only the optical quality of this glass, parallelity of internal and external surfaces, and the index of refraction as well as a possible curvature, is of importance. If, however, fiber optical windows are utilized, the field flattening properties of such components and possibly lens equivalent effects (in the case of tapered fiber bundles) will have to be considered. The optical requirements of the tube envelope, while previously of only secondary importance, are now assuming a greater weight in tube design.

f) *The tube envelope should be an integral part of an energy converting system.*—The devices discussed here, while referred to as information presentation devices, belong actually to the larger group of energy converting devices. This means that the energy fed into the device experiences one or more conversions before it is utilized at the output. Conventionally, the energy conversion occurs in certain tube components enclosed by the tube envelope. It is, however, quite possible to visualize that, for instance, the entrance window of an image tube serves as energy converter for X-rays (X-ray fluorescent glasses).

Energy converting layers, such as encountered in X-ray image tubes and conventionally housed inside the vacuum enclosure, may be arranged outside the entrance window if a fiber optical element is used on the tube entrance. For the obvious reason of maintaining resolution, such an energy converting layer has to be in intimate contact with the fiber component;

thus, chemical interaction, indices of refraction, microgeometry of the fiber surface, etc., are points of concern.

3.2 *Envelope Material*

In principle, four types of envelope materials appear to be applicable, namely glass, metals, ceramic and plastics.

Glass as envelope material has the advantage of a long history in this use. It can be worked relatively easy; seals of various types to other glasses and metals of matching or non-matching coefficient of expansion can be achieved. Some of the glasses available nowadays are quite transparent to most of the electromagnetic radiations one might be interested in, namely visible light, X-rays, infrared, etc. However, the chemical and vacuum properties of certain glasses are not beyond reproach. It is, for instance, quite difficult to outgas and clean a glass surface thoroughly. The well known application of vacuum heating combined with a glow discharge may not be suitable in all instances. Further, the mechanical rigidity and the ability to withstand accelerations of high g-values and high energy impact may be undesirably low.

Thus, *ceramic* as tube envelope material appears to be gaining increased importance. However, the sealability of ceramics, necessitating special techniques, as well as surface resistance properties do not appear to facilitate a universal application.

Metal envelopes have certain advantages such as weight and relative ease in forming techniques, but may show a higher permeability to gases and suffer from the lack of electrical insulation. However, special presentation devices have been constructed successfully with metal envelopes (including aluminum).[2]

Mentioning *plastics* in conjunction with vacuum systems appears to be a rather surprising undertaking. It is well known that the vapor pressure at room temperature of common plastics is relatively high, making it nearly impossible to achieve low residual pressure values in a vacuum enclosure. It should be noted, however, that developments in the field of plastic are progressing at a very rapid pace. Some of the modern plastics and thermo-setting resins can be utilized and are actually applied in high vacuum tubes.[3] The vapor pressure after proper treatment is sufficiently low to permit such a use. Thus, it may not be too far fetched to anticipate a possible application of re-enforced plastics for certain parts of tube envelopes.

3.3 *Envelope Assembly*

In general, the envelope of a vacuum device consists of several parts which have to be assembled either before or after certain critical processing steps have been carried out. These processing steps pertain in general to energy converting components enclosed by the envelope and are mostly carried out under high vacuum conditions. This means that the technique applied to sealing tube components is subjected to certain limitations such as temperature, humidity, chemical interactions, etc.

Furthermore, the tube envelope may consist of unlike parts such as glass and metal, glasses of different coefficient of expansion, clear glass

and fiber components, etc. It will be appreciated that some of the seals required are indeed quite difficult to make.

It has been inferred here that the sealing of the tube envelope is one of the decisive steps in making a successful device. Some of the sealing techniques presently applied will be discussed as examples. Thereafter, the system functionality of the envelope shall be elaborated on in detail. Finally, techniques of opening an envelope without destructing sensitive energy converting components and necessitated by specific applications such as in electronography shall be described.

4. ENVELOPE SEALS

It is not the task of this paper to develop a complete listing of all possible seals which could be utilized between all possible envelope materials. Specifically, ceramic-to-metal seals and the potential application of plastic materials as part of the tube envelope will not be elaborated on.

The application of conventional and some novel sealing techniques will be described of selected on hand examples only.

4. *Hot Seals*

Hot seals between glass and glass are based in principle on diffusion of the liquefied glasses. In the case of the glass-to-metal seal a reliable bond can be achieved between the molten glass and an oxide layer on the metal. A hot seal can be applied only if the developed heat does not effect adversely components already in the tube envelope.

The necessary heat may be applied either by flame heating or by radio-frequency heating. As a variance, Joule heating may supplement other heat sources after the glass conductivity has been increased due to preheating.

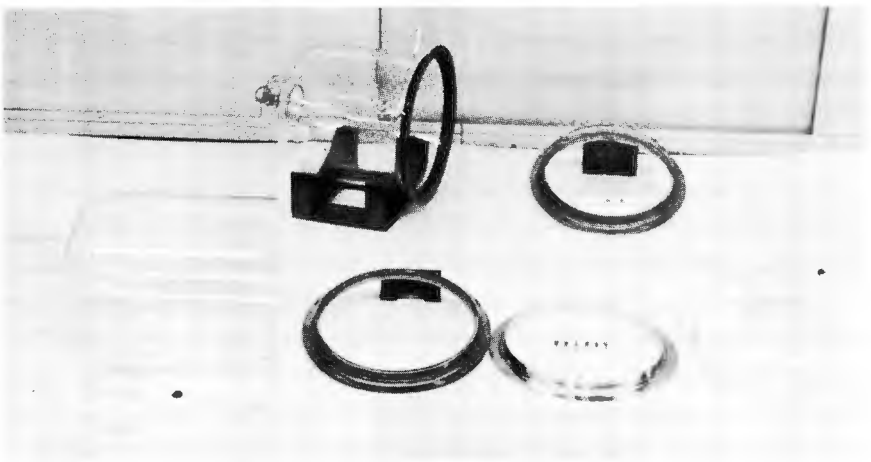

Figure 2
Consecutive Steps in Manufacturing a Large Diameter, Hard Glass Image Tube Envelope (Housekeeper Seal)

As an example of flame seals of the glass-to-glass and glass-to-metal type, the manufacture of a large diameter, hard glass image tube envelope will be described (Fig. 2). In this case, a 10″ diameter cylindrical envelope consisting of kovar sealing Corning glass, type #7052, is joined to a 10″ diameter kovar metal flange by means of a "housekeeper" seal. The large diameter kovar metal flange is hydrogen fired, subsequently oxidized and glazed with Corning #7052 glass. The final seal is made between the glazing and the cylindrical glass envelope.

At the other end of the cylindrical glass envelope a re-entrant type seal is made between a cup shaped part and a bottle-neck type termination of the tube envelope. The output window carried in the cup shaped part consists of optically clear kovar sealing glass Corning Type #7056, and the rest of Corning glass #7052 or Kimble glass #650.

A glass-to-metal seal as described here has varying properties depending on the degree of metal oxidation. A silvery appearance of the glass-to-metal sealing area indicates a "metallic seal" or a lack of oxide formation. A seal of this type is mechanically rather weak. A sealing area appearing quite black might indicate overoxidation of the metal part. Such a seal may show small leaks.

While glass-to-metal seals of the type described here may prove to be perfectly vacuum tight after annealing, subsequent (chemical) treatment of the sealing areas may result in leaks.

It is obvious that the metal kovar flange will experience surface oxidation over its entirety during the sealing process. These surface oxides have to be removed as they may lead to deterioration of the tube performance or may make it impossible to carry out subsequent assembly steps. Thus, the flanged tube envelope is subjected to a chemical cleaning process ("pickling"). If the sealing area has been overoxidized, the chemicals used in pickling may penetrate into the micropores of the oxide and create a leakage path.

Furthermore, chemicals having penetrated into the oxide interface layer are difficult to be removed and may represent a virtual leak after completion of the tube.

As the envelope discussed here is the vacuum enclosure of an image tube, the seal-areas are exposed to highly reactive alkali metal vapors during processing of the photocathode. Vapors such as cesium may reduce the metal oxides and may result in leaks developed during tube life. Thus, it is obvious that the oxide formation will have to be controlled with utmost care.

The same tube envelope carries electrical contacts of the conventional small ball type. Overoxidation or burning of these contacts before sealing, combined with the subsequent chemical cleaning, may lead to a high occurrence of vacuum leaks in this area, particularly as these contacts are subjected to a spot welding operation.

While the hot seals described here are made in conventional manner by the use of burners and are novel possibly only in their dimensions and with respect to the stringent requirement on the oxide interface layer, heat seals of the *butt type* may be carried out by radio-frequency heating

Figure 3
Image Tube Envelope with Butt-Seals

of a metal component (Fig. 3). In these cases, the metal flange is flat and a cylindrical glass section is pressed against it in a lava jig. Preliminary auxiliary heating may be carried out by the application of burners and, subsequently, the metal component is heated by induction at radio-frequencies. While the housekeeper type seal described above does not lend itself readily to tight axial tolerances, an RF seal as mentioned here permits axial tolerances of ± .002″ with proper lava jigging. It will be appreciated that the above remarks, pertaining to the oxide layer, are also applicable here if the envelope in question is used for an image tube.

As mentioned already, heat seals are not always applicable. Thus, the next section will deal with so-called "cold" seals, that is, seals carried out at room temperature or at temperatures appreciably below the softening point of glass.

4.2 *Cold Seals*

4.2.1 *Frit Seals*

A glass frit seal is not a truly cold seal as the entire tube envelope is generally heated to the melting temperature of the glass frit. However, low melting glass frits are available which permit achieving a vacuum tight seal at temperatures appreciably below the softening point of the envelope material.

The main advantage of a frit seal is its relative freedom of distortion in the sealing area. Thus, a frit seal may be applied with advantage to the sealing of fiber optics components (see later).

After completion of such a seal, a frit surface may be exposed to the vacuum volume of the tube envelope. As frits consist of powdered glass and are generally applied by forming a paste of the powdered glass and a suitable binder (for example, nitrocellulose, oxidized by air-baking), the vacuum properties of the exposed frit as well as the surface geometry warrant some consideration. In general, frits may have a rough (or porous) surface and may be difficult to outgas. Further, the rough surface may act as getter for, say, alkali metal vapors liberated in the envelope volume during certain processing steps. It is of advantage to seal off exposed

frit surfaces by evaporating a metal layer after proper surface polishing whenever possible. More about frit sealing will be said in Section 4.3.

4.2.2 *Arc Welding*

The kovar flange envelope construction discussed previously lends itself readily to effecting a final envelope seal by arc welding along the rim of the kovar flange (Fig. 4). Such a sealing method, a truly cold seal, is not new but has been applied extensively in tube technology, among others also in the construction of early color TV picture tubes. It should be noted, that the heat sinks normally applied from both sides in the form of copper cooling rings, pressed against the components to be joined together, subject the kovar flanges easily to a bending momentum which in turn may lead to cracking of the glass-to-metal seal.

4.2.3 *Conventional Indium Seals*

Envelope components may be joined together in a vacuum tight manner by the use of an indium washer exercising a pressure of approximately 600 psi. As the indium (or in some instances "indalloy" consisting of 50 parts indium and 50 parts tin) is a soft material, it binds rather well to a glass surface effecting vacuum tightness. It is important that the sealing surface is properly polished and cleaned.

As the melting point of indium is low (150°C., indalloy 125°C.), envelopes prepared by indium seals are restricted in their exhaust temperature. A novel type of indium seal circumvents this draw-back.

4.2.4 *Bakeable Indium Seal*

A bakeable indium seal[4] takes advantage of the low vapor pressure of molten indium (10^{-11} Torr at 350°C.). The seal geometry restrains the indium in such a way that even in the molten stage it can not reach the

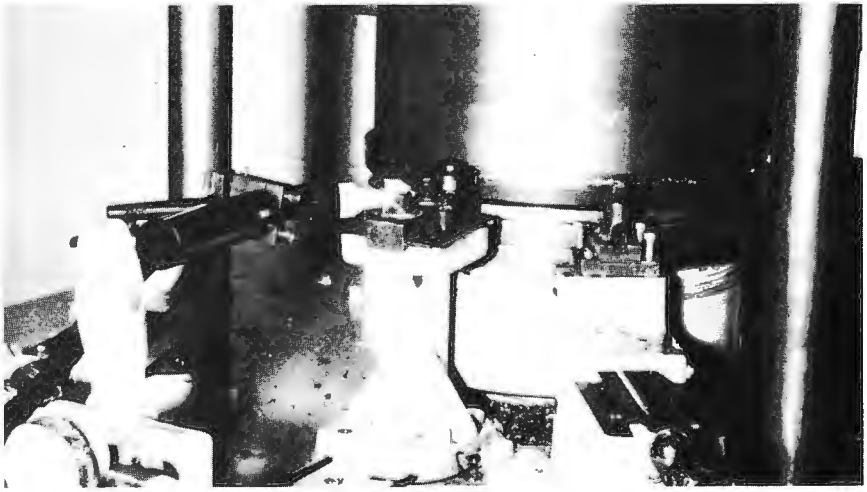

Figure 4
Arc-welding of Image Tube Envelopes

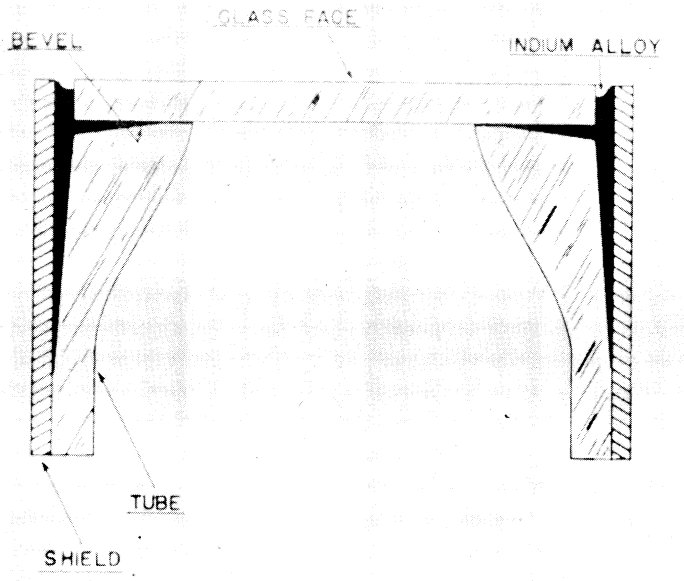

Figure 5
Geometry of a Bakeable Indium Seal

vacuum enclosure and can not leave the sealing area (Fig. 5). Seals of this type have been made successfully between components of different thermal expansion such as soft glass (type G-12) and pyrex. These envelopes have been exhausted at temperatures of 380°C.

4.2.5 *Pinch Seals*

Soft metal such as copper may form a vacuum tight seal by simply pressing two surfaces together with considerable force (300,000 psi). Tube parts may be sealed together by pinching copper in a similar manner as copper tubulation may be pinched off. This seal is made, of course, at room temperature and is thus a genuine cold seal. However, care has to be taken that the extremely high pressure, necessary to effect a vacuum tight copper pinch seal, does not damage the seal between the copper surfaces and the tube envelope.

4.3 *Sealing of Fiber Optical Components*

The sealing of fiber optical components warrants special considerations. The difficulties of joining a fiber optical component to a tube envelope are caused by the coefficients of thermal expansion of the core and cladding of the individual fibers forming the fiber component, as well as by difficult seal geometries required for proper device design.

As one will recall, a fiber optical component consists of a fused mosaic of (small diameter) glass fibers of high index of refraction each surrounded by a thin cladding of low index of refraction (Fig. 6). The cladding may be rendered partially light absorbing by diffusing a dye from the outside into the cladding during the fiber pulling process (extramural

Figure 6
Examples of Fiber Optical Components

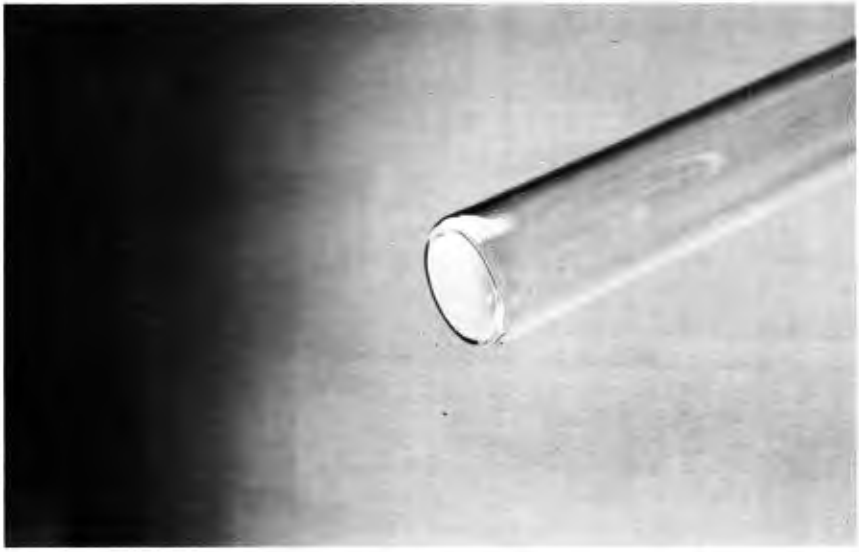

Figure 7
Flame Seal of a Fiber Component to Glass

absorption, EMA). Interstitial absorption by essentially opaque fibers may be introduced to enhance the obtainable contrast in a similar manner as achieved by EMA.

In some instances, the fiber component is enclosed into a clear glass cylinder. The effective thermal expansion of a fiber component is an average of the different thermal expansions of core and cladding glass. The small diameter of the cores makes it possible that the cladding may be fused to the core even at appreciable differences in thermal expansion.

Flame sealing of fiber components has to be carried out with utmost care to avoid excessive distortions of the fibers in the seal area. A typical flame seal is shown in Fig. 7.

Frit sealing may be the preferred method due to the lower probability of distortion. However, frit sealing should, by preference, be carried out between a clear glass skirt surrounding the fiber component and the tube envelope, as the locally different coefficient of expansion in the fiber area may lead to difficulties.

A typical geometry for a frit seal between a fiber component and a metal flange is shown in Fig. 8. One will notice that the external atmospheric pressure the tube envelope experiences after evacuation drives the frustoconical fiber component into the aperture of the metal flange, thus strengthening the seal. Butt type frit seals between fiber components and metal flanges are only advisable if the pressure on both sides of the component is comparable, as otherwise cracking of the frit seal might occur.

The optical properties of fiber components depend upon the indices of refraction of the core and the cladding and thus upon the glass composition and the coefficients of thermal expansion. Unfortunately, some otherwise preferable fiber optical components possess an expansion of approximately $80 \times 10^{-7}/°C$ (at 300°C). This expansion range is not very well covered by suitable envelope materials but the possibility of sealing such fiber components to metal flanges (such as columbium) exists. Indium type seals as discussed above are normally considered an advantage here.

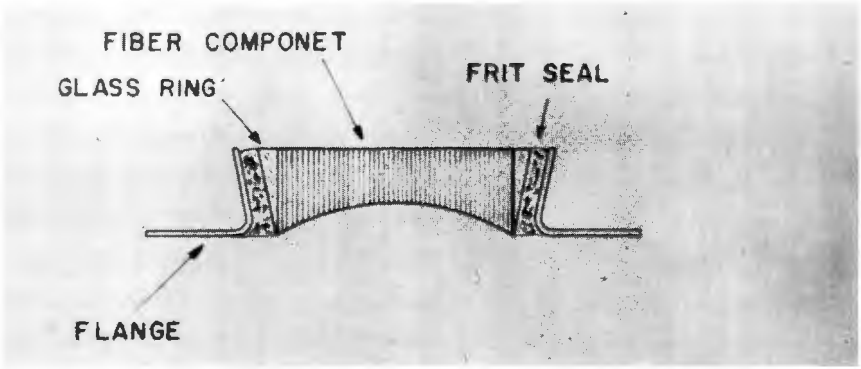

Figure 8
Frit Seal Between Fiber Component and Metal Flange

It should be noted that a certain mismatch between the thermal expansion of fiber components and the envelope material may be tolerated provided the seal geometry preserves a certain elasticity or the fiber component has a rather small diameter. A re-entrant type seal mentioned previously is a flexible seal. For the seal geometry shown in Fig. 9 it was possible to flame seal pyrex against kovar glass without experiencing cracking.

An unusual and somewhat difficult seal is the insertion of a fiber optical component into the faceplate of a relatively large cathode ray tube. Such seals have been made by fritting using seal geometry similar to that shown in Fig. 8. A photograph of such a seal, showing the faceplate of a special radar display tube, is depicted in Fig. 10.

5. TUBE ENVELOPE AS FUNCTIONAL PART OF THE ELECTRON OPTICAL SYSTEM

Every information display device uses an electron optical system and a phosphor screen. While conventional types of display devices utilize an electron optical structure entirely independent from the tube envelope and mounted to the vacuum enclosure for reasons of mechanical support, some of the novel display devices such as large diameter image tubes utilize a metal coating evaporated onto the inside of the tube envelope as part of the electron optical system. In these cases, the requirements on the roundness of the cylindrical tube part, axial dimensions, etc., are rather tight ones. For instance, the image tube structure, shown in Fig. 11, necessitates roundness tolerances of ± 0.6% in 10" diameter and axial dimensional tolerances of ± 10% in 16" overall length. It is obvious that selected

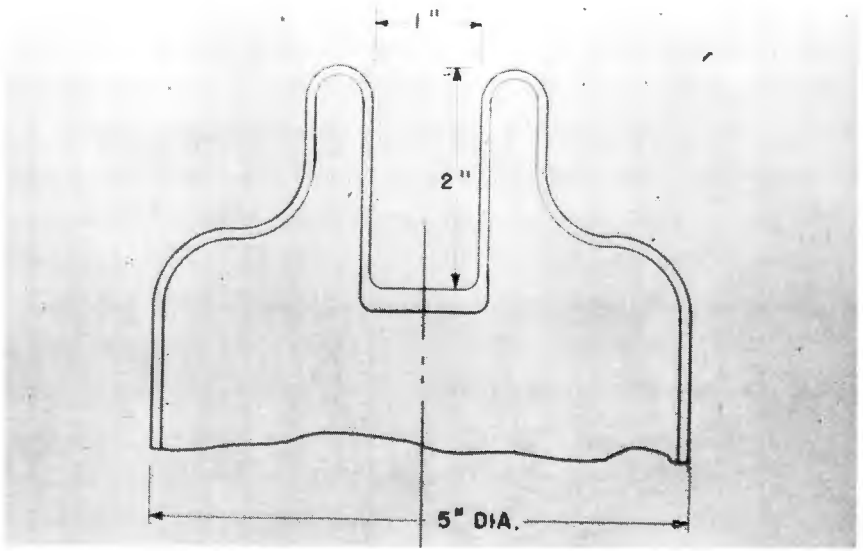

Figure 9
Flexible Re-Entrant Type Seal

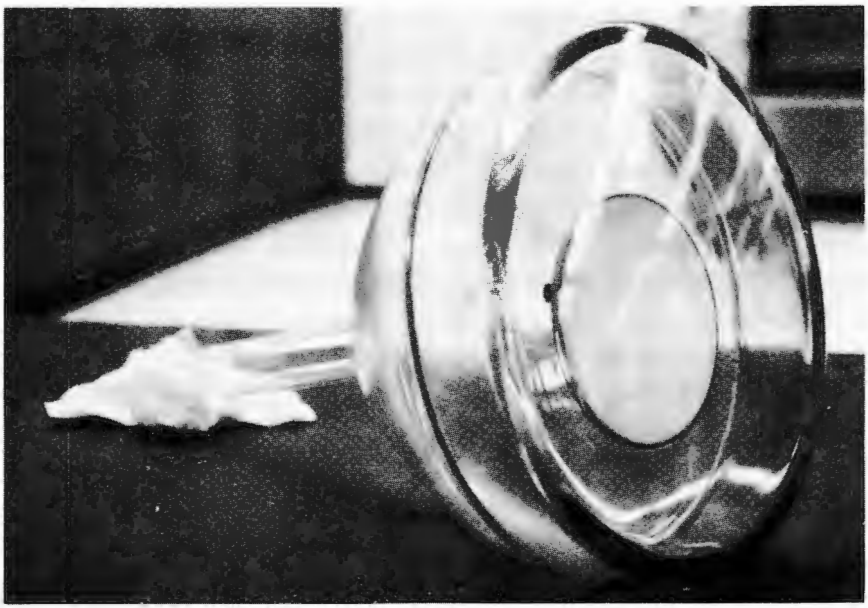

Figure 10
Fiber Optical Component Sealed into a Large Area Clear Glass Tube Faceplate

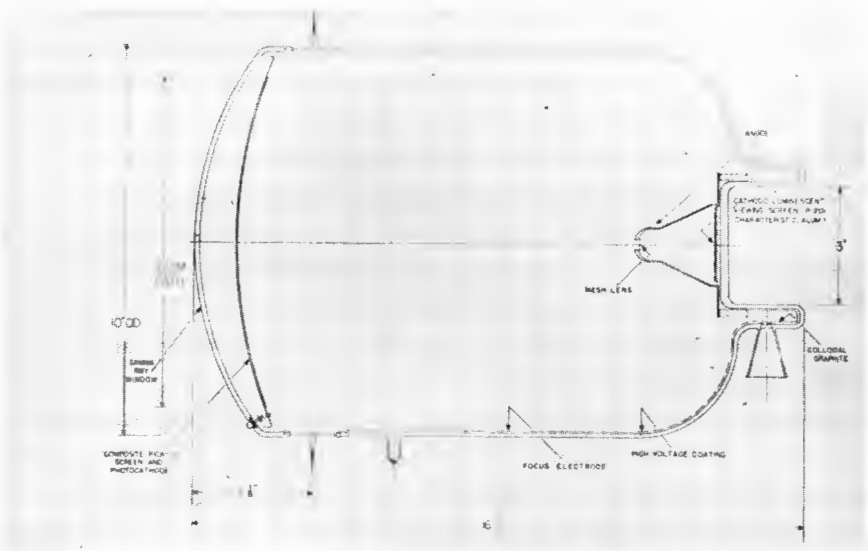

Figure 11
Image Tube Structure with the Tube Envelope Forming an Integral Part of the Electron-Optical System

tubing will have to be used in some instances and that utmost care has to be taken to avoid local deformation during sealing operations.

It has been mentioned already previously that input and output windows of image tubes form inherent parts of external light optical systems. In these cases, the unavoidable deformation in the sealing area should be restricted so that the usable diameter approaches the physical tube diameter.

6. CHEMICAL AND PHYSICAL PROPERTIES OF THE ENVELOPE MATERIAL

6.1 *Envelope Material and Signal-to-Noise Ratio*

The signal-to-noise ratio in image tubes should be maintained at as high a level as possible to facilitate proper contrast-detail reproduction.[5] This means that the noise introduced by the device itself should be minimized so as to permit the image tube to operate at the noise level of the photosensitive cathode.

One of the noise sources encountered in image tubes is electron emission at room temperature from low potential electrodes (either metal electrodes supported by the tube envelope or metallic evaporated wall coatings). The probability for "cold" emission is enhanced by the adsorption of alkali metal vapors used in tube processing.

The problem of device noise and cold emission is a very serious one in image tube technology. It is nearly impossible to keep an internal uncoated glass surface sufficiently clean as to inhibit the (semi) permanent adsorption of alkali metal vapors. While the potential distribution along a clean glass surface between a low potential and a high potential region may be described as shown in Fig. 12 (curve A), the formation of islands of high conductivity due to alkali metal vapor adsorption alters the potential distribution as depicted in Curve B, of the same figure. As the probability of cold emission increases strongly with increasing slope of the potential distribution, the device noise is higher for the distribution of Curve B.

The strongly varying slope of the potential distribution can be smoothed in the region under consideration by either increasing the bulk or surface conductivity of the glass. In the neck region of TV picture tubes, where similar considerations hold true, European glass technology has chosen to experiment with increased *bulk* conductivity. In the case of image tubes it proved worthwhile to increase the *surface* conductivity of the glass by application of a suitable coating, gettering alkali metal vapors during processing.[6]

As ceramic materials have in general a resistivity exceeding that of glass, the application of ceramic envelopes to certain image tube structures may lead to difficulties. Specifically, the high resistivity of ceramic suggests avoiding choosing the tube envelope as integral part of an electron optical system.

6.2 *Chemical Interaction between Envelope Material and Electron Sources*

Thermionic or photoelectric cathodes, used as electron sources in practically all information presentation devices, show the tendency to be

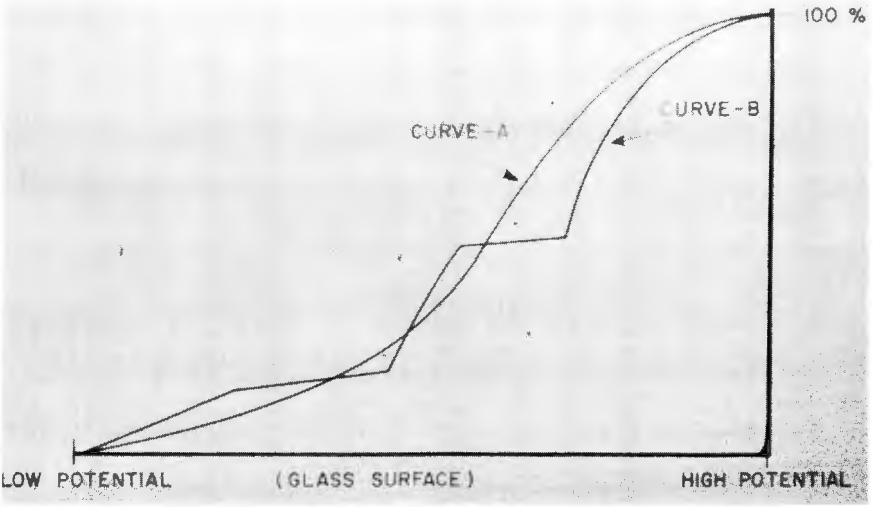

Figure 12

Potential Distribution Between the Low and High Potential Region of an Image Tube Along a Glass Surface Shown Schematically:

Curve A: Clean Glass Surface

Curve B: Glass Surface with Locally Adsorbed Metal Vapors (such as Cesium)

poisoned or deactivated quite readily by a large number of materials. For instance, oxygen, sulphur, carbon dioxide, chlorine, alkali halides, etc. may trigger chemical reactions virtually destroying these electron sources. Thus, it is an understandable desire that the envelope material used should not release these materials neither during sealing, during vacuum exhaust nor during activation of the electron sources.

Experience has indicated that certain glasses, otherwise quite suitable for the envelopes of information presentation devices, release alkali halides during sealing operations damaging thermionic sources. Suitable sealing techniques or the use of special getters in the tube envelope[7] inhibit the damaging effects of the alkali halides to some extent. However, the application of such glasses should be avoided whenever possible.

The same type of glass proves also troublesome in photoelectric devices. There appears to be a chemical interaction between alkali metal vapors and the glass to such an extent that heating of the tube envelope after exposure to alkali metal vapors, releases poisoning agents deactivating photosensitive cathodes.

One possible remedy in this case is covering the internal surfaces of the envelopes with suitable coatings such as evaporated aluminum, tin oxides, chromium oxide, etc. In these cases, poisoning effects are not observed or at least reduced greatly.

6.3 *Considerations pertaining to the External Envelope Surface*

As glasses may have a rather high dielectric constant, charging of a glass surface by capacitive coupling to the surround is quite possible. It

has been observed, for instance, that image tubes operated in the reverse, that is, the output screen grounded and the electron source at a high negative potential, may experience a periodic discharge rendering these devices inapplicable for the intended task. Increasing the conductivity of the external glass surface by use of a lacquer coating of a resistivity by 2-3 orders of magnitude lower than that of glass is generally found to be of advantage. Equally, the use of a so-called Leyden-bottle external electrostatic shield inhibits such periodic discharges.[8]

As the tube envelope forms an integral part of the electron optical system in some image tube designs, as referred to above, external charging of the envelope with the ensuing capacitive coupling to the inside, yielding internal charging, may introduce a slow, time dependent variation of the electron optical performance of such devices. As the external charging may not only be capacitive but may also be due to charge leakage cause, for instance, by humidity condensation, the external glass surface should be water repellent. Unfortunately, this problem does not appear to be an easy one to solve. It is well known that extremely clean glass surfaces adsorb water molecules under high ambient humidity conditions. The application of so-called water repellent lacquer coatings is not always very successful.

7. OPENING OF VACUUM ENCLOSURES

In some instances, the opposite of sealing vacuum enclosures, namely opening of tube envelopes, is required to render tubes operable. For instance, in an electronographic system, an image tube is prepared without a phosphor screen. Subsequently, the anode end of the image tube is inserted in a continuously pumped vacuum system and a previously vacuum tight enclosure has to be removed to permit electrons to impinge upon a photographic emulsion enclosed by the continuously pumped vacuum system.

It is possible to crack a glass envelope in vacuum along a pre-ground groove.[6] While cracking of glass in air is based upon differential heating of the envelope thus introducing strain, differential heating of a tube envelope in vacuum can not be achieved quite readily due to structural difficulties and due to the absence of convection cooling as effected by the presence of room air. However, surrounding a radial groove, pre-ground into the glass envelope, by threaded tungsten wire and heating the tungsten by current flow results in localized wetting of the hot tungsten wire to the (kovar) glass envelope. In cooling, the differential thermal expansion of tungsten and glass results in strain and yields a clean glass cut.

8. SUMMARY AND CONCLUSION

Information presentation devices have gained increasing importance in visual telecommunication, data processing, nuclear instrumentation, space sciences, medicine and warfare. As most of these devices require a vacuum enclosure and at least one window transparent to visual radiation, glass is utilized for the tube envelope as a whole or in part. The impact of glass technology on device design and performance is illustrated in this paper by selected examples.

Some of the solid state and electron physical components utilized in modern presentation devices necessitate low temperature seals. Examples for such techniques are elaborated on in this discussion.

The progress achieved in the field of fiber optics permits constructing the tube envelope as part of an (external) light optical system. Glass technological problems, pertaining to the fabrication of vacuum enclosures with fiber optic windows, are discussed in a summarizing form.

The fundamental importance of the tube envelope may exceed that of a mere vacuum enclosure. In image intensifiers, for instance, the envelope may be an integral part of the electron optical system requiring assembly techniques which yield tight tolerances.

In addition to the geometric form of the (glass) envelope, the physical and chemical properties of internal glass surfaces are of great importance for proper device performance. Resistivity against interaction with highly reactive chemicals used in tube processing, surface conductivity and micro geometry, etc., co-determine the device noise, one of the most important parameters.

The practicability of (vacuum) electronography is dependent upon opening vacuum devices in a controlled manner in a vacuum ambient. A relevant technique is described.

In conclusion it can be stated that the solution of glass technological problems is still the prerequisite for the successful development of novel information presentation devices.

ACKNOWLEDGMENT

Information presentation devices can neither be developed nor produced without the assistance of an excellent glass technological department. It is only proper to acknowledge here the technological contributions made by members of the Glass Department of the Rauland Corporation, particularly Mr. Harry Voelz, supervisor and Mr. Sam Galfano, assistant supervisor. The continuous encouragement and guidance by Dr. C. S. Szegho, Vice President in charge of research, was decisive in executing the Rauland's Corporation program in the field of information presentation devices.

REFERENCES

1. Bartholomew, C. Y., "Impurities Introduced into Kovar Envelope Electron Tubes by Atmospheric Corrosion", Lect., Electron Devices Meeting IRE-PGED, Washington, D. C., (1958).
2. Lueckerath, W., Fink, K., Flossman, R., Stahl und Eisen, 79/22, p. 1637 (1959).
3. Niklas, W. F., *Am. J. Roetgenol Rad. Therapy and Nuclear Med.*, 85, p. 323 (1961).
4. Pakswer, S., Dowd, J., *Rev. Sc. Inst.*, 39/7, p. 789 (1962).
5. Dolon, P. J., Niklas, W. F., "Quantum Statistics of X-Ray Image Intensifying Systems for Fluoroscopy", Lect., Colloquium on Diagnostic Radiologic Instrumentation, University of Chicago, (1962).
6. Hiltner, W. A., Niklas, W. F., Advances in Electronics and Electron Physics, Acad. Press New York and London, XVI, p. 37 (1962).
7. Kern, H. E., Graney, E. T., Feder, D. O., "Glass Envelope Composition as a Factor in Oxide Cathode Poisoning", Lect., Electron Devices Meeting IRE-PGED, Washington, D. C., (1958).
8. Hiltner, W. A., Priv. Comm. (1963).

RADIATION EFFECTS ON GLASS

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Scientists who are fortunate enough to have experienced glassblowers available learn to rely on their knowledge and judgment as to the proper glasses to use in the fabrication of apparatus. This knowledge comes from training, experience, technical papers and symposia such as this.

Due to the increased use of radioactive substances in research and development, the scientific glassblower is being called upon more often to know about radiation effects on glass. From the viewpoint of fabrication of apparatus, discoloration and radiation damage are the most important effects. However, thermoluminescence, the emission of light upon heating, and triboluminescence, the emission of light upon applying mechanical strain, subsequent to irradiation are also important phenomena.

Before discussing these effects it may be advisable to briefly survey the principles involved. High energy radiations or ionizing radiations are emitted from radioactive substances. They are also produced in high energy accelerators such as the Van de Graaff generator, cyclotron, etc. and in nuclear reactors.

These ionizing radiations fall into three general classes; photons, charged particles and neutral particles. Some of the more common ionizing radiations and their physical properties are shown in Table I. Photons

SOME COMMON HIGH ENERGY RADIATIONS

RADIATION	SYMBOL	CHARGE	MASS (AMU)
I. PHOTONS			
X-RAYS	X-RAY	0	0
GAMMA-RAYS	γ-RAY	0	0
II. CHARGED PARTICLES			
ELECTRON (NEGATRON)	e^- or β^-	−	$\sim 1/2000$
POSITRON	β^+	+	$\sim 1/2000$
PROTON	p or H^+	+	1
ALPHA PARTICLE	He^{++} or α	++	4
III. NEUTRAL PARTICLE			
NEUTRON	n	0	1

Table I

*Operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission.

have neither mass nor charge. The charged particles all have mass and charge, whereas the neutron, a neutral particle, has only mass.

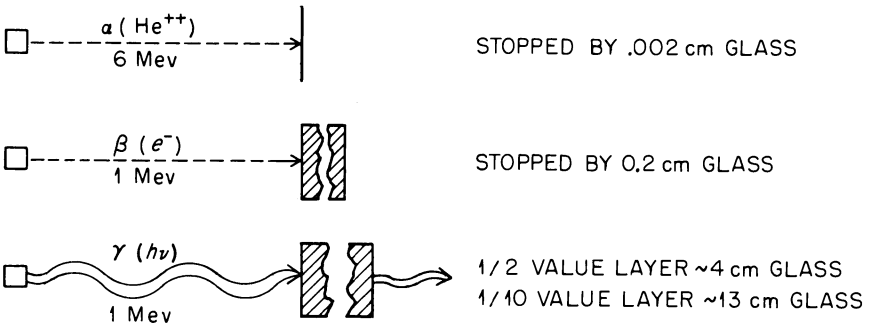

Figure 1
The range of several ionizing radiations in glass of normal density.

Various radiations have different ranges in a given medium. This is shown in Fig. 1 for three different radiations as they traverse glass having a density of about 2.3 gm/cc. Due to their heavy mass, alpha particles (α-particles) which are doubly charged helium ions (He^{++}) lose their energy very rapidly. A 6 Mev (million electron volts) α-particle will be completely stopped by 0.002 cm of glass. An electron (e^-) of 1 Mev will traverse 0.2 cm of glass before it is stopped. Gamma-rays (γ-rays) are so penetrating that instead of considering the thickness of material necessary to stop them, we consider the thickness of material necessary to reduce the energy of the emergent photon to a given fraction of the incident photon. Thus, after a 1 Mev γ-ray passes through 4 cm of glass it will have a residual energy of ½ Mev. This is referred to as the ½ thickness layer.

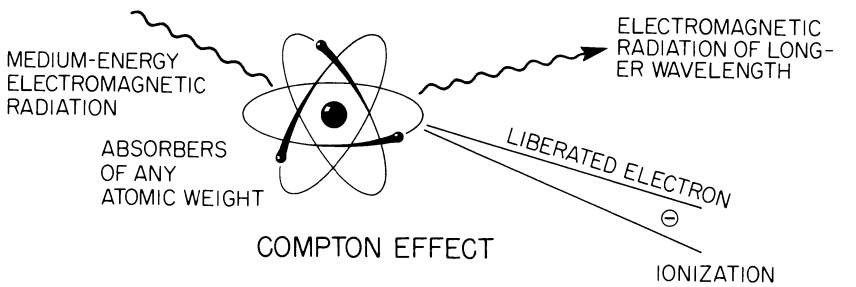

Figure 2
Energy loss of gamma-rays of about 0.2 to 2 Mev by the Compton process.

In each class, the radiations lose their energy, as they traverse a medium, by different processes. The photons transfer energy to electrons of the molecules being irradiated. This energy may be much greater than the binding energy of the electron in which case the electron is ejected from its molecule leaving an ion. Since the original molecule was electrically neutral the loss of an electron leaves the residual with a positive charge. This charged residual is an ion. There are three processes involved in the attenuation of photons, however, only the Compton effect is important in the irradiation of glasses. This is illustrated in Fig. 2. Energy from a photon of about 0.2 to 2.0 Mev is absorbed by a molecule liberating an energetic electron and a photon of less energy than the incident photon. The liberated electron can produce further ionizations by the process for charged particles.

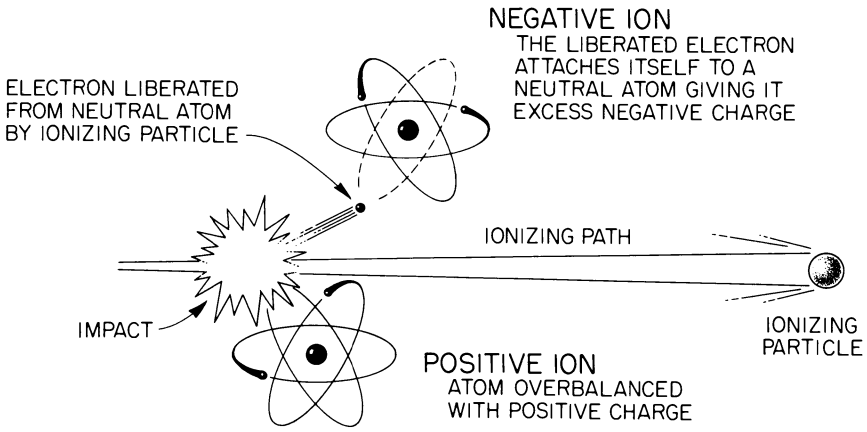

Figure 3
A schematic representation of the process of ionization by a charged particle.

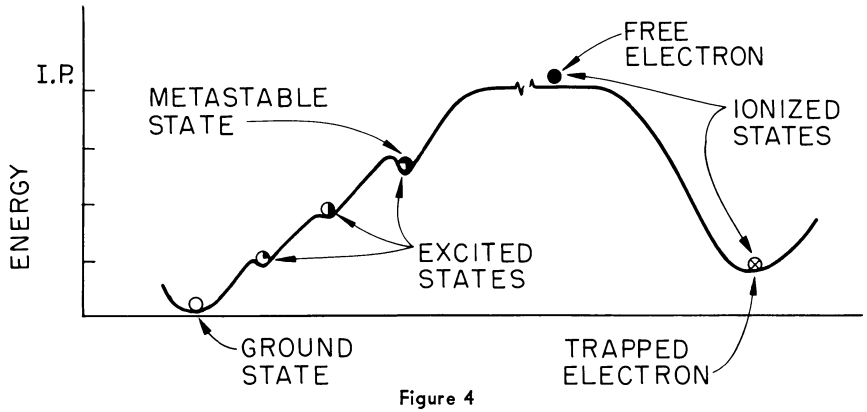

Figure 4
Schematic model of various energy states of an atom or molecule subjected to ionizing radiation.

High velocity charged particles lose energy by "collisions" with molecules due to electrical interaction with the electrons of the traversed medium. This is illustrated in Fig. 3. The electrons thus affected may be ejected from their molecules (ionization). The original particle produces many ionizations and each of the ejected electrons can cause additional ionizations until the particles (original particle and secondary electrons) lose most of their energy (thermalization). These degraded electrons (primary and secondary) can, in some cases, be captured by a neutral molecule to produce a negative ion, can neutralize a positive ion to reform a neutral molecule, or excite electrons within a molecule to a higher energy level (excitation) or can be captured by lattice defects in the case of solids. Fig. 4 shows a schematic model for some of these processes. An electron in its ground state, on absorption of energy, can be raised to a higher electronic level or excited state within its own molecule. These electrons usually fall back to the ground state with the emission of light. If the excited state is a metastable level, the electron will remain there until it receives, by some process, enough energy to get out of the "well" and fall back to the ground state with the emission of light.

If the electron absorbs sufficient energy to overcome the binding energy it can be liberated from its original molecule. This free electron can travel appreciable distances compared to the size of a molecule. When this electron has degraded below the binding energy, or ionization potential (I.P.), it can be captured or trapped by a hole in a solid.[1] Holes are defects in solids due to electrical unbalance. The discoloration of glass is due to these trapped electrons. The effects of the above phenomena produced in a one-inch diameter silica rod are demonstrated in the photographs[2] below.

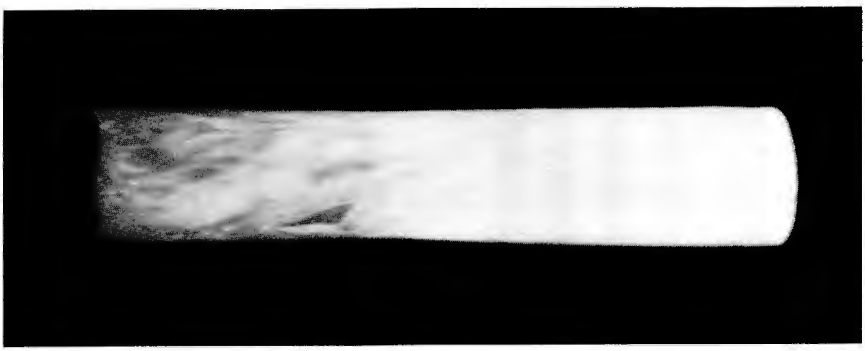

Figure 5

Brilliant pale blue, low temperature thermoluminescence of a one inch quartz rod which was irradiated with gamma-rays (1.3 Mev) at liquid nitrogen temperature. When the rod was removed from the liquid nitrogen and allowed to warm up in the air, it luminesced as shown. (Photo taken in darkened room).*

*Figs. 5 through 8 are a sequence of photographs taken in numerical order

[1]Solid State Physicists use different terminology to explain these phenomena. However, the fundamental principles are the same.

[2]The original pictures shown at the Symposium were in color.

The silica rod was irradiated at liquid nitrogen temperature with γ-rays and maintained at that temperature until photographed. The rod was removed from the liquid nitrogen and as it warmed up it luminesced with a brilliant pale blue light as shown in Fig. 5 (photo taken in darkened room). This luminescence was due to excited electrons, which were "frozen" in their higher energy states, falling back to the ground state. In doing so, they released their excess energy as light.

Figure 6
The quartz rod, colored deep purple, after low temperature thermoluminescence ceased.

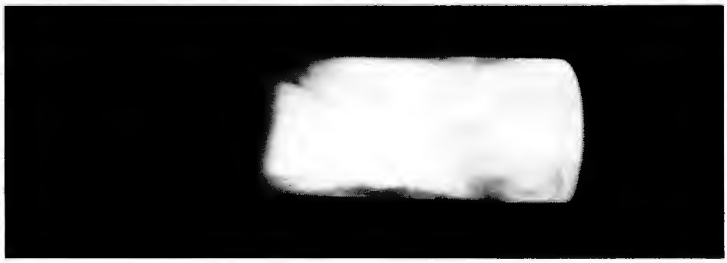

Figure 7
Deeper blue, high temperature thermoluminescence, produced by heating the end of the room-temperature rod with a gas-oxygen flame. (Photo taken in darkened room.)

After this initial luminescence stopped, the rod was colored deep purple as shown in Fig. 6. Part of the rod was then heated with a gas-oxygen flame and it luminesced again as demonstrated in Fig. 7 (photographed by its own light). This luminescence was a deeper blue than the low-temperature luminescence. The high temperature gave the trapped electrons sufficient energy to leave the holes and return to the ground state releasing their excess energy by the emission of light.

Figure 8

The heated end of rod shows complete disappearance of discoloration after high temperature luminescence ceases.

After the high-temperature luminescence subsided the heated portion of the rod was decolored as seen in Fig. 8. This series of photographs illustrates luminescence as excited and trapped electrons lose their excess energy, discoloration due to trapped electrons and the annealing[3] of the radiation effects.

If the rod had been irradiated at room temperature there would have been no visible post-irradiation low-temperature thermoluminescence. In this case the excited electrons would continuously cascade back to the ground state during the irradiation. The color due to trapped electrons, the high temperature luminescence and annealing could all be observed after room temperature irradiation.

Various glasses take on different colors upon irradiation due to their composition. For example, Pyrex turns brown, and phosphate glass becomes a ruby red. Ordinary silica becomes blue or purple, whereas, ultra-pure silica does not discolor under irradiation. The irradiation cell shown in Fig. 9 has a Pyrex stopper (brown), ordinary silica body (blue) and ultra-pure silica windows (colorless). Since the windows of this cell do not discolor, the same cell can be used for both irradiation of the sample and analysis by ultraviolet spectroscopy, eliminating the numerous transfers that were formerly required when separate cells were used for irradiation and analysis.

Glasses undergo changes other than discoloration when irradiated. These radiation damage effects are a function of both glass composition and the type of irradiation.

[3]Annealing as used herein means releasing radiation effects, hence, has a different context than annealing in the art of glassblowing.

Figure 9

An irradiation cell subjected to gamma irradiation. The body of the cell, made of ordinary quartz is blue. The windows made of ultra-pure quartz are colorless and the stopper made of Pyrex is dark brown.

SOME NUCLEAR REACTIONS RESULTING FROM SLOW NEUTRON BOMBARDMENT OF ATOMS COMMONLY FOUND IN GLASSES[a]

% ABUNDANCE OF TARGET ISOTOPE	NUCLEAR REACTION	RELATIVE CROSS SECTION	ENERGY RELEASE (Mev)
20	$^{10}B(n,\alpha)\ ^{7}Li$	35000.	2.8
100	$^{23}Na(n,\gamma)\ ^{24}Na^{*}$	4.8	7.0
0.037	$^{17}O(n,\alpha)\ ^{14}C^{*}$	3.6	1.8
97	$^{40}Ca(n,\gamma)\ ^{41}Ca^{*}$	1.8	8.4
3.1	$^{30}Si(n,\gamma)\ ^{31}Si^{*}$	1.0	6.6

*Product radioactive.

[a]Data from:

(1) D. T. Goldman and J. R. Stehn, "Chart of the Nuclides" (Knolls Atomic Power Laboratory) December, 1961.

(2) F. Everling, et al., "1960 Nuclear Data Tables" Part I (National Academy of Sciences) 1961.

Table II

In Table I a neutral particle, the neutron, of 1 AMU[4] was shown. The neutron can produce ionizations by indirect processes. However, more important, especially relative to effects on glass, is its power to produce nuclear reactions. Since the neutron is uncharged it can penetrate the electron cloud surrounding the nucleus of an atom and produce changes in this nucleus. A few nuclear reactions involving elements commonly found in glasses are shown in Table II. The first reaction will be discussed to explain this table. The naturally occurring isotopes of Boron are boron of 10 AMU's (^{10}B) and boron of 11 AMU's (^{11}B). The lighter isotope, ^{10}B, makes up about 20% of the naturally occurring boron. If ^{10}B is bombarded with a slow neutron it has a very high probability (cross-section) of absorbing the neutron and emitting an α-particle producing a new element, Lithium of 7 AMU's. The total energy released by this nuclear transformation is 2.8 Mev per event. The nuclear reactions depicted in Table II show: Target isotope (the bombarding particle, the radiation emitted) and the product isotope. The overall probability of a given reaction occurring can be considered as the product of percent abundance and cross-section. Thus the overall probability of the nuclear reaction with ^{10}B is 7000 compared to 4.8 for ^{23}Na for the same number of naturally occurring atoms in the same neutron flux. The product isotopes may be stable or radioactive.

The radiation damage due to high energy radiations as a function of glass composition is well illustrated in the case of neutron bombardment. Due to the ^{10}B content of Pyrex, apparatus made from it cannot be used in a neutron flux. The nuclear reaction causes rapid deterioration of the glass. It becomes brittle, develops cracks and breaks. Further, due to the high absorption of neutrons by the ^{10}B the neutron density inside the apparatus is low and variable, thus the scientist would have difficulty in calculating dose rates.

Soda-lime glasses and, to a lesser extent, Pyrex become radioactive due to the neutron reaction with the sodium component. The product isotope ^{24}Na is a very potent γ-emitter and represents a radiation and contamination hazard.

Even silica, which is used exclusively for reactor irradiations, becomes radioactive. However, the small cross section for nuclear reactions and low percent abundances of ^{30}Si and $^{17,18}O$ which give radioactive-product isotopes make silica the best glass for fabricating apparatus for reactor irradiations.

Silica, Pyrex and "soft" glass apparatus of normal wall thickness are stable to γ-rays under ordinary irradiation conditions. These photons produce Compton electrons in the glasses causing discolorations due to the trapping of the electrons. However, prolonged exposure to relatively high intensities of γ-rays does not produce structural radiation damages.

Pyrex and soft glass are not reliably stable to high intensity electron beams such as produced by a Van de Graaff generator. This appears to be a thermal effect due to the spot heating where the electron beam enters

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[4]AMU represents atomic mass uits, *i.e.*, 1/16 of the mass of 1 neutral $^{16}0$ atom, (*e.g.*, hydrogen atom (H) has $\sim$ 1 AMU, whereas, molecular hydrogen (H_2) has $\sim$ 2 AMU's).

the thin glass windows used in such applications. The localized high temperatures produced cause strains and consequent cracking.

Prolonged storage of α-emitters in silica or Pyrex produces cracks in these glasses. However, soda-lime and potash-soda-lead glasses can withstand α-irradiation for many years without visible signs of radiation damage. These glasses do, however, discolor.

High density (6.2 gm/cc) lead-silicate glasses have been developed for x-ray and γ-ray shielding purposes. Glasses containing as much as 81% lead oxide (75% lead metal) are produced commercially. Many of these high density lead glasses contain cerium oxide (CeO_2) which retards discoloration.

Figure 10

Triboluminescence, mechanically induced luminescence, of a lead-cerium glass. The glass had been irradiated with 1.5 Mev electrons and the discharge produced by tapping with a sharp tool just visible on the top center. Photo taken in a darkened room by the light of the discharge.

Presumably, the Ce^{+4} is reduced to Ce^{+3} by free electrons thus diminishing the trapping process. Prolonged exposure to very intense γ-radiation has cracked this glass by building up a static charge in the glass. Upon discharge it emits a burst of light and cracks develop in the glass. The same effect can be produced in short periods of time by irradiation with an intense electron beam. Fig. 10 is a photograph of this type of discharge. A piece of lead-cerium glass, 1″ x 1″ x 3/8″ was irradiated with 1.5 Mev Van de Graaff electrons at 10 microamperes for 20 seconds. The discharge was subsequently produced by a sharp tap with a centerpunch (just visible at top center of glass). The discharge produced all the light. This is an example of triboluminescence previously mentioned.

Research is in progress in many laboratories on radiation effects on glass. Relatively little is known about the fundamental processes producing these effects. These processes must be learned so that better glass, for use in the atomic age, can be developed.

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SUGGESTED REFERENCES FOR FURTHER READING

1. C. J. Hochanadel, "Absorption of Ionizing Radiations" in *Radiation Chemistry of Gases* by S. C. Lind (Reinhold Publishing Corp., N. Y., 1961).
2. N. J. Kreidl and J. R. Hensler, "Special Glasses for Nuclear Engineering Applications in *Modern Materials*, Vol. I, H. H. Hausner, Ed. (Academic Press, N. Y., 1958).
3. Proc. 4th Inter. Congr. on Glass, Paris, July, 1956.
4. D. S. Billington and J. H. Crawford, Jr., *Radiation Damage in Solids*, (Princeton Univ. Press, Princeton, 1961).
5. P. S. Rudolph, "The Irradiation of Glasses," *Fusion*, **9**, 9 (Feb. 1962).
6. K-H Sun and N. J. Kreidl, "Coloration of Glass by Irradiation," *Glass Ind.*, **33**, 511, 589, 651 (1952).

FIELD EMISSION MICROSCOPY

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I. INTRODUCTION

With the development of ultrahigh vacuum techniques in the last ten or fifteen years, several new methods for the study of surface chemistry and physics are now available. Three of the more outstanding of these are thin films, field emission, and field ionization. Scientists working on catalysis and adsorption have probably made more elaborate use of glass apparatus than any of the other sciences for the past forty years, and the involved systems for gas handling and purification employed are quite familiar.

However, the vacuum obtainable in unbakeable systems is inadequate for many investigations of surface phenomena. To illustrate, a system with a diffusion pump and glass stop cocks generally can attain a pressure not much better than 10^{-6} mm Hg or so. If in such a vacuum one prepares a surface which reacts with the gases present, it will be completely contaminated in about one second. Clearly, much better vacuums are necessary to keep surfaces clean for a time long enough to perform experiments on them. A pressure of 10^{-9} mm Hg is sufficient to keep a surface clean for about ten minutes, and this is about the upper pressure limit for experiments requiring "clean" surfaces. Further, although metal vacuum systems have been competing with glass in many applications, all glass systems have been used almost exclusively in field emission, and probably will continue to be preferred over metal.

II. PRINCIPLES OF OPERATION

The field emission microscope is a device for studying metal surfaces and reactions at these surfaces. It consists essentially of a metal needle or tip and a phosphorescent screen on which an image of the tip is produced.

The wire from which the tip is to be formed is attached to a heatable metal loop and then etched chemically to a fine point, generally having an end diameter of less than 1000 Å. This is then mounted on a high vacuum system. In operation a high voltage is applied between the loop and the screen such that the screen is at high potential. The small diameter of the tip causes an extremely high electric field near its surface. Voltages of about one kilovolt produce electric fields of about 0.3 v/Å, and this is sufficient to draw electrons from the cold metal tip. These electrons travel outward radially from the tip and strike the phosphorescent screen. An image of the metal tip is thus produced on the screen. Magnification of the tip is over 100,000, and the limit of resolution is about 10 Å. The field emission tip is almost always a single crystal so one can easily identify the various crystal planes by the relative intensity of electrons emitted from them.

To obtain a clean metal surface, the tip must be heated to high temperature by passing a current through the loop. This generally limits field

emission to refractory metals, although such metals as nickel and iron can be cleaned by the method of field evaporation.

III. MICROSCOPE CONSTRUCTION

The field emission tube is constructed of pyrex with electrodes in pyrex-nonex press seals. Many types of vacuum systems are used by various field emission groups. We obtain adequate pressures with a very simple system consisting of a two-stage mercury pump backed by a mechanical pump. The entire high vacuum side of the system is bakeable and consists of liquid nitrogen traps, a Bayard-Alpert ion gauge, and the field emission tube. Gas admission is *via* mercury cutoffs from gas sources when needed. After a two-hour bakeout and flashing metal parts, a pressure of 10^{-9} mm Hg is easily obtained.

Most of the microscope tube is of standard construction, but several features deserve mention:

A. *Transparent Conductive Glass Coating*

Since the screen must be conductive and transparent to permit observation of the tip image, a tin oxide coating is used. This is obtained by depositing stannous chloride vapor on the walls of the tube, which is heated in an oven or flame to about 600°C. Parts of the tube which are to remain nonconducting are protected with Aquadag during conductivizing operation.

B. *Electrical Contacts to Conductive Coating*

These are provided by sealing in a tungsten wire in a pyrex-nonex seal, and making contact with the conductive coating using Hanovia platinum, which can be applied as a liquid and heated to produce a low resistance film which gives no vacuum problems.

C. *Phosphorescent Screens*

A Willemite screen is deposited on the conductivized glass region of the field emission tube by blowing finely ground Willemite powder onto the glass with a binder of phosphoric acid in acetone. When the tube is baked, a stable coating of Willemite is produced.

IV. OPERATION

A. *On Vacuum Line*

This procedure is used when experiments produce gases which must be pumped from the system. This is frequently true when large metal which cannot be outgassed must be used. Often evaporated metal films of tantalum or molybdenum are used as "getters" to further reduce pressures to about 10^{-10} mm Hg. The disadvantage of this system is that the pumps and traps require constant attention.

B. *Cryogenic Pumping*

This method is being used increasingly in field emission. A tube is sealed off with a conventional vacuum system and cooled with liquid hydrogen or helium. The pressures obtained in this manner are inmeasurably low, with hydrogen or helium being the only gases with measurable vapor pressure at these temperatures.

Gases which are to be adsorbed on the field emission tip are prepared in a metal crucible. This is "loaded" either by preparing a suitable chemical compound which will decompose when heated to yield the gas desired, or the gas can be made to condense on the crucible by filling the tube with the desired gas before sealoff and cooling the source assembly with liquid hydrogen or helium keeping the rest of the tube warm. After condensation the entire tube is submerged in liquid hydrogen or helium and is ready for operation.

A tip is "dosed" with the adsorbate by heating the source crucible to give the desired deposit. All gas liberated is immediately frozen out on the walls of the tube so that only the portion of the tip that "sees" the source directly is covered.

A tip may also be covered with low melting metal films using a slightly different source. A tungsten loop may be wrapped with a wire of the metal to be deposited. This loop is then heated electrically to evaporate the desired amount of metal on the tip.

V. APPLICATIONS OF THE FIELD EMISSION MICROSCOPE TO SURFACE PHENOMENA

Field emission is ideally suited to the study of all gases (except perhaps helium) on high melting metal surfaces. It has also been used to study adsorption on semiconductors, and to study the crystal structure of clean metals. Further, since gases can be adsorbed on one side of a field emission tip only, the rate and mechanism of surface diffusion can be examined. The details of these applications are interesting but involved and so beyond the scope of this paper.

Much remains to be learned about surfaces and the field emission microscope promises to be a valuable tool in this research. In just the last several years field emission from semiconductors has been used; also, metal whiskers have been found to be suitable as field emitters. This makes field emission possible with essentially all metals.

The necessary high vacuum techniques are now routine and the application of field emission and similar methods of surface study should reveal much more about the structure and reactions of solid surfaces.

BIBLIOGRAPHY

1. R. Gomer, *Field Emission and Field Ionization,* Harvard University Press, 1956.
2. R. H. Good and E. W. Müller, in "Handbuch der Physik," 2nd ed., Vol. 21, p. 185, Springer, Berlin, 1956.
3. E. W. Müller, "Field Ionization and Field Ion Microscopy," *Advances in Electronics and Electron Physics,* Vol. XIII, p. 83, Academic Press, 1960.

GLASS AND CRYOGENICS

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Cryogenics is the generation and application of very low temperatures. Cryogenics had its beginning in 1877 when a "permanent" gas was first liquefied simultaneously by Cailletet in France and Pictet in Switzerland. They obtained only a fog of liquid air, but this was the stimulus for further experimentation. The next break-through was in 1883 when two Polish scientists, Wroblewski and Olszewski, obtained oxygen and nitrogen in a completely liquid state, to be followed the following year with their liquefaction of a few drops of hydrogen. Large scale gas liquefaction as well as extended cryogenic experimentation was quite impossible at that time as the liquefied gases would evaporate in a very short time. In 1892 Dewar was the first to use the glass vacuum flask as a storage vessel for the liquefied gases and also as the experimental chamber for low temperature research. Dewar found that an evacuated double walled glass container would retain liquefied gases five times longer than a single walled uninsulated vessel and this could be improved by a factor of six if the surfaces within the vacuum space were silvered. Dewar, therefore, made a major contribution to the field of cryogenics and the device he used still bears his name. It is evident that from its earliest history, cryogenics has had a dependence on glass.

With the dewar flask available Kamerlingh Omnes liquefied the last of the "permanent" gases. At the University of Leyden in 1908, Omnes was successful in liquefying helium, thereby reaching a temperature just 4.2° above the absolute zero. Gradually, gas liquefication became the task of the engineer and the scientist found in cryogenics a new and exciting expanse for experimentation. With this tool he could slow up the motion of molecules in matter, he could achieve resistance-free flow of electric current in certain conductors, he could attain a degree of vacuum before unheard of.

Today, gas liquefaction is rapidly becoming a commercial art. New industrial applications for cryogenic fluids are being discovered daily. Cryogenic technology is changing the methods for large volume gas storage and transport, refrigeration in transit, food processing and of course, space simulation and rocketry, to mention but a few.

In the laboratory, however, the surface has hardly been scratched. Much is yet to be learned about matter by studying it at extremely low temperatures.

CRYOSTATS

Many factors have to be considered when designing storage vessels and experimental chambers employing cyrogenic fluids.Very low heats of vaporization of these liquids require careful consideration of:

1. thermal conductance of the materials used in construction of the container and in tubes, wires, rods, etc., leading into the experimental area.

2. thermal radiation into the cryogenic liquid through the walls of the container, as well as radiation from the top. Table I[1] shows the latent heats of vaporization of some common gases and their atmospheric boiling points.

TABLE I

Gas	O_2	A	N_2	Ne	H_2	He
Latent heat (cal./cm^3)	58.1	53.5	38.6	25	7.56	0.65
Boiling Point (°K)	90.1	87.4	77.3	27.3	20.4	4.2

It is interesting to compare the above with the heat of vaporization of water at its normal boiling point (540 cal.cm^3). Liquid helium, therefore, is 830 times more volatile than boiling water and 90 times more volatile than liquid oxygen.

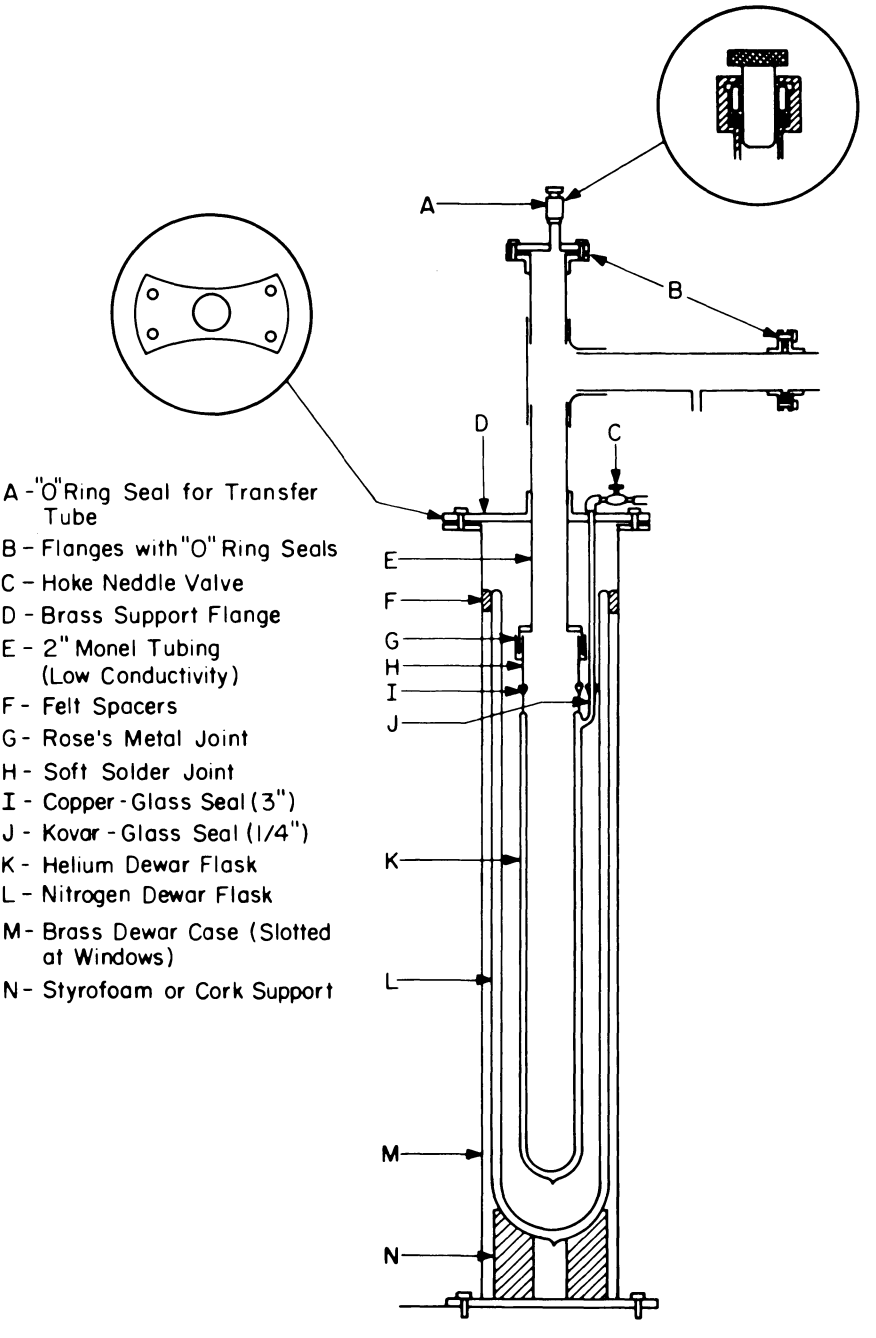
Ordinary dewar flasks are adequate for storing liquid oxygen, argon and nitrogen. Liquid neon and hydrogen can be kept for short periods of time in a single dewar flask. The very high evaporation rate of helium, however, makes it impractical to store or use this liquid in ordinary dewar flasks. The cryostat (Figure 1) developed for handling liquid helium consists of two dewar flasks, one inside the other. The inner vessel contains the liquid helium. It is surrounded by liquid nitrogen, contained in the outer flask. The liquid helium, therefore, receives heat radiation not from ambient room temperature but rather from the liquid nitrogen surrounding it which is over 200° colder.

In a properly designed cryostat other precautions are taken to prevent thermal conduction down the walls and through wires and tubes, etc. into the liquid helium. These are placed in thermal contact with the outer bath rather than conducting room temperature heat into the helium. Radiation shields in thermal contact with the outer liquid can also be placed in the neck of the helium container to further reduce evaporation. Such shields also act as heat exchangers to exploit the refrigeration remaining in the helium gas which when emerging from the dewar is only a few degrees warmer than the liquid. With such an experimental cryostat it is possible to keep liquid helium for many hours and even days. A carefully designed storage vessel will retain liquid helium for as long as a year.

Dewar Construction and Evacuation

Dewar making is an art well known by glass blowers and it is not the purpose of this paper to teach glass blowing, but it might be wise to point out the necessary precautions to make a good cryogenic dewar.

1. Spacers between the walls should be such that they can be removed. Corrugated sheet copper or copper gauze makes excellent spacer material. Copper can stand the heat of annealing and can be easily dissolved in nitric acid before evacuation and sealing.
2. Dewars should be properly annealed. Any strains left in the glass are liable to cause cracking with the extreme and sudden changes in temperature a cryogenic dewar is subjected to.



Helium Cryostat

Figure 1

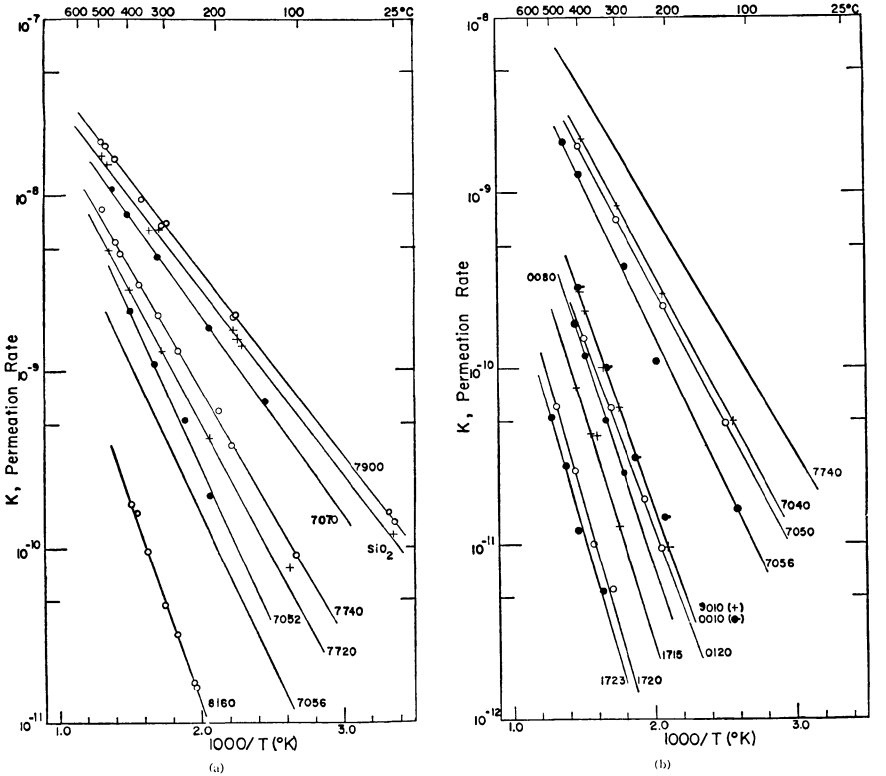
3. Silvering of the walls in the vacuum space can be done successfully every time if cleanliness is observed. The glass surfaces must be cleaned with hot chromic acid cleaning solution. All chemicals used should be reagent grade and carefully measured. All water used in making solutions should be distilled. Some silvering formulae call for adding ice to solutions. If this is done the ice should be made from distilled water. A complete description of the silvering process is published in *Experimental Cryophysics* by F. E. Hoare, L. C. Jackson and N. Kurti, 7.11.3, page 160.
4. The pump-out tube should be completely cleaned of silver and all foreign substances. It should be constricted for easy seal-off.
5. Permanently sealed off dewars should be baked for several hours during evacuation at temperatures in excess of 350°C. to drive off the adsorbed gas on its surface. A good vacuum (10-7 mm Hg) should be attained before heating is begun as the silver will deteriorate rapidly at high temperatures in the presence of air. It must be remembered that the visible silver surfaces are not the important ones, but rather those within the vacuum space of the dewar. These must be effective infra-red reflectors. Temperature must be controlled to avoid reaching the softening point of the glass, in which case sagging, misalignment and even collapse may occur.
6. Dewars should be sealed off hot, then removed from the furnace immediately for rapid cool down. Seal off tips should be checked with a Tesla spark coil for pin holes.

Borosilicate glass, such as PYREX and KIMAX, is an ideal material for dewar manufacture. It resists the thermal shocks or rapid cool down, it has a very low thermal conductivity, it can be blown into various intricate shapes suitable for cryogenics, seals can be easily made high vacuum tight and even more easily tested for vacuum tightness, its surfaces can be silvered by a relatively simple chemical process, unsilvered slits can give visual access with little sacrifice of cryogenic liquids, it can be baked at a high enough temperature during evacuation to drive out residual gases.

CRYOPUMPING

All of the above precautions are quite necessary for dewars to be used for liquid nitrogen and oxygen, but when it comes to liquid helium and hydrogen, one can forget about the careful baking and evacuation to extremely low pressures. Air, at liquid helium and hydrogen temperatures has a vapor pressure so low that a little air left in the vacuum space is of no consequence. It will condense as a solid on the inside as soon as the cryogenic liquid is introduced. An excellent vacuum is immediately attained. The process of producing a vacuum by freezing out residual gases is called cryopumping. This technique has been used for creating proper environment in space simulators. A giant wind tunnel at California Institute of Technology employs cryopumping. Very low pressures can be maintained without conventional vacuum pumps. Professor Hiltner at Yerkes Observatory employs cryopumping with one liter of liquid hydrogen within a telescope to keep light amplifier cells at operating pressure without the vibration and the weight ballast of conventional vacuum pumping equipment.

It is common practice to leave some air (about 50 microns) in the vacuum space of helium and hydrogen dewars. This much gas provides thermal conduction from the liquid nitrogen space to the interior of the helium dewar. In this way, the apparatus can be precooled at the expense of liquid nitrogen, and much less liquid helium or hydrogen will be used. At the moment liquid helium or hydrogen is introduced to the inner space, an excellent insulating vacuum results. Liquid helium and liquid hydrogen are quite capable, because of their temperature, to produce their own insulating vacuum.



Permeation rate K of helium through various glasses. Log$K$ is plotted vs reciprocal of absolute temperature, $1000/T°K$. Units of K are cc(STP)/sec/cm² area/mm thickness/cm Hg pressure difference.

Figure 2

HELIUM DIFFUSION

Most cryogenic researchers prefer to use helium dewar flasks that have accessible pump out tubes on their vacuum space. This is accomplished by using a metal to glass seal on the pump out tube and leading a line of metal tubing out of the cold region terminating with a valve. Between uses the insulating space can be flushed with air and evacuated. The reason for this is that helium is capable of diffusing through glass.

The rate of diffusion is practically non-existent at cryogenic temperatures, but as the cryostat warms up with helium gas in it the insulating vacuum is ruined in several hours. V. O. Altemose[2] of Corning Glass Works has shown the rate of diffusion of helium through various glasses identified by their Corning Code No. as a function of temperature (Figure 2). As the temperature rises the permeation of helium increases significantly. When a helium dewar is equipped with a pump out tube the insulating space can be purged with air and evacuated several times before each use, insuring a helium free and adequate insulating vacuum when filled with liquid helium. It is not impossible to use a permanently evacuated and sealed dewar flask for liquid helium. It is important, however, that no helium gas is left in the dewar as it warms up. When the last trace of liquid helium is gone, the helium space can be evacuated and kept under vacuum until warm or flushed with liquid nitrogen or nitrogen gas. The pump out tube permits the experimenter the luxury of leaving the apparatus when the experiment is completed with no concern of ruining the dewar even if liquid helium is still left in it.

Helium diffusion through glass is the limiting factor in the production of ultra high vacua. This phenomena has also been put to practical use. Since the rate of diffusion is constant at a specific temperature, a standard leak can be easily produced by sealing an atmosphere of helium into a glass container. Such leaks employing helium filled sealed quartz tubes are used for calibrating mass spectrometer leak detectors.

GLASS VERSUS METAL

In recent years metal dewars have been introduced for cryogenic uses. They have certain advantages over glass dewars and also disadvantages. Metal dewars are:

1. not as fragile as glass.
2. a thinner material is possible so there is less mass to cool down.
3. It is possible to make metal dewars with less space between outer and inner walls placing exterior apparatus in closer proximity to that which is located within the dewar flask, such as an exterior magnet acting on a sample within.
4. Complete ready to use metal cryostats are commercially available.

Metal dewars have disadvantages. There is a complete lack of visibility into the inner space. One must rely completely on instruments for liquid level location. When using a metal dewar the researcher must spend time with such instruments and very often have some doubts. This situation does not exist with glass dewars as a glance through the clear slit in a strip silvered dewar tells him where the level is and if his sample is covered. Periodic visible checks into a cryostat can very often tell more about an experiment instantly than weeks of calculating data taken on instruments alone.

Vacuum leaks occurring after a cryostat is in operation are much more probable with metal dewars than with glass. A simple Tesla coil check on a glass dewar is generally all that is needed as far a vacuum testing goes, but with metal dewars much more sophisticated testing is required. Testing a metal dewar at room temperature, even with a mass

spectrometer leak detector is no guarantee that it will remain tight when cooled to cryogenic temperatures.

When it comes to choosing between metal and glass there is also an economic factor. Glass dewars can be made at much less expense than dewars made of metal. It is economically feasible in most cases to buy two glass dewars, having one as a spare, for less than the price of one metal dewar.

The complete metal cryostats are generally of the type having a common vacuum space. This means that any malfunction makes the entire unit inoperable. Glass cryostats generally consist of two independent dewar flasks. If one dewar fails, it can be replaced with a spare and research can quickly go on.

There is no question that metal dewars are much better for large capacity storage of cryogenic liquids. Such storage vessels can be stationary or mobile. They will take more abuse and rough handling than glass. Metal cryostats have certain distinct advantages in particular applications. However, for general laboratory use glass dewars are more practical, dependable, functional and economical.

There is one more option that is available to the cryogenic researcher, namely, combining glass and metal. With the use of metal to glass seals the best of both (metal and glass) can be gainfully exploited. Copper to glass and kovar to glass seals withstand cryogenic temperatures without ill effect. Of course, cooling down should be done gradually and carefully.

Many cryogenic experiments depend on electrical measurements. It is easy to see, therefore, that kovar and tungsten to glass seals play an important role in cryogenic research. Solid and tubular, single and multiple wire seals have extensive cryogenic applications. It is important to note that seals having a hollow bell-shaped glass part between the two metal parts are generally more reliable than the solid glass type since thermal expansion is taken up in the glass bell even when these seals are soldered into massive blocks of metal. The solid glass type are useable when soldered into the ends of thin tubes somewhat duplicating the "housekeeper" seal.

ADHESIVES

Until the advent of the epoxy resins there was no good adhesive to be used at cryogenic temperatures. The expoxies, however, have changed that completely. If one is careful to follow the mixing and curing instructions of epoxy cements, such as "Aralaldite," it is possible to make seals that will remain high vacuum tight even at liquid helium temperatures. It is important to carefully consider the thermal expansion of the components being cemented as differential expansion may cause cracking of the joints and very often cracking of the components when subjected to these extremes of temperature.

TEMPERATURE CONTROL

The normal boiling points of cryogenic liquids are fixed temperatures that can be used as standards for calibration of instruments. The experimentalist is not limited to these fixed temperatures since by varying the

vapor pressure each liquefied gas gives an entire range of temperatures to work with. The temperature of a boiling liquid is dependent on the pressure above it so the control of that pressure is in effect a control of the temperature. By using a vacuum pump and pumping through a good metering valve it is quite easy to accurately control the temperature of any of the cryogenic liquids. Glass manometers play an important role in pressure measurement. Mercury and oil "U" tube manometers are a very accurate and dependable means of pressure measurement. Differential oil manometers are extremely useful in manually controlling temperature by keeping pressure constant. This control can be even more accurate by using a tilted oil manometer. With one leg of the manometer inclined it is possible to observe ten or more units of travel of the meniscus for each unit of rise.

THE FUTURE OF CRYOGENICS

The field of cryogenics has great growth potential. It is just in recent years that cryogenics has been applied to industry, and each application results in new growth and expansion. It is becoming standard practice to store oxygen as a liquid in places where large quantities of this gas are consumed, such as hospitals, steel mills, welding shops and glass shops as well. Nitrogen is also stored as liquid and new applications for this substance are constantly being found. Both of these cryogenic liquids are easily and conveniently transported as liquids. Recently the Linde Company announced a method of mobile refrigeration in railroad cars and trucks utilizing the low temperature of liquid nitrogen. With a single thermostatic valve any desired temperature could be controlled. This unit requires no mechanical devices of any sort, just a storage space for liquid nitrogen. Cost per B.T.U. of refrigeration is to be comparable to that of mechanical refrigeration with none of the upkeep problems.

With increased interest in the use of liquid hydrogen as a rocket propellent the cryogenic industry responded in building huge hydrogen liquefaction facilities. The Saturn rocket uses liquid hydrogen as a fuel and liquid oxygen as an oxidizer, making it a completely cryogenic rocket. Since hydrogen is the lightest element it gives the most thrust per pound of any rocket fuel. Since rocket parts come in contact with these extremely low temperatures it is necessary to test components in liquid hydrogen before they can be accepted. Cryogenic laboratories, as a result, have sprung up in many unrelated industries.

Cryobiology is a quite recent application of very low temperatures. For several years biologists have been keeping lower form specimens in a sort of suspended animation by a rapid freeze technique and storage at cryogenic temperatures. There is some experimental evidence that extremely rapid freezing of tissue results in the absence of water crystal formation, which with slower freezing methods injuries or destroys the cells. Dr. Fernandez-Moran[3]* has done some work in this field at the Massachusetts Institute of Technology, employing liquid helium temperatures. Dr. Stumpf of the University of Chicago Pharmacology Department is presently engaged in experiments employing cryogenic freezing.

*Now at the University of Chicago.

Until very recently research with liquid helium was limited to laboratories with elaborate helium liquefaction facilities. At first these liquefiers had to be designed and constructed by the people who used them. Later, a unique commercial helium liquefier designed by Samuel C. Collins was placed on the market by Arthur D. Little, Inc. Hundreds were sold but the price is such as to prevent small universities and industrial laboratories from experimenting with liquid helium. This picture is now changing. The Linde Company already has a helium liquefaction facility at Amarillo, Texas, close to the source of the nation's supply of helium. At present Kerr McGee is in the process of building a large helium liquefier at Navajo, Arizona, at their own helium well and they expect to be delivering liquid helium to customers early in 1964. Future plans include storage depots for liquid helium in various locations throughout the country. This will minimize transportation costs and lower the price of liquid helium so that it will come into the economic range of even the very small laboratories.

In the near future cryogenics will play an important role in various diverse fields. In electronics, work done with superconductors and semiconductors will develop into useful applications. Cryogenic lasers have opened up a new field of investigation as did superconducting magnets with their extremely high fields. I have recently observed cryogenic techniques developed in the field of metallurgy being deployed to study nonmetallic elements. Professors Meyer and Barrett of the University of Chicago are currently engaged in a series of experiments investigating solid crystals of various inert gases employing X-ray diffraction in a specially designed cryostat.

Many facets of research that have thus far been done at higher temperatures will be investigated in the cryogenic range. More and more research people are making investigations in the much broader range of temperatures made available by cryogenics.

How does all of this affect the scientific glass blower? It is evident that as more people get interested in cryogenics, more dewars, manometers, etc., will be needed. More effort on the part of the dewar manufacturer will have to be expended into the design of dewars and complete cryostats, as researchers entering this new field will expect to purchase a functional, ready-to-use piece of equipment.

As cryogenics had to rely on the scientific glass blower for its very beginning, it will continue to rely on him for its future.

REFERENCES

1. White, G. K., *Experimental Techniques in Low Temperature Physics,* (Oxford University Press), II, p. 37.
2. Altemose, V. O., *Journal of Applied Physics,* **32**, 1309 July, 1961.
3. Fernandez-Moran, *H. Annals of the New York Academy of Sciences,* Vol. **85**, Art. 2, P. 689.

OPTICAL CRYOSTATS*

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1. INTRODUCTION

A study of the various properties of a substance as a function of temperature reveals many interesting features. The behaviour of the optical properties of solids at low temperature is of particular importance. It is the purpose of the present paper to describe several versions of cryostats developed during the course of extensive work by the authors on the optical properties of semiconductors at low temperatures.

2. GENERAL CONSIDERATIONS

The purpose of a cryostat is to maintain a sample at a desired temperature for a length of time adequate for the observation being made. Thus the sample and the coolant must be thermally isolated from its surroundings as much as is feasible. Hence, the sample and coolant are enclosed in a vacuum and surrounded by a radiation shield. Also conductive losses must be minimized. Radiation shielding is provided by interposing between the refrigerant and the ambient a surface of intermediate temperature. Liquid nitrogen is ideal for cooling the shield. Radiative heating can be minimized by coating the relevant surfaces with a low emissive material such as silver. Conduction losses are reduced by constructing the cryostat from a low thermal conductivity material such as glass.

For optical measurements, light from a suitable source must, in general, enter and leave the cryostat. Appropriate optical windows must then be provided as part of the vacuum enclosure while, in the vicinity of the sample, the radiation shield must be transparent to the desired radiation. In many spectral regions this requires that the radiation shield be provided with apertures. Thus, in providing access for the light beam, one inadvertently exposes the sample to room temperature radiation. In order to minimize the resultant heating of the sample, efficient thermal contact between the sample and the coolant must be achieved.

Thermal contact between the sample and the cooling bath can be obtained in a variety of ways. The most efficient method is to immerse the sample directly into the liquid coolant. Another way by which the sample may be cooled is to clamp the sample to a copper block, one end of which is in direct contact with the coolant. Here the cooling is limited by the thermal contact[1] between the sample and the block. The efficiency of this method may be improved by soldering short strands of copper from the sample to the copper block; soldering of the sample directly to the copper block is ill-advised as undesirable inhomogeneous thermal strains are produced. Closer thermal contact between the sample and the cold copper block can be obtained by enclosing the sample and block in a gas-filled can; helium, in view of its light mass and low liquification temperature, is used as the exchange gas. In this case, as in the immersion case, one must provide low temperature optical windows.

*Work supported in part by the Office of Naval Research and the U. S. Army Research Contract.

It is necessary that a facility exist by means of which the sample can be moved in and out of the light beam in order that its transmission may be determined. Also easy access to the sample is desirable.

3. SIMPLE TRANSMISSION CRYOSTAT[1]

The simplest form of the cryostats to be described is shown in Fig. 1. As can be seen from this diagram the cryostat consists of two parts. One unit consists of the liquid coolant reservoir and sample block and will be called the center-piece. The remainder we shall call the outer-piece. These two units can be separated at the 71/60 cone joint.

(i) *The center-piece*: The sample block is of copper and has two identical apertures over one of which the sample is clamped. Either can be interposed in the light beam by rotating the center-piece at the 29/42 joint. The sample block is soldered to either a Kovar, platinum or copper tube which is in turn sealed to the appropriate glass. It has been found that platinum or copper give the most satisfactory seal particularly when used with superfluid helium. Of these two, copper seals are preferred because there are commercially[2] available seals of good quality in which the copper tube is sealed directly to Pyrex. This is a distinct advantage as the rest of the liquid coolant reservoir is also of Pyrex.

In Fig. 1, the top 35/20 ball can be used to connect the volume containing the coolant to a high-speed vacuum pump so that one can reduce the vapor pressure of the gas above the liquid and thus lower the bath temperature and still allow rotation about 29/42. When liquid hydrogen is used at room pressure, the lower 35/20 provides a means for making a reliable seal for the venting system while the top 35/20 is sealed immediately after the hydrogen has been transferred.

(ii) *The outer-piece*: From Fig. 1, it can be seen that the outer-piece consists of three co-axial tubes. The outermost tube forms the vacuum wall of the cryostat, the inner two constitute the liquid nitrogen radiation shield and are joined to the outer tube at the top in two ring seals and thence to the 71/60 cone. Thus the liquid nitrogen is open to the atmosphere only at the 24/40 cone which is used as the filling port. Hence the liquid nitrogen can be vented in such a way as to minimize the condensation of atmospheric water vapor into the nitrogen. If excessive water is allowed to accumulate in the bottom of the nitrogen jacket, subsequent cooling will cause damage. As an additional precaution, the liquid nitrogen shield is evacuated through the 24/40 before filling. The inner and outer vacuum spaces are interconnected via the apertures through the two walls of the nitrogen jacket. The sizes of these apertures are chosen to just accommodate the light beam and so minimize the undesired room temperature radiation reaching the sample. Since the two walls of the nitrogen shield are rigidly connected at the top and the bottom, bellows are provided to permit independent expansion and contraction of these two tubes.

[1]The design for this cryostat in its original form was introduced to the authors by W. G. Spitzer and R. A. Laff who received their information via a private communication. The original design is very similar to that given by H. M. Hersh, *Phys. Rev.* **105**, 1158 (1957). A similar version of this latter cryostat is illustrated by H. S. Martin and Son, Catalog 70, Section D, p. 42.

[2]Available from Larson Electronic Glass, P. O. Box 371, 2840 Bay Road, Redwood City, California.

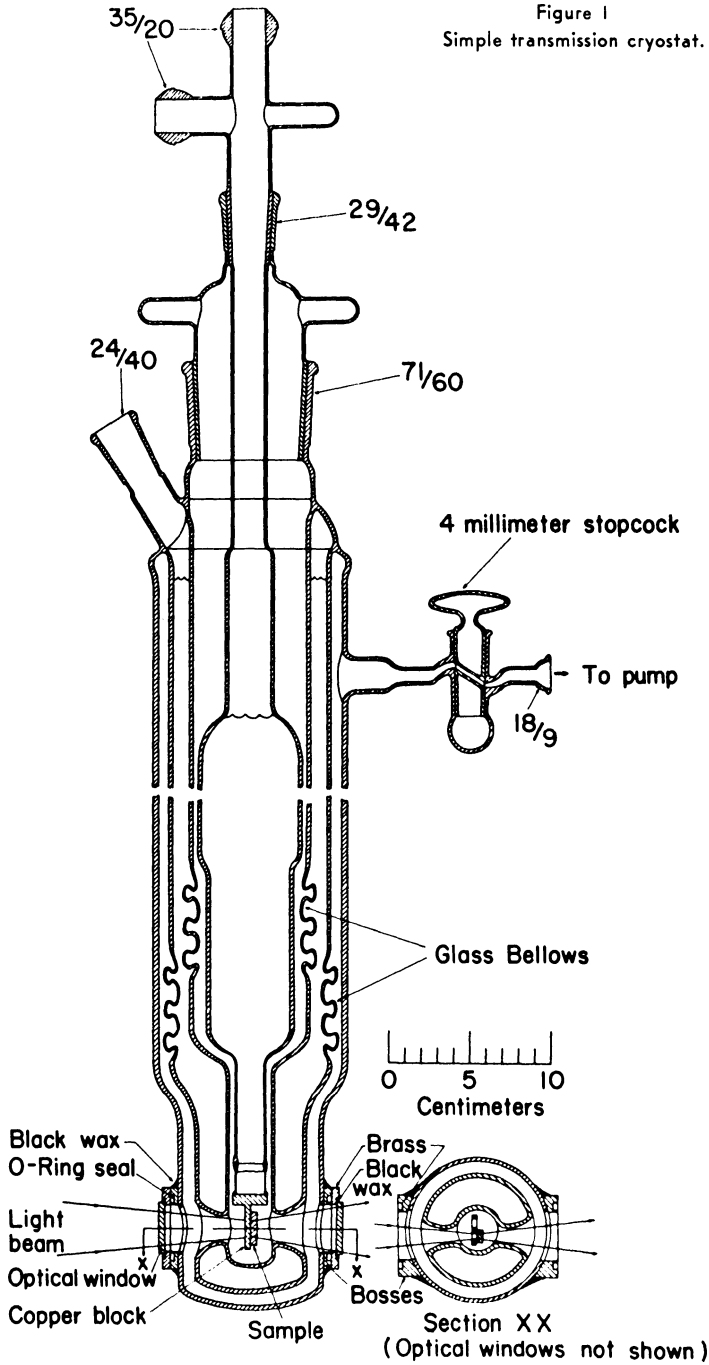

Figure 1
Simple transmission cryostat.

The lower diameter of the outer-piece has been optimized with regard to window size, solid angle through the nitrogen shield for room temperature radiation and location of the cell in the spectrometer. The optical windows are mounted onto brass plates with black wax. Using O-rings for seals the plates are bolted to brass bosses waxed to the outside surface of the outer-piece in which there are holes of appropriate size. These bosses are made such that the optical windows, when in position, are normal to the light beam. This method of attaching the windows to the cryostat greatly facilitates their interchange. When windows such as the alkali halides, sapphire, quartz and other materials are used one keeps a selection on hand mounted permanently on brass plates. If one desires to use plastic window material such as Mylar, the plastic film is simply clamped between the O-ring and a brass window blank.

The center-piece has a capacity of one liter to the level indicated, while the nitrogen jacket has a capacity of one and a half litres.

In constructing the cell the major difficulty encountered is that of aligning the various co-axial tubes. In particular, the center-piece should

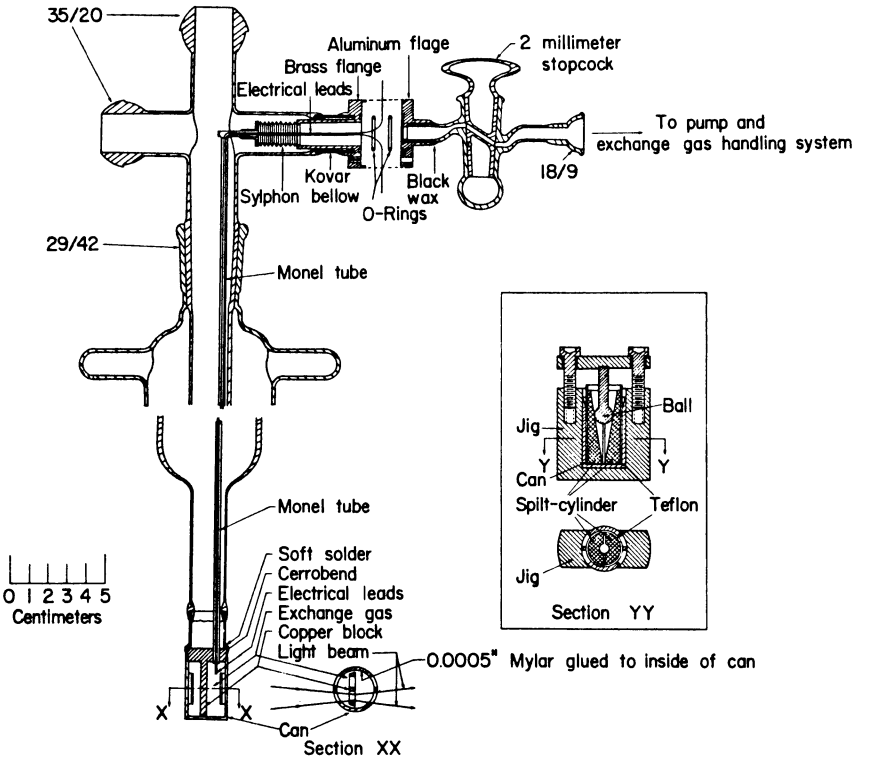

Figure 2

Center-piece for exchange gas cryostat. Inset shows jig for mounting Mylar windows on the exchange gas can.

rotate symmetrically within the nitrogen shield. Unfortunately the commercial 71/60 cone is usually not axial with respect to its attached tube. Thus one must take care to align the cone axis with that of the inner tube of the nitrogen jacket.

4. EXCHANGE GAS TRANSMISSION CRYOSTAT[3]

The outer-piece for the exchange gas transmission cryostat is identical to that shown in Fig. 1. The center-piece is modified as shown in Fig. 2. For the modified center-piece, an exchange gas can is provided. The can, with windows attached, fits over the taper on the copper block, thus enclosing the sample. The present design is for use with Mylar windows which are sealed to the inside surface of the copper can by use of the jig shown in the inset[4] to Fig. 2. To avoid destroying the Mylar-copper seal one solders the exchange can to the copper block with a low melting point solder such as cerrobend.

The exchange gas can is evacuated through the Monel tube which also serves to introduce the exchange gas. Electrical leads to a resistance thermometer located on the sample are taken out through the same Monel tube. The sylphon bellows incorporated in the exchange gas line takes up the differential expansion of the Monel tube and the glass center-piece. The electrical leads are taken out of the exchange gas system at the two O-rings shown in Fig. 2; these thin wires are clamped between the O-rings when the aluminum and brass flanges are bolted together.

An illustration of the helium time which is obtained with the present cryostat is given in Fig. 3. The volume of helium as a function of time, is indicated for three situations: (*a*) no exchange gas can, helium unpumped, (*b*) with exchange gas can, helium unpumped and (*c*) with exchange gas can, helium pumped to a temperature of 1.5°K. For all three cases the outside surface of the center-piece was unsilvered.

5. IMMERSION TRANSMISSION CRYOSTAT

The outer piece for the immersion cryostat is the same as that shown in Fig. 1; the center-piece is illustrated in Fig. 4. It is seen in Fig. 4 that the center-piece consists, now, of two parts, a helium reservoir and a sample holder that fits into this reservoir at the 29/42 cone. This cone also permits rotation of the sample holder. The helium reservoir fits the outer-piece at the 71/60 cone joint and is terminated at the bottom in a short length of fused quartz (one may use sapphire instead of quartz) through which the light beam passes. A standard graded seal provides

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[3]Some of the constructional details of this cryostat are similar to those used by R. A. Laff in the design of a photoconductivity cryostat, *Tech. Rpt.*, Purdue University, Contract Nonr 1100(04), NR 015-221, Office of Naval Research.

[4]The method used to bond the Mylar windows to the inside surface of the exchange gas can is somewhat similar to that described by J. C. Corelli, M. Livingston and L. Seidlitz, *Rev. Sci. Instr.* **28**, 471 (1957). The inside of the can is first highly polished and then coated with two layers of Du Pont 46950 adhesive which is allowed to dry. Armstrong Thinner, Type 1, is used with the adhesive. A strip of Mylar is fitted to the inside surface of the can and then covered with a strip of Teflon. The can is placed inside the jig shown in the inset to Fig. 2. A split-cylinder with a tapered bore is now placed inside the Teflon and is forced open by the ball, thus tightly pressing the Mylar against the inside wall of the can. The degree to which the split-cylinder has been expanded is gauged by measuring the outside diameter of the can as the ball is forced into the taper. The whole assembly is now placed into an oven and the cement cured for 10 mins. at 170°C. The Teflon sleeve between the Mylar and split-cylinder serves to prevent extruded cement from bonding the Mylar to the split-cylinder during the curing operation.

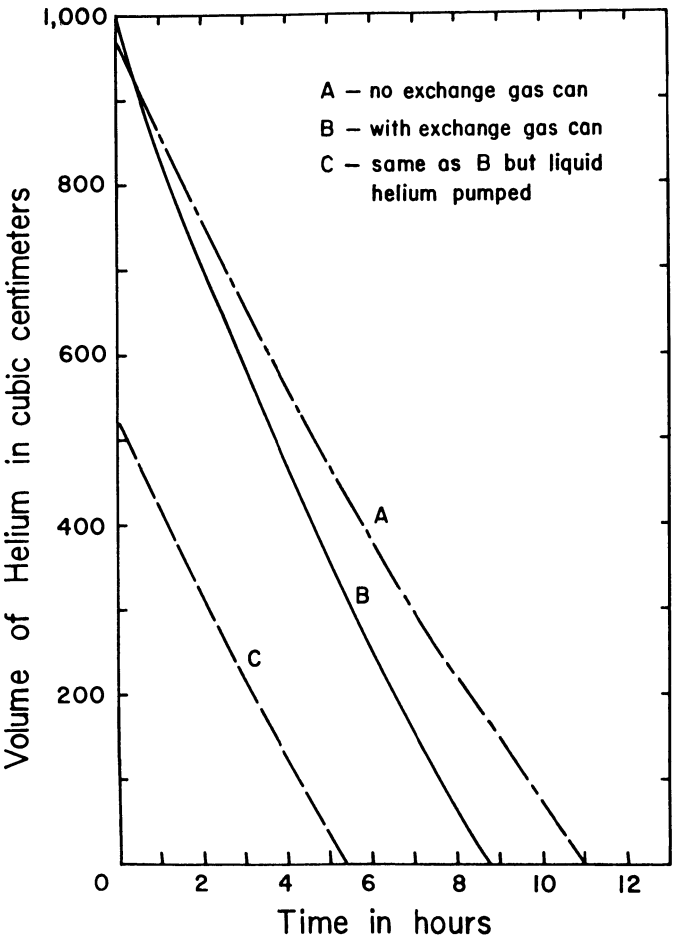


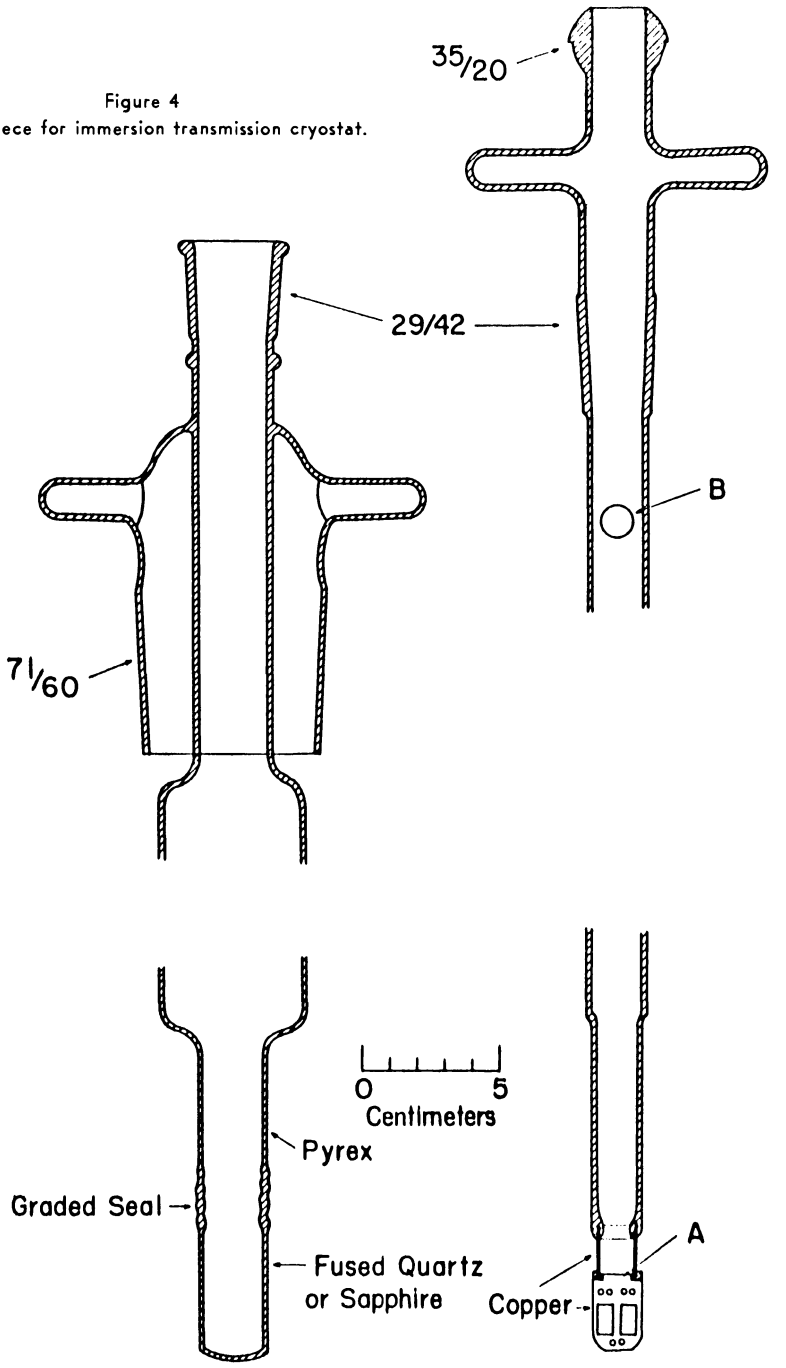
Figure 3

Quantity of helium left in exchange gas center-piece as a function of time.

the transition from quartz to Pyrex. The sample to be examined is attached to the copper tail of the sample holder; this tail is secured to the glass via a copper-pyrex seal. The inside volume of the glass part of the sample holder is connected to the helium reservoir through the two holes, A and B. Hole A is in the copper tail while B is in the upper part of the glass tube, thus providing entrance and exit for pre-cooling gas and for the liquid helium and its vapor. During the operations of pre-cooling, and filling with liquid helium, one must take careful precautions to prevent condensation of any substance onto the sample and into the reservoir.

The bubbles in normal helium scatter the light beam producing intensity loss and introducing intensity fluctuations. In order to eliminate these bubbles and to achieve the lowest temperature, the reservoir

Figure 4
Center-piece for immersion transmission cryostat.



is attached to a high speed vacuum pump which causes the helium to become superfluid.

6. MAGNETO-OPTICAL CRYOSTAT

A study of the optical properties of a substance subjected to an applied magnetic field and at low temperature is frequently necessary. For this purpose one needs to redesign the lower section of the transmission cryostats so far discussed to enable one to locate the cold sample between the magnet pole pieces set to give the minimum air-gap feasible. Fig. 5 shows a cryostat designed to fit a 4″ Varian magnet provided with one and a half-inch tapered pole caps set to give a 9/16″ air-gap. As the prime object of the measurement is to obtain the largest magnetic field possible, the reference beam aperture has been sacrificed. In Fig. 5a, the lower part of the outer-piece is shown; the top portion is of the same construction as that given in Fig. 1. For convenience and compactness, the optical windows are waxed directly to the outside vacuum wall of the tail-piece of the center-piece. For this reason, that portion of the tail-piece which fits between the pole-pieces is of square cross-section and is formed by shrinking the glass tubing onto a carbon jig. The tail-piece is waxed to the rest

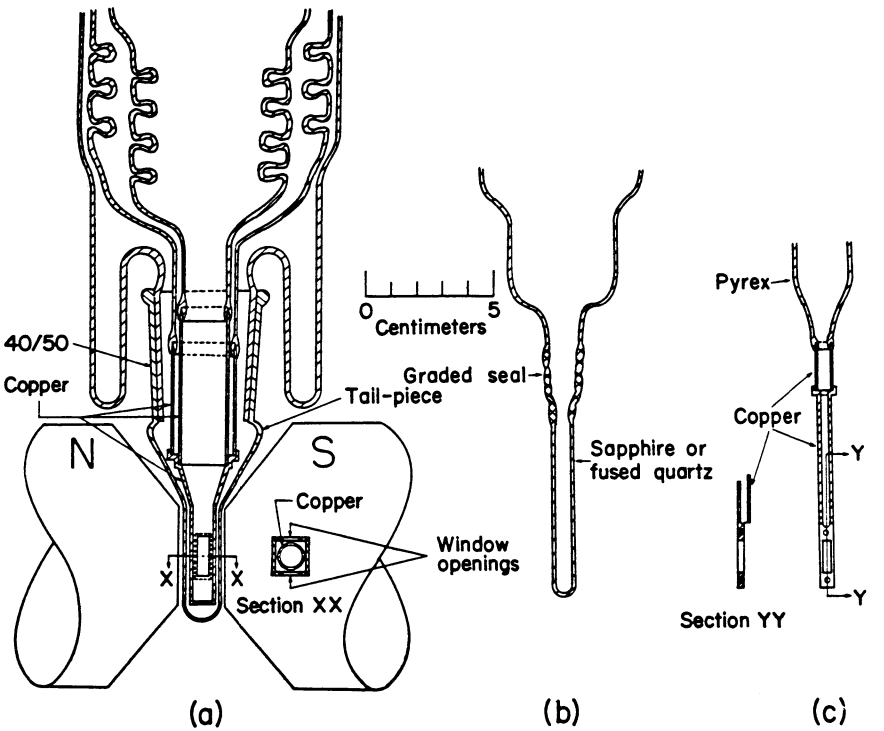


Figure 5
Lower portion of magneto-optical cryostat:
(a) outer-piece (b) immersion reservoir (c) sample holder for (b).

of the outer-piece at the cone joint 40/50. The feature of a detachable tail-piece simplifies interchange of windows and allows one to use a supersonic cookie-cutter for cutting the window openings. Space is further economized by the use of a thin copper cylinder as the radiation shield in the air-gap. This shield is in contact with liquid nitrogen where it is soldered to the two copper-Pyrex seals which terminate the glass portion of the nitrogen jacket. The elaborate shape of the bottom part of the outer wall is merely to facilitate clamping the cell into position. It should be noted that one can provide for measurement of the reference beam by supplying an additional pair of optical windows below those shown and by raising and lowering the cell as required.

Figs. 5(b) and (c) show the lower portions of an immersion type center-piece designed to fit the outer-piece just discussed. These serve the same purpose, and are of a design similar to, the corresponding parts discussed in Section 5. When the helium reservoir is terminated in sapphire, the sapphire-pyrex seal is made using the technique described by Nelson and Spindler[2] except that the graded seal has been modified by replacing the diffused 3320 glass in the 7280 glass with two glasses. The sequence used was 7740, 3320, 7510, 7520 and 7280. The length of 7280 used was a little longer than the seal required to further remove the low softening point glasses from the hottest region of the furnace where the sapphire was located. The sapphire was obtained[5] in the form of a short tube with one end closed and with the inside surface polished. The outside was ground and polished to size in our laboratory.

7. OPTICAL CRYOSTAT FOR ELECTRON BOMBARDMENT

For some investigations, it has been found necessary to irradiate samples with high energy electrons and subsequently to measure the effect of this irradiation on the optical properties of the sample while always maintaining the sample at the temperature of the irradiation. The cryostat shown in Fig. 6 is designed to be used for this type of observation at liquid nitrogen temperature. In the figure it will be noted that no radiation shield has been provided as this introduces additional complications.

The electron beam for the irradiation enters the cryostat normal to the window W_3 (see Fig. 6) which consists of a 1 mil aluminum foil. This foil is mounted using the same technique as that described for the Mylar windows mentioned in Section 3. D is an electrically grounded copper slab which contains a defining aperture; during an irradiation the charge delivered to the collector, C, and the sample block, B, (which are electrically connected) is stored on a capacitor and is periodically measured with a ballistic galvanometer. Thus, knowing the area of the aperture in D and the charge collected, the electron flux can be computed. It should be noted that in Fig. 6, B has been rotated at the 24/40 joint to the position used for the optical measurement to show the constructional details clearly. In the cross-section XX, B is shown rotated so that the sample S is positioned for the electron irradiation. Leads from C and D are taken out of the cryostat through the Tubes T_1 and T_2; heavy gauge tungsten wire has been used for the glass-metal seals, the lower pair of

[5]Supplied by Linde Air Products Company.

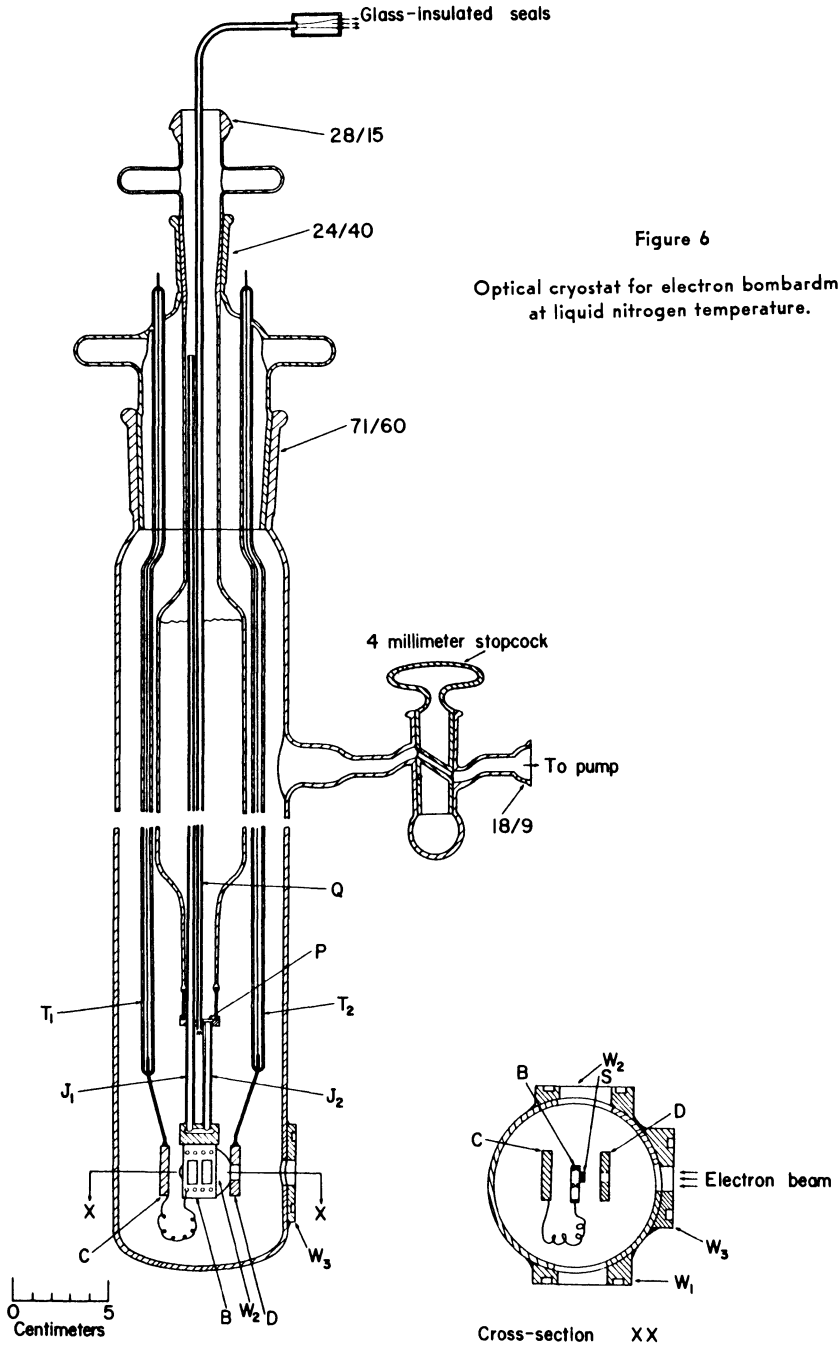


Figure 6

Optical cryostat for electron bombardment at liquid nitrogen temperature.

wires supporting C and D. In both T_1 and T_2, nickel wires, spot-welded to the tungsten provide the necessary leads.

The sample block is cooled by liquid nitrogen via the Monel tubes J_1 and J_2. The sample block can be partially thermally isolated from the reservoir by plugging the open end, P, of J_2; the open end of J_1 extends above the level of the liquid nitrogen. Thus the sample block can be raised to higher temperatures by the use of a heater. The central Monel tube, Q, provides access to the sample block for leads to a thermometer and the heater.

The optical windows are mounted at W_1 and W_2. Use of this cell has been confined, so far, to the near infrared region of the spectrum for which it has been found that the transparency of sodium chloride and potassium iodide is not affected by the discoloration produced in them by the x-rays generated during an irradiation. The glass becomes discolored but this does not affect its mechanical properties.

8. DISCUSSION

The simple transmission cryostat discussed in Section 3 can be used to study the optical properties of a substance over a wide range of the electromagnetic spectrum with comparative ease. This is because the preparation and installation of the room temperature optical windows (the only windows in the light beam) involve no technical difficulties. A typical set of windows[3] consisting of lithium fluoride, cesium iodide, Mylar[6] and crystalline quartz can, for example, cover the region from the vacuum ultraviolet to the submillimeter wavelength range. The limitation of this type of cryostat is that the sample temperature is significantly higher than that of the bath. For example, with the sample simply clipped to the copper block, a temperature of about 12°K is obtained with liquid helium. The exchange gas system enables one to attain a sample temperature of 2.0°K when the bath temperature is at 1.5°K. By suitably varying the exchange gas pressure and the temperature of the helium bath any temperature in the range 2° to 8°K can be obtained. For the immersion magnet cell and with the pumping installation used the lowest sample temperature attained is 1.4°K. Still lower temperatures should be obtainable using higher pumping speeds.

As already mentioned, the exchange gas and the immersion cryostats require low temperature optical windows. The 0.5 mil Mylar exchange gas window cannot be used in the range from 5 microns to about 16 microns due to the presence of absorption bands; the ultraviolet cut-off is not known. The 0.5 mm. wall thickness sapphire used for the immersion cell can be utilized from the extreme ultraviolet to about 6 microns. Fused quartz of the same thickness has a somewhat smaller range but presents less technical difficulties. Both fused quartz[4] and sapphire[5] transmit in the submillimeter wavelength range; fused quartz should be usable from about 100 microns and beyond. There is an obvious need for techniques to be developed so that the tail of the immersion reservoir can be made from materials transparent[7] beyond 6 microns.

[6]Mylar conveniently fills in the range between the long wavelength cut-off of cesium iodide and the onset of usable transmission of crystalline quartz in the long wavelength.

[7]C. J. Rauch and W. C. Kernan at Lincoln Laboratory, M.I.T. has had success with immersed calcium fluoride using a technique similar to that described by V. Roberts, *J. Sci. Instrum.* **31**, 251 (1954). For details see *Rev. Sci. Instrum.* **33**, 496 (1962)

ACKNOWLEDGMENTS

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REFERENCES

(1) R. Berman and C. F. Mate, *Nature* **182,** 1661 (1958).
(2) L. S. Nelson and G. P. Spindler, *Rev. Sci. Instr.* **29,** 324 (1958).
(3) IRIA State-of-the-Art report *Optical Materials for Infrared Instrumentation* (Report No. 2389-11-S). The University of Michigan, Willow Run Laboratories. Compiled by S. S. Ballard, K. A. McCarthy and W. L. Wolfe.
(4) M. Czerny and H. Roder, *Erg. der Exakt. Natwis.* **17**, 71 (1938).
(5) Ernest V. Loewenstein, *J.O.S.A.* **51,** 108 (1961).

THE USE OF NEW FLUOROCARBON MATERIALS IN THE DESIGN OF GLASS HIGH-VACUUM VALVES AND JOINTS

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The traditional use of hydrocarbon based lubricants for ground stopcocks and standard tapers suffers from many serious limitations. The utility of apparatus assembled with lubricated joints and stopcocks is limited for the chemist by the chemical reactivity and physical properties of the lubricant. New chemically inert lubricants such as the fluorocarbon greases and waxes overcome some of these limitations but are usable only at temperatures near room temperature.

The discovery of fluorocarbon plastics and elastomers and the easy availability of these new materials allow new methods of overcoming most of the traditional shortcomings of lubricated joints and stopcocks.

The successful use of such materials require extensive changes in design. These changes must be compatible with the properties of glass. For example, the problem of obtaining suitable compression of elastomer O-rings necessary for good seal characteristics without fracture of the glass portions of a given seal has to be solved. This and other design problems were discussed and a new series of self-lubricating, grease-free stopcocks and joints, usable at pressures as low as 10^{-7} mm and temperatures as high as 200°C., were described.

GLASS TECHNOLOGY IN THE COMPUTER INDUSTRY

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The electronic computer, a newcomer to the electronics industry, had its beginning in the mid 40's in the laboratories of the University of Pennsylvania. Dr. Mauchly and Mr. Eckert, with the help of many others, developed the idea that computations, *i.e.*, addition, substraction and multiplication could be accomplished much faster by replacing the slower forms of mechanical and electromechanical devices with electronic units.

Man's need for counting devices continues to grow. Beads were counted on the abacus thousands of years ago, pebbles were used in ancient Rome, manual or electromechanical calculators with their gearboxes and counters served until World War II. Since then military requirements for higher speed computation to solve logistics and transportation problems needed speedier and more capable computing means.

The first all-electronic machine, the Eniac - **E**lectronic **N**umerical **I**ntegrator **A**nd **C**omputer contained 18,000 vacuum tubes and could compute the trajectory of a shell in four seconds—or about 1/10 of its flying time. Before Eniac, this computation took an experienced operator two or three days with the aid of an electric desk calculator.

A modern scientific computer with a magnetic film memory can store 1,000,000,000 bits of information in one second. A computer of this type used in our atomic energy program, could in weeks, solve a single problem which twenty years ago would have taken an army of mathematicians several hundreds of years. The present dollar volume of the computer industry in the U.S.A. is approximately 3.5 billion dollars per year with the cost of an individual computer system ranging from ten thousand dollars to ten million dollars per system.

A computer system consists of a central processor in which arithmetic operations are performed, a memory unit which stores data and provides results, and an input/output system which serves to convey information to and from memory, all under the control of a program of instructions.

As the keyboards of an electronic organ are connected by wires via a switching unit to the sound generators, so the central processor of a computer is connected to its circuit modules or cards. Mounted on these cards are solid state components, such as diodes and transistors, combined into integrated circuits that serve to switch electronic impulses into various channels. For example, a train of electronic impulses representing data, may be switched to the memory unit where small ferrite crystal doughnuts, called cores, one-half mm. in diameter are strung on a matrix of copper wires. Each electron pulse causes the magnetic field of a core to be switched in accordance with the information represented by that electron pulse. Thus the transient pulse train is stored in a static condition by these cores. When this data is required the polarity of the magnetic field of each core is recognized by the computer as a one or a zero. It requires about one millionth of a second to switch a memory core from zero to one, or vice versa, and one million switches can be performed in

one second. A new device, consisting of a magnetic film on glass, will switch 1000 times faster, *i.e.*, it requires one nanosecond to switch or 1,000,000,000 switches in one second. Since electricity travels at a speed of one foot per nanosecond or 1 foot in 1/1,000,000,000 second, one can see that these devices have to be small and compact so as not to lose time by interconnection.

There is a similarity between electrical current conducted by a wire and a fluid carried by a pipe: as the cross section area of the wire, or the pipe increases, friction and loss of pressure decreases. The resistance to the flow of electricity in a metal conductor is based on the electron transfer in the outer shell of the atom, which vibrates through thermal agitation in a crystalling structure. If the temperature of the conductor is increased in any way, the metal expands, the thermal vibration increases and its resistance to the conductance of electricity also increases.

Should we, however, cool the metal to minus 270°C. one finds that quite a few metals become superconducting, *i.e.*, there is no resistance to the flow of electricity.

Now, by using the above concepts, we can construct a magnetic memory and logic circuits, which will switch, interrograte, remember and recall, within a nanosecond, any information which had previously been stored in its magnetic memory.

This high-speed magnetic memory consists of a very thin glass plate 50 x 70 mm., 0.1 mm. thick, or roughly 2″ x3″ x 4 mil, coated on one surface with a nickel-iron alloy of 82/18 composition about 1000 Angstroms thick (*i.e.*, 5000 films equal thickness of one human hair). In order to make these films smooth, uniform in composition and stress-free, the substrate has to be nearly perfect. The surfaces of glasses used for substrates for magnetic films or microcircuit components were studied, using an electron microscope and replica technique giving a resolution 15-20 Angstrom and magnification as high as 200,000 times. For comparison, flat drawn sheet glass was produced by different processes such as Pennvernon, Corning, Fourcault, Pilkington, Colburn, and St. Gobain, and for plate glass by grinding and polishing; twin ground, rouge polished and acid polished and Pilkington Float glass.

All methods showed similar imperfections and defect patterns, caused by a similarity in the melting and refining process, plus waviness introduced by the traction rolls, drawingbar and debiteuse or drawing slot or orifice. Also, many tiny gas bubbles, called seeds, containing residues from the melting and refining process, and lenses or bumps of circular shape where drops of a higher viscosity glass have not been fully blended with the main composition, ranging in size from 100-10,000Å in diameter were observed. These cords differ in refractive index and density because their composition is slightly different than the surrounding glass-matrix. Many of these fine cords and inhomogeneities are caused by incomplete mixing of the glass batch or contamination from the refractory material in which the glasses are melted.

Ground and polished glasses show a characteristic scratched surface caused by the grinding and polishing medium and must be acid polished,

i.e., its surface dissolved with a mixture of Hydrofluoric Acid and Sulfuric Acid, to be usable at all.

The best results were obtained from a fire-polished sheet, etched to the required thickness by an acid etch which removed most of the impurities and scum imbedded in its surface during the manufacturing process.

There is room for the development of ultra pure and smooth glasses which will match the thermal expansion of their coating, be shockproof, impact resistant, suitable for soldering of terminals (thermal shockproof) and have an amorphous (non-crystalline) surface structure free of pores and impurities for use in the new low temperature microcircuit technique. The saving in space and cost would be enormous. A plate 20 x 20 x $\frac{1}{8}$" would contain 25 million bits and a memory block of 20 x 20 x 5" could store 1,000,000,000 bits of information.

The cost per bit must be very low. For example, insurance companies are looking today for a 10^{14} bit memory storage. At 0.1 cent per bit this memory would cost $100,000,000,000, a sum equal to our national budget per year, a price nobody could afford.

The solution to this problem will be found in most-production-techniques and scientific breakthrough where material technology, skill, and automated process will form, control and correct and standardize a product which will serve humanity for better values in life.

10 electron microphotographs of glass surfaces and magnetic coating on glass were shown.

Specimens of magnetic core memories, magnetic film memories, integrated logic devices and a book sized computer were displayed.

UNIQUE GLASS-TO-METAL SEALS WHICH ARE THERMALLY CYCLICAL AND VACUUM TIGHT

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Warren, Michigan

1. INTRODUCTION

In the study of gas filled tubes in and out of nuclear reactors by the Electron Converter and Plasma Group of the Physics Department, it was found that the standard oxide type glass-metal seal would not meet the stringent conditions imposed upon it. It was therefore imperative that a new type seal be found that would be satisfactory.

Examinations on oxide glass-metal seals after exposure to the high temperature and plasma environment, invariably showed that the oxide interface was attacked and decomposed sufficiently to cause electron tubes to become "leakers". From this initial observation it was decided that if the oxide seal was eliminated perhaps a dependable seal could be produced.

2. HISTORICAL DISCUSSION

The wide use of vacuum devices during the past 2 decades has focused attention on glass-to-metal seals and the many problems involved. In fact today's research and development programs with their wide range of temperature and ultra high vacuum conditions and the use of alkali metal materials for plasma generation has placed new and unusual demands upon glass-to-metal seal technology.

Almost any of the general books on glass blowing or glassworking make some very specific remarks as to the fundamental principles involved in making glass-to-metal seals. Among those fundamental statements there will always be one which states (and I quote now from *Scientific Glass Blowing* by Barr and Anhorn): "The degree of oxidation is very important. If the oxide layer is too thin, the glass cannot form a strong bond with the metal and a good durable seal is not obtained. If the oxide layer is too thick, the glass cannot dissolve to the required depth in the layer and poor seals result. The success in covering the metal with a suitable oxide film is best attained by experience."

To a glass blower, a good glass-to-metal seal is in fact evidenced by a certain specific or characteristic color. For this reason most of you would have discarded the oxide-free types of seals which we made in our investigation as not being sufficiently oxidized inasmuch as the characteristic color was metallic or silvery. The affinity of clean, pure metals for glass is generally assumed to be small. In fact appearing in *Physics* 1934 there is the "Oxide Layer Hypothesis" of Hull and Burger[2] which can be supported to an extent by the examination of broken seals. The fracture usually occurs either in the glass, a layer of which remains attached to the metal, or at the oxide metal boundary leaving oxide firmly attached to the glass. It rarely occurs between the glass and oxide. The adhesion between glass and oxide is strong because of the apparent ionic structures.

A gradual change in structure is apparently indicated wherein ions of the sealing metal displace silicon ions in the glass. It is said that metal oxide dissolves into the glass.

Adhesion between the metal and its oxide is even more difficult to explain, even though the oxide may be slightly soluble in the metal. It appears that if the metal or alloy is marked by the formation of multiple oxides then these oxides will depend upon the temperature ranges and the amount of oxygen present. Some of these oxides are then, more or less soluble in glass and more or less adhesive to the parent metal, but lattice structures, etc., must be compatible at the same instant. In general then, many factors appear to influence the adhesion or sealing properties of glasses to metals.

Hull and Burger state that molten glass will not spread over the surface of clean metal in an atmosphere of hydrogen, pure nitrogen or carbon dioxide, provided that the surface remains unoxidized. They also state that the glass will spread rapidly if the metal surface is oxidized, in fact, the affinity is so strong as to cause the glass to creep up the surface of a vertically inclined metal plate.

With all this in mind, we still deemed it necessary, to go somehow from glass-to-metal without an oxide layer. At least we wanted to keep the oxide layer to an extremely thin film that is not naturally visible. To accomplish this we made the seals in a reducing atmosphere.

GENERAL PROPERTIES OF PERTINENT GLASSES AND METALS

C.O.E. Low to High	Glass	Coeff. of Exp.	Annealed °C Normal Service	Annealed °C Extreme Limit	Strain Point °C	Annealing Pt °C	Soft Pt °C	Working Pt °C	Glass Name	Glass Lab #
1	7740	32.5x10-7	230	490	520	565	820	1220	Chemical Pyrex	G726-MX
2	7720	36x10-7	230	460	485	525	755	1110	Nonex	G7702-P
3	3320	40x10-7	200	480	495	540	780	1155	Uranium	G371-BN
4	1720	42x10-7	200	650	670	715	915	1200	Aluminosilicate	G172-AJ
5	7052	46x10-7	200	420	435	480	708	1135	Kovar Sealing	G705-FN
6	7056	51.5x10-7	200	460	472	512	718	1050	Halide Free Kovar Sealing	G840-MF

Metal	Molt. Wt.	Melt Pt. °C	Coeff. of Exp.	Boil Pt. °C
Tungsten	184.0	3370	45x10-7	5900
Molybdenum	96.0	2620 ± 10	49x10-7	3700
Kovar	-	Approx. 1450 °C	44-52 x10-7	-

Table I

3. EXPERIMENTAL WORK

We decided upon some of the standard metals and glasses used in the vacuum industry. The metals were tungsten, molybdenum and Kovar. The glasses were Corning numbers 7740, 7720, 3320, 1720, 7052 and 7056.

A chart of the general properties of the glasses as related to each other and to the concerned metals is shown in Table I. The order of the glasses is according to the thermal coefficient of expansion from low to high. It is obvious from the table that the softening point and the working point do not bear a similar sequential relationship to each other or to the thermal coefficient of expansion.

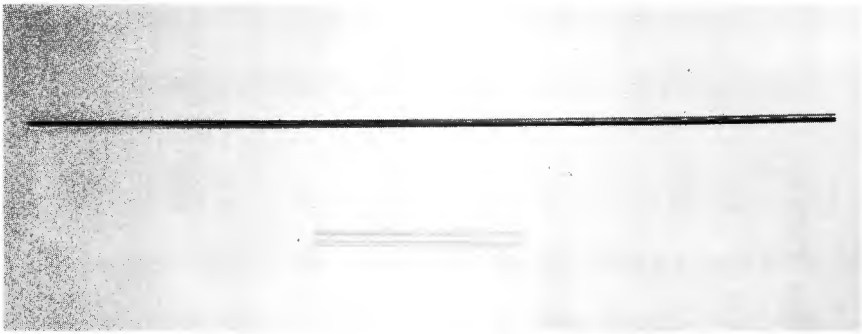

Figure 1
Wire and glass sleeve 2X.

The metals were in the form of wires 0.040 inch diameter by 4 inches in length. The glasses were in the form of sleeves approximately 1 inch long and just large enough in diameter to slip over the wires. These sleeves were located on the wires one inch from one end. Figure 1 shows a typical glass sleeve and metal wire. After being fired the glass had shrunk to about ¾ of an inch in length.

The centerless ground wires and glass sleeves were ultrasonically cleaned in trichlorethylene; washed in alcohol and dried. The tungsten and molybdenum wires were fired in dry hydrogen at 1175°C. for one-half hour. The Kovar was fired in wet hydrogen at 1175°C. for one-half hour and the chromallized wires were fired in very wet hydrogen at 1175°C. for one hour.

The desired combination of glass and metal wire assemblies were loaded into a fixture for hydrogen firing, as depicted in Figure 2. One glass-metal assembly is shown in place. As many as 500 glass-metal assemblies could be processed at one time in the particular fixture that was fabricated. The number of assemblies that can be processed simultaneously is limited only by the number of holes and overall size of the fixture. The fixture was made from stainless steel. The end sections were bent from the bottom piece to serve as stops for the wires. Two perforated sections were located between the two ends to serve as supports for the wires and as a stop for the glass sleeves.

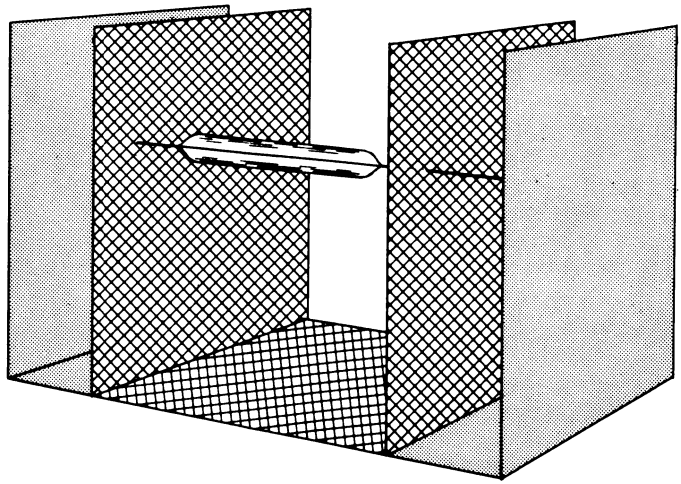

Figure 2
Fixture for glass-metal assemblies.

The fixture was loaded with the glass-metal assemblies and inserted into a Stewart type hydrogen furnace. After the furnace was purged with nitrogen it was operated with dry hydrogen and brought up to the desired temperature is approximately 20 minutes. It was found that the temperature and the time at temperature were critical. The furnace was then lowered to room temperature and purged with nitrogen. This phase also required about 20 minutes. Figure 3 shows three typical oxide-free seals at a magnification of 3X.

In general, the seals were clear, metallic and silvery in color. The seals involving chromium were green in color. Some of the unusual features in the wires after beading were as follows: Some of the Kovar group wires showed a bubble alignment longitudinally along the wire. They were not harmful in any way. Some of the molybdenum pieces showed a mottled appearance with a sort of square crystalline like structure at the glass metal interface. The Nonex beads all reduced quite badly, turning black.

At least 500 of the glass-metal assemblies were made of various combinations. Several of these assemblies were tried which did not hold up at all. If the wire and bead did not unite effectively in the furnace treatment no attempt was made to seal the assembly into a tube unit.

After the wires were beaded in the hydrogen furnace we processed them by conventional glass working techniques into the tube units as shown in Figure 4.

The basic design of the unit was a one pin seal which was inserted into a round ended tube about 20 mm in O.D. This extended for about 4 inches and reduced to a seal-off constriction. Uranium glass was used as the intermediate glass between the tube unit and the chemical borosilicate glass manifold which was used for evacuation and bake-out.

The tubes were decaled with ceramic decals originated by The American Scientific Glass Blowers Society.

With the aluminosilicate glasses we had to be careful to present reboil and reduction. Natural gas bubbled through ethyl-orthosilicate, careful adjustment of fires, and extreme cleanliness are critically important. Hydrogen used as the gas is also effective in the prevention of reboil and makes it unnecessary to use the ethyl-orthosilicate. The black Nonex beads were very sensitive and did not have a typical wet angle with the metal. The Kovar sealing glass, the chemical borosilicate glass and the uranium glass acted normally when being manipulated.

The tubes were attached to the manifold of a vacuum station through uranium grades where necessary. They were baked out at 425°C. for a minimum of 6 hours and sealed-off at a pressure of 10^{-7} torr. About ten tube units were pumped on the manifold at one time. See Figure 5.

4. TEST RESULTS

After a two week lapse the tube units were tested with a tesla coil and those which exhibited any tendency towards being gassy were rejected. All the tube units were checked macroscopically and also examined with a hand lens and binocular microscope at powers from 3X to 20X.

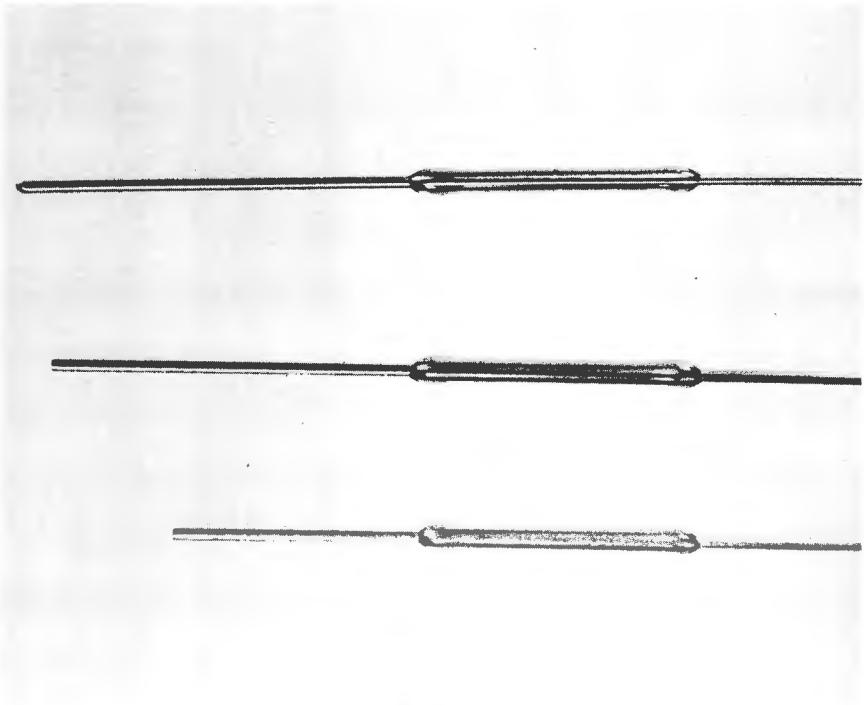

Figure 3
Typical oxide free seals 3X.

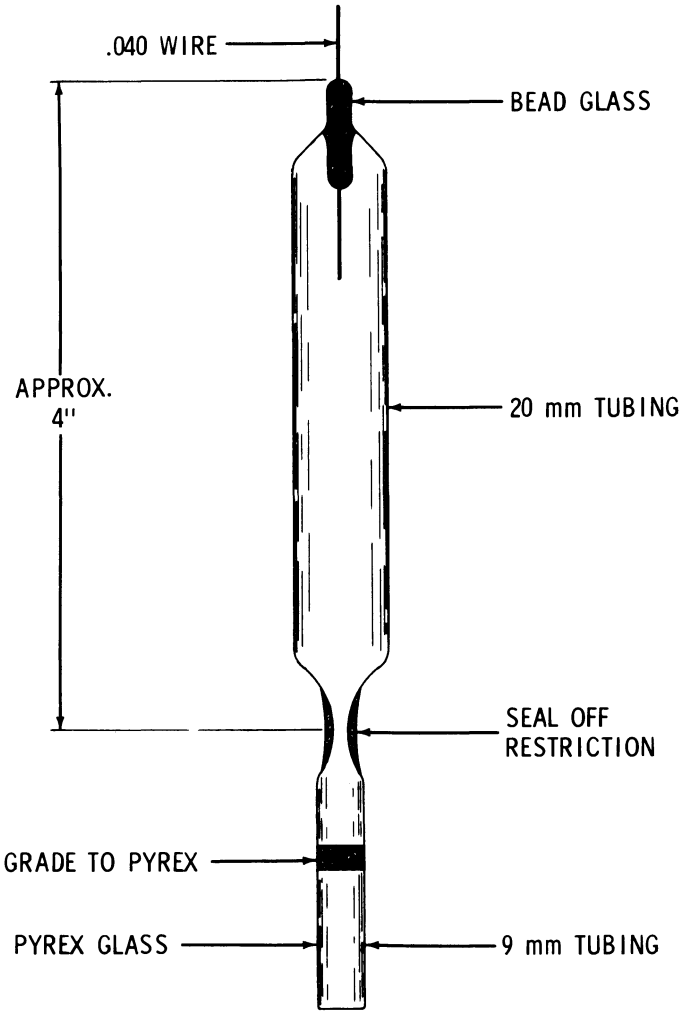

Figure 4
Oxide free test unit.

A composite of all hydrogen treated glass-metal assemblies is shown in Table II. Potentially satisfactory seals are indicated by G. Unsatisfactory seals are indicated by B. Some of the seal work was inconclusive, these are marked with an I. It is evident from Table II that many combinations not routinely considered effective by glass blowers appeared to be successful seals under vacuum conditions and with thermal cycling. For example, tungsten and 7052 or molybdenum and 7720 are not normally considered compatible.

Figure 5
Test units ready for exhausting.

Approximately 100 glass-metal tube units were fabricated. Out of this number 20 some were not completed into the tube units because of inherent stresses in some of the glass-metal combinations. Another 15 tube units failed during the exhausting and bakeout cycle. This was especially true of the Nonex combinations. Twenty-five of the tube units were of the oxide variety and were used for comparison. The remaining 40 were of the oxide free type were involved in these tests which included thermal cycling over an extended period of time and checking for vacuum tightness. Some of these glass-metal assemblies were inserted into multiple pin presses. Figure 6 shows one of these presses which has been used in a practical application.

SUMMARY OF HYDROGEN TREATED GLASS-METAL ASSEMBLIES

Metal \ Glass	7740	7720	3320	1720	7052	7056
W	G	G	G	G	G	B
MO	G	G	G	G	G	G
Kovar	B	B	B	B	G	G
Chromallized Moly	-	-	G	I	G	I
Chromallized Kovar	-	-	G	I	G	G
Chrome Pl. Moly	-	-	-	G	G	-

G = Good Seals
B = Bad Seals
I = Inconclusive

Table II

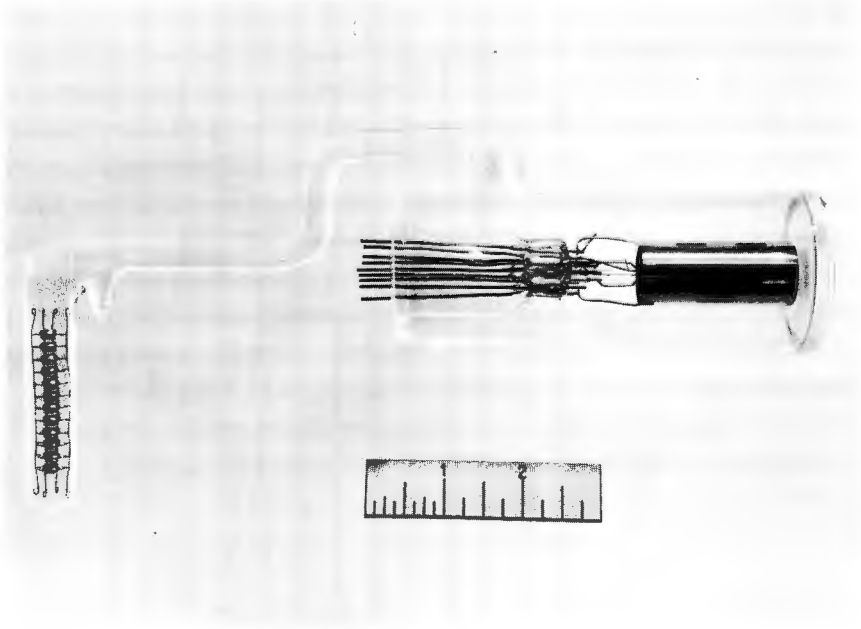

Figure 6
Multiple pin oxide free press in experimental tube.

6. SUMMARY

One of the main advantages of the oxide free seal over the conventional type seal is that there appears to be a greater freedom of choice in the types of metals and glasses that may be utilized. This type of seal also lends itself admirably to mass production methods. Economics could also be an important factor in favor of this type of seal.

These glass-metal seals do not rely upon the individualistic color characterization denoted by the glass blower. It should also be mentioned that this type of seal is not necessarily limited to wires alone as cylinders and rods might also be considered. Although hydrogen was employed in this program, other gases; *i.e.* forming gas, inert gases or possibly a vacuum atmosphere, may be equally effective.

ACKNOWLEDGMENTS

Mr. C. Williams for the hydrogen processing of the sample wires and geads.

Mr. J. Palazzolo for the construction of many of the tube units.

Mr. D. L. Fry and Dr. F. E. Jamerson for their support and encouragement of our work in this area.

BIBLIOGRAPHY

1. *Scientific and Industrial Glass Blowing and Laboratory Techniques*, W. E. Barr and V. J. Anhorn, Instruments Publishing Company (1949), Pittsburgh 12, Pa.
2. "Glass-to-Metal Seals", A. W. Hull and E. E. Burger, *Physics*, Volume V, December, 1934.
3. *Engineering with Glass*, Corning Glass Works, Corning, New York.

OXYGEN OUTGASSING CAUSED BY ELECTRON BOMBARDMENT OF GLASS

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A system employing a mass spectrometer as a continuous flow gauge has been used to study the oxygen evolved from aluminum coated glass as a result of electron bombardment. The outgassing from most glasses is found to fit the empirical equation $Q = Q_\infty (1 - \exp\text{-}t/K)$. In this equation, Q is the sum of the oxygen released during the bombardment time t and that evolved during a subsequent thermal outgas and Q_∞ is the maximum amount of oxygen expected from a sample bombarded for long times. Experimental results from Code 8603 glass indicate that Q_∞ is a measure of the range of 10 to 27 kev electrons in glass, K varies inversely with electron current per unit mass of glass affected and that electron current density may have a secondary effect on electron range in bulk glass. Oxygen outgassing data is presented from 12 commercial glasses subjected to 150μa of 20 kev electrons bombarding a 3 x ¾ inch area. A mechanism of oxygen release is proposed which involves the dissipation of electron energy, the charge produced in the glass by the electrons, and the availability of non-bridging oxygen atoms in the glass structure.

Data resulting from bombardment of two to four component glasses containing SiO_2, Na_2O, K_2O, BaO, CaO, MgO, Al_2O_3 and B_2O_3 are included. Results show that Na_2O and K_2O are the only oxides, of those studied, responsible for the oxygen release with Al_2O_3 demonstrating a temporary effect in reducing this oxygen.

INTRODUCTION

The widespread use of glass in the construction of electron devices employing oxide cathodes has always posed numerous questions with regard to the effect of the glass on cathode life. In particular, with reference to cathode ray tubes, the question is "what gases, if any, are evolved from well baked out glass when it is subjected to bombardment with electrons?" It was reported in an earlier paper on this work[1] that studies of aluminum coated glass bombarded with 20 kev electrons showed oxygen to comprise at least 95% of the gas evolved.

This paper describes the techniques we are using to study the outgassing of glass caused by electron bombardment and relates the outgassing characteristics of ten glasses to two parameters of an empirical formula. A mechanism of oxygen release is proposed which is based on: (1) changes in the glass that have been observed as a result of electron bombardment, (2) studies of the dependence of oxygen outgassing on electron energy and current density, (3) studies of two to four component glasses.

APPARATUS AND METHOD

In brief, the samples for test are mounted near the face of a small cathode ray tube where a television type raster is used to scan the samples

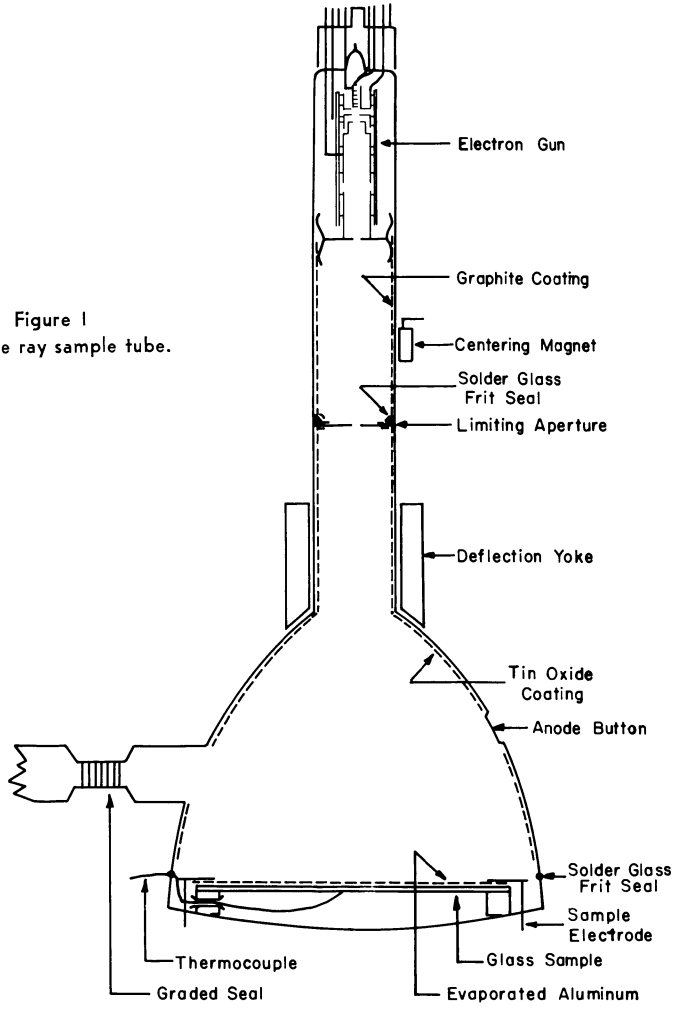

Figure 1
Cathode ray sample tube.

with electrons. A flow system in which the cathode ray tube is sealed directly to the source of a mass spectrometer is used to obtain continuous measurement of the outgassing rate as a function of time.

Outgassing produced by bombardment with 10 to 27 kev electrons is of particular interest since this is within the range of energies used in cathode ray tubes. However, glass bombarded with such electrons acquires a negative charge which destroys the raster and diminishes the bombarding electron energy. In order to avoid this, a conductive coating must be applied. The coating we use is 5000 Å nitrocellulose film, followed by 1000Å of vacuum evaporated aluminum. During subsequent thermal cycles, the nitrocellulose film is volatilized, leaving a conductive aluminum

film loosely adhering to the glass. This coating scheme was found to maximize oxygen outgassing. To insure constant surface conditions and to enhance temperature control for all tests, the samples are ground to 0.060 inches, polished on the bombardment side, washed in 2% hydrofluoric acid for two minutes and are well rinsed in distilled water prior to the application of the coating. Temperature control of the samples is provided by 40 gauge chromel-alumel thermocouples located on the bare side of the samples at the center of the raster. Small spots of Saureisen cement and waterglass are used to attach the thermocouples to the samples. The thermocouple leads are embedded in the solder glass frit panel-to-funnel seal of the sample tube.

The sample tube, shown schematically in Fig. 1, is made from a lead glass faceplate and funnel. The glass samples are held in place near the faceplate by a stainless steel and aluminum rack which is anchored to two pins sealed through the faceplate. The rack can hold a single 4 x 5 inch sample or four 1¼ x 4 inch samples. The pins and rack provide electrical contact to the aluminum sample coating.

Gettering of oxygen within the sample tube is limited by the platinum aperture sealed in the neck of the tube and the use of inert materials within the sample cavity. The control circuitry produces a standard television raster on the sample, using electromagnetic scanning of the electron beam. The beam is centered through the .060 inch aperture hole with the external centering magnet. The raster size is variable in both dimensions from the focused spot size to five inches and the raster may

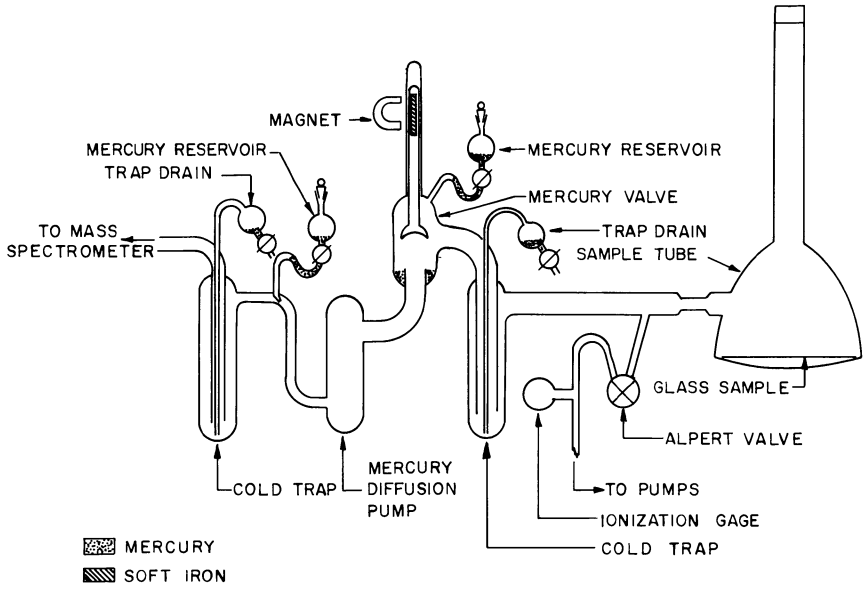

Figure 2
Connecting vacuum system.

be positioned on any area of the sample. A calibrated monitor tube is used to show the position and size of the raster on the sample area. The electron gun is one-third of a color television gun and employs electrostatic focusing. The energy of the bombarding primary electrons is taken as the potential difference between the cathode of the electron gun and the aluminum conductive coating.

The sample tube is connected to the mass spectrometer by way of the relatively high conductance system shown schematically in Fig. 2. The mercury diffusion pump and the one-inch glass system provide a pumping speed of 1.5 liters per second at the sample cavity. Since gettering within the tube is limited primarily by the 0.2 liter per second conductance of the neck aperture, at least 85% of the oxygen evolved should be measured by the mass spectrometer.

The one-inch magnetically operated mercury valve, Fig. 2, is used to isolate the mass spectrometer from atmospheric pressure when sample tubes are changed or processed. Mercury in the reservoir seals the mating surfaces of a glass ball joint. During all outgassing measurements, the mercury diffusion pump is operating and the cold traps are cooled to −78°C. After a period of about one week, sufficient mercury is cryogenically pumped into the right trap to lower the mercury level below the lip of the dome. When this happens, the level is restored by opening the stopcock to the reservoir. Each time the pressure in the system on the right of the mercury valve is increased to an atmosphere, the mercury in the right trap is pushed into the trap drain where it is easily removed from the system. The other reservoir and trap drain service the mercury pump in the same manner. Small amounts of mercury are maintained between the stopcocks and the vacuum in an attempt to hide the stopcock grease from the system.

The tube is processed (baked out for one hour at 400°C., gun outgassed by induction heating, and cathode activated) while pumping through the Alpert valve with the mercury valve closed. After completion of tube processing, the Alpert valve is closed and the mercury valve is opened. The system is then ready for outgassing measurements.

The mass spectrometer used is the Consolidated Electrodynamics Corporation Model 21-620 with the gold leak removed so that the oxygen evolved is pumped directly into the ion source region by the mercury diffusion pump. Flow calibration of the instrument is accomplished by a separate gas handling system and a calibrated leak.

SAMPLE CURRENT MEASUREMENT

The bombarding electron current is measured by placing a meter in series with the sample electrode and ground. Therefore, the sample current measured in this work is that of the primary electrons minus backscattered and secondary electrons which leave the aluminum sample coating and are collected by the funnel coating. It is generally accepted that when electrons leave a surface being bombarded with primary electrons, the secondary electrons are those with energies less than 50 ev whereas the backscattered (rediffused and reflected primary electrons) may be as energetic as the primary electrons. According to Young[2], an initial electron energy of about 2 kev is required to penetrate a 1000 Å aluminum film. Therefore, all of the secondary electrons must originate in

the aluminum and only backscattered electrons originating in the glass with initial energies greater than 2 kev will be collected by the funnel coating. Although the ratio of secondary to primary electrons may vary with primary energy, the ratio would be the same for all samples at a given primary energy. The backscattered electrons having energies approaching the primary electron energy, may originate in the glass. Archard[3] reports that the backscattered fraction depends upon the atomic number, and roughly upon the density, of the material bombarded. Therefore, the primary electron current necessary to maintain a given sample current would be expected to depend upon the glass sample.

A more complete understanding of the controlling oxygen release factors is necessary in determining the importance of considering these currents. As a matter of interest, however, the ratio of secondary (including true secondary plus backscattered electrons) to primary electron current, I_S/I_P, has been measured for four samples with large differences in density. The measurement was made in a cathode ray tube similar to that of Fig. 1. The aperture and neck coating between the aperture and the electron gun were electrically isolated from the funnel coating. In addition to the I_A meter which measures the net sample current, a meter was placed in series with the funnel coating and ground for measuring I_S. The measurements were made using a $3 \times \frac{3}{4}$ inch raster, electron energies, Vp, of 10, 20 and 28 kev and I_A values of 25, 50, 75 and 150 μa. No major differences were noted in the I_A/I_P ratios for either I_A or Vp variations. Table I lists the values determined, the I_P/I_A ratio, and the densities of all glasses mentioned in this paper.

TABLE I

Glass Densities and Electron Current Ratios

Corning Glass Code	Density	I_S/I_P	I_P/I_A
7070	2.13	0.12	1.14
7740	2.23		
7800	2.36		
8603	2.36		
0081	2.47		
9019	2.59		
1723	2.63		
9010	2.64		
0129	2.78		
0041	2.89		
0120	3.05	0.23	1.31
8870	4.28	0.34	1.52
8363	6.22	0.35	1.54

OUTGASSING MEASUREMENTS

Samples of aluminum coated glass are maintained at 200°C. during bombardment by placing a small furnace around the sample end of the tube. The amount of oxygen evolved during the electron bombardment, Q_E, is determined by integration of the flow data recorded by a strip chart recorder on the output of the mass spectrometer. When the electron beam is turned off, oxygen will continue to be evolved from the sample if the sample temperature is maintained at the temperature of bombardment. To accelerate the depletion of this thermally evolved oxygen, Q_T, the sample temperature is increased to 350°C.

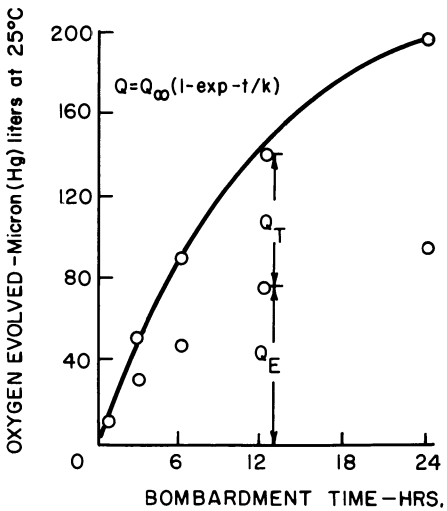

Figure 3
Outgassing of Code 8603 glass.

Figure 3 is a plot of the oxygen outgassing data from Code 8603 glass bombarded with 150 μa of 20 kev electrons using a 3 × $\frac{3}{4}$ inch raster. These data were obtained using a new area of glass for each of the Q_E points. Following each bombardment, the sample was baked out until the oxygen had been depleted.

If one assumes a quantity of oxygen of uniform distribution within a volume of glass and if a constant energy or force is applied to cause it to become available for removal, one would expect the Q data, where $Q = Q_E + Q_T$, to fit an equation of the formula $Q = Q_\infty (1 - \exp -t/K)$. In this equation t is the actual time of bombardment, Q_∞ is the total amount of oxygen which can be produced and measured and K is a measure of the time dependence of the phenomenon. The Q data from most glasses have been found to fit this equation rather well. In these cases the Q_∞ and K parameters provide a concise means of describing the outgassing characteristics under a given set of conditions.

COMMERCIAL GLASSES

Twelve commercial glasses were bombarded using 150 μa of 20 kev electrons and a 3 × $\frac{3}{4}$ inch raster with bombardment time t as the only

variable. The data from ten of these were found to fit the empirical formula rather well. The Q_∞ and K parameters are listed in Table II. These values were determined with the aid of an electronic computer as the values which minimize the average fractional deviations of the Q data. For values of $t<4K$, the average deviation is less than 12% for any particular glass. For values of $t>4K$, the observed Q data are somewhat larger than one would expect for several glasses.

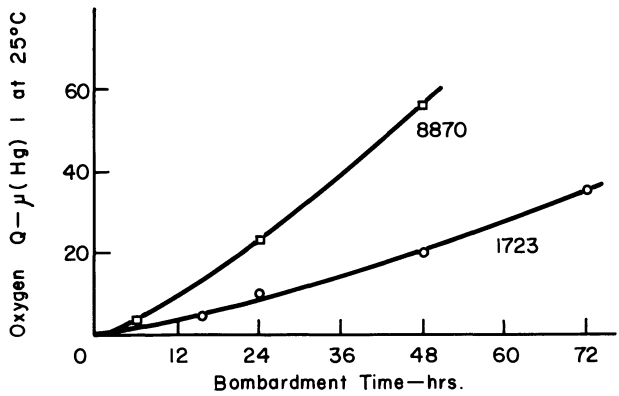

Figure 4

Outgassing of Code 1723 and 8870 Glasses.

The oxygen data from Code 1723 and 8870 glasses do not fit the empirical equation. These data are plotted in Fig. 4. Glasses have been measured which evolve less than 1 μ (Hg) liter as a result of 24 hours of bombardment. This is considered to be the background of the system.

TABLE II

Q_∞ and K for glasses bombarded with 150 μa of 20 kev electrons using a 3 x¾ inch raster

Corning Glass Code	Q_∞ μ (Hg) liters at 25°C.	K (Hour)
0081	247	23.4
8603	227	12.4
9019	178	23.7
9010	170	20.6
0041	83	5.9
0120	72	7.7
7740	60	5.5
0129	60	5.4
7070	51	12.5
7800	49	3.2

ELECTRON ENERGY AND CURRENT DENSITY DEPENDENCE

The dependence of electron energy and current density on the oxygen outgassing of Code 8603 glass has been studied. Electron energies, Vp, of 10, 20 and 27 kev with total sample currents, I_A, of 25, 75 and 150 μa bombarding a 3 × $\frac{3}{4}$ inch area were used. The Q_∞ and K values determined are listed in Table II.

From the work of Kanter[4], the average electron energy loss in the 1000 A aluminum conductive coating has been determined to be 460, 270 and 220 ev for primary energies of 10, 20 and 27 kev respectively (the 27 kev value was extrapolated from the 2 to 20 kev data). This leaves average electron energies of 9.5, 19.7 and 26.8 kev entering the glass. According to the Thomson-Widdington law and the work of Spear[5], the depth of electron penetration, x, in cm is determined by the relation

$$x = \frac{V_p^2}{\beta d} \qquad (1)$$

where Vp is in volts, d is the density in gm cm^{-3} and β is a constant of $6.2 \times 10^{11} V^2 gm^{-1} cm^2$ for a borosilicate glass. The mass of glass affected, M, is given by

$$M = Axd \qquad (2)$$

where A is the bombarded area in cm^2. Combining 1 and 2,

$$M = \frac{AV_p^2}{\beta} \qquad (3)$$

In this work, A is held constant at 14.5 cm^2. From equation (3), assuming the value of β to be reasonably good for all glasses, one notes that the mass of glass affected is proportional to the square of the electron energy and independent of glass density. Therefore, the 9.5, 19.7 and 26.8 kev electrons will affect 2.1, 9.1 and 16.9 mg of glass respectively. If Q_∞ is expected to be a measure of the removable oxygen in the glass affected as is proposed in the next section, one would expect the Q_∞ values at the three energy levels to be in the ratio 2.1:9.1:16.9 or 1:4.3:8.0, which we indeed found to be the case. If one simply takes the average of the Q_∞ values at the three energies from Table III (60.5, 256 and 468 μ (Hg) liters at 10, 20 and 27 kev respectively), the ratio of these values is 1:4.2:7.8 and is in reasonably close agreement with the mass ratios. However, it is interesting to note that, with the exception of the 150 μa 10 kev value, Q_∞ tends to increase with decreasing electron current density at a given energy. This phenomenon will also be considered in the next section.

The time dependence factor K of the oxygen outgassing has been found to be a function of the beam current per unit mass of glass affected. Figure 5 is a plot of K as a function of I_A/M with M computed from equation (3). The values used are listed in Table IV.

TABLE III

Q_∞ and K for Code 8603 glass bombarded with variations of sample current (IA) and electron energy (VP) using a 3 x ¾ inch area

VP (kev)	IA (μa)	Q_∞ μ (Hg) liters at 25°C.	K (Hour)
10	150	78	5.5
	75	48	5.4
	25	56	20.9
20	150	227	11.7
	75	243	26.9
	25	298	118
27	150	468	30.2

TABLE IV

Ratio of electron current to mass of glass affected, (IA/M), for various bombardment conditions

VP (kev)	IA (μa)	IA/M (ma/gm)	K (hour)
27	150	8.88	30.2
20	25	2.75	118
	75	8.25	29.6
	150	16.5	11.7
10	25	11.9	20.9
	75	35.8	5.4
	150	71.5	5.5

OXYGEN RELEASE MECHANISM

An examination of glass samples after electron bombardment has revealed the following as partially depicted by the schematic cross-section in Fig. 6:

1. The surface is displaced from the original surface plane of the glass in the direction of the bombarding electrons. As observed with a Zeiss interference microscope, the displacement increases with increasing Q and is in the order of tenths of microns as Q approaches Q_∞.
2. There is a very sharp density change with depth in the bombarded area of the glass as evidenced by interference colors. Judging from the brilliance of the transmitted fringe, the transition from the less to more dense layers is less than 100 Å thick.
3. The depth at which the transition in 2 occurs increases progressively with bombardment time and approaches the estimated depth of electron penetration as Q approaches Q_∞. The depth of 20 kev electron penetration in Code 7740 glass is estimated at 2.7 μ based on the Thomson-Widdington law and the work of Spear[5].

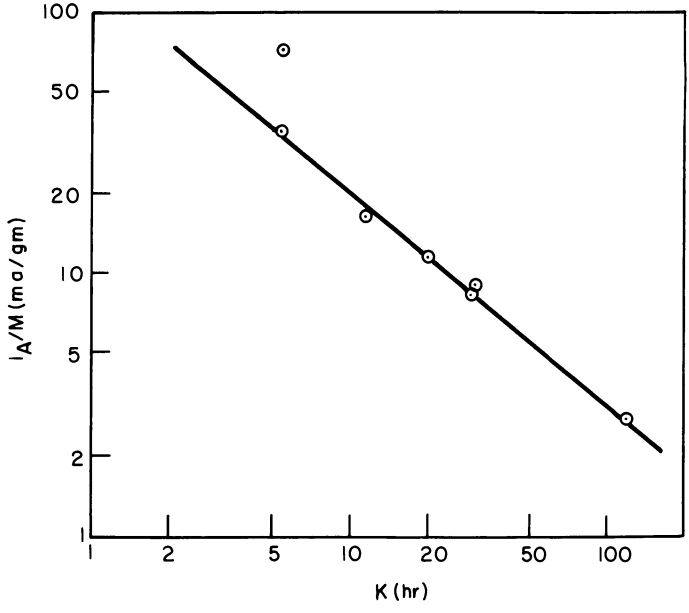

Figure 5
Outgassing time dependence factor K as a function of current per unit mass of glass affected, $I_{A/M}$

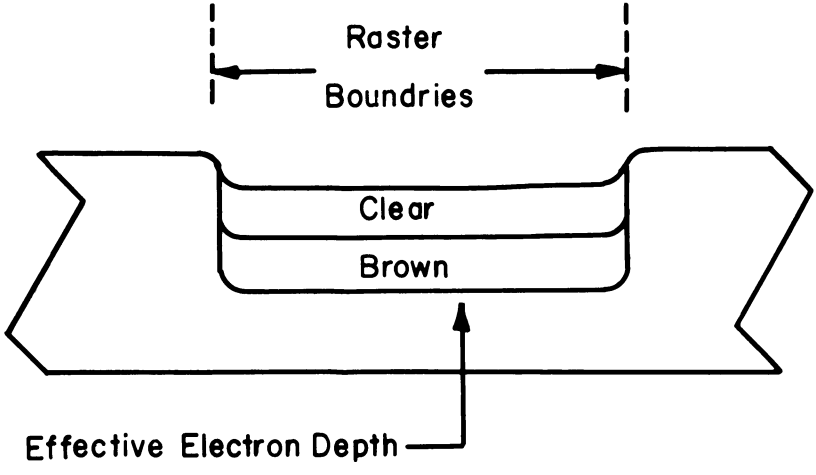

Figure 6
Schematic cross section of bombarded glass.

4. The familiar electron browning begins at the bottom of the layer described in 2 and 3 and is continuous to the depth of electron penetration with x-ray browning going much deeper. This was determined by etching away the bombarded surface in steps and measuring the sample thickness loss and visible transmission increase between each step. Measurements of thickness changes were made with a Sheffield gauge. The sample was carefully indexed so that all measurements were taken at the same spot.
5. It is not possible to produce reboil in a heavily bombarded area of the glass when the glass is reheated in an open flame. (Reboil is the term used to describe the evolution of gas, in the form of bubbles, in molten glass.)
6. As much as 10% of the total oxygen, from the affected volume of some glasses, is removed as a result of electron bombardment. Obviously, the oxygen within the glass structure itself is removed.

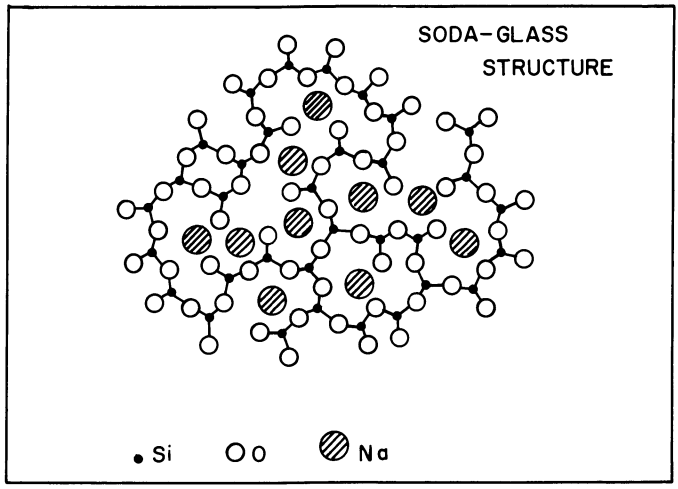

Figure 7
Schematic in two dimensions of a soda-silica glass after Warren[6].

In proposing any oxygen release mechanism, the structure of a simple soda-silica glass is considered. Figure 7 is a two-dimensional picture of such a structure as deduced by Warren[6] and is in agreement with the theoretical deductions of Zachariason[7]. In three dimensions, each silicon atom is actually surrounded by four oxygen atoms. It is noted that when Na_2O is added to SiO_2, the oxygen from the Na_2O attaches itself to a Si atom thus breaking one link of the normal Si-O-Si bond. This leaves two oxygen atoms bonded to only one Si with the two Na atoms in the nearby interstices to provide charge neutrality. It is these non-bridging oxygen atoms, or oxygen half-ions that are important in the release mechanism. Figure 8A is a simplified section of Fig. 7.

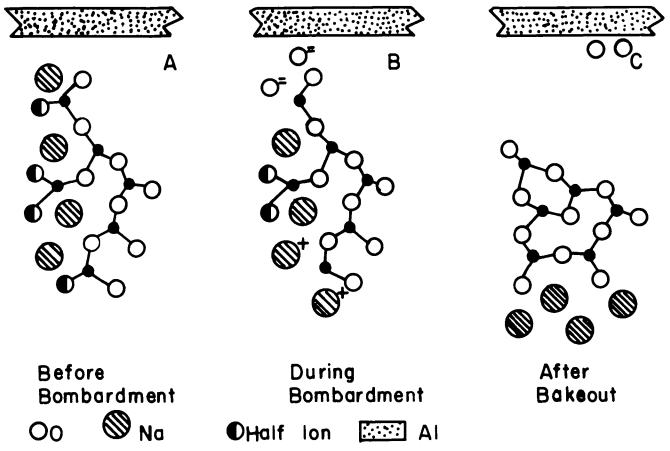

Figure 8
Schematic of Oxygen Release Mechanism.

The high energy electrons penetrate the aluminum coating, enter the glass and dissipate their energy by ionization and excitation of the atoms of the glass structure. They come to rest at some depth within the glass, producing a net negative charge. This charge and the grounded aluminum electrode set up a field in the glass layer between these two in a direction necessary to move positive sodium ions toward the negative charge region. (Reference will be made to sodium ions for simplicity since these are generally considered to be the major charge carrier in glass.) A potential equilibrium is reached in which the arrival of primary electrons is balanced by the arrival of sodium ions together with the diffusion of electrons back to the surface electrode. As the sodium ions become separated from the oxygen half-ions their net positive charge can be satisfied by oxygen half-ions at a lower level (Fig. 8B) or electrons diffusing back toward the aluminum electrode. Metallic ions which have become neutralized by electrons exist within the glass in an elemental form and produce the color commonly referred to as electron browning. Bombarding electrons re-ionize these atoms, or separate sodium atoms from their new oxygen half-ion position, and they move a step deeper into the glass concentrating themselves at a depth approaching that of the effective primary electron penetration as Q approaches Q_∞, (Fig. 8C).

Concurrent with the movement of the sodium, oxygen atoms are freed from the oxygen half-ion positions. They can move into vacated half-ion positions nearer the surface (provided sufficient sodium ions are on hand to provide charge neutrality) and stop migrating temporarily (Fig. 8B), or they can lose their electrons to the aluminum electrode and become detected by the mass spectrometer, (Fig. 8C). Therefore, as the brown region moves deeper into the glass, more and more of the network's removable oxygen is left between this layer and the aluminum electrode in the form of ions. During the thermal outgassing cycle following electron bombardment, the excess primary electrons diffuse to the surface

electrode along with all negative oxygen ions which cannot find half-ion positions to satisfy. This leaves a layer of glass far different in composition and properties from the original sample between the browned region and the aluminum. This layer is deficient in sodium and oxygen half-ions (Fig. 8C). The remaining loose structure would tend to pull itself together and reform the normal SiO_2 tetrahedron, thus reducing the density and lowering the surface plane.

Several researchers in this laboratory have observed that reboil resistance is inversely proportional to the helium diffusion rate. Altemose[8] has shown that the addition of soda to glass reduces the diffusion rate. Conversely, the removal of soda from the structure should increase the diffusion rate and reduce reboil. Removal of the more weakly bound oxygen from the structure, which may cause reboil given sufficient thermal energy, may also contribute to the reduction of reboil.

It is interesting to speculate on the mechanism causing the increase of Q_∞ with decreasing current density at a given electron energy as was pointed out in the electron energy current density studies. Such a phenomenon could be explained by considering the repulsion of the primary electrons by the charge built up within the glass at different current densities. Under equilibrium conditions, the primary electrons which have entered the glass are diffusing back to the aluminum electrode at the same rate that new primaries are arriving. The time required for this equilibrium is apparently a matter of seconds since the net sample current becomes reasonably steady almost immediately after the electron beam is turned on. Therefore, the total charge within a given glass increases as the bombarding electron current increases. This charge has a retarding effect on the normal penetration of the primary electrons and an increase in the primary electron current would reduce the effective depth of penetration of primary electrons. This would result in a reduction in the depth of the most negative potential in the glass. From the proposed release mechanism, the depth of most negative potential would become the effective depth for the removal of oxygen since oxygen ions produced at a greater depth would be repelled by the more negative charge level.

SIMPLE GLASS STUDIES

The oxygen release mechanism proposed that modifying oxides used in glass melting, such as Na_2O, were responsible for the oxygen outgassing of glass caused by electron bombardment. In an attempt to obtain an understanding of the complete mechanism and to determine which oxides are responsible for the release, studies of two to four component glasses were begun. Since one to two months is required for a good Q_∞ determination on a single glass, care was taken to test only stable and amorphous glasses. Mole percentages of the various oxides were used as the basis of computing glass composition so that outgassing data could be compared to glass structure on a molecular basis. Care was taken to use glass batch materials with a 99% plus purity with chemically pure materials being used whenever available. All melts were made in clean platinum or platinum-rhodium crucibles. Whenever possible, the glasses were stirred during melting; otherwise, they were poured in water (dry gauged),

ground and remelted to enhance homogeneity. As a precaution against batch errors, each melt was checked by analysis of the resulting glass. The samples were then prepared for electron bombardment tests in the normal manner. Table V lists the glass batch oxide composition in mole percentages.

TABLE V

Composition of Simple Glasses by Mole Percent of Oxide

Glass	SiO_2	CaO	BaO	B_2O_3	MgO	Al_2O_3	Na_2O	K_2O
124ART	83.0						17.0	
124ARU	75.0					8.0	17.0	
124ARV	75.0	17.0				8.0		
865N	75.0		17.0			8.0		
865O	75.0				8.0		17.0	
865P	83.0	8.5					8.5	
865AB	75.0	8.5				8.0	8.5	
865S	66.0					17.0	17.0	
865Y	83.0							17.0
865T	75.0			25.0				
865V	65.0			25.0			10.0	
865W	65.0			25.0				10.0

The outgassing tests were made, using 150 μa of 20 kev electrons and a 3 $\times$ $\frac{3}{4}$ inch raster with bombardment time as the only variable. The Q_∞ and K parameters determined are listed in Table VI along with the oxygen put into 9.1 mg (the affected mass) of the glasses with the various oxides.

DISCUSSION

The binary soda-silica glass, 124 ART, shows Q_∞ to be 53% of the oxygen in the glass associated with the soda. In reference to the proposed release mechanism, apparently the oxygen half ions bonded ionically to the sodium are the oxygen source. The substitution of Al_2O_3 for SiO_2 in this glass, as in glass 124 ARU, reduces Q_∞ to 22% of the soda's oxygen. If one assumes that the Al_2O_3 uses the oxygen of the Na_2O to become four coordinated (bonded to four oxygen atoms with the sodium providing charge neutrality, as proposed by Ainsworth[9]), it requires one-third oxygen of the remaining soda is 120 μl of which Q_∞ is 42% and is in reasonably close agreement with the glass 124 ART data. However, the Q data of this glass begins to rise again after 15 hours of bombardment. Apparently the effect of the alumina is temporary since the 48 hour data point, which is also asymptomatic, is 131 μl or 58% of the soda's oxygen. This would indicate that the Al_2O_4 coordination is temporarily effective in preventing oxygen release. It is felt that the short term effect is of practical significance since the bombardment conditions used in these experiments are extremely severe as compared to those expected in electron devices.

TABLE VI

Oxygen in and Q_∞ from (in μ (Hg) Liters) and K (in hours) in Volume of Glass Affected by Bombardment with 20 kev Electrons using a 3 x ¾ inch Raster

Glass	SiO_2	CaO	BaO	B_2O_3	MgO	Al_2O_3	Na_2O	K_2O	Q_∞	K
124ART	2335						239		127	9.1
124ARU	1998					320	227		50[1]	5.8
124ARV	2030	230				325			<1	—
865N	1606		182			258			<1	—
865O	2165				116		245		147	14.0
865P	2353	121					121		86	12.4
865AB	2014	114				322	114		50[2]	—
865S	1660					642	214		77	10.0
865Y	1345							193	130[3]	17.0[3]
865T	2039			1020					<1	—
865V	1760			1010			135		106	6.5
865W	1670			965				129	123	23.1

1. The Q curve approaches an asumptomatic value in 10 to 15 hours of bombardment. However, after that the Q data are larger than one would expect with the 48-hour point being 131 μ (Hg) Liters and again asmyptomatic.
2. These data do not appear to have an exponential plot. The 50 μ (Hg) liters is the 24-hour Q point.
3. These values are approximate; more data is required for a good Q_∞ determination.

ABBREVIATIONS

Å	angstrom unit
cm	centimeter
ev	electron volt
kev	kilo electron volt (10^{+3} ev)
gm	gram
mg	milligram (10^{-3} grams)
μ	micron (10^{-6} meters)
μa	microamperes (10^{-6} amperes)

The substitution of CaO for the Na_2O of glass 124 ARU, as in glass 124 ARV, shows that the oxygen associated with CaO in the glass cannot be released by bombardment. This is explained by considering that Ca^{++} must bridge two oxygen half-ions, whereas, Na^+ is bonded to only one. This requires that both Ca ionic bonds be broken in close proximity and

the Ca^{++} moved before the single covalent oxygen to silicon bond can be broken and the oxygen released. Apparently the chance of this happening is small.

The possibility of the lower field strength (ionic charge divided by the square of the ionic radius) of the Na^{+} (1.11) as compared to the Ca^{++} (2.04) being responsible for oxygen release was also considered since this would be a measure of the strength of the bond. In glass 865-N, barium (field strength 1.10) oxide was substituted for the CaO in glass 124 ARV. The lack of oxygen release from 865-N would indicate that the devalency, bridging of two half-ions of the Ba^{++} and Ca^{++}, prevents oxygen release rather than the field strength.

Ainsworth[9] also reports that intermediate oxides such as MgO, ZnO, BeO and NiO also use the oxygen from fluxing oxides to go into the network by becoming four coordinated. In glass 865-O, MgO was substituted for the Al_2O_4 in glass 124 ARU. It is seen that Q_∞ from this glass is 60% of the soda's oxygen—essentially unchanged from the 124 ARU data. This indicates that the Mg_2O_4 cordination is even less effective than the Al_2O_4 coordination in preventing oxygen release. However, a slight effect is noticed in the form of an increase in the K value which reduces Q for a given t. As a matter of interest, it is noted that the bulk resistivities of glasses 124 ART, 124 ARU and 8650 are identical, thus precluding a resistivity effect.

The Q_∞ value, when equal amounts of CaO and Na_2O are used, as in 865 AB, was expected to show an effect similar to the one observed in glass 124 ARU. However, Q is essentially linear with t up to t = 24 hours and not asymptomatic. However, compared to glass 865 P, Q is reduced for a given t.

In glass 865 S, an attempt was made to tie up all of the oxygen by using equal mole percentages of Na_2O and Al_2O_3. Although the desired result was not achieved, Q_∞ was reduced to a permanent 36% of the soda's oxygen. Compared to the 53% of 124 ART, this reduction seems significant. However, compared to the temporary 22% of glass 124 ARU, the result is bewildering.

The use of K_2O in glass 865 Y in place of the Na_2O in glass 124 ART produces a Q_∞ of approximately 67% of the alkali's oxygen. Although a good determination of Q_∞ requires more data, it seems reasonably safe to assume that K_2O and Na_2O produce approximately the same effect in terms of oxygen outgassing with K_2O perhaps allowing a larger percentage of the alkali oxygen to be released.

In the borosilicate systems tested, it is seen that the binary borosilicate glass 865 T evolves no oxygen. The addition of Na_2O and K_2O, as illustrated with glasses 865 V and 865 W, produces Q_∞ values of 78% and 95% of the alkali oxygen respectively. The larger percentages in the boron glasses, as compared to boron-free systems, is considered real.

CONCLUSIONS

Studies of two to four component glasses clearly indicate that of those studied the alkali rather than the alkaline earth oxides in glass are responsible for the oxygen evolved as a result of electron bombardment. It has also been shown that the quantity of oxygen evolved is propor-

tional to the square of the primary electron energy as one would expect. The β value, equation (3), of $6.2 \times 10^{11} V^2 gm^{-1} cm^2$ (determined by Spear[5] for a borosilicate glass) was assumed in this work to be reasonably good for all glasses. However, a variation in β from glass to glass would also vary M and might be responsible for the differences in the Q_∞ to alkali oxygen ratio and could explain the large difference between the boron and boron-free systems. For this reason, no significance is attached in small differences in the Q_∞ to alkali oxygen ratio at this time.

In addition to Q_∞, the K values listed are necessary in determining the shape of the outgassing curve. Although K was determined to be a function of the I_A/M for Code 8603 glass, no relation between K and glass structure or properties is evident at this time.

It is important to remember that, in many electron device applications, coatings with thicknesses of many microns are applied to the glass. Earlier work has shown that such coatings reduce the substrate to a common denominator and that the oxygen evolved originates in the coating.

This work is continuing toward a more complete understanding of the oxygen release mechanism and includes continued studies of simple glass systems.

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REFERENCES

1. B. J. Todd, J. L. Lineweaver, and J. T. Kerr, *J. Appl. Phys.* 31, 51, (1960).
2. J. R. Young, *Phys. Rev.* 103, 292 (1956).
3. G. D. Archard, *J. Appl. Phys.* 32, 1505 (1961).
4. H. Kanter, *Phys. Rev.* 121, 677 (1961).
5. W. E. Spear, *Proc. Phys. Soc.* (London) B68, 991 (1955).
6. B. E. Warren, *J. Appl. Phys* 8, 645 (1937).
7. W. H. Zachariasen, *J. Am. Chem. Soc.* 54, 3841 (1932).
8. V. O. Altemose, *J. Appl. Phys.* 32, 1309 (1961).
9. Ainsworth, *J. Soc. Glass Tech.* 38, 501 (1954).

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The following are on record as having attended the Eighth Symposium on the Art of Glassblowing held at the Sherman House Hotel, Chicago, Illinois, June 5, 6, 7, 1963. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

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