Proceedings

THE ELEVENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1966

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

Proceedings
THE ELEVENTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

Sponsored by

THE AMERICAN SCIENTIFIC
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THE NEW ENGLAND SECTION
OF THE A.S.G.S.

STATLER HILTON HOTEL
BOSTON, MASSACHUSETTS

JUNE 8, 9, 10, 1966

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

FOREWORD

Boston, a city steeped in heritage and tradition, was the site of our Eleventh Annual Symposium. We were surrounded by landmarks of our country's early struggles to break the bonds of tyranny and oppression and to conceive our great nation. This provided inspiration for the American Scientific Glassblowers Society in its continuing struggle to break the bonds of secrecy and apprehension within our profession.

The annual Symposium is an educational forum which is designed to keep us alert to a changing technology. Through this annual meeting our society members pursue their quest for knowledge. It is our attempt to shorten the time between discovery and application of knowledge, since we believe that knowledge is the wealth of our nation which even tyrants cannot despoil. We shall continue to pursue our obligation to advance and disseminate scientific and technical information about glass working.

The American Scientific Glassblowers Society gratefully acknowledges the work of Mr. Anthony Velluto and his Committees of the Eleventh Symposium; Mr. Jules Benbenek and his Technical Papers Committee; and Mr. Karl Walther and his Guidance Committee. Their effort is rewarded by the enthusiasm which was shown by record breaking interest and attendance.

We are also indebted to the many authors with diverse experiences and varied kinds of information who shared their thoughts with us and gave us the opportunity for interpersonal contact.

Mr. George Sites who assembles all of these talks into this unified whole called "Proceedings" is to be complimented for his excellent and untiring efforts.

Finally, I would like to dedicate this technical work to some not so technically inclined women who have managed to help and care about all of the proceedings throughout this year: To Virginia Velluto, Dolores Sites, and my wife, Carol.

ARTHUR DOLENGA
President

June, 1965 - June, 1966

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DESIGN CONSIDERATIONS FOR HIGH TEMPERATURE VACUUM SYSTEMS USED IN GAS ANALYSIS

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INTRODUCTION

The liberation of gases in vacuum from materials, and the subsequent analysis of them requires an apparatus which is capable of being pumped down to vacuums in the order of 10^{-8} Torr. The system should be inert to the gases liberated and all subsequent reactions ensuing from the analysis of such material. An ideal material for such uses is glass. To me, glass is an amorphous noncrystalline material with reasonable workability, durability and not subject to reaction with gases or other materials at ordinary temperatures. The general term of "glass" will be used throughout this paper to include boro-silicate glasses, quartz and Vycor.®

We will discuss the apparatus parameters, which are shown in Figure 1, in general. The first thing to be considered, in building an apparatus made of glass, is the choice of glass for the various parts (Fig. 2). Most of the time, we use quartz for the furnace tubes, which constitute the high temperature part of the system. The joints attached to the quartz usually are Vycor. The low temperature parts of the apparatus, which are normally at room temperature, usually are made of Pyrex.®

In the ensuing illustrations, I will show examples of the effects of some gas reactions with quartz; as well as, other examples of degradation of Pyrex and Vycor and the properties of these materials.

Many times the dimensions of the equipment (by dimensions we refer to the thickness of the glass, the diameter, the length and all other measurements which affect design) make the designer compromise to favor certain parameters which are more critical. Generally, one tries

APPARATUS PARAMETERS

1. CHOICE OF GLASS
2. DIMENSIONS
3. SHAPE
4. LOCATION OF INTERNAL ELEMENTS
5. EASE OF CONSTRUCTION

Figure 1

TYPES AND USES

QUARTZ - HIGH TEMP. - FURNACE TUBES, ETC.
VYCOR - JOINTS - WITH QUARTZ
PYREX - LOW TEMP. AND ROOM TEMP.

Figure 2

to keep the size of equipment down to reasonable dimensions, but other factors have to be considered which might make our system larger than desirable. An example of this is the location of internal elements within the glass walls of the outer shell to prevent radiant heating from inner elements.

Another case of the effect of the dimension is the condensation of metals and carbon on the surfaces of the glass systems. Sometimes it is possible to keep the condensate or the plated-out metals down in a certain part of the apparatus by merely making it longer. There are many other dimension factors which I will point out as we go along. They will be obvious as we discuss the figures that follow.

MAIN BODY

The properties of glass, which appear to be important for vacuum use, are listed in Figure 3. Special properties that affect performance, such as, degassing of certain types of glasses, workability, and deformation at certain temperatures are all considered.

Thermal shock is a property which we must always consider; but with the glass used in most furnaces tubes today, has minor significance.

GLASS PROPERTIES

1. SPECIAL PROPERTIES
2. DEFORMATION
3. THERMAL SHOCK
4. WORKABILITY
5. GEOMETRY
6. LOCATION OF ACCESSORIES

Figure 3

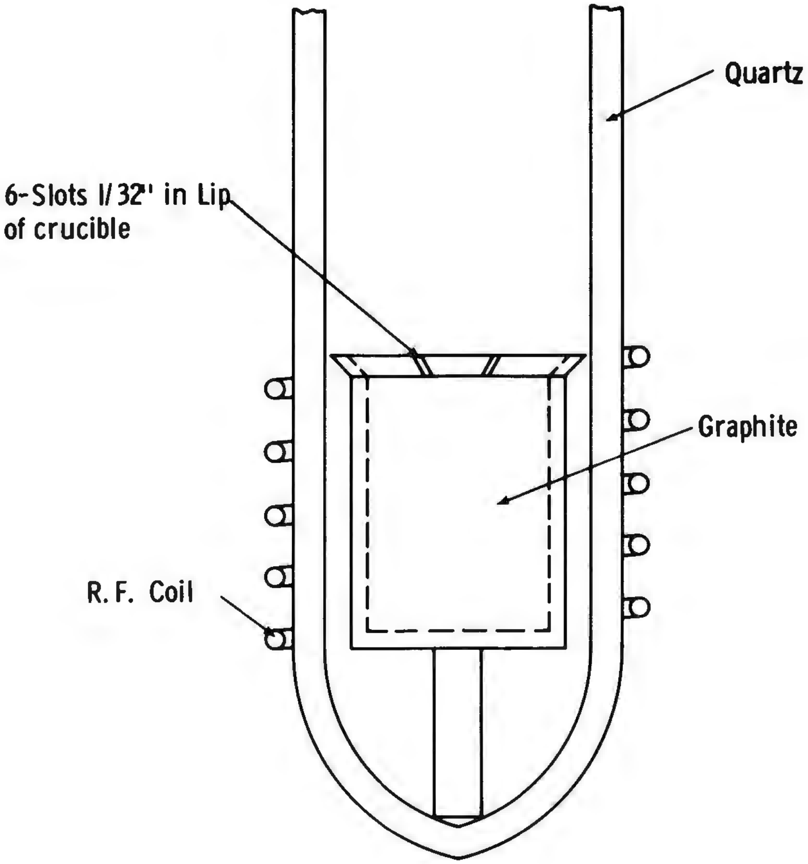

Figure 4
Schematic of early furnace tube.

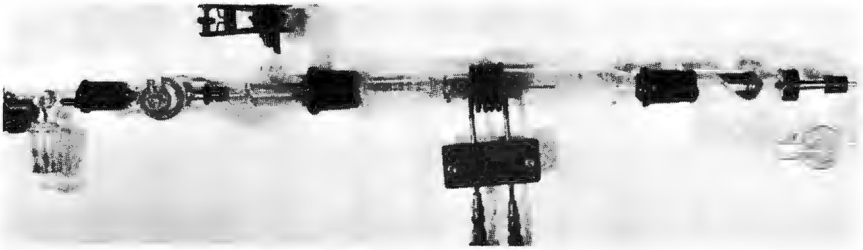

Figure 5
"Leco" assembly.

Most of the glass-like materials we have used are fairly devoid of this weakness. We have had no noticeable occurrence of thermal shock.

Geometry has been a major factor in all of our vacuum system designs. Some have had to be abandoned because of this factor. Accessories, which might be close to the walls of the system, often have caused the alteration of design. Many of the materials we use inside the glass envelope have an obverse effect, especially on design considerations, not only from a geometry standpoint, but also from a standpoint of decomposition under operation conditions.

Figure 4 shows a typical furnace tube in a hot extraction apparatus usually operating at 1000°C. The proximity of the RF coil, the diameter

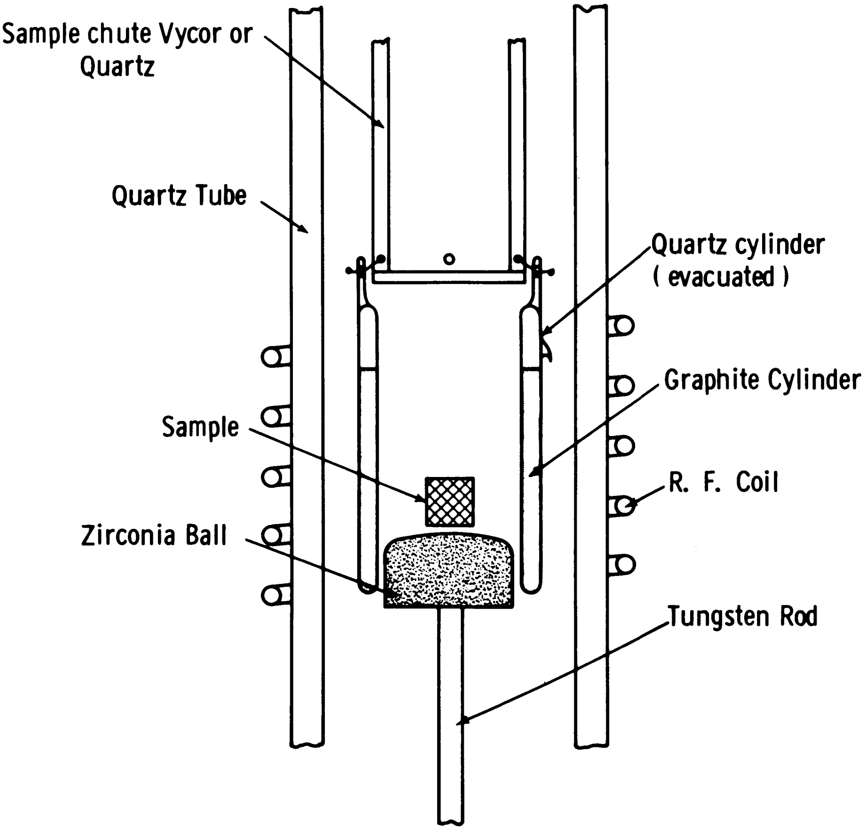

Figure 6
Schematic of Leco crucible.

of the furnace tube and the location of the hot crucible in this system are shown.

The features illustrated here are: RF coil in close proximity to the graphite crucible, slotted lip on the crucible to reduce inductive heating of the glass, with the pedestal barely touching the bottom of the tube walls. This design proved to be very successful up to 1000°C. A water jacketed modification of this furnace tube allowed operation up to 1200°C.

This tube and crucible assembly withstood many months of operational use without failure. The disadvantage of this design became obvious when the operator discovered his crucible was full of spent samples. The vacuum system must be opened to empty the crucible thus creating "downtime" for the analytical system.

A more efficient system designed by LECO is shown in Figures 5 and 6. The entire tube shown in Figure 5 includes an air-lock at the top to

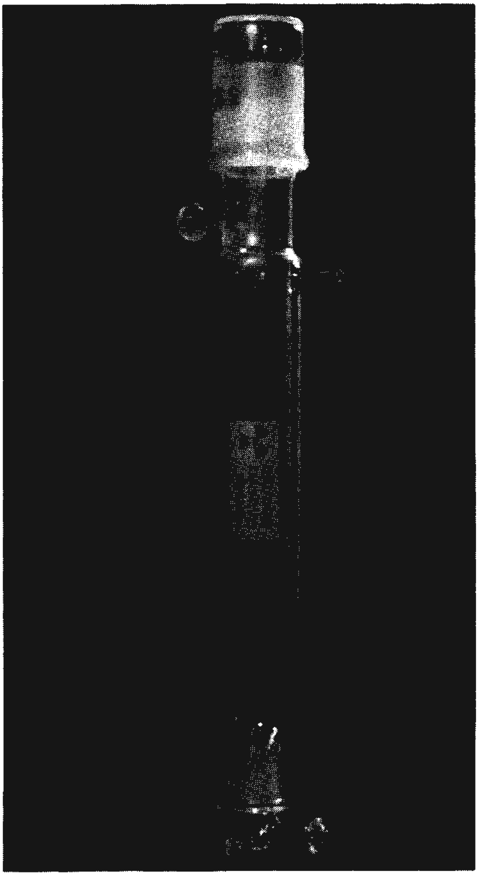

Figure 7
Dual temperature assembly.

get the sample into the vacuum system without undue flooding with air. This entry device proved to be a very practical design and has withstood several thousand cycles without failure.

Figure 6 is a schematic of the inner crucible and associated parts showing some design features mentioned in the introduction. The hanging crucible on the sample chute is especially note worthy since this arrangement prevents conductive heating of the end of the chute. The false-bottom zirconia ball and tungsten rod assembly allow the sample to be released from the crucible and fall into a collector at the base of the tube. The entire design has many operational advantages and is an example of good design.

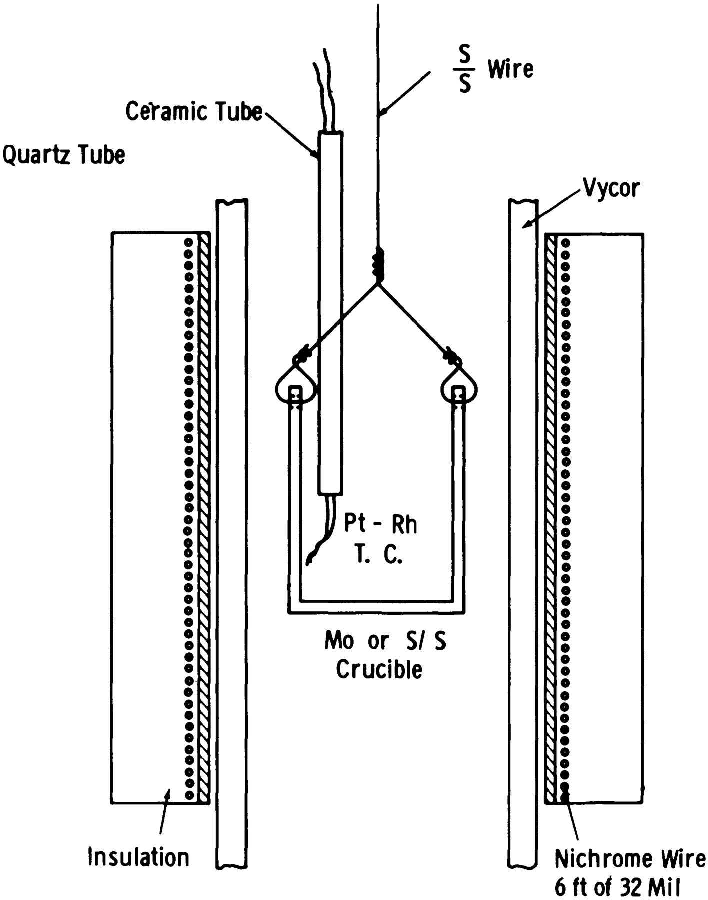

Figure 8
Assembly for thermocouple control.

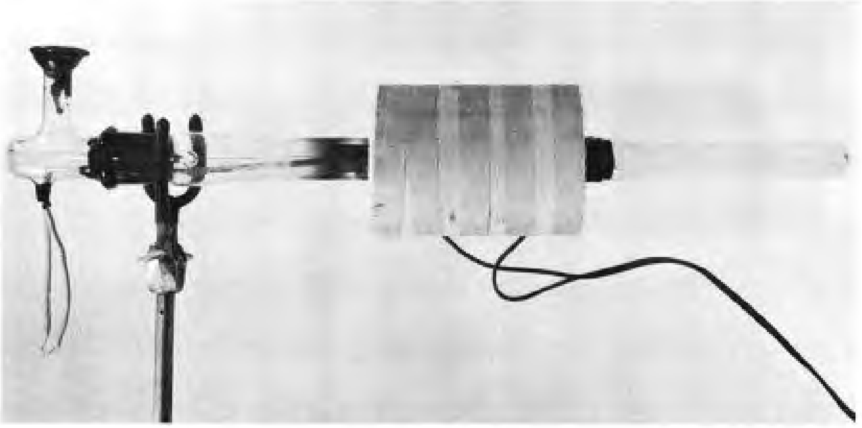

Figure 9
Resistance heater and thermocouple assembly.

The furnace assembly shown in Figure 7 was designed by me to allow heating materials at two temperatures allowing deposition of more volatile metals on the tantalum sleeve with subsequent higher heating of the residue.

The tube is water jacketed and has a specially oriented water inlet to allow placing the radio-frequency coil around the tube from the bottom. This little innovation saves many hours of labor and allows the use of a close-fitting removable coil on the outer jacket.

The crucible mount shown is simple to build but effective and proved to be very durable. The design of the bottom closure allows removal of the crucible assembly for loading and disposal. This equipment was used up to 1000°C. for several months with no evidence of failure.

A quartz tube, for use in a system which had to be heated to several temperatures for long periods of time, was required in these laboratories. The temperature of the crucible was to be measured by thermocouples which do not behave very well in radio-frequency fields. Figure 8 shows the schematic details of this assembly and Figure 9, the entire apparatus with the thermocouple leads entering the top adapter, The resistance furnace was wound directly on the quartz tube and coated with insulation. This design allowed heating and temperature control with excellent success for many hours of operation.

A typical vacuum fusion set-up used in our laboratories is shown in Figure 10. With this equipment, samples are heated as high as 2400°C. in a shielded crucible. The furnace tube is 18″ long through bottom to the first graphite joint. This length, above the hot zone, allows the condensation of vapors before they are swept into the transfer pump orifice. A case where geometry has been the controlling factor in the success of this equipment.

CONCLUSIONS

The success or failure of many glass systems, when used for high temperature is dependent, for the most part, on proper design considerations. Extremely important are dimensions, choice of glass, location of accessory parts, shape and temperature of operation. Lesser considerations in vacuum systems are special properties, thermal shocks, and workability. These factors, do however, enter into certain specialized equipment and control the cost of construction.

The capabilities of the modern scientific glassblowing shops have made the designs discussed here possible.

Figure 10
Vacuum fusion furnace tube.

MATHEMATICS AND THE GLASSBLOWER

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Generally speaking there are three ways of determining the volume of a vessel: calculation, direct measurement by filling it with the required amount of water, or by inspired guesswork. Of the three alternatives the second is the most common, the third is adopted when no measuring cylinder is available, while the first is avoided like the plague because the answers never seem to bear any relation to the intended result.

The problem involved in calculation of volume is that it always involves squares or cubes of the radius or diameter and during the process the decimal point gets lost. Bearing this fact in mind I have prepared sets of tables which remove the burdensome r^2's, r^3's etc. from the calculation which the glassblower has to perform. These tables apply to regular shapes either spherical or cylindrical. So far as the spheres are concerned provided the size corresponds to these set out in the table you can have your answer immediately. If you can't find it there revert to methods 2 or 3 or use the formulae or draw a graph. I will deal with this solution in a moment.

First of all I want to talk about cylindrical vessels. The calculations vary according to the shape of the ends. If they are flat they are obtained by using $\pi r^2 h$, Tables II, III and IV give the cross-sectional areas for the commercially available standard. Medium, and Heavy wall tubes based on the internal diameter within the limitation of tolerance as sets out in the catalogues of Corning and Owens Illinois. In case you have never noticed, they are identical. Look up the area which corresponds to the outside diameter, multiply this number by the height of the vessel and you have its volume. If your cylinder has hemispherical or cone shaped ends it is still simple. Tackle it thus—2 hemispheres = 1 sphere the diameter being that of the tube. Find the volume of a sphere based on this diameter in Table I and add this volume to the volume of the straight cylinder. If the ends are cone shaped find the volume of a cone which has the same height as the diameter of the tube on which it is sitting—this figure is obtainable in Tables II, III, V depending on the wall thickness. If there is a cone at each end add twice this volume to the cylinder, if there is only one end coned don't multiply by 2. Should you have to deal with a cone and a hemisphere, look up the volume of the corresponding sphere, divide by 2 and add this volume to the cylinder.

While I am on the subject of cones and hemispheres it is appropriate to mention the McLeod gauge bulb. There are soulless people who use a sphere. However most of us prefer to fashion a cone shaped vessel with a rounded base. The volume of a cone having a height (h) equal to the diameter of the hemisphere on which it is sitting is almost equal to the volume of the sphere with the same diameter. There is a small difference but it is insignificant on bulbs of 500 ml and under, bearing in mind that wall thicknesses will vary, and angles will not be mathematically exact etc. If you are asked to make a bulb 350 ml capacity and you can produce one of 345 or 355 ml it will fall within the requirements of simple common sense, such bulbs are usually calibrated most carefully in order to give exact readings on a calculated scale as a function of their volume and that of the capillary which is attached thereto irrespective of the actual size of the bulb itself.

Although regular shapes such as I have indicated will satisfy most requirements it is sometimes necessary to modify the shape of the end of the vessel. To save yourself much grief if a hemispherical; adopt a cone, because figuring the volume of a cone the height of which differs from the simple one to one relationship set out in the table is easy. Trying to figure out a flatend hemisphere is not so simple. The modified cone is straight forward because the cross-sectional area remains the same. If we take as an example a regular cone made on a tube 51 mms OD, its volume is 26.99, or let us say 27 ccs. Its height is 47 mm because this is the ID of a 51 mm tube, Now if you double the height of the cone you double its volume, if you halve the height you halve the volume, and that's all there is to that.

Before I leave the subject of cylinders and their volumes I would like to discuss briefly the calibration of a capillary tube for application to a McLeod gauge. The simplest answer and the one most commonly resorted to, is to use a precision bore tube where the accuracy of the bore is such that no checking is necessary. If this is the case it is only necessary to calculate the volume contained within unit length. To facilitate this I have prepared in Table V a list of the cross-sectional areas of precision bore tubing available under the name of Trubore® Tubing and supplied by Ace Glass Incorporated. So far as the gauges are concerned the smaller tubes will be of interest. However, calculations for the flow of liquid through an orifice have to be made from time to time and the basis for these calculations in the cross-sectional area. For this reason I have calculated πr^2 for all the Trubore tubing listed in the Ace catalogue.

Should you be faced with the construction of a gauge using normal capillary, steps must be taken to determine the consistency of the bore over the whole length of the tube and, assuming that it is suitable, to determine the true diameter.

Firstly the question of consistency. Place within the horizontally mounted capillary a small amount of pure mercury so that it forms a continuous thread of about 5 cms in length. Measure the length accurately with a venier caliper or rule to an accuracy of 0.1 mm. Make a note the length then move the thread about 4 cms. along the tube and re-measure it. Repeat this procedure until sufficient tubing has been checked to provide the material needed to construct the bulb and side arm. The variation should not exceed 0.2 mms. over the whole length of material. Having obtained this information, carefully weigh the mercury. Armed with these data the calculation of volume per millimeter of length is simple:—

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*Registered trademark of the Ace Glass Co.

$$\text{cc per mm} = \frac{\text{weight of mercury in grams}}{13.6 \times \text{length of mercury thread}}$$

13.6 is the density of mercury

From this information the actual diameter of the capillary may be determined, using $\pi r^2 h = V$

h = length of thread

hence $V = h \times$ cc per mm

hence $\pi \times r^2 \times h = V$

(known = 3.142) (unknown) (known) (known)

$$\text{hence } r^2 = \frac{V}{\pi h}$$

$$r = \sqrt{\frac{V}{\pi h}}$$

To find square roots—buy, beg, borrow or steal a slide rule. The scales on the outer edges of the sliding scale are so arranged that if the number given by

$$r^2 = \frac{V}{\pi h}$$

are located on the upper scale (0-100) the square root is immediately below it on the lower scale of the slide (0-10). If no slide rules exist look up the logarithm of the number, divide it by two and look up the answer in the antilogarithm table. This will give you (r).

While I am still playing with formulae I would like to spend a few moments on the problem of how tall and or fat a cylinder should be to contain an appropriate volume. First, consider the cylinder in relation to the equipment to which it must be attached, and the purpose for which it will be used. If there is plenty of height it may be of small diameter, but if height is at a premium compensation must be made by increasing the diameter. Referring to the data in Table II, III, IV and considering with their use the simplest solution to the problem a variation of length as a function of a selected size of tubing. Taking as an example a cylinder of 1000 ccs. using a tube 60 mms. OD, from Table II, we find that a 60 mm. OD tube has a cross-section of 2380 mms^2 or 23.8 cms^2.
Now $23.8 = \pi r^2$ and $\pi r^2 h = 1000$ ccs.

$$\text{hence } \frac{1000}{23.8} = h$$

$$= 42 \text{ cms.}$$

Where height is fixed and volume is known we have to tackle the problem the other way around. Let's stay with 1000 ccs and have height 30 cms. now:—

$$\pi r^2 \underset{(h)}{30} = 1000$$

$$\text{hence } r^2 = \frac{1000}{\pi \times 30}$$

$$= \frac{1000}{3.142 \times 30}$$

$$= \frac{1000}{94.2}$$

$$r^2 = 10.62$$

$$r = \sqrt{10.62}$$

$$= 3.26$$

hence ID of tubes = $2 \times 3.26 = 65.2$ mms.

Using the same figuring, a 1000 cc vessel 18 cms high would have an ID of 84 mms.

Finally I have a few more words for you on the subject of spheres. Because small changes in diameter produce large changes in volume the judging of size against one which is known is inaccurate. For example, you need a 300 ml. bulb and you have for comparison a 200 ml. and a 500 ml. flask, their rough measurements taken with a rule in a shaky hand 72 and 97 (they are actually 72.6 and 98.2) so you divide the difference 25 into 3 = 8.3 and add this to the size of the 200 ml flask to give a diameter of 80.3 mms which is about 275 ml. If we use the exact measurements for the reference flasks the difference is 25.6, dividing by 3 = 8.5, 8.5 + 72.6 = 81.1 = 285. The true diameter is 83.2. If you try this with larger volumes 2000 ml and up the error becomes very large.

Table I which gives volumes and diameters for spheres does not cover every possible size but has been designed to cover most needs. If you require volumes not listed herein they may be obtained by drawing a graph using known volumes and diameters, selecting at least four points on either side of the desired figure so that a good curve can be obtained. If this is too troublesome the diameter may be calculated from the standard formulae.

$$V = 4/3\ \pi r^3$$

OR $4.189\, r^3 = V$ which is the same thing.

So, taking one lst example, a bulb is needed of a size to contain 765 ml

$$4.189 r^3 = 765$$

$$r^3 = \frac{765}{4.189}$$

$$= 183$$

$$r = \sqrt[3]{183}$$

$$= 5.68$$

hence D = 11.32 cms or 113.2 mms.

In my closing remarks at the 10th symposium I referred to vacuum as a tool; mathematics is just another tool. It is indispensable to us if we are to perform our work effectively. Like it or not we are stuck with it.

My thanks to the University of Toronto for allowing me to wear out one of their calculating machines, and to the typist who pounded out all these figures.

TABLE I

Volumes of spheres as functions of their internal diameter. When measuring add twice the estimated wall thickness to give external diameter.

Volume in mls.	*ID in mms.*	*Volume in mls.*	*ID in mms.*
0.10	5.7	80	53.4
0.25	7.8	90	55.6
0.5	9.9	100	57.6
0.75	11.3	125	62.2
1.0	12.5	150	66.0
1.5	14.2	175	69.4
2.0	15.7	200	72.6
2.5	16.9	250	78.2
3.0	17.9	300	83.2
3.5	18.8	350	87.2
4.0	19.7	400	91.2
4.5	20.6	450	94.8
5.0	21.2	500	98.2
5.5	21.8	600	104.6
6.0	22.6	700	110.2
6.5	23.0	800	115.2
7.0	28.8	900	119.2
7.5	24.3	1000	124.0
8.0	24.7	1100	128.0
8.5	25.2	1200	131.8
9.0	25.8	1300	135.4
9.5	26.4	1400	138.8
10.0	26.8	1500	142.0
11.0	27.5	1600	145.0
12.0	28.4	1700	148.0
13.0	28.8	1800	150.8
14.0	29.6	1900	153.6
15.0	30.6	2000	156.4
16.0	31.2	2500	168.4
17.0	31.6	3000	178.8
18.0	32.6	3500	188.4
19.0	32.8	4000	197.0
20.0	33.6	4500	204.6
21.0	34.2	5000	212.0
22.0	34.6	6000	225.6
23.0	35.2	7000	237.8
24.0	35.6	8000	248.0
25.0	36.2	9000	257.0
30.0	38.4	10000	267.4
40.0	42.2	12000	284.2
50.0	45.6	22000	347.6
60	48.4	50000	457.2
70	51.0	72000	515.8

TABLE II

Cross-sectional areas and volumes of cones having a vertical height equal to diameter of cross-section. Based on catalogue specifications for 7740 and KG-33 glasses.

STANDARD WALL

OD, mms	*ID, mms*	*Cross-section, mms²*	*Volume of Cone, ccs*
2	1.0	0.78	0.00026
3	1.8	3.14	0.0015
4	2.4	4.50	0.0036
5	3.4	9.08	0.0102
6	4.0	12.56	0.0166
7	5.0	19.60	0.0325
8	6.0	28.30	0.0561
9	7.0	38.50	0.0891
10	8.0	50.20	0.133
11	9.0	63.60	0.185
12	10.0	78.50	0.260
13	10.6	88.10	0.309
14	11.6	105.00	0.405
15	12.6	124	0.520
16	13.6	145	0.654
17	14.6	167	0.809
18	15.6	191	0.987
19	16.6	216	1.189
20	17.6	233	1.417
22	19.0	283	1.783
25	22.0	380	2.76
28	25.0	490	4.06
30	26.4	545	4.78
32	28.4	633	5.95
35	31.0	755	7.74
38	34.0	908	10.21
41	37.0	1075	13.16
45	41.0	1320	17.91
48	44.0	1520	22.14
51	47.0	1735	26.99
54	49.2	1900	31.72
57	52.2	2140	36.97
60	55.2	2380	43.72
64	59.2	2750	53.93
70	65.2	3340	72.04
75	70.2	3860	89.92
80	75.2	4450	110.54
85	80.2	5050	134.09
90	85.2	5700	160.77
95	90.2	6390	190.77
100	95.2	7120	224.19
110	104.8	8600	299.09
120	114.0	10207	385.09
125	119.0	11122	430.78
130	124.0	12076	495.62
140	133.0	13892	611.53
150	143.0	16060	760.18
178	171.0	22965	1299.94

TABLE III

Cross-sectional areas and cone volumes

Medium Wall

OD, ins″	*OD, mms*	*ID, mms*	*Area, mm*^{2}	*Cone Vol., ccs*
¼	6.3	4.0	12.57	0.016
½	12.7	9.6	78.50	0.23
⅝	15.8	12.7	126.50	0.52
¾	19.0	15.9	198	1.03
1	25.4	20.6	334	2.3
1¼	31.7	26.9	568	5.1
1½	38.0	33.2	864	9.5
1¾	44.4	39.6	1230	16.1
2	50.8	44.5	1555	22.8
2¼	57.1	50.8	2040	34
2½	63.4	57.1	2555	48
2¾	69.8	63.5	3160	66
3	76.2	69.9	3840	89
3¼	82.5	76.2	4560	115
3½	88.9	81.3	5200	139
4	101.6	92.1	6650	184
4½	114.2	104.7	8600	297

TABLE IV

Cross-sectional Areas and Cone Values

Heavy Wall

OD, ins″	*OD, mms*	*ID, mms*	*Area, mm*^{2}	*Cone Vol., ccs*
¼	9.5	5.6	24.6	0.04
½	12.7	7.9	49.0	0.12
⅝	15.8	11.0	95.0	0.34
¾	19.0	12.7	126.5	0.52
1	25.4	17.5	240	1.37
1¼	31.7	23.8	444	3.50
1½	38.0	30.1	710	7.04
1¾	44.4	36.5	1045	12.57
2	50.8	41.3	1340	18.22
2¼	57.1	47.6	1470	28.04
2½	63.4	53.5	2240	39.66
2¾	69.8	59.9	2820	56.06
3	76.2	66.7	3490	76.90
3¼	82.5	73.0	4180	101.10
3½	88.9	79.4	4950	130.13
4	101.6	88.9	6200	183.04
4½	114.2	101.5	8090	271.30
5	127.0	114.3	10300	387.60
5½	139.6	126.9	12600	532.1
6	152.3	136.5	14650	660
6½	165.1	149.3	17500	864
7	177.8	158.8	19700	1041

TABLE V

Cross-sectional Areas of Ace Glass Trubore* Tubing

ID, ins″	*ID, mms*	*Area, mms²*
0.008	0.203	0.032
0.010	0.254	0.051
0.012	0.305	0.073
0.013	0.330	0.086
0.015	0.381	0.114
0.016	0.406	0.129
0.018	0.457	0.164
0.020	0.508	0.203
0.022	0.559	0.245
0.024	0.610	0.292
0.027	0.686	0.370
0.029	0.737	0.426
0.030	0.762	0.456
0.031	0.787	0.487
0.035	0.890	0.620
0.039	0.991	0.770
0.040	1.016	0.810
0.047	1.194	1.119
0.051	1.295	1.317
0.059	1.499	1.763
0.060	1.524	1.823
0.065	1.651	2.140
0.070	1.778	2.482
0.076	1.930	2.925
0.079	2.007	3.161
0.080	2.032	3.241
0.089	2.261	4.012
0.095	2.413	4.571
0.096	2.438	4.667
0.100	2.540	5.064
0.111	2.819	6.240
0.117	2.972	6.933
0.126	3.200	8.040
0.135	3.429	9.230
0.142	3.607	10.212
0.153	3.886	11.855
0.163	4.140	13.456
0.169	4.293	14.465
0.177	4.495	15.867
0.186	4.724	17.521
0.198	5.029	19.855
0.227	5.766	26.097
0.236	5.994	28.207
0.240	6.096	29.171
0.275	6.985	38.300
0.286	7.264	41.426
0.312	7.925	49.300
0.319	8.103	51.537
0.324	8.230	53.204
0.350	8.890	62.040
0.396	10.058	79.419
0.419	10.643	88.913
0.441	11.201	98.495
0.455	11.557	104.848
0.460	11.684	107.165
0.478	12.141	115.716
0.484	12.294	118.639
0.515	13.081	134.323
0.520	13.208	136.944
0.537	13.639	146.045
0.551	13.995	153.759
0.585	14.859	173.320
0.610	15.494	188.450
0.625	15.875	197.832
0.655	16.637	217.280
0.724	18.390	265.469
0.781	19.837	308.915
0.789	20.041	315.276
0.795	20.193	320.089
0.829	21.057	348.053
0.875	22.225	387.751
0.945	24.003	452.273
1.010	25.654	516.630
1.070	27.178	579.835
1.119	28.423	634.158
1.184	30.099	711.202
1.197	30.404	725.646
1.223	31.064	757.513
1.295	32.893	849.330
1.380	35.052	964.484
1.465	37.211	1086.957
1.576	40.030	1257.910
1.643	41.732	1367.137
1.892	48.057	1812.923
1.971	50.063	1967.480
2.007	50.978	2040.008

THE SCIENTIFIC GLASSBLOWER IN PETROLEUM EXPLORATION RESEARCH

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ABSTRACT

Recent trends in petroleum exploration research demand a quantitative physical and chemical approach for solution of many complex problems. Developments in analytical instrumentation have been largely responsible for providing the techniques with which to solve the hitherto mysterious problems of petroleum formation and location. The scientific glassblower has played a key role in working with other scientists of many professions in development of basic components and specialty items for these apparatus. Geochemical exploration activities involve specialization in a number of areas of physics and chemistry including: Thermochemistry, Cryogenics, Mass Spectrometry, Optical and Resonance Spectroscopy, Ion Exchange Systems, and Molecular Properties of Molecules. The role of the scientific glassblower in several of these areas related to petroleum exploration will be discussed.

INTRODUCTION

Exploration developments within the oil industry during the past ten years have seen the increased utilization of scientists in the fields of chemistry, physics, and mathematics to solve problems formerly considered the province of the geologist and geophysicist. The scientific glassblower has cooperated with the experimentalists in these fields in developing the new techniques for petroleum exploration. Their influence has been a steady and significant one in the progress made. A detailed discussion of the specific glassware involved in the development of significant exploration techniques would require much more time in elaboration than has been allotted for this talk. It is therefore proposed to summarize several of the more significant recent accomplishments in the area of petroleum exploration research in which the glassblower has figured prominently without pursuing the specific aspects of the glass apparatus or glassblowing techniques.

It is the objective of all concerned with increasing our energy reserves in the form of fossil fuels to carry out productive research to increase effectiveness in attaining the following objectives:

1. To better understand the chemical composition of the petroleum deposits of the world.
2. To devise new and better chemical and physical methods for the detection of petroleum and natural gas.

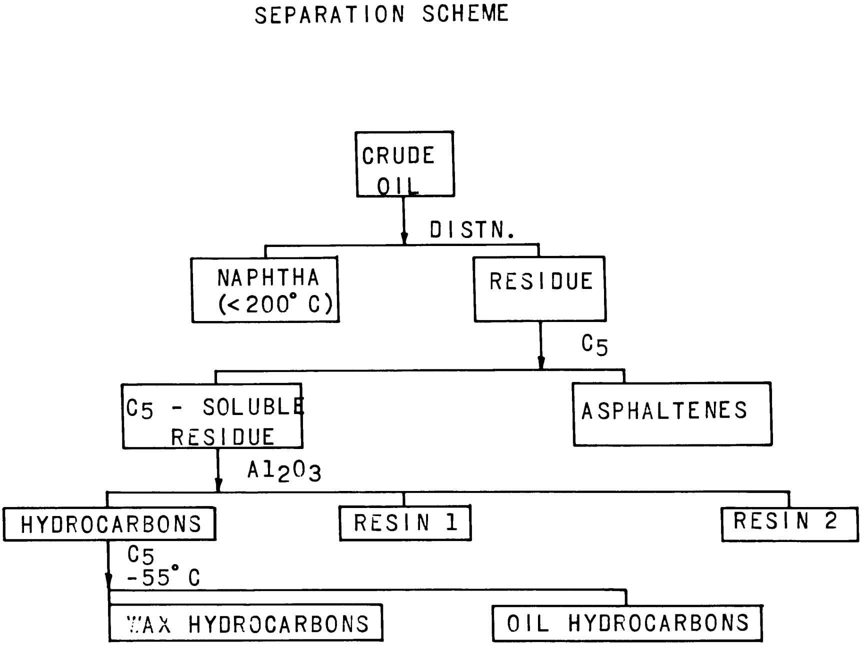


Figure I

METHODS USED IN CHEMICAL CHARACTERIZATION OF PETROLEUM

One scheme for obtaining a breakdown in the components of petroleum is shown in Figure 1. Here, a combination of physical methods is employed to obtain fractions of a crude oil for further characterization by chemical and physical methods. The crude is first subjected to a thermal distillation to remove the more volatile components in the naphtha range. This consists of many of the light hydrocarbons found in the gasoline normally supplied for automotive consumption. In the laboratory, the chemist has been assisted by the glassblower in the development of highly efficient fractional distillation apparatus for this separation, as well as equipment for the determination of molecular weights and other physical properties necessary for characterization of these chemical constituents. Following this "stripping" operation, an extraction of the residue is carried out leaving behind a highly asphaltic material of complex chemical structure called asphaltenes. The soluble portion of the crude may be separated on chromatographic columns supplied by the glassblower into a hydrocarbon fraction not unlike the lubricating oils used in your automobile, a wax fraction, and several fractions called resins which contain polymeric material incorporating sulfur and nitrogen. All of these operations are completed in a quantitative fashion to yield information which enables the geochemist to fingerprint a given crude oil for comparison with other crude oils in a given petroleum-producing province.

EXPLORATION CRITERIA AND TECHNIQUES

Exploration for petroleum deposits involves several distinct phases of operation. First, a region must be evaluated for the possibility of the occurrence of oil or gas. Second, a choice of most probable location for the deposit must be made. Finally, the prospect must be tested by the actual well drilling operation.

The initial phase of the exploration process is usually carried out by geologists and geophysicists who utilize surface features and seismic and magnetic data to determine the type of subsurface structure in an area. Following this initial evaluation of the province, one or more holes may be drilled to test the predictions of these scientists. If these initial efforts do not produce a commercial accumulation of petroleum, it is desirable to obtain as much information concerning the oil potential of the province from this "dry" hole as possible. Actually, all wells produce some fluid—small amounts of liquid hydrocarbon similar to oil or brines containing small amounts of dissolved hydrocarbons, often in the parts per million range. The geochemist will utilize the method of characterizing a petroleum, outlined in Figure 1, to determine the type of petroleum to be found in the region in a more suitable trap. Additional information may be obtained from the subsurface fluids or brine samples. These contain such dissolved chemical constituents as propane, butane, pentane, cyclopentane, hexane, methylcyclohexane, and benzene. Benzene, an aromatic hydrocarbon, has been found extremely useful in predicting the occurrence of oil in the subsurface. The concentration of benzene in fluids

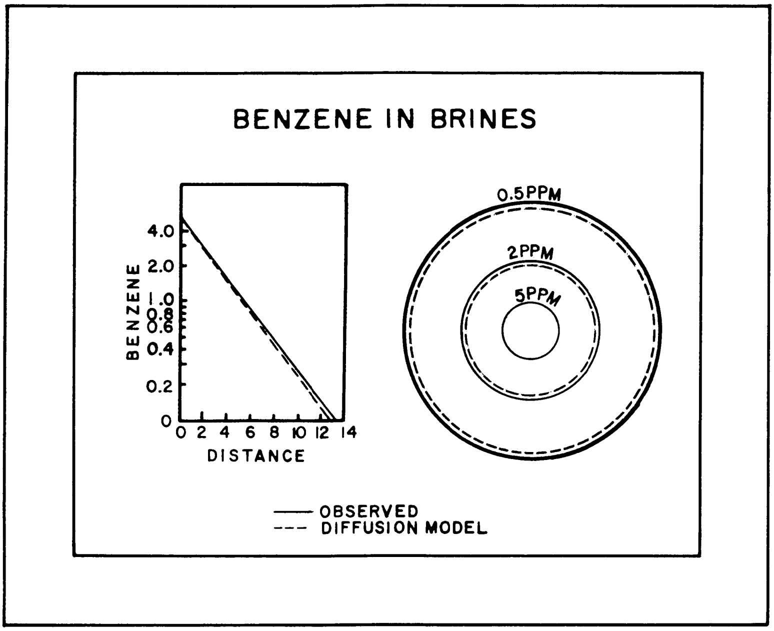


Figure 2

associated with crude oils is of the order of 5 parts per million in the immediate area of contact of the fluid with the oil pool. It has been found that this concentration decreases as the distance from the oil accumulation increases. The relationship observed for a typical oil field-subsurface brine is shown in Figure 2. This behavior of benzene concentration versus distance can be explained on the basis of a diffusion model, involving the outward flow of benzene from the oil-water contact at the edge of the oil pool. This method was developed at the Gulf Research & Development Laboratories and has now been made available to the industry where it has seen widespread application. The glassblower has been involved in the fabrication of the specialized apparatus for the gas chromatographic procedures involved in the determination of the hydrocarbon content and in the design of cells used directly in the spectrophotometers for the diffusion experiments.

The advent of the atomic age has brought the term "isotope" into the language of the layman. It has also introduced radiotracers into most research laboratories for elucidation of reaction mechanisms and for following the movement of fluids through areas inaccessible to visual observation. The area of petroleum exploration research is no exception. Both radioactive isotopes and those which are stable have been employed successfully to increase exploration results. A number of these methods are shown schematically in Figure 3. The potassium-argon method of geochronology has found direct application in solving drilling problems and

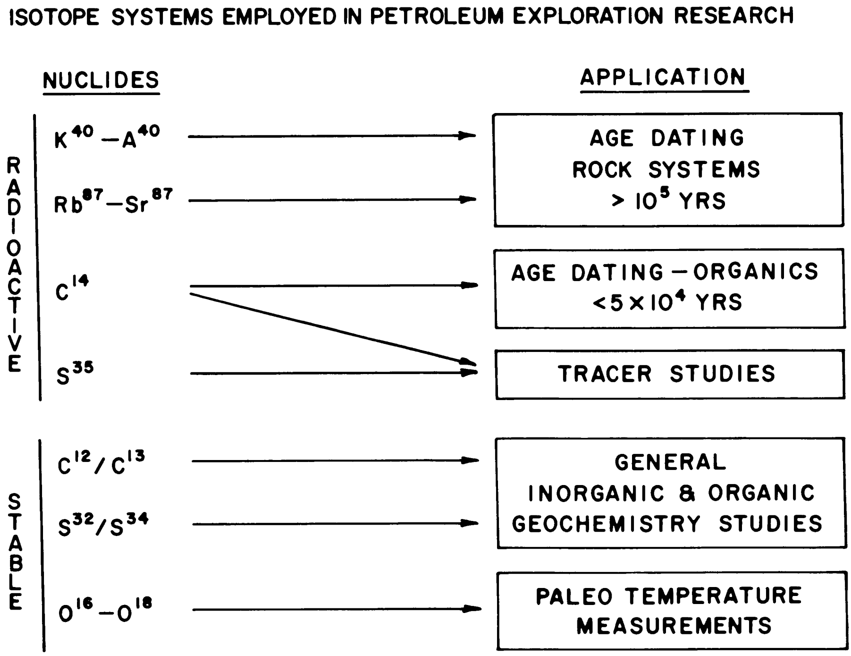
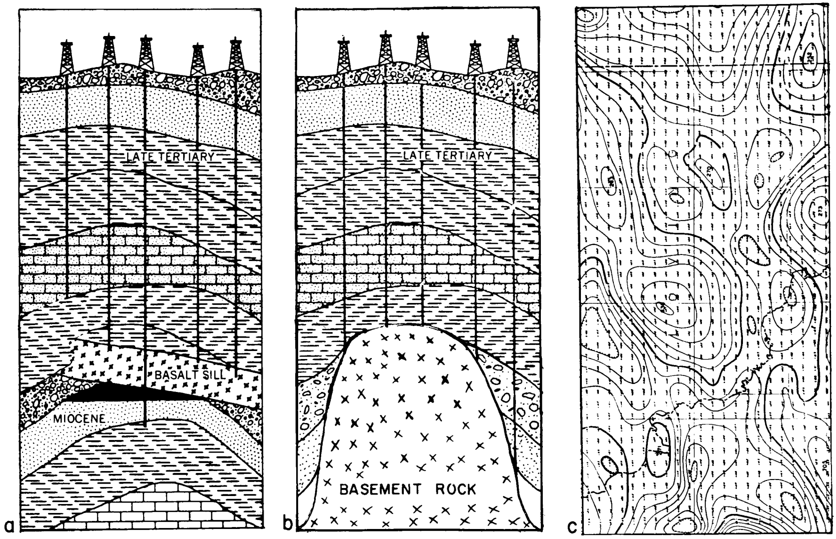


Figure 3



INTRUSIVE OR BASEMENT HIGH?

Figure 4

in initial evaluation of the time-sequence of the geologic section. It is widely accepted that oil is not likely to be found in the Precambrian or basement rock section of the earth's crust. Most of the mechanisms for oil formation point to an origin within sedimentary systems above this older igneous rock mass. As shown in Figure 4, it is not uncommon while drilling for oil to encounter a rock system called a dike or basalt sill in an area where the geologist expects to find sedimentary rock. From surface measurements, the geophysicist obtains a map similar to that shown in Figure 4c, which enables the determination of the distance from the surface to the top of the basement or granitic rock. It does not enable the determination of the age of this rock, nor does it always allow for the possibility that a normal sedimentary sequence with oil production potential lies beneath a granite placed high in the column. When such a system is encountered, the geochronologist has a tool to enable dating the rock. True basement will have an age in excess of 600 million years. Many intrustive rocks are much younger in age, perhaps 20 or 30 million years. The principle of radiodating by the potassium-argon method is based upon the occurrence of a radioactive isotope of potassium which occurs in all potassium-bearing minerals. This potassium decays to produce argon, a gas which remains trapped in the rock until liberated by heating. This can be done in the laboratory and the amount of the gas liberated measured very accurately. In addition to the argon gas extraction, a determination of the potassium content of the mineral is necessary to permit the calculation of the duration of the decay process, hence, the time of formation of the rock in which the mineral was formed. The amounts of

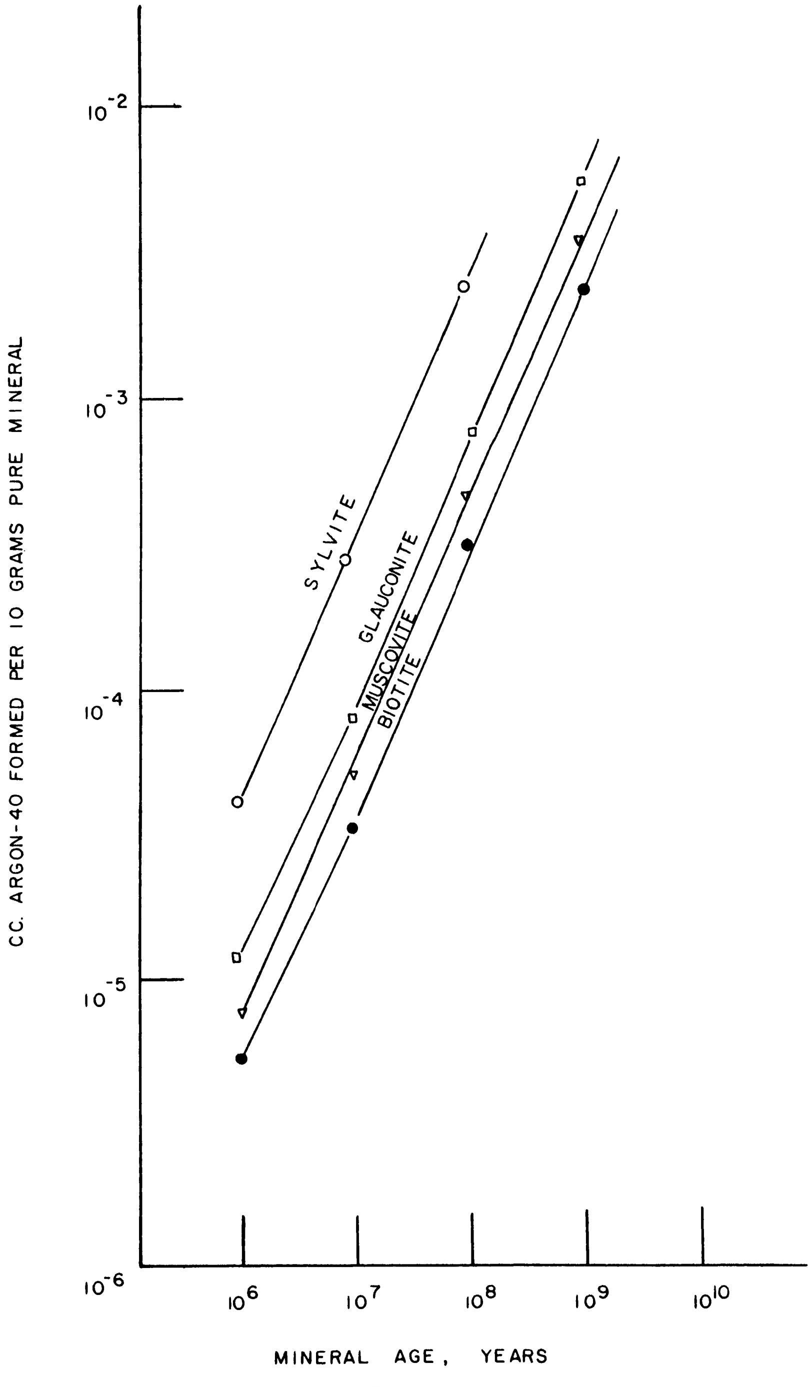

CC. ARGON-40 FORMED PER 10 GRAMS PURE MINERAL
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
SYLVITE
GLAUCONITE
MUSCOVITE
BIOTITE
10^{6}
10^{7}
10^{8}
10^{9}
10^{10}
MINERAL AGE, YEARS

Figure 5

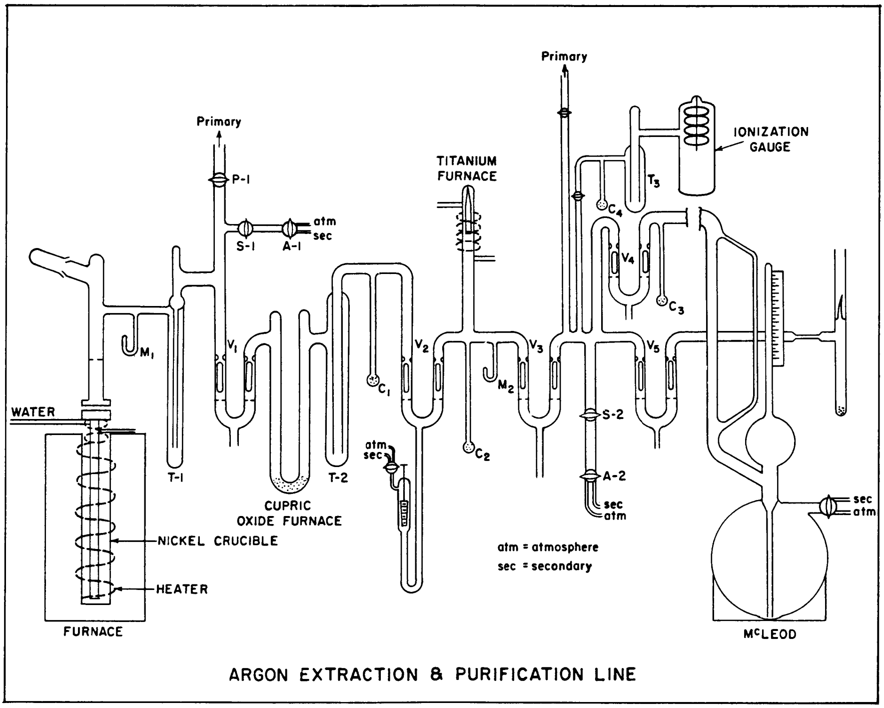


Figure 6

material formed per 10 grams of pure mineral are shown in Figure 5 as a function of age for several minerals. Even for material of a billion years of age, the amount of gas formed is very small—about 10^{-4} grams per gram of material. This requires that the extraction process be carried out under vacuum. A schematic diagram of a typical extraction and purification system is shown in Figure 6 and in the photograph in Figure 7. One additional complication is encountered in the process which requires the use of the elaborate mass spectrometric equipment shown in Figure 8. This involves the accumulation of argon from the atmosphere in the sediment or at the time the rock material is exposed in the laboratory. Atmospheric argon contains several additional isotopes of argon in addition to the radiogenically produced argon-40 which must be determined using mass spectrometry techniques prior to making the age calculation.

The dating process described above is applicable to materials over 1 million years in age owing to practical experimental problems. For very young material, from present day to 50,000 years, the carbon-14 method is employed. One of the techniques available for carbon dating is shown in Figure 9. This involves destruction of the sample by converting the carbonaceous material to carbon dioxide, then to a more suitable organic form for the actual radioactivity counting determination.

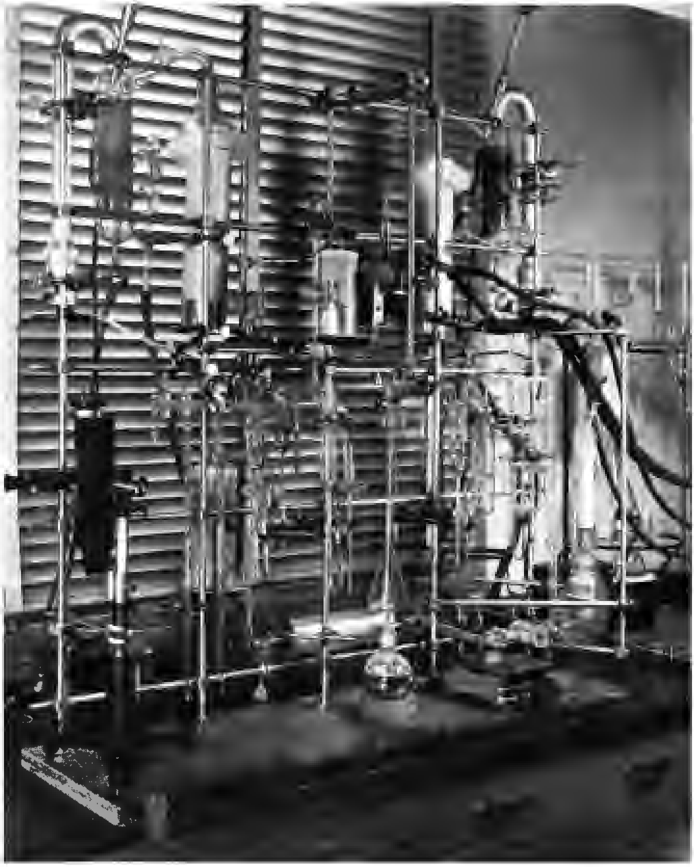


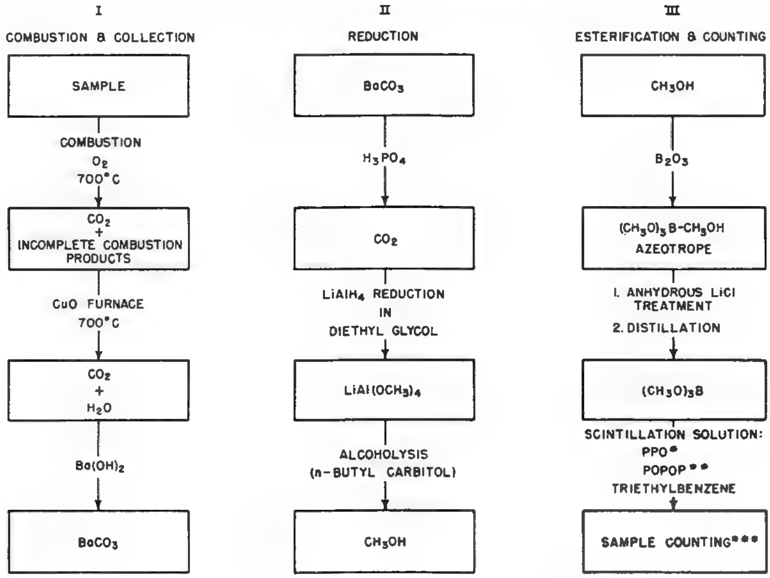
Figure 7

Applications of isotope techniques in petroleum exploration research are not limited to age-dating of sedimentary rocks or recent organic sediments. Stable oxygen isotope determination is employed in the establishment of paleotemperatures based on the equilibrium between the carbonate and water oxygen-18 isotope which is dependent on temperature, as shown in Figure 10. The carbonate containing a temperature determined isotope value is incorporated into the shells of mollusks and into the structure of foraminifera which are preserved in the sediments and may be utilized in the temperature reconstruction of an exploration area.

These represent some of the modern techniques which are utilized in the search for petroleum and in which the glassblower has figured prominently in providing much of the laboratory apparatus to permit the establishment of these techniques.

Figure 8

FLOW DIAGRAM — RADIOCARBON DATING PROCESS



* 2,5-DIPHENYLOXAZOLE
** 1,4-bis-2-(5-PHENYLOXAZOLYL)-BENZENE
*** LIQUID SCINTILLATION METHOD USING TRI-CARB SPECTROMETER

Figure 9

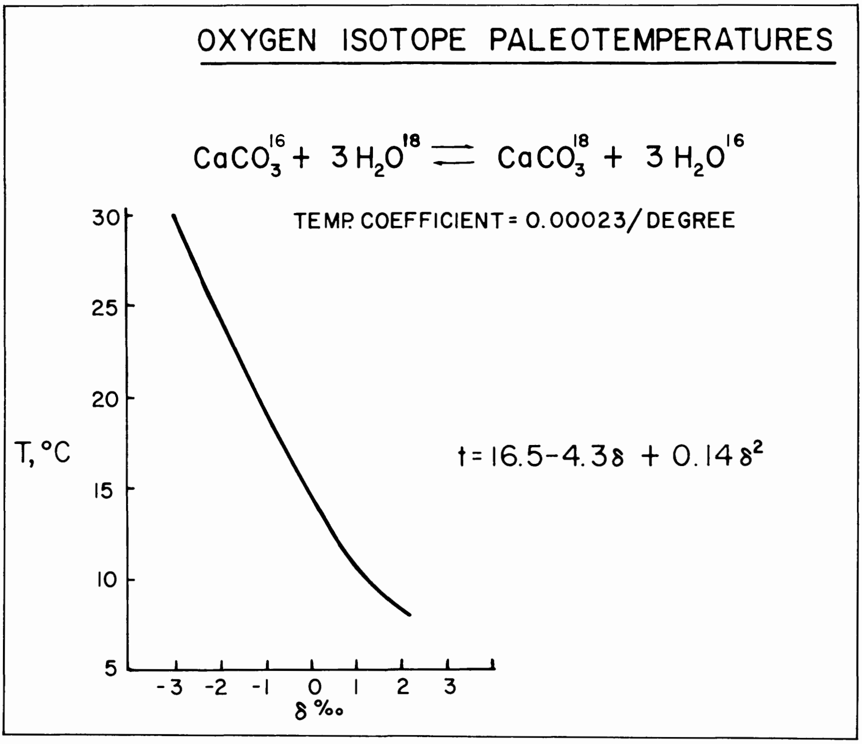


Figure 10

ACKNOWLEDGMENT

The author is indebted to Messrs. W. E. Barr, C. F. Hepler, L. J. Hitson, J. P. Sylba, and W. W. Kravenko for their significant contributions to the establishment of the techniques described above. Appreciation is also extended to Mr. Gene R. Beck for help in providing the illustrations.

THE GLASS BLOWER AND THE OPTICAL PUMPING OF LASERS

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INTRODUCTION

The work of the glass blower was involved in the very beginning of the lasers. Maiman used a quartz helical flash tube to excite the first laser which was of ruby. The gas lasers of Javan, Bennett and Herriott were the result of expertise in the blowing of glass.

I would like to discuss today three areas of laser research and development that demonstrate the interaction of the man working on lasers and the glass blower. The first area, which is that closest to my interests, is the optical pumping of solid state lasers. In this, I shall discuss our recent work upon highly radiative arc discharges of the types used to pump lasers of both the continuous and pulsed varieties. The second area will be concerned with new laser types requiring considerable glass blowing, and the third area will examine some situations in which the laser may be of use to the glass blower.

STUDIES OF HIGHLY RADIATIVE ARCS

The optical radiation emitted by an arc consist of relatively monochromatic spectral lines (such as those from mercury lamp), and a continuum similar to that of a tungsten filament lamp. The lines originate from the electrons undergoing transitions between discrete or bound states

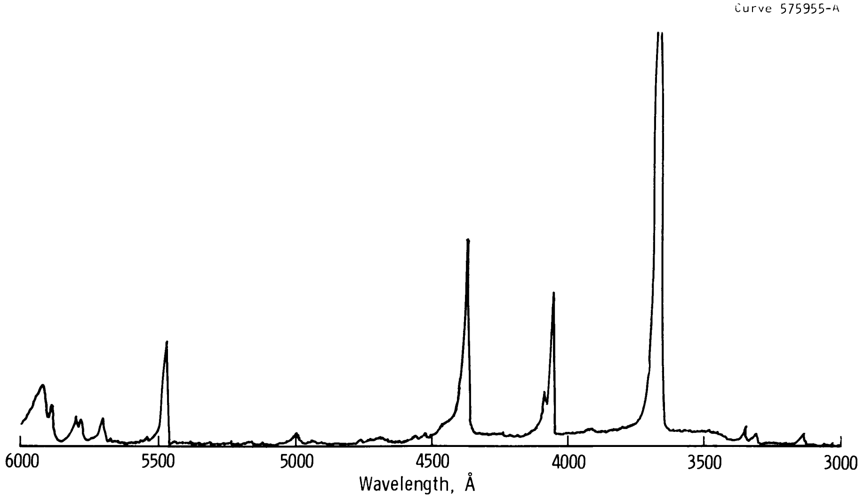
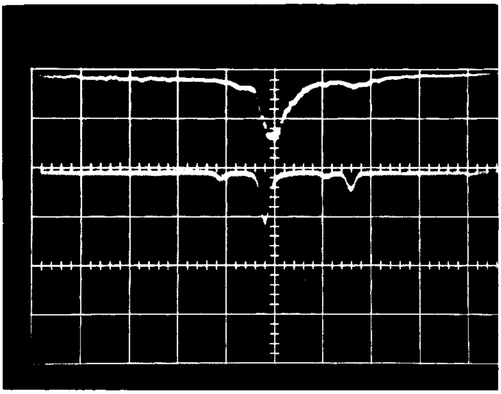
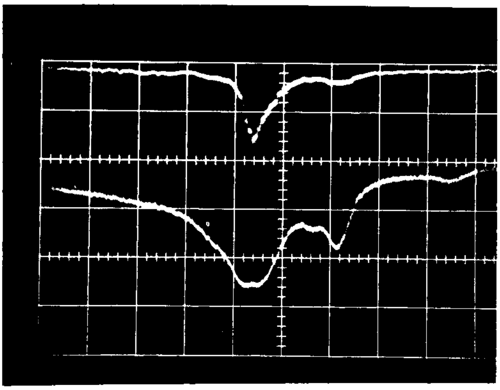


Figure I
Spectrum of NaI Lamp.

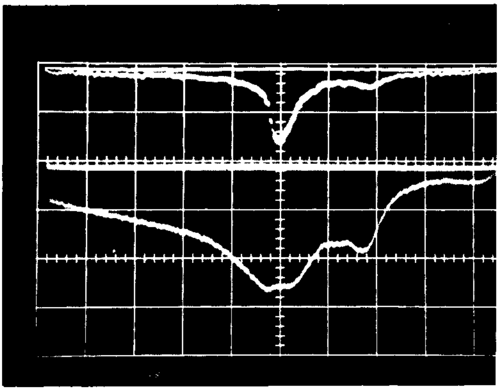


a) Current Density

$J = 890$ Amps/cm^2



b) $J = 1300$ Amps/cm^2



c) $J = 1550$ Amps/cm^2

Figure 2

Spectral Radiance around 8231.6 A line of xenon for 200 μ sec time delay and varying input voltage (i.e.: current) scanning rate 5 μ sec/cm ➔ 4.3 A/μ sec (From reference 1). PEKX-75 reference spectra upper trace.

of the atoms of the discharge. The continuum arise for the electrons going to bound states for free states, or undergoing transitions between two free states. The first continuum is called recombination (or inversely photoionizing radiation); the latter continuum is called bremstrahlung or "retarding" radiation. As an atom becomes excited, the line radiation is emitted first. As the atom is excited more strongly, the lines broaden and the continuum increases. The point at which the lines become buried in the continuum depends upon the atomic system and the conditions in the arc. Under the right conditions, which in general are a low atomic number gas at low pressures and high temperatures, the lines for the ionized states of the atom will appear. In one phase of our work, we are developing theoretical methods for calculating the emission for line and for continuum from the basic physical principles.

We have investigated for use in pumping lasers the line emission from continuous arc discharges consisting of metallic halides in mercury discharges, and the continuum and broadened line emission from pulsed arcs discharges in xenon. As the power density on the arc increases, the continuum level which arises for the processes mentioned earlier and the wings of the lines goes from many or less orders of magnitude lower in intensity than the peaks of the lines until equal in intensity to the lines. Figure 1 shows the spectra arising from a sodium iodide in a Hg discharge. The lines are very distinct and narrow. Figure 2 taken from reference 1 shows a sequence of spectra taken on a xenon flash lamp fired at successively higher levels using a new rapid scanning spectrometer we have developed.[1] To be noted is the broadening of the xenon line and the increase in the continuum with increasing current density.

We are using this information to allow the design of better laser pumps. We are also using it to develop new light sources for the more usual lighting applications, and to gain more information on arcs of the type that may occur in lightning strokes, in switches, and in many other situations in the commercial and military world.

THE WORK OF THE GLASS BLOWER

It is well and good to speak of these studies. To make the measurements and to construct the new laser pumps has required and is requiring exacting glass blowing. In the pulsed lamps, we are dealing with arcs that may have power densities of 1 to 10 megawatts/1 cm^3 or even higher, that are generated by currents of 15,000 to 50,000 amperes. These conditions require quartz construction and place harsh requirements on the quartz to electrode seals. The present graded glass seals may be used if properly protected from thermal and mechanical shock, but present one of the weakest parts in the flash tube. Other seals such as the indium seals and compression seals are being used, but still require further development, particularly for the larger sizes.

Figures 3 and 4 show some lamps that we are using for the pulsed studies. The lamp in Figure 3 has a rectangular cross section to present a uniform cross section. (The electrode seals are epoxy glued.) Using the lamp, in Figure 4, we can measure the spectral radiance (*i.e.* brightness or intensity to those not used to these terms), on a diameter and

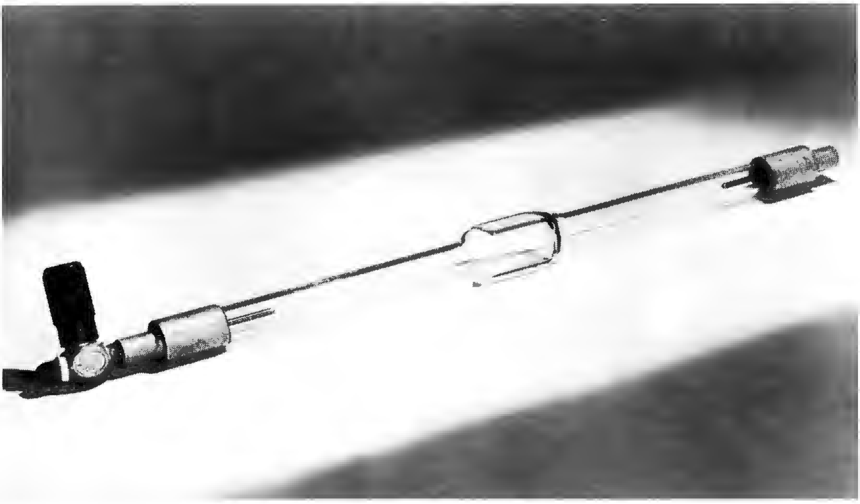


Figure 3
Flash lamp with a rectangular section for plasma studies.

down the length. Since the arc plasma is homogeneous in temperature[2] we can obtain a variation of ten or more in optical thickness (or opacity) which is very useful for studying gases half way between that one of widely varying optical thickness.

Figure 4
Flash lamp for viewing arc plasma side-on and end-on.

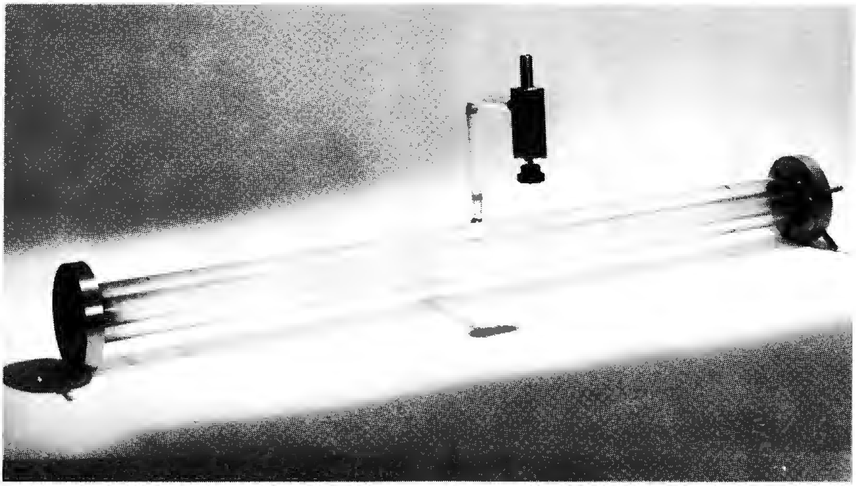


Figure 5
High energy coaxial flash lamp.

Figures 5 and 6 present two new laser pumps that have come from this work. Figure 5 is a high energy coaxial laser pump of the type which has achieved slope efficiency exceeding 5%[3] when used with a good Nd: glass laser rod. Figure 6 shows a small diameter metallic iodide mercury lamp which has been used for continuous laser pumping.[4] The thick quartz wall allows operation in air without an outer envelope as would be found in the more usual mercury street lamp.

Figure 6
Sodium Iodide-Mercury Lamp—The type used for the continuous pumping of lasers.

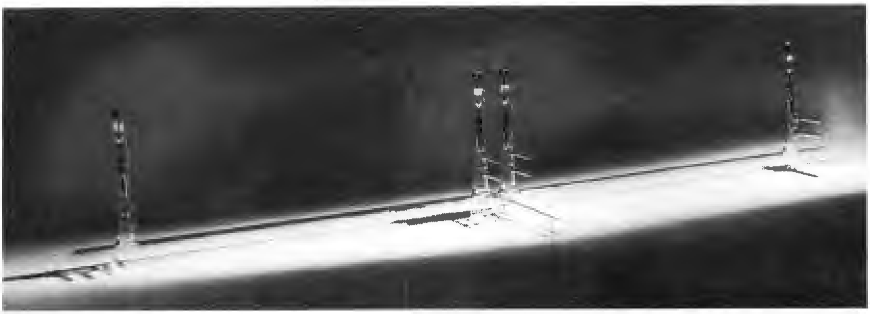


Figure 7
CO_2-N_2-He continuous laser tube.

NEW GAS LASERS

Figure 7 and 8 present two new gas laser systems which require extensive glass blowing. Figure 7 shows the arc tube (which is in Pyrex) CO_2-N_2-He laser of the type developed by Patel. This laster operates at 10.6 μ with 10 to 20 output, watt and has a nominal efficiency of 5% or more. Others of this type may range at present up to 300 to 500 watts in size. Figure 8 shows the much more intricate (from the glass blowers point of view) arc tube of the DC excited ionized argon laser (due to Bell, Bridges, Labuda and Gordon). The laser operates in the blue-green with a power of about .1 to 1 watt (1 watt of coherent energy is a surprisingly bright light even when viewed from the side. Viewed end on, it would damage if not destroy entirely the retina of the eye). Many of these lasers operate in the infrared requiring windows of materials such as BaF_2, ZnSe, etc. which are not in the usual glass blower's inventory. These new laser systems, as the new laser pumps, will require new techniques and many changes in the old techniques. For example, the cleanliness required in many of these new laser devices is considerably beyond that of many previous glass devices, approaching that of the ultra high vacuum systems.

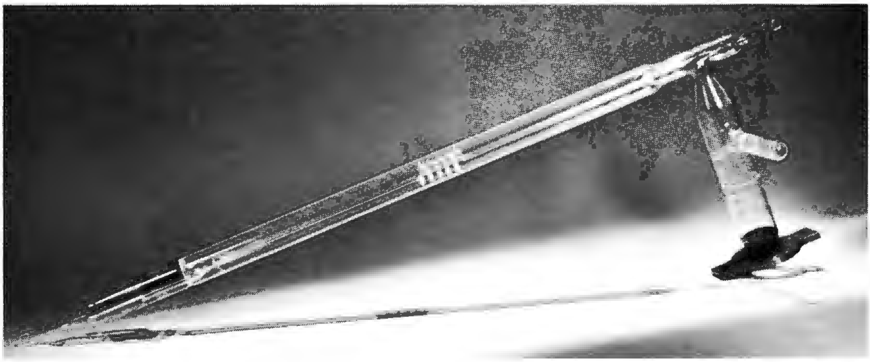


Figure 8
DC excited ionized argon laser tube.

APPLICATION OF THE LASER

There are some applications of the laser that may be useful to the glass blower. One of these is the welding or cutting of metallic materials through the glass envelope, allowing post-assembly fabrication or repairing. If the laser beam is focussed at a point within the envelope the energy density at the envelope can be kept low enough to avoid damage to the glass. The laser can also be used to weld or cut many materials not readily weldable, such as tungsten. We have made tungsten to tungsten welds in fabricating the electrodes of our tubes.

The advent of the CO_2-N_2-He laser offers the glass blower a tool for cutting, or for locally heating glass. Glass absorbs the 10.6μ laser radiative, allowing good coupling of the energy of the optical beam into the glass.

CONCLUSION

The glass blower has been of great service to the laser scientist and engineer in the development of new light sources for exciting lasers, and in making new lasers. Sometimes I feel that every new laser, or laser pump, has added a few (or many) grey hairs to some glass blower somewhere. The cooperation of the glass blowing community has made possible many of these new devices which have lead to whole new areas in technically. In conslusion, I would like to acknowledge the assistance of my colleagues and co-workers in this work, and of C. J. Cassidy and the men of the glass blowing shop of the Westinghouse Research Laboratories who were responsible for the glass work shown in the previous figures.

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THE GLASS LASER

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INTRODUCTION

The word " Laser" is an acronym for Light Amplification by Stimulated Emission of Radiation. The theory of lasers has been described in a number of publications.[1] For the present purposes, it is sufficient to give the basic principles of how a laser differs from ordinary sources of light.

Light is most often the result of energy transitions within atoms, ions or molecules. If the energy of the transition is sufficiently large, a photon of visible energy is produced. For the light to be of sufficient intensity to be observed, a large number of atoms must be radiating at the same or nearly the same time.

In general the excited atoms act independently of one another, radiating their energy in all directions. The result is that in most cases light is emitted more or less equally in all directions, with little or no correlation between the photons emitted in one direction and another. Such light is called 'incoherent" and is typical of the ordinary sources of light generated for illumination. The difference between ordinary sources and laser sources is that in the latter the light is "coherent", that is to say, the photons are all emitted in essentially the same direction, and more important, they all have a definite relation to one another.

In order for atoms to effect transitions from higher energy states to lower energy states and thus produce photons, they must somehow get to the states of higher energy; in other words, they must be excited. This requires that energy be put into the assembly of atoms. This energy can take a variety of forms. It may be thermal energy, as in incandescent sources, electrical energy, as in gas discharge lamps, or optical energy. If optical energy is used, it must generally consist of photons whose energy is equal to or greater than the photons being emitted.

The process of generation and emission of light in a single atom is shown schematically in the left hand diagram of Figure 1*a*. The state labeled 1 is the ground state, or state of lowest energy. States 2 and 3 are energy states of progressively higher energy. Excitation consists in raising an atom from its ground state to a higher state 3, whence it may decay by means of a photon or by lattice vibrations to the state labeled 2. Here it spends a very short, but significant amount of time, which may range from 10^{-9} seconds or less to many milliseconds; seconds in some instances. The transition from 2 to 1 is the significant one for us, since it results in the emission of a photon. In the case of a four level laser, shown on the right of Figure 1*a*, excitation occurs from levels 1 to 4, and emission occurs from 3 to 2.

As stated earlier, photons are usually produced in a random fashion. There is a way, however, in which photons may be produced so that they are correlated with one another. This process is called stimulation, and

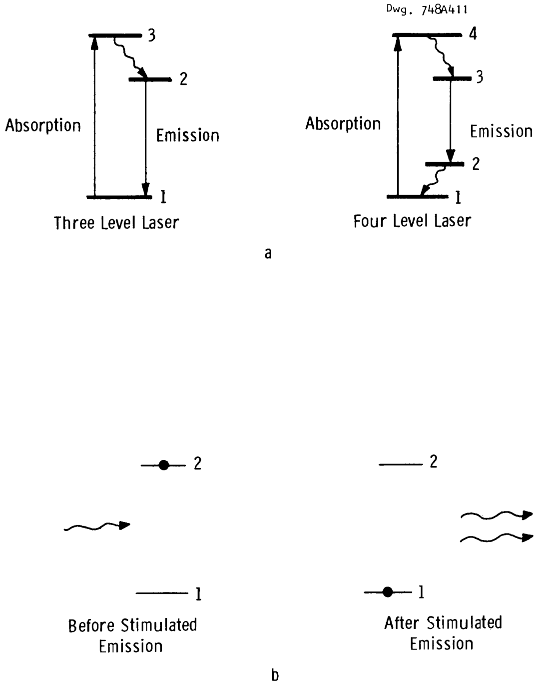

Figure I

a) Absorption and emission of three and four level laser systems.

b) Stimulated emission process.

was first described by Einstein. Because an atom spends some time in the excited state 2, it can remain excited while another photon comes along. If this photon has exactly the same energy as the energy difference between 2 and 1, it can cause the excited atom to give up its energy prematurely. In such a case, the new photon has exactly the same wavelength as the first, is in phase with it, and travels in exactly the same direction. Such a process is called stimulation. In order to obtain stimulated emission, one must have an inverted population; that is, for the three level system, there must be more ions in state 2 than in state 1. In a four level system, population inversion automatically occurs as soon as one or more ions are excited into the state labeled 3 providing level 2 is unoccupied. Once inversion is attained, one photon gives rise to two, two to four, four to eight, and so on, through the process of stimulation. Thus we have amplification, but just as important, because all of the photons so produced are in phase with one another, and of the same wavelength, they give rise to a bundle of radiation which is coherent. This process is schematically shown in Figure 1*b*, and is the essential process in a laser. The fact that many materials, including solids, liquids and gases can be made to perform in this fashion (and many forms of excitation can be used) is the reason for the large variety of lasers which are possible, such as liquid, solid or gas lasers.

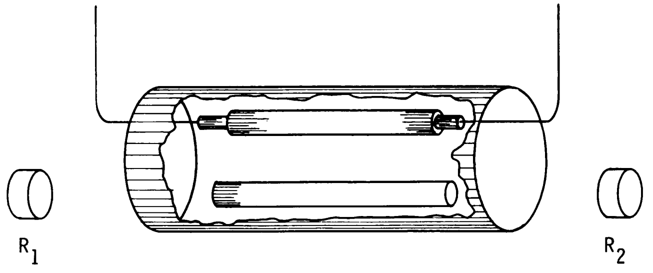

Figure 2
Laser cavity showing reflectors, R and R_2, flashlamp and rod.

Figure 2 shows one very common way in which laser action is obtained in practice. The laser rod, which may, in the present case, be either of glass or of a suitable crystalline material appropriately doped with active ions, is placed within a pump cavity in close proximity to a xenon flashlamp. The laser rod is usually cylindrical in shape, with its end polished flat and parallel to a very high degree of accuracy, in order to prevent losses at the ends. The flashlamp is usually, though not necessarily, also cylindrical in shape, with a length and diameter approximately equal to that of the rod. The pump cavity usually consists of a reflecting cylinder, whose purpose is to insure that a maximum amount of the radiation from the flashlamp enters the laser rod. The objects labeled R_1 and R_2 consist of two mirrors, either flat or slightly concave, which have a very specific and predetermined reflectivity at the wavelength of the laser emission. The purpose of these mirrors, or resonators, is to feed some of the light emitted by the laser rod back into the rod, thereby increasing the overall gain of the system. Typically, the resonator labeled R_1 has a high reflectivity very close to 1, whereas R_2 has a reflectivity somewhat below 1 in order to enable the laser emission to escape to the outside. The reflecting coatings that constitute R_1 and R_2 are often applied to the end of the rod itself, although in many cases, external mirrors are used, as shown in the figure.

Figure 3 shows some typical glass laser rods and illustrates the range of sizes of useful glass lasers. These rods and the laser glass were made for Westinghouse by the Pittsburght Plate Glass Co., and the final fabrication of the rods was performed at the Westinghouse Research Laboratories. The smallest of the rods is 3″ long by ¼″ diameter, and the largest is 1 meter long by nearly 1″ diameter. Both larger and smaller laser rods have been made. The center rod is 12″ long by ½″ diameter, and has a roof prism at one end to replace the 100 percent resonator R_1.

We now want to consider some characteristics that give rise to a good laser. Since our main concern is with glass lasers, we emphasize these characteristics which are of primary importance to glass lasers. The first of these is perhaps efficiency. Since glass lasers are used where high energy or high power is usually the most important characteristic, high conversion efficiency becomes important. Glass lasers are optically pumped lasers, and most often, xenon gas flashlamps are used for excitation to ob-

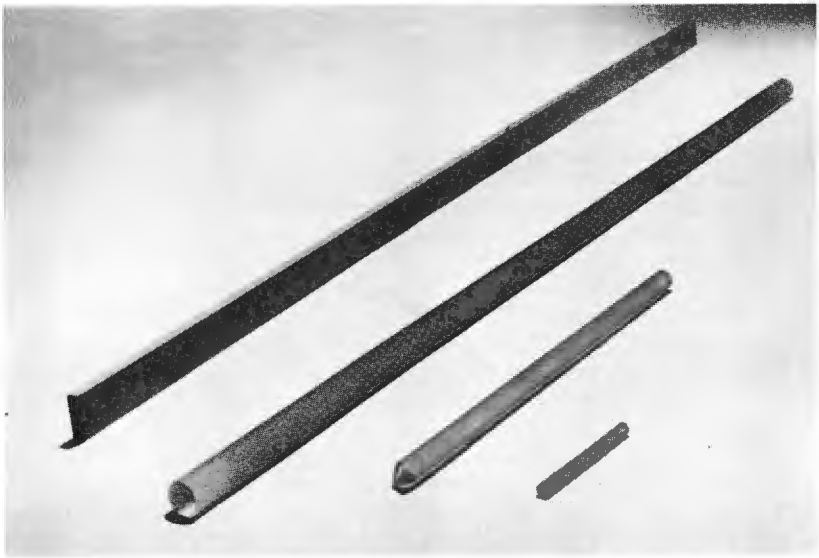

Figure 3
Nd^{3+}-doped laser rods of barium crown silicate glass.

tain efficient operation. The active ion, that is, the one whose emission gives rise to coherent radiation, must have sufficiently broad and strong absorption bands to be able to utilize a maximum amount of the radiant energy emitted by the flashlamp. The most commonly used active ion in glass lasers is trivalent neodymium, which is added to the basic glass as several percent of Nd_2O_3. Like most rare earth ions, Nd^{3+} has an absorption characterized by a number of comparatively narrow bands, which for Nd^{3+}, are somewhat broader than for most rare earths. Those most useful for optical pumping are shown in Figure 4, as they occur in a typical silicate laser glass. Also shown in this figure is a xenon lamp emission spectrum. The emission of Nd^{3+} occurs at about 1.06μ, which is in the near infrared, and the fluorescence band width is typically 300 Å. This band narrows to about 25 Å during laser action.

A second important requirement is that the quantum efficiency of the fluorescence band in question be as high as possible. The quantum efficiency is the efficiency with which the energy absorbed in the laser material is converted to the desired fluorescence band. For Nd^{3+} measured values of quantum efficience lie around 30%. Other important features will become clear in the following sections.

GLASS LASERS

Advantages

Glass has certain inherent advantages as a laser host which makes it attractive and very promising for many applications, particularly as a high-power device. The technology of optical glass melting and fabrication is certainly much older than that of crystal growth, and the present state of the art of the former is more advanced. It is much easier to fabricate glass rods of extremely fine optical quality in which the homogeneity may be good to the sixth decimal place in refractive index, whereas most single crystals usually contain some imperfections. The optical quality of the laser rod is of great importance in obtaining the theoretical limit of the laser beam divergence. Glass laser rods have been fabricated with beam divergence of a few tenths of a radian. An obvious advantage, from the consideration just mentioned, is that glass laser rods of almost any practical dimension and configuration may be fabricated. For example, glass rods of up to one meter length have been prepared with excellent quality. On the other hand crystalline materials are still limited to relatively small dimensions because of the difficulty in growing large, defect-free single crystals.

Because a glass may be considered as a supercooled liquid solution, its chemistry allows relatively high concentrations of transition metal ions to be dissolved in the glass "solvent". Thus, for example, it is possible to dope a glass with up to about 10% by weight of neodymium oxide. The degree of doping as well as the type of ion in single crystals are somewhat limited by the crystal structure of the host. An important property of glass is that the fluorescence property of the dopant may be easily varied by simply modifying the glass composition. The absorption and emission characteristics of the transition metal ion in any host is strongly influenced by the environment of this ion. Therefore, by changing the composition of the glass, the environment of the ion, for example Nd^{3+}, is also changed. Consequently, there may be slight changes in the optical absorption strength or the shape of the bands. More important is the marked influence this environmental change will have on the fluorescence decay time and on the width of the fluorescence band. Both these properties are fundamental parameters of the laser.

As an example of the environmental effect, we have shown that the decay time of Nd^{3+} in potassium silicate glass is 635 microsec, while that in a lithium silicate glass of corresponding composition is only 235 microsec. Also, the fluorescence bandwidth in the former glass is about 275 Å as compared to about 300 Å in the lithium silicate. A more drastic change is obtained by doping the Nd^{3+} ion into a borate glass where the decay time is reduced to about 50 microsec. Since the gain per unit length and threshold of the laser are dependent on the decay time and on the fluorescence bandwidth, it is seen that these fundamental laser properties will vary from glass to glass.

Because glass laser rods may be fabricated with dimensions up to one meter or longer, with relatively high dopings of a rare earth ion, one is able to obtain a laser of extremely high power and energy. For example, powers of the order of 1000 megawatts have been obtained with one meter rods doped with Nd^{3+}. The 6% slope efficiency of these long rods is also the highest for optically pumped lasers.

Although there are many advantages to glass as a laser host, there are some serious limitations. The most important of these, which is fundamental to the material, is the broad fluorescence emission bands which are characteristic of the glass host. One of the requirements of an optically pumped laser is a narrow emission band. The broad band arises from the fact that there are a greater variety of sites in the glass, and that there are also distortions in a given type of site. In most crystalline laser hosts, on the other hand, the transition metal ion has a very well defined environment with a low electronic interaction between the ion and the crystalline lattice. The consequence is the extremely narrow emission bands in crystals. It is also possible to dope crystals with rare earth ions in different valence states, so that lasers may be obtained from the visible to the infrared. The glass laser, so far, has been limited to the infrared emitting ions Nd^{3+}, Yb^{3+}, Ho^{3+}, and Er^{3+}. No visible laser has been developed to date. It is a serious disadvantage of the glass in this respect, in that it is difficult to prepare an ingot in which the fluorescing ion is completely in an oxidation state other than in its normal one. For example, the rare earth ions are always in their trivalent state when melted under ordinary conditions; even when melted under extremely drastic reducing condition the equilibrium in the glass system very often is one in which there is still some trivalent ion. This property is typical of the liquid-like property of the glass.

The broader emission bands and somewhat lower quantum efficiencies in glass is reflected in higher laser threshold. The result of this aspect is that a continuous glass laser has not yet been obtained by using a rod. The only glass CW laser obtained to date is one using a fiber optic technique.

Some of the other fundamental disadvantages, which may or may not be serious, depending on the application, are: (1) relatively low thermal shock resistance of glasses; (2) somewhat lower mechanical strength when compared to a ruby rod; (3) some tendency toward solarization, which is especially serious with certain combinations of transition metal ions; and (4) the tendency of some glasses to attack by moisture.

The types of glasses which have to date been used for the commercial manufacture of Nd^{3+} doped glass laser rods are: (1) barium crown (a potassium barium silicate), (2) soda lime (a sodium calcium silicate), and (3) a lanthanum borate. Other types of glasses have also been reported by a number of workers, but these are primarily laboratory samples used in the study of laser processes. It should be mentioned that a phosphate glass is normally a poor laser host which results in very high laser thresholds. However, by a sensitization process it is possible to greatly improve the laser properties of this class of glasses.

The most widely used glass laser at the present time is the Nd-doped barium crown. This glass system is characterized by a relatively long Nd^{3+} fluorescence decay time (ca. 0.57 millisec at 5 wt%Nd_2O_3) with bandwidth of about 250 Å. On small rods the laser threshold can be as low as 10 joules with 99% - 95% resonators. The laser slope efficiency with ¼ × 3 inch rods is around 2%. The glass may be prepared with extremely high optical quality.

Preparation and Fabrication

The glasses must be prepared from pure materials which contain the minimum of ions which interfere with the laser properties. For example, Fe^{2+} is one of the worst contaminants for the Nd-doped laser since the iron, a common contaminant, has a strong absorption band at 1.06μ.

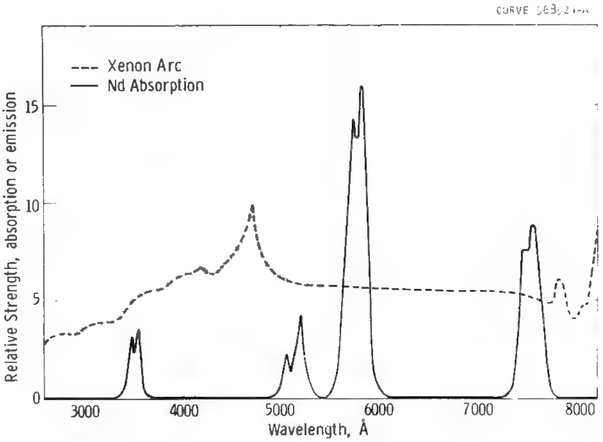

Figure 4
Nd^{3+} absorption spectrum (solid line) and Xenon arc emission (dashed line).

There must also be no contamination introduced from the furnace and crucible. Provided these requirements are fulfilled, the technique of the melting process is similar to the manufacture of extremely high quality optical glass. Depending upon the size of rods desired, the quality of the batch may be slightly different; fabrication of a meter rod obviously requires a more homogeneous melt. The glasses are melted to homogeneity, then either cast into a large slab, or extruded. In some instances, the extruded laser glass is cladded by fiber-optic techniques with a non-activated glass of matching refractive index. The glasses must be carefully annealed to remove all strain. The cylindrical rods are finished by grinding faces to less than 5 seconds parallelism, and polished to less than 0.1 wavelength smoothness.

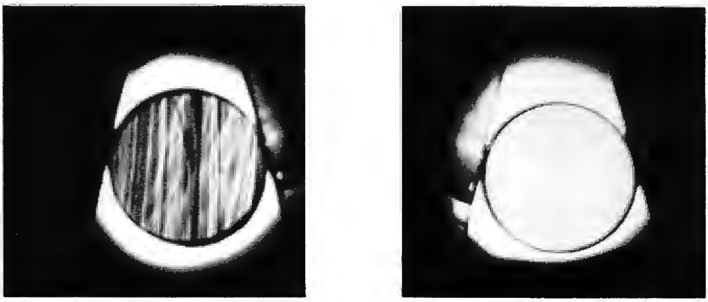

Figure 5
Schlieren pattern of inhomogeneous and homogeneous glass laser rods.

Figure 5 shows a schlieren photograph taken through a 12 inch laser rod. This method which is commonly used to determine rod quality is extremely sensitive to various types of defects, notably those due to variations of refractive index within the rod. The absence of striae or other defects is evident in the lower rod by the absence of any disturbances in the photograph. The upper rod shows the presence of striae, and is therefore not of equal quality.

It has been shown by a number of workers that platinum inclusion may be a serious problem when glasses are melted in platinum crucibles. Consequently, glasses have also been melted in high-quality ceramic crucibles.

New Developments and Improvements

We will briefly discuss recent developments which show promise for improving the glass laser. As it was earlier shown, the fluorescing ion must first absorb energy to raise its energy state. If the pump lamp has a radiation spectrum extending from the ultraviolet to the infrared, the only energy utilized in the fluorescence process will be that absorbed, for example, by the Nd^{3+} ion. Figure 4 shows the xenon arc emission and the Nd^{3+} absorption spectra. Now, by incorporating Mn^{2+} also into the same glass it is possible to effectively broaden the Nd^{3+} absorption band by an energy transfer process whereby the energy absorbed by the Mn^{2+} is transferred to the Nd^{3+} by a nonradiative process. Figure 6 shows the

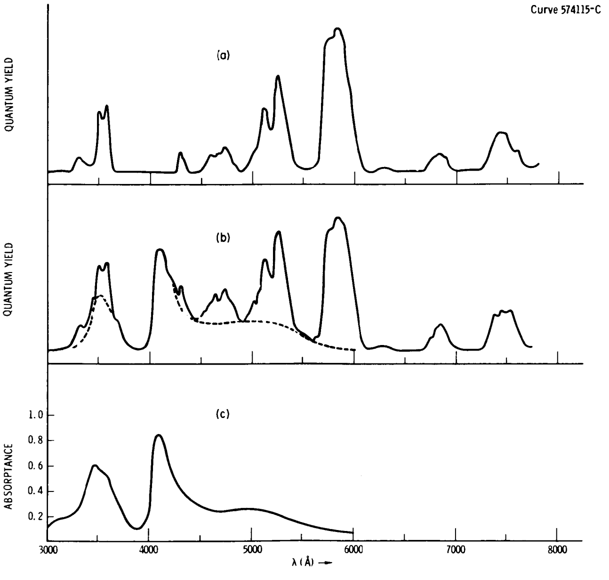

Figure 6

a) Nd^{3+} excitation spectrum in phosphate glass.
b) Mn^{2+} sensitized excitation of Nd^{3+} in a phosphate glass.
c) Mn^{2+} absorption in phosphate glass.

excitation spectrum for the Nd^{3+} + Mn^{2+} combinations when pumped with a xenon lamp and observing the fluorescence intensity at 1.06μ. Note that the Mn has filled in a large void in the Nd^{3+} spectrum. The Mn transfers a large part of its absorbed energy to the Nd, which subsequently fluoresces in the near infrared. By this sensitization process, we have improved the laser output efficiencies of Nd^{3+} in phosphate glasses, and the increase in effective pump utilization was about 35% over that for the glass without Mn. Similar types of energy transfer processes have been shown by other workers for other systems containing two rare earth ions or a rare earth with a transition metal ion; however, these latter systems are of relatively lower efficiency.

The second development which utilizes a doubly-doped system is a barium crown glass doped with Nd^{3+} and UO_2^{2+}. The uranyl ion in this system acts as a saturable filter for the Nd laser emission. When the laser rod containing these ions is pumped, both the UO_2^{2+} and the Nd^{3+} are excited. However, the uranyl, when excited by the blue or ultraviolet radiation, is raised to a metastable upper state which has its own absorption which extends to the near infrared. Consequently, part of the Nd^{3+} fluorescence is absorbed by the uranyl metastable state, and this process continues until the latter state becomes saturated. During this process there is no laser action, since the UO_2^{2+} lowers the Q of the optical cavity. Simultaneously, the Nd is allowed to reach a higher population inversion level than is otherwise possible. The system finally reaches a point where the gain in the rod reaches a level sufficient for laser action to begin. This in turn bleaches the induced uranyl absorption in its metastable state by saturation and results in a giant spike. The spikes are spaced at fairly regular intervals as shown in Figure 7.

APPLICATIONS

Applications of Glass Lasers

The laser is in principle simply another light source. But, because of its unique properties of high intensity and high degree of coherence, it lends itself to an extremely wide range of applications. At the present time, no one application has become so extensive as to dominate the field of laser applications. Rather, the uses of laser have tended to be widespread and specialized, and many of the potentially important applications are still in the research or development stages. This will probably change in time with certain applications assuming a more dominant role as the special properties of lasers become more firmly established in our technology. Because of the present widespread nature of laser applications, no effort will be made to single out any particular application; instead, a number of applications will be briefly described in order to demonstrate the range and versatility of lasers. Many of the following applications involve the use of glass lasers, although a number of them are common to other laser materials, notably crystal and gas lasers.

Material Processing by Means of Lasers

One of the earliest applications of lasers was to materials processing, mainly in the areas of welding and machining. The ability to concentrate

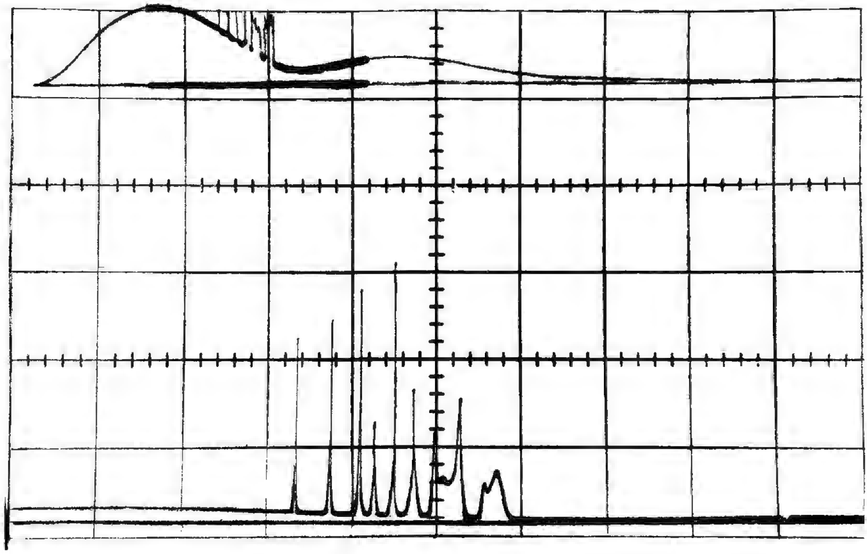

Figure 7
Integral giant spike in UO_2^{2+} sensitized Nd^{3+} laser in barium crown silicate glass. Lower trace is expanded time trace of upper oscillogram.

a great deal of energy onto a very small area, by means of optical techniques, makes it possible to machine and weld with a very high degree of accuracy. In many instances the functions performed by lasers were previously either very difficult or impossible to perform. Glass lasers are particularly useful in these applications because of the wide range of

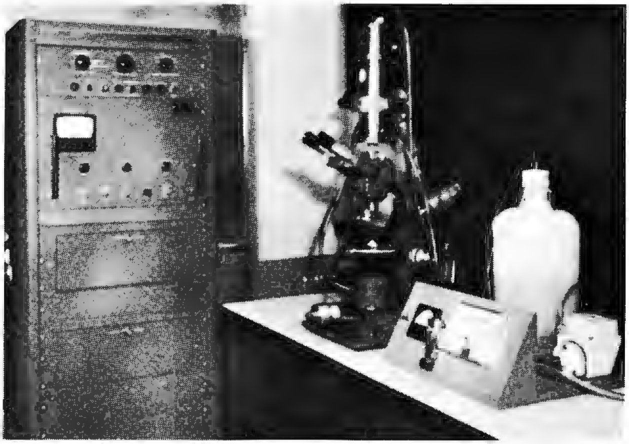

Figure 8
Laser welding equipment.

sizes, hence of energy capabilities, that are available. A typical laser welding apparatus may have an energy output up to perhaps 20 joules, with a pulse duration of perhaps 1 millisecond. This corresponds to a peak power of 20,000 watts, which, when focussed to a spot diameter of approximately 2×10^{-3} inches, represents a power density at the focal point of approximately 7×10^{9} watts/in^2. Such high power densities permit either welding or machining, depending on the manner in which the energy is applied.

Figure 8 shows a typical laser welding apparatus. The basic optical system utilizes a trinocular microscope for accurate focussing and positioning. The laser head, mounted above the miscroscope eyepieces, utilizes the same microscope objectives to insure accuracy. Figure 9 shows a series of flat packs (miniature electronic components) laser welded to a slotted printed circuit board. Figure 10 shows a cross section of a laser hole drilled through a 0.210 inch cast iron plate.

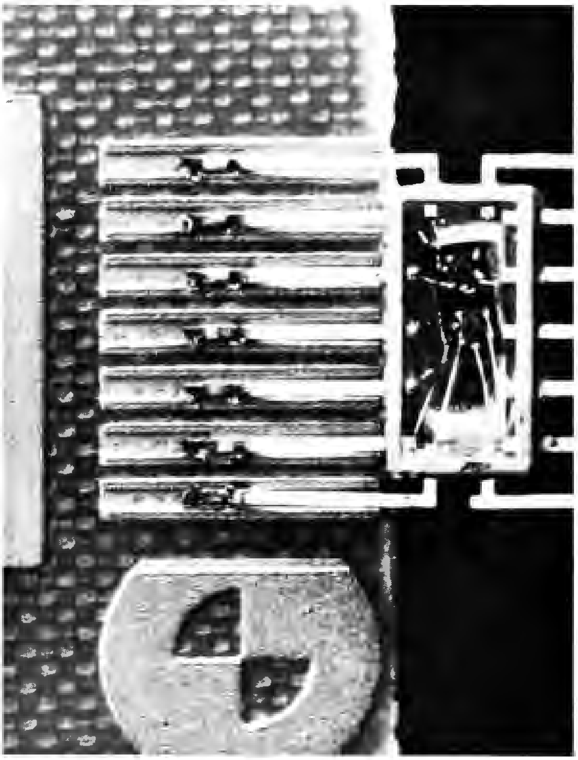

Figure 9
Laser-welded microelectronic flat-pack.

Among the advantages of laser welding are: avoidance of contact with external electrodes or foreign materials, hence freedom from contamination and mechanical deformation; applicablity to a wide range of ma-

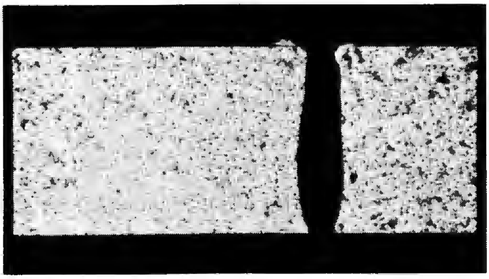

Figure 10
Laser drilling through 0.210" cast iron.

terials, including very refractory materials; a high degree of accuracy and control. The latter advantages are extremely useful in applications involving miniature or microminiature electronic components. Figure 11 shows a variety of miniature electronic modules which contain one or more laser welds. Figure 12 provides another example of laser machining. In this case, a matrix of holes was laser machined in the side of a 1 inch O.D. zirconia tube. Finally, a unique example of a laser welding application is provided by Figure 13. In this case, the weld, indicated by the arrow, was made through the envelope of an image orthicon tube, after the tube had been evacuated and sealed. A plant for drilling holes in diamonds for use as wire drawing dies is currently being constructed by the Western Electric Co. These are but a few examples of the wide range of application of laser welding and machining.

Laser Ranging, Illuminating and Communication

By far the largest consumers of lasers and laser components are the military services. Many of the applications involve ranging and target illumination, and many of these are equally useful in non-military applications.

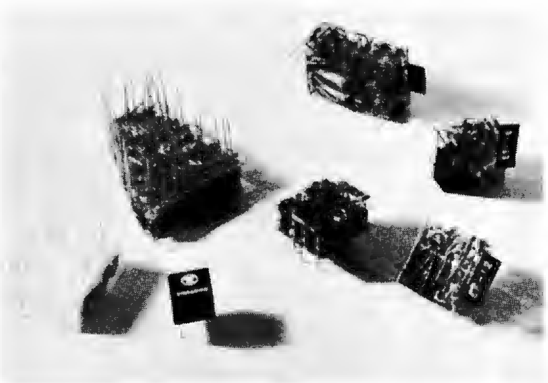

Figure 11
Wire welded modules.

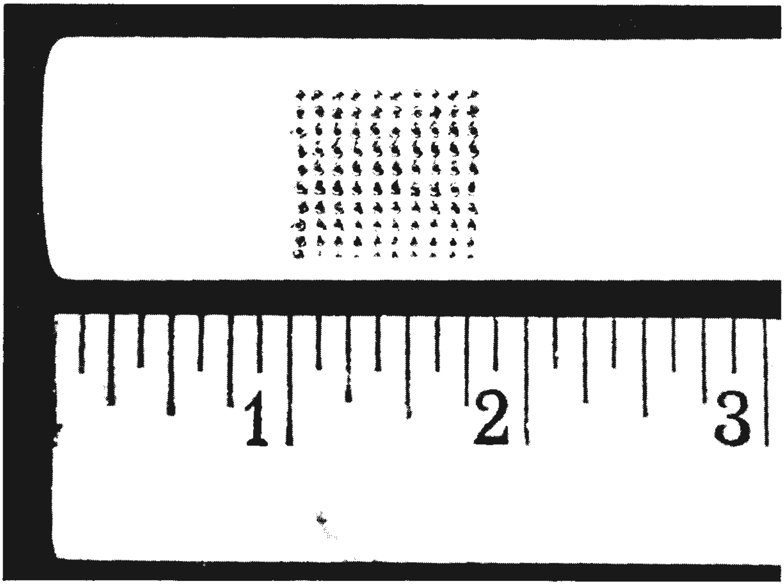

Figure 12
Zirconia tube with matrix of laser drilled holes.

Perhaps the most direct application is in range finding of either fixed or moving objects. The application is straightforward, and in its broadest sense, may be classified as laser radar. An object whose distance is to be determined is sighted either through a telescope or sighting tube which is mounted along side of the laser head so that its line of view closely corresponds to the path of the laser beam. A pulse of laser energy is directed at the target, and a portion of the reflected or scattered radiation is detected by means of a detector often located on or near the laser head. Since the velocity of light is known with considerable accuracy, the time taken for a light pulse to make a round trip from the laser to the object and back to the detector is a measure of the distance of the target to the observer. To obtain good resolution, very short pulses are desirable, and pulses as short as 10^{-8} seconds can be generated. Ranging can be accomplished over a distance of up to several miles with an accuracy of several feet. Glass lasers have been successfully used in this application as well as lasers of other materials. The equipment can be small enough and light enough to be carried by hand.

A much more exciting, and potentially broader, application of lasers lies in the area of communications. Lasers are particularly attractive because of their extremely high radiance, low beam divergence, and high frequencies. Like radar communication, lasers would have to be used in line of sight, or point to point communication systems. Their very high radiance and low beam divergence permits information to be transmitted over vastly greater distances than by presently available techniques. In-

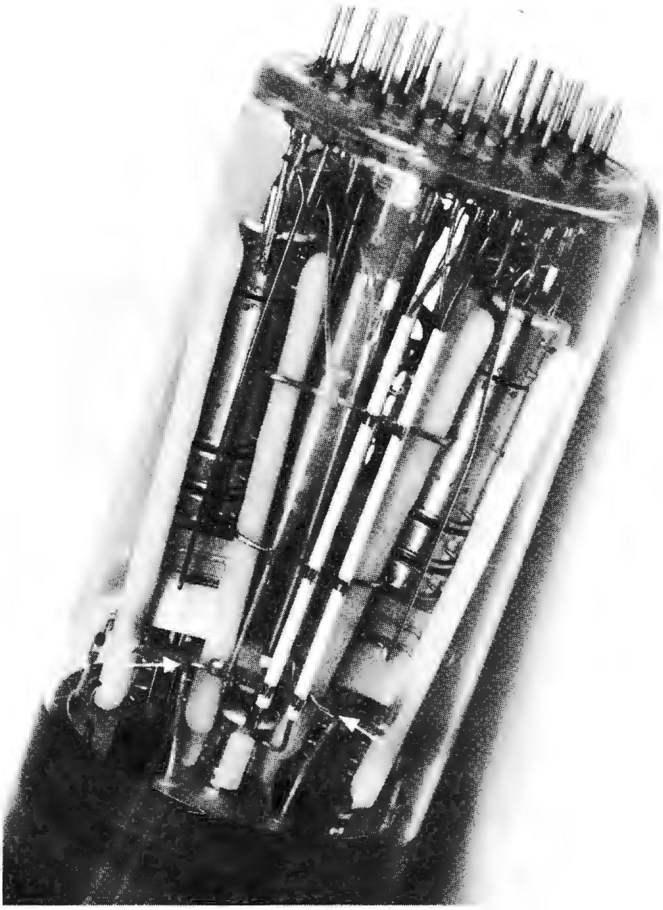

Figure 13
Welding (at arrow) within image orthicon tube.

deed, lasers may provide the most effective means for deep space communications. In addition, the very high frequencies at which lasers operate, permit, in principle, the transmission of an extremely large number of individual channels on a single carrier wave, with a very high signal to noise ratio.

Most of these applications are still in the early experimental or development stages. In many instances C.W. lasers are desirable. For this reason, glass lasers have not been prominent in these applications, but there is no reason why they cannot find a place in this area in the future. The problems are centered mainly on the development of successful modulation techniques. However, the principles underlying these applications are well established.

Miscellaneous Applications

The potential applications of lasers are so numerous and in such diverse fields that only brief mention can be made of a few of the more interesting uses, to illustrate the range of activities which are currently being explored. Among them are the following:

(*a*) Data processing and pattern recognition.

(*b*) Medical applications, including such applications as retinal coagulation for the treatment of detached retinas and the treatment of tumors. In retinal coagulation, a controlled laser pulse, usually from a ruby laser, although a glass laser may be used, form a tiny spot-weld which at-

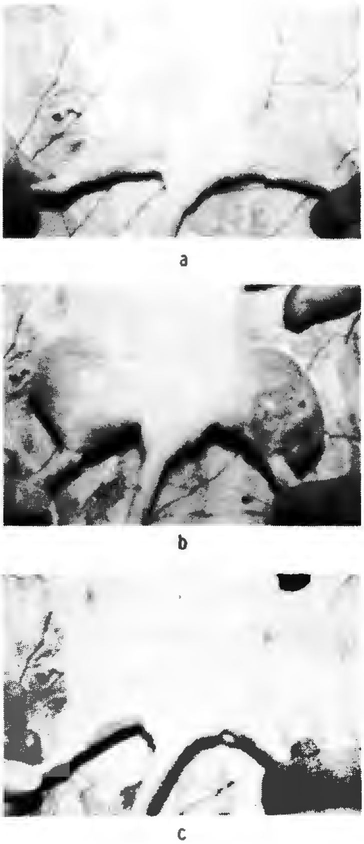

Figure 14

Treatment of Walker's sarcoma in rat by laser irradiation.
a) Control.
b) tumor after inoculation.
c) after irradiation of tumor showing remission.

taches the retina to the choroid, the membrane that normally supports the retina. In the treatment of tumors, it has been observed that irradiating a tumor in an experimental animal often produces remission of the tumor, and occasionally, also of nearby tumors. Figure 14 illustrates this effect in a series of experiments performed at the Westinghouse Research Laboratories in conjunction with the University of Pittsburgh Medical School. This potential application has aroused a great deal of interest, but the results are not fully understood, and insufficiently investigated to be regarded, at this time, as a potential treatment of human tumors.

(*c*) Holography. This is a new and most interesting application of lasers to photography. In holography, instead of photographing the real image of an object by means of a lens focussed on the film plane, a photograph is made of the diffraction pattern produced by the object when it is illuminated by coherent radiation. The diffraction pattern seen on the exposed film bears no apparent relation to the object when viewed in ordinary light; the film appears uniformly grey. When viewed with coherent or monochromatic radiation, a three dimensional image appears in space, with a size and position depending on the relative position of the observed. The potential uses of holography are themselves so numerous and varied as to open an entire new field of applications.

CONCLUSIONS

Most applications of lasers are in various stages of development, some of them in very early stages of development. Few, if any, applications have reached a state where they can be regarded as fully established procedures or techniques. Lasers themselves are still in various stages of development with new materials and properties constantly being discovered and studied. Perhaps because of the diverse and varied nature of their applications, no one area of application can be regarded as having reached a state of maturity. Nevertheless, all of the indications are that lasers will find many important uses in the future. Glass lasers, because of their ease of fabrication, high optical quality, and availability in such a wide range of sizes, shapes and power outputs will have a very important role in laser applications and laser technology.

ACKNOWLEDGMENT

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PRESSURE SINTERING—A VERSATILE METHOD OF MATERIALS' PREPARATION

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ABSTRACT

Pressure sintering has been increasingly used in the past decade to prepare conventional and novel materials more cheaply and more efficiently. The broad choice of experimental conditions concerning time, temperature, pressure, ambients, die materials as well as powder characteristics determine the physics of compaction mechanisms and the resulting properties. Ceramics, metals, metalloids, semiconductors, and composite structures lend themselves readily to the process improving existing and opening interesting new applications.

INTRODUCTION

Pressure sintering may be defined as the compaction of powders at elevated temperatures with the simultaneous application of pressure carried out in a controlled medium, such as vacuum or atmosphere of any kind. The method has been derived from the conventional sintering technique, differing only in the time relationship of pressure and temperature application.

Figure 1 illustrates pressure sintering as an intermediate method of

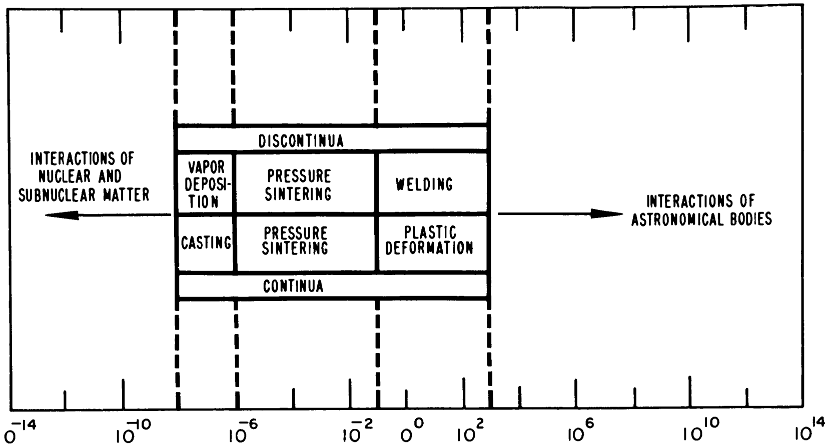

Figure 1

Approximate particle size ranges in material's preparation processes materials' preparation. The basic building blocks are powder particles ranging from approximately 0.01 to 1000 microns in average diameter and thus border both the microscopic and macroscopic state of matter. This suggests that the mechanisms governing powder compaction must be recruited from a broad range of metal physics: Newtonian and plastic flow, diffusion, evaporation, condensation, nucleation, grain growth phenomena, etc. Proper understanding and control of this diversity of mechanisms is fit to produce a wide variety of materials which cannot be obtained by other means.

METHODS AND EQUIPMENT

Figure 2 shows a basic pressure sintering apparatus. The most essen-

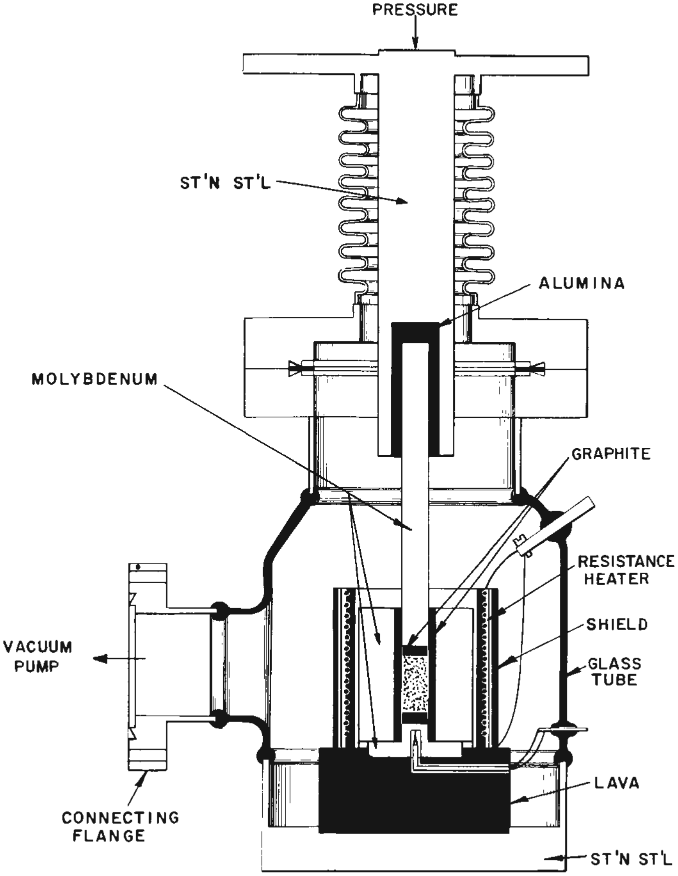

Figure 2

Air cooled hot pressing chamber

tial parts are the pressure transmitting device (top and bottom plunger), the heat supply, the powder container (die), and the chamber envelope encompassing the ambient.

Pressures can be generated in numerous ways. Although proposed methods include, among others, sophisticated press equipment,[1] isostatic pressing,[2] electrically and explosion generated shock waves,[2] and pinched magnetic fields[3], they have found only very limited entry into the field of pressure sintering. By far most cases still utilize pneumatically or hydraulically propagated uniaxial slow rate pressurization applied in a fashion similar to that shown in Figure 2. Ultimate achievable conditions at the present state of the art allow continuous uniaxial pressures of approximately 100 kbar[1] ($=1.5 \times 10^6$ psi) at moderate temperatures.

Future processes leave room for improvement in the control of

(1) pressurization rates, dP/dt,
(2) higher absolute pressures, and
(3) isostatic pressing.

(1) Reproducible pressurization as well as depressurization rates and their control will help to understand densification mechanisms better and, accordingly, permit a more direct control of the process. This has been almost completely neglected in the past.

(2) Higher absolute pressures will not only permit to compact refractory materials at lower temperatures, but will also open to pressure sintering the field of metastable modifications which often exhibit valuable properties.

(3) Isostatic pressure propagation is particularly desirable, if uniformly densified samples are required. Lines of equal pressure in Figure 3, observed in an Al_2O_3-matrix hot pressed composite, demonstrate the uneven pressure distibution which is caused by wall friction and verifies observations that have been long known to occur in uniaxially cold pressed specimens. This effect is responsible for appreciable density variations (Figure 3). For this reason height to width rations of $H/D = 4$ should not normally be exceeded. Hot gas isostatic pressing[4] represents one possible solution to this problem.

Heating methods vary significantly. As shown in Figure 4, they range from induction, resistance, radiation, and convection heating to the tapping of chemical energy from an exothermic process in "reaction hot pressing".[5,6] For rapid operations, unless continuous hot pressing can be utilized, either rf or direct resistance heating must be employed. Temperatures around 3000°C. at moderate pressures have been reported.[7] Room for improvement is, again, given in the heating and cooling rates, dT/dt, over a large range of values which will help to control the compaction processes more reproducibly.

Die materials and designs are other parameters subject to improvement. The reason for the limited number of usable materials is due to requirements which are not normally combined in one material:

(1) good lubricating properties,
(2) high strength at elevated temperatures, and
(3) chemical compatibility with ambient and powder.

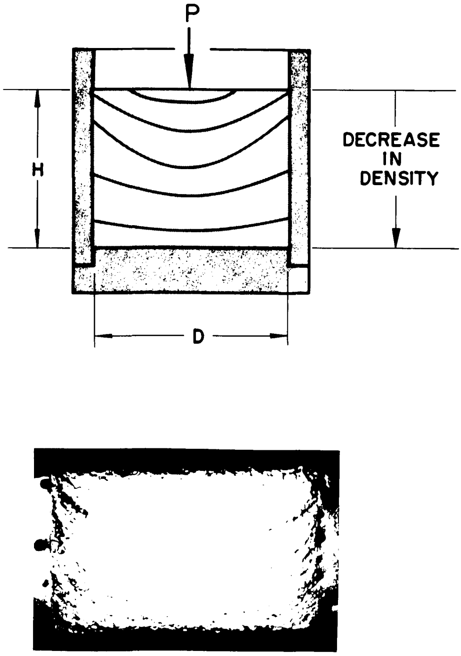

Figure 3

Lines of equal pressure in hot pressed specimen

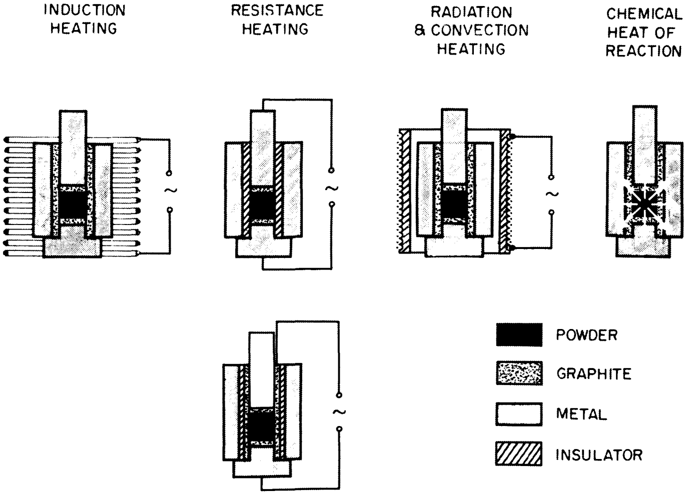

Figure 4

Heating methods in pressure sintering

Graphite is most widely used because of its excellent lubricating properties. Due to its limited strength, however (normally 10,000 psi, hot pressed to theoretical density +25,000 psi compressive strength), other materials like metals[8] (steel, cast iron, W, Mo, TZM, etc.), ceramics[9] (steatite, Al_2O_3, MgO, ZrO_2, etc.), metalloids (refractory carbides and borides) have been proposed or used in special applications. The best results are obtained with combinations of compatible linings which are in direct contact with the powder, reinforced by stronger outside walls (Figure 2). High pressure applications utilize prestrained[1] or segmented[10] designs. To insure chemical compatibility coatings (graphite, Al_2O_3, etc.), spacers (graphite, Al_2O_3, SiC, etc.), and liners (graphite sleeves, refractory or noble metal foils) are employed. Figure 2 shows the arrangement of liner and spacer in a typical experiment. Numerous media are encountered in normal operations, partly to create inert conditions (inert gas, vacuum), partly to suppress evaporation of equipment components (inert gases).

WORKING PARAMETERS

Hot pressing of powders encompasses many mechanisms of material transport. Before the correct models can be assigned to a particular problem, several factors must be defined. The basic parameters are

(1) type of material,
(2) powder condition, and
(3) external conditions.

(1) The type of material is important because certain critical properties, which determine the prevailing compaction mechanism, like vapor pressure, diffusion constants, elastic and plastic properties, etc., lastly depend on the type of bonding (Figure 5). Crystals with metallic bonds, for instance, have a broader temperature range in which they are ductile

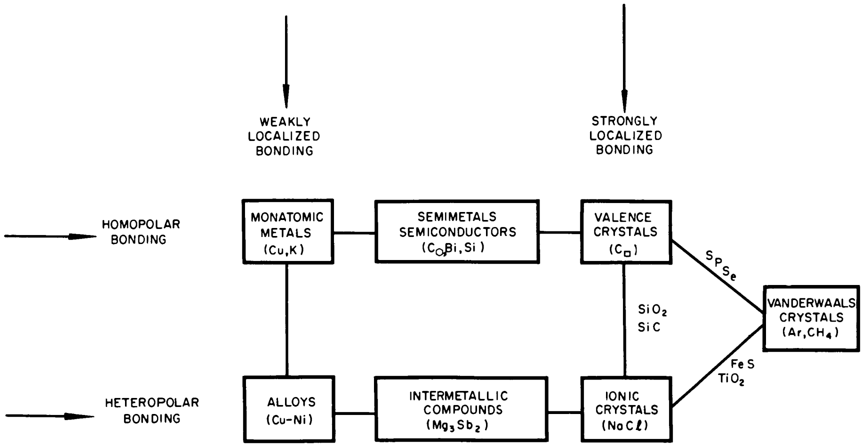

Figure 5

Bonding relationships between solids

and thus yield to plastic flow; ionic crystals are normally brittle over large temperature ranges and thus would be expected to obey other mechanisms, etc. Experimental conditions are most strongly determined by the type of material.

(2) The powder condition is evenly important. Table I comprises factors which influence the densification process. Alone the particle size is an extremely effective way to change powder properties. This is borne out by Table II which shows that the surface energy increase as well as Kelvin's vapor pressure (and thus activity) ratio become determining factors in submicron powders. The amount of surface adsorption is also directly proportional to the specific surface area of the powder. The associated electrostatic and gravity effects are believed to be the reason that fine powders pack less densely[11] than coarse ones. On the other hand, fine powders normally densify much more rapidly than coarse powders (Figure 6) and also result in higher absolute densities. A rough qualitative correlation between particle size, shape, ductility and favored densification mechanism is given in Table III. The aforesaid emphasizes the impor-

TABLE I

CHARACTERIZATION OF POWDERS

Chemical Composition	*Particle Geometry*	*Physical Powder Properties*
Particle bulk composition	Particle size	State of lattice
Distribution of phases	Absolute size range	Powder particle crystallinity
State of surface absorption	Size distribution	Degree of distortion
	Particle shapes	Electrical properties
	Qualitative range of shapes	Thermal properties
	Distribution of shapes	Magnetic properties
	Microscopic surface roughness	Optical properties

TABLE II

POWDER PARTICLE PROPERTIES AS A FUNCTION OF PARTICLE SIZE**

Particle Diameter (cm)	10^{0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Particle Surface (cm^2)	3	3×10^{-2}	3×10^{-4}	3×10^{-6}	3×10^{-8}	3×10^{-10}	3×10^{-12}
Particle Volume (cm^3)	5×10^{-1}	5×10^{-4}	5×10^{-7}	5×10^{-10}	5×10^{-13}	5×10^{-16}	5×10^{-19}
Ratio of Bulk to Surface Atoms	5.3×10^{6}	5.3×10^{5}	5.3×10^{4}	5.3×10^{3}	5.3×10^{2}	5.3×10^{1}	5.3
Thompson's Small Particle Vapor Pressure Ratio $\triangle p/p_\infty$ ($\triangle p = p_r - p_\infty$)	$e^{5\times10^{-7}}\frac{V^*}{T}$	$e^{5\times10^{-6}}\frac{V}{T}$	$e^{5\times10^{-5}}\frac{V}{T}$	$e^{5\times10^{-4}}\frac{V}{T}$	$e^{5\times10^{-3}}\frac{V}{T}$	$e^{5\times10^{-2}}\frac{V}{T}$	$e^{5\times10^{-1}}\frac{V}{T}$

*V = molar volume (cm^3/mol), T = temperature (°K) **Spherical Particles

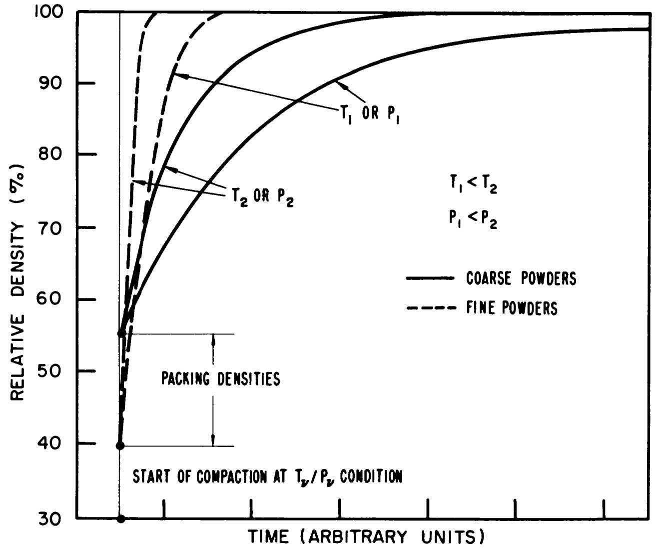

Figure 6

General densification curves in pressure sintering

tance of powder preparation techniques[8,12] the most common of which are arranged in Table IV. Without powder characterization a hot pressing process cannot be made reproducible.

TABLE III

COMPACTION MECHANISM, STRUCTURAL EFFECTS, AND POWDER PROPERTIES

Compaction Mechanisms	*Powder Property Favoring Compaction Mechanism*			*Structural Effects in Compact*
	Size	*Shape*	*Plasticity*	
Rearrangement	fine	round	brittle, ductile	Densification
Fracture	coarse	sharp edges	brittle	Densification, Grain Size Reduction
Viscous Flow (Boundary Gliding)	fine	round	brittle, ductile	Densification
Plastic Flow	coarse	. . .	ductile	Densification, Grain Shape Change (Recrystallization)
Diffusion	fine	. . .	ductile, brittle	Densification, Grain Growth
Solution-Redeposition	fine	sharp edges	brittle, ductile	Densification, Grain Growth
Evaporation-Condensation	fine	sharp edges	brittle, ductile	Densification, Grain Growth

TABLE IV

POWDER PREPARATION TECHNIQUES

Mechanical Comminution

- Grinding mill,
- Ball mill,
- Vibrational mill,
- Jet mill

Chemical Reduction of Compounds

- H_2-Reduction of Oxides,
- Alkali Reduction of Halides

Solution and Subsequent Distillation

- Amalgamation,
- Freeze-Dry Technique

Chemical Decomposition

- Metal Hydride,
- Carbonyl,
- Halide

Electrolysis

Atomization of Liquid Metals

Evaporation-Condensation

- Against Inert Gas Atmosphere,
- Plasma Jet and Arc Disintegration

(3) Finally, external conditions, like temperature T, pressure P, time t, dT/dt, and dP/dt, die materials, and atmosphere influence the compaction behavior. This is illustrated in Figure 6. The initial rise of the curves is a strong function of dT/dt and dP/dt and re-emphasizes the importance of close control of these parameters as mentioned earlier. Generally, high temperatures and high pressures enhance both rate and degree of densification. Die materials and the kind of medium present in the chamber[13] also contribute to the compaction behavior. Chemical interaction and adsorption effects, for instance, change the substance of grain boundaries and thus may affect macroscopic flow characteristics, and porous compacts with gas filled pores sinter more reluctantly than evacuated ones.

MODELS OF COMPACTION

Phenomenologically, the entire compaction cycle may be divided into the continuous and the isolated pore stage. During the first the interparticle bonding and main shrinkage phases occur, during the latter a slow, final densification takes place (Figure 6) according to one or more of the basic mechanisms listed in Table III. A short definition and outline of each is in order. Since the occasion does not permit to present a complete mathematical treatment, only the general direction of procedure will be indicated.

(1) Rearrangement signifies the relocation of powder particles after those bridges collapse which encompass unstable voids (Figure 7). Spherical particles of equal size and a combination of face centered cubic (fcc) and hexagonal-closely packed (hcp) arrangement assumed, the theoretical packing density cannot exceed 74.1 vol.-%. Real conglomerates, with irregularly shaped and sized particles, can fill out voids formed by a large particle matrix. W. D. Kingery has, indeed, observed a minimum porosity to exist in binary systems of coarse and fine particles.[14] Controlled, as opposed to statistical, arrangements should result in near theoretical densities, if the proper adjustment of particle sizes, shapes, and numbers could be possible.

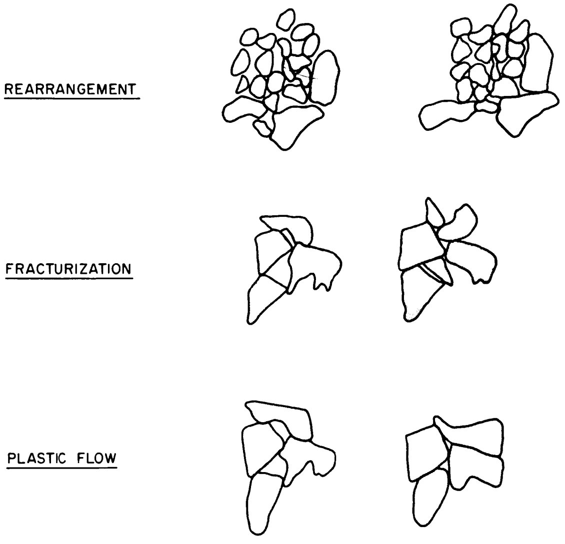

Figure 7

Illustration of compaction mechanisms

(2) Fracturization takes place in the initial stages of pressing, if the material is brittle and coarse grained (Figure 7). Fragmentation leads to rearrangement and thus enhances densification. The combined effect should, again, yield near 100% dense material in the extreme case. This could, undoubtedly, be verified, if high enough pressures and suf-

ficiently brittle material are employed. Evidence for such behavior may possibly be given by observations of Spriggs *et al.*[15] who prepared dense, but weakly bonded NiO at high pressures.

(3) Diffusion is a basic mechanism of atomic movement. Among the numerous details proposed for atomic transport[16] that of vacancy movement is most relevant to the process of powder compaction.[17] Figure 8 illustrates several possibilities of vacancy migration. Vacancy gradients exist along the differently curved neck regions and between surface, grain boundary, and lattice. Generally, atomic flow is directed toward small radius areas to reduce the surface energy. Observed rates of compaction by pressure sintering always exceed diffusion rates during the main shrinkage stage.[18] This either indicates that other mechanisms are active or that diffusion rates are enhanced under pressure. Several authors have, indeed, reported that stress can increase diffusion coefficients by several orders of magnitude through the introduction of concentration and defect gradients.[19,20] In such cases diffusional creep models may be applicable. This prompted T. Vasilos and R. M. Spriggs to calculate diffusion coefficients for several hot pressed ceramics[21] using the Nabarro-Herring creep model[22] modified with respect to the stress term, σ:

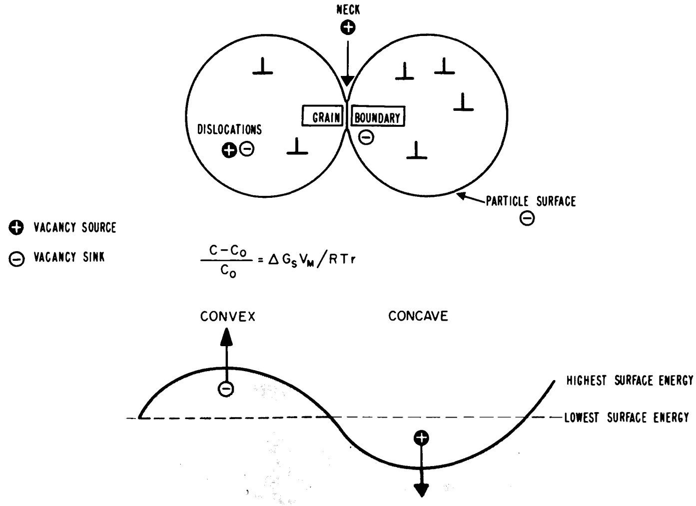

Figure 8
Distribution and diffusion of vacancies on powder particles during sintering

$$D = \zeta d^2 k T / 16 V_v \sigma$$

where d = grain diameter in cm,
ζ = strain rate in s^{-1},
k = Boltzman constant, 1.38×10^{-16} erg/°K.,
T = absolute temperature in °K.,
V_v = vacancy volume in cm^3,
σ = effective stress in erg/cm^3, modified by $P(1 + 2\pi) = \sigma$, where P = applied pressure, π = porosity in vol. %.

As a general rule, diffusion mechanisms are more significant during the last stages of the densification cycle (see Figure 6) and as long as temperature and pressure stay below critical shear stress conditions.

(4) Viscous and plastic flow are the only mechanisms that contain, by definition, a pressure dependent term and thus appear predestined to describe pressure sintering processes. Both terms are characterized by the viscosity, η, and differ only by the "activation pressure" (critical shear stress, T_{crit}) required to initiate plastic flow. The free flow of fine powders approximates viscous flow behavior (low viscosities) and thus, to a certain extent governs rearrangement of particles, whereas plastic flow (high viscosities) concerns the deformation of individual particles (Figure 7) due to introduced stresses. Using the plastic flow model of Mackenzie and Shuttleworth[23] Livey, Murray, and Williams[18] derived the following relationship to describe the main shrinkage phase of certain ceramics:

$$ln\,(\pi/\pi_0) = -3Pt/4\eta$$

for $P \gg 2\gamma/r$ (capillary driving force) and $P \gg T_{crit}$. *Here*

π/π_0 = ratio of porosity, π, and starting porosity, π_0,

η = viscosity in gs/cm^2

t = time in s.

A modified version of this model considers grain growth during densification[24]:

$$ln(\pi/\pi_0) = -3P\,ln(1 + bt)/4\eta b$$

where b = proportionality constant. These phenomenological models do not reflect much of the real microstructural events during compaction. Normally these follow the strain stress relationship of polycrystalline aggregrates[16] as characterized by elastic strain, yield, and plastic deformation (and finally fracture, if conditions permit).

(5) Solution-redeposition[25] and evaporation-condensation[26] have certain aspects in common. The first is encountered in compacts with minor admixtures of liquid phase which is also sometimes generated by the pressed material itself, like in the reported case of cast iron powder.[27,28] The latter is obviously found in high vapor pressure materials, for instance, alkali halides. A schematical presentation of the process is given in Figure 9. After initial rearrangement, which is enhanced appreciably by the presence of a liquid film, "erosion" of sharp corners and edges by solution in the liquid or evaporation takes place (exterminating very small particles entirely), enhanced by Kelvin's vapor pressure (or activity) ratio of strongly curved surfaces (Figure 9). Redeposition occurs on more stable sites and thus evens out pore irregularities and closes the pores (Figure 9). Theoretically, the densification should stop at the isolated pore stage, in particular, in the case of evaporation-condensation. In pressure sintering these processes are never alone active, however, such that the final stage of densification is masked by other, pressure favored, mechanisms.

EXPERIMENTAL ASPECTS

Experimental control serves to verify the hypothetical compaction models. Since the mathematical description normally considers the time dependent relative porosity, $d\pi/dt$, densification rates must be measured.

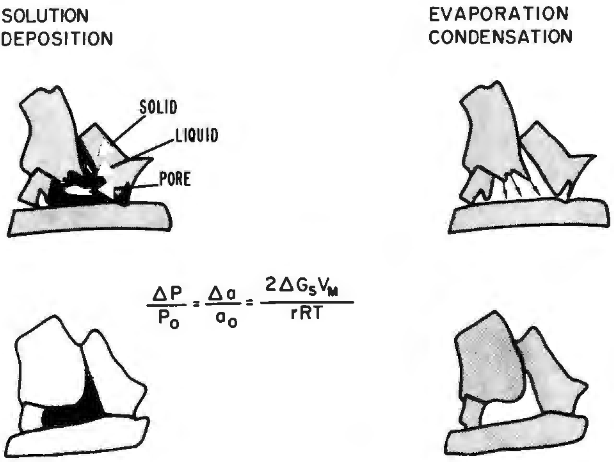

Figure 9
Shrinking of powder compacts through evaporation-condensation and solution-redeposition

In addition, a qualitative analysis will help to identify the compaction mechanism by comparison of the following characteristics of the powder and hot pressed compact:

(1) number of powder particles and grains (cm^{-3}),
(2) average power particle and grain diameter (cm),
(3) size distribution of powder particles and grains,
(4) powder particle and grain shapes, the latter in directions parallel and perpendicular to pressure propagation.

An example of such analysis, concerning point (4), is shown in Figure 10. In this case obviously a plastic deformation model must be considered (see also Table III).

To conclude the general section and lead over into the applications the versatility of the hot pressing method is demonstrated by data on hot pressed cast iron powder[27,28] (Table V). Cast iron is a three-phase structure of γ-Fe matrix, graphite second phase, and a ternary eutectic Fe_3P/Fe^3C/γ-Fe grain boundary phase. The macroscopic melting point lies at 1150°C, but the grain boundary phase melts at 950°C.[29] This peculiarity and the relative brittleness of cast iron dictate the compaction mechanism, hot pressing conditions, and the possible applications (Table V).

APPLICATION

Pressure sintering is applied for two basic reasons:

(1) It is a unique method of materials' preparation, and
(2) it provides better properties when compared to conventional powder metallurgical products.

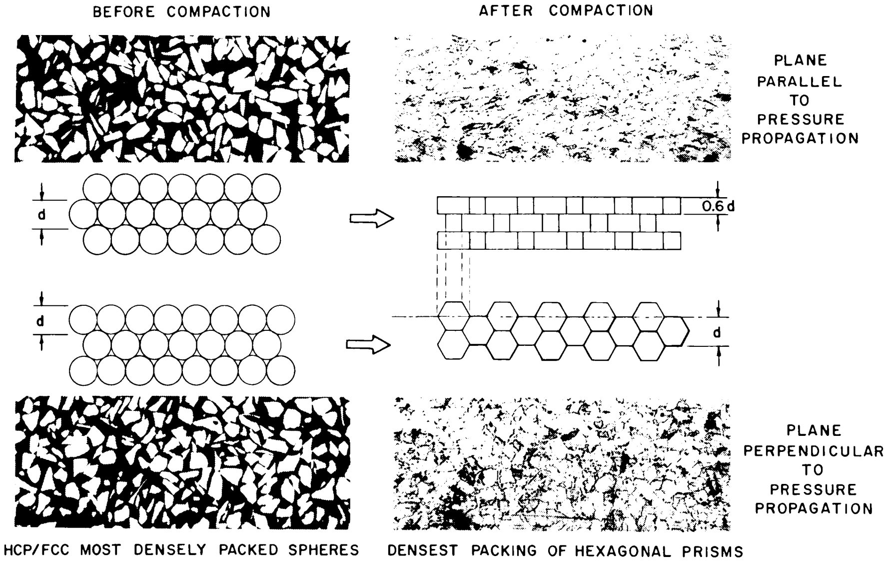

Figure 10
Compaction model of coarse grained GaSb powders (20-500μ)

(1) Casting is often uneconomical or impossible for high melting point materials due to the lack of compatible crucibles and molds. Also other shortcomings, like chemical immiscibility of components, highly differing vapor pressures and densities often make it difficult to work with melts. For instance, metal matrices with imbedded diamond particles cannot normally be cast due to gravity segregation, but are easily compacted by hot pressing. With respect to vapor deposition it has the advantage of producing larger objects much more economically and compared to conventional sintering it works faster, yielding materials with improved properties. In addition, bonding to other components can often be carried out simultaneously.

(2) The improved properties are a result of the high densities achieved. Also property combinations in composite structures are a most valuable asset of pressure sintering techniques. The essential improvements are achieved in

(1) mechanical properties (strength, hardness, elongation),
(2) thermal, electrical(conducting or insulating), magnetic and optical properties, and
(3) (if anisotropic matter is involved) isotropic properties.

METALS are among the oldest hot pressed materials.[28] Soon after the first patent was granted (1912) for the hot pressing of boron refractory metals entered the scene. The technique was an obvious extension of the old Pt-sintering technology.[8] Very soon all conventional metals had become part of the "repertoire".[8] They found use wherever better densities,

TABLE V

THREE CASES OF CAST IRON HOT PRESSING

	1		2	3	4	5
	Condition		*Densification Model*	*Hot Pressed Structure Under Condition 1*	*Required Pressure for Dense Structure*	*Application of Structure under 3*
	Temperature (°C)	*Particle Size*				
I	<950	fine or coarse	fracturization, diffusion	porous	very high	self-lubricating bearing
II	>950	coarse	diffusion plastic flow	porous/dense	medium	machine parts
III	>950	fine	solution-redeposition, diffusion	dense	low	machine parts with special strength requirements

strength and hardness, electrical conduction, and form stability (no shrinkage) were required. The development today emphasizes the preparation of refractory metals,[30] alloys,[31] and compounds[32] with and without minor second phase additions. Many of these materials find use in astronautical engineering for parts with stringent mechanical requirements (against abrasion, rupture, thermal stress failure, etc.).

METALLOIDS represent another old field of hot pressed materials.[8,28] Although they are rarely used as single phase materials (WC for high temperature furnace parts,[33] TiB_2 as high temperature arc electrodes[34]), they serve widely as hard components in composite structures. Work on carbides like TaC, HfC, ZrC,[7,35,36] and SiC[37] is being reported. UC[35] and solid solutions with ZrC[6] have found interest as thermionic emitters in reactor powered energy converters.[35] One of the most consequential developments was the hot pressing of graphite. It made feasible near theoretical densities and strength properties never before attained. A similar material made available through hot pressing is BN[38] which is used as electrical insulator and thermal cycling resistant wall liner.

IONIC CRYSTALS entered the scene relatively late. Most of the applications are found in ceramics and are mostly concerned with crystalline rather than with amorphous materials (glasses). The main incentive is given by the fact that some materials cannot easily or not at all be obtained in single phase or dense form. Like with metals, also here mechanical as well as electrical (insulating) properties are signficantly improved.[39] Conventional ceramics like Al_2O_3 and MgO,[40] but also more unusual types like BeO[34], TiO_2, ZnO, Nb_2O_5,WO_3, Y_2O_3, Cr_2O_3, NiO,[15] or Si_3N_4[41] have been compacted to densities never before attained in polycrystalline form. Al_2O_3 finds use as cutting tool material, spray nozzles, extrusion dies, etc.[34] Another area of endeavor is in magnetic materials.[42,43] Again, the mere fact that theoretical densities can be obtained improves their resistivity as well as magnetic properties. For instance, the economical production of improved YIG-recorder heads (yttrium-iron garnet) has been reported.[44]. Other areas are represented by infrared and radar transmitting elements.[34] Optically excellent properties were obtained with MgF_2, CaF_2, and MgO. Also polycrystalline light transparent MgO and translucent BeO and CaO have been hot pressed.[34] Even a pressure sintered laser was prepared[45] with properties that were nearly equal to corresponding single crystals. Hot pressing of glass is not widely spread, although glass-bonded mica (in st'n st'l dies) and compacted glass (in cast iron dies) have found industrial application.[56] Pressure sintered fused silica[46] is used for radar transmitting windows in space vehicles.

SEMICONDUCTORS are the youngest in the family of hot pressed materials. Interest arose especially in thermoelectrics. Probably the first semiconductor to be hot pressed on a production scale was PbTe.[47] The extremely low mechanical strength of melt grown PbTe made hot pressing a "conditio sine qua non". Another advantage is that bonding to other converter components can be accomplished in one operation with the compaction.[48] Bi_2Te_3-Sb_2Te_3 and Bi_2Te_3-Bi_2Se_3 alloys[49,50] also demonstrated the feasibility of hot pressing for thermoelectric materials preparation, in some cases with superior properties. Pressure sintered cubic Th_3X_4[51] compounds showed that the technique can serve as a convenient method to prepare new materials for exploratory work. Electroluminescent materials, like ZnS,[52] have been likewise compacted by hot pressing.

COMPOSITE STRUCTURES probably possess the largest potential for the technique of hot pressing. The wide range of possible combinations invite the property engineer to synthesize the most controversial conglomerates, the most obvious of which are porous (not completely densified) structures. Solid-solid combinations could, for instance, include inorganic, organic, structural, amorphous, ceramic, metallic, semiconducting, magnetic, insulating, superconducting materials, etc.

Composite structures were among the first hot pressed materials.[28] The first combinations were ductile metal matrices with hard inclusions of diamond or carbides which became the classical "cemented hard metals" like TiC, TaC, and WC with Co- or Ni-binder. Newer developments in the field of tool steels are combinations of other metalloids, like transition metal borides and nitrides, with metal or ceramic matrices.[53] In space technology and related fields metal (honeycomb and wire) reinforced ceramics are of interest with respect to thermal stress stability (re-entry systems).[54] In semiconductors PbTe has been reinforced by Mo-, W-, and Al_2O_3-inclusions.[48] More sophisticated applications of pressure sintered composites have not become widely accepted, however, although the general field presently enjoys a tremendous growth utilizing a multitude of related or more sophisticated preparational methods.[55]

OUTLOOK

As methods become more refined high pressure compaction will gain in significance, not only for economic reasons or to produce old materials with better properties, but also to synthesize entirely new materials where no other method is applicable. Higher pressures and better control of time dependent conditions will expand possibilities still further. The field of composite structures, by its very nature of nearly unlimited combinations, will contribute many a new material and perhaps even concept.

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GAS LASER TUBE SYSTEM

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ABSTRACT

A new glass laser tube with self-contained optics which are self-aligning is described. The system accommodates severe thermal or mechanical stresses which do not disrupt the laser beam. Also contained are the gas exciting electrodes and their respective glass-to-metal sealed feed through terminals. The latter protrude through the laser envelope for electrical power input connection. Either the visible (6328Å) or the infrared can be produced. One modification allows low voltage operation of the device. This new laser design includes considerations which embrace: scientific glassblowing; optical surface grinding and polishing; geometric-optics; thin-film depositions; and, ultra high purification and evacuation. Power output data are not completed but the new laser compares well with the output of either plano-to-plano, or confocal, laser tube design. A so-called corner-cube is used at one or both ends of the new design, inside the envelope. Borosilica glass is used entirely, excepting in those cases of the infrared type, the latter necessitating a suitable transmitting material for the window.

INTRODUCTION

The advancement of gas laser tube design since its inception[1] has been one of a truly scientific progress and technologically engineered accomplishment. All those who have taken part in this effort must be grateful to have participated.

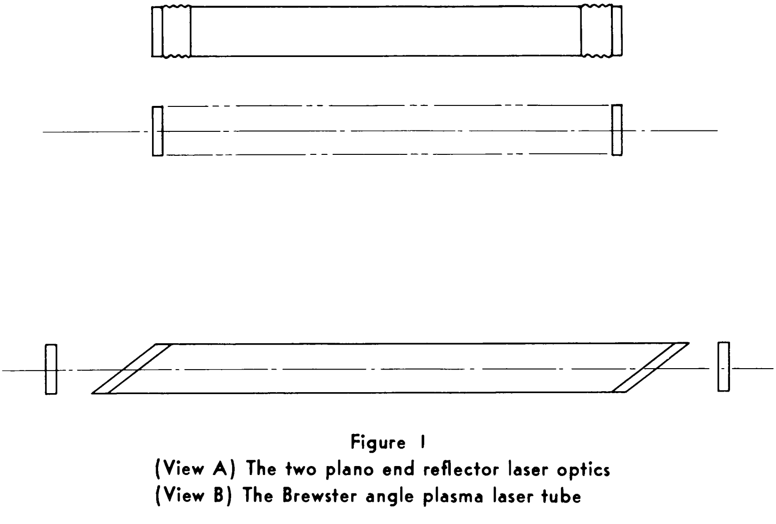

Figure I
(View A) The two plano end reflector laser optics
(View B) The Brewster angle plasma laser tube

Until recently the theory and practice appears to have been confined to the optics of either two plano-reflectors, or to the confocal using at least one spherical-reflector. Also, the usual practice has called out an external optical system.

There is no doubt that one or more investigators—the physicist, the engineer, and the technologically trained scientific glassblower, have considered the use of an optical system apart and different from the two end plano or the confocal; that would accomplish the required intensification of the laser beam and, too, somewhat simplify the alignment problem.

During the Fall (1965) this writer was contracted to design and develop a two-meter, high output, IR generator. In effect, a laser tube. Prior laser experience dated back to a few early brewster-angle prototype tube (plasma) units, during 1962-63. However, a design was promptly submitted for a dynamically operated unit using the conventional two plano end-reflectors, with metal bellows to facilitate the necessary alignment for final true parallelism. The design accepted, the unit was promptly fabricated and set up. The time-consuming problem of parallelism resulted in his own original design and development of a gas laser tube system which has the unique and inherent ability to be self-aligning; also to have all optical components and the electrode elements self-contained in his laser tube.

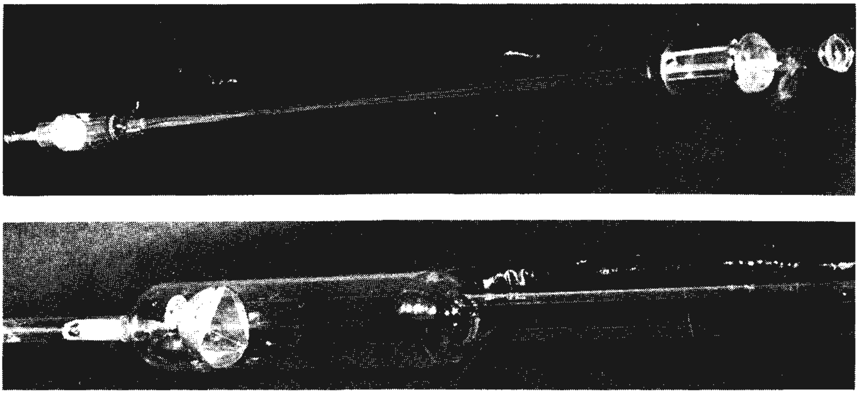

Figure 2

New gas laser tube system using right tetrahedral reflector group with self-aligning and self-contained optics, and with internal gas excitation mechanism.

This paper describes the new gas laser tube system. The entire unit is illustrated in Fig. 3 which is a sectional drawing. The glass envelope is Corning No. 7740. The window arm and its disc closure may also be of Pyrex® if only the visible is to be required. However, if the infrared is to be investigated this window arm then becomes, in effect, the graded seal portion required to go from the Corning No. 7740 to quartz, sapphire, and other infrared transmitting materials; each material dictating the particular series of glass grades to be used to effect the graded seal—inclusive of the window material itself.

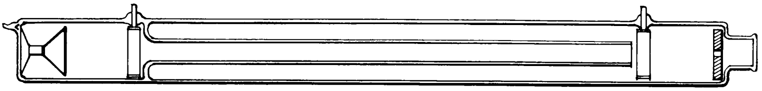

Figure 3
The gas laser tube system in section—schematic.

The two electrodes in the laser tube are of pure nickel. A suitable cathodic emissive coating is used on the electrode surface. Each electrode lead pin is tungsten, beaded with Corning No. 7720 (nonex), and press stem mounted into a flare of uranium, Corning No. 3320. The flare of the stem, in turn, is ring or re-entrance sealed to a short tubular port located on the lateral side of the laser envelope.

The optical arrangement of the new gas laser tube system is relatively simple. It has indicated both reliable and successful results. The components for the optics are made up in the following sequence: Three glass flats are cut so as to form equal sized 45° 90° triangular pieces. The three are ground and polished, washed, and then assembled so as to form mutual perpendicularity to one another—thus resulting in a right tetrahedral group. The group then is thoroughly chem-cleaned and dried. Thin-film depositions are then executed; the first being a thin-film of chromium, the second a thin-film of aluminum, and the third (optional) a thin-film of silicon monoxide. Note: The first two depositions are successively applied, or phased so as not to require the admittance of atmospheric gas pressures between the two depositions. The third deposition is indicated when there is storage (and handling problems) prior to final assembly and evacuation. It is a protective film. These depositions result in excellent front-surface reflection for the interior of the tetrahedral group. The latter is frequently referred to as a "corner-cube" although some prefer to remark the "hollowed corner of a cube." In several instances the tetrahedral reflector group was successfully assembled using Corning No. 45 "Pyroceram." (Note: The Pyroceram schedule should be followed closely.)

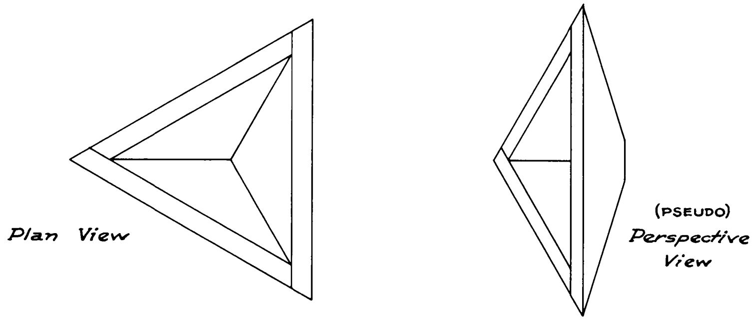

Figure 4
The right tetrahedral reflector group.

The tetrahedral reflector group is mounted on a flare stem and sealed to one end of the laser envelope. At this point it is advisable to tubulate to facilitate final glass section assembly, and to provide for the evacuation, purification, and filling. The tip or final seal, of course, will be made at the base of this tubulation.

A plano mirror disc having front-surface depositions matching those of the tetrahedral reflector group is drilled through at its center. The diameter of this through-hole is considered as an arbitrary matter. It may, however, be held with safety between one-tenth and one-fifth of the disc diameter. The hole becomes the beam aperture during operation of the completed laser tube, hence it will limit the laser beam-width which can pass. This plano mirror disc is then positioned inside the laser envelope at its opposite end from the tetrahedral reflector. The disc is fastened having its aperture properly centered. (Pyroceram No. 45)

The individual glassblower will have his own method of fabrication for any one given project with regard to the convenience of its successful assembly. In the case at hand the main body or envelope started out as a three piece group and its eventual and final assembly, though now appearing as a single tubular member, is actually that of the original three sections abutted by the glassblower.

At this stage we have a laser tube unit ready for its vacuum processing. (Note: If the vacuum process can not follow final tube assembly, storage can be for indefinite periods providing it is rough-pumped and temporarily sealed against the atmosphere.)

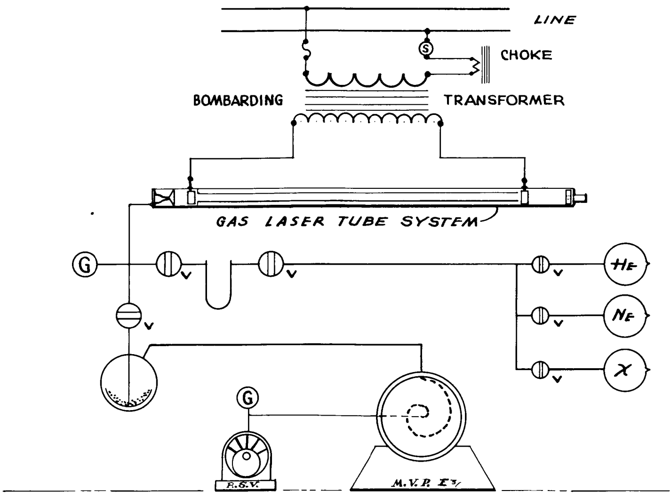

Figure 5

The vacuum system, bombarding equipment, and gas fill apparatus used to process the gas laser tube system.

(Schematics)

One time-proven method for the vacuum processing follows: The laser tube unit is sealed onto the vacuum system manifold and roughed out. At a pressure of approximately one to five millimeters (Hg) the pump valve is closed and a leak check may be made. The electrode leads of the laser tube are connected to a high-current (5 KVA; 15,000 v. Secondary) transformer. It is usually called a bombarding transformer, and a sliding choke control is a part of the equipment. The choke allows a variation of output currents and is mandatory. (Note: Such equipment is considered as dangerous, it can destroy life, and should be used only by one qualified and experienced (trained) to handle such power, manually). The pump valve is opened, a fraction, and as soon as the pressure in the unit is low enough to support a sustained discharge, the valve is again closed. The envelope glass between electrodes will be heated directly by the discharge, using moderate currents. As gas is released from the glass, and other contained components, it will be necessary to reduce the pressure in the tube in order to maintain the bombing current. The reduction of the pressure is done with full control, the pump valve being opened very slightly and reclosed as soon as high current and steady bombing discharge is evident. (*e.g.* Relative high pressure during discharge heats the tube portions during bombing, whereas a lowered pressure will heat the electrodes, and allow the tube portion to cool. Avoid the latter during the first bombarding heat.) After some several minutes of continued high current discharge the tube will attain a safe maximum purification temperature; 435°C.

This first heat is followed by an extended period of evacuation, the current of course off and the vacuum pump valve wide open. It is suggested that during this protracted period of extended pumping a careful application of heat be applied to those sections of the laser tube unit which do not come under the direct influence of the internal bombardment—between electrodes. A hand torch may be used, or external electric heater elements. The temperature is monitored. Low pressure measurements following this prolonged evacuation and localized degassing should indicate no more, say, than mid-10^{-6} Torr.

A second bombarding heat is now applied for conversion of the electrode coating. The pump valve is again closed off and a trace pressure of gas is admitted into the tube. (1 to 3 Torr.) Current is again applied, and sustained at a high level to attain electrode visible red-heat temperature. Profuse carbon-dioxide is liberated from the coating and it will be necessary to maintain lowered gas pressures in the tube by simply partially opening the pump valve. The electrode conversion heat should be carried forward promptly, or otherwise the tube would (needlessly) be overheated. When the electrodes have attained a full and uniform visible red-heat, and the evacuation of the liberated carbon-dioxide has been accomplished the pump valve is opened wide and the current discontinued. The tube unit is allowed to cool to about 100° Fahrenheit—warm to the touch. The laser tube may be considered as well purified at this point. Its ultimate low pressure evacuation will be stated later.

A third and, usually, a final test flush heat is applied. Any of the noble gases may be used. Helium is preferred. Approximately three to four Torr of helium is admitted into the tube, the pump valve of course again being closed off. A moderate application of current, 75 to 100 MA will result in a discharge giving the well-known and characteristic spectral color of helium. This true color will be sustained for several moments of continued discharge, and will indicate a relatively high state of purity of both the tube unit itself, and the helium gas used. Were the helium discharge to lose its characteristic spectral color quickly, this would indicate an impure condition, within, and a subsequent bombarding heat (using helium) should be applied; or, even the complete repetition of the foregoing procedure. Usually, the purity is observed as excellent, at this point of the process. The tube is cooled and well evacuated down to 5×10^{-7} Torr, or better. It is then "filled" with the gas, or the vapor(s), or the gases which have been selected for this particular laser tube.

The laser tube is then tip-sealed, and completed.

Generally, the power supply considerations are an optional matter, since one of several types of voltage supply sources may be used. Direct-current; alternating-current; high-frequency; and, even a pulsed discharge from a charged bank of capacitors. However, the voltages in all cases will be sufficient to meet the starting drop across the particular laser tube electrodes. Once started, when continuous operation is the order, this voltage falls to a lower level depending on the geometry, the gas pressure, the electrode drop, and so forth. However, the operating voltage is accepted as quite constant for one particular discharge tube. Indeed, one simple modification added to a small model of this type of laser tube system, (Six inch total length), was to make use of the Machlett Strip,[2] and using a cesium compound for its emissive surface coating. In this manner the operation of the laser was kept within the limits of normal single phase line voltage, or 240 volts, and less.

The operation of the gas laser tube system should be, and is, with a full control of the operating current. Again, this is a matter which is

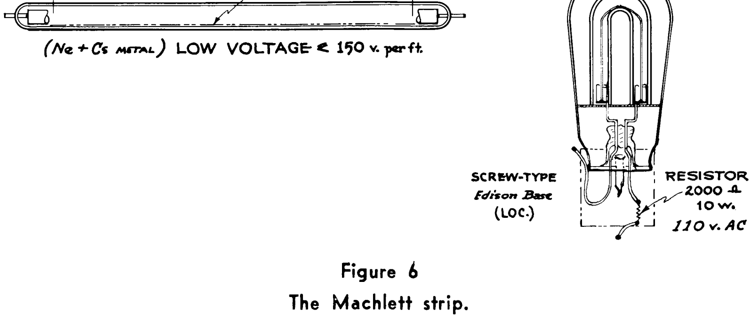

Figure 6
The Machlett strip.

Figure 7
Miniaturized gas laser tube.

limited to the individual design and structure of any one particular laser. One rule-of-thumb would be to not apply currents in excess of the calculated current-density of 1.0 ampere per square decimeter;[3] the area of the single electrode surface being the limiting factor in this approximation. Of several laser prototypes made, using this new tetrahedral configuration, the output power for a continuous operating unit is measurable. In excess of 15 milliwatts has been observed, using an aperture of 0.100 in. diameter, and an applied operating discharge current of less than 0.025 amperes, 60 cycle. Pulsed input power, as may be applied is of course another serious matter, and when it is used caution should be practiced with respect to personal safety; also the destruction of the window material is one possibility.

The optics involved in the new gas laser tube system are very simple from the elementary geometrical optics viewpoint; however, from the physical optics standpoint the optics involve a more comprehensive study. Furthermore, since the gas laser tube is essentially an interferometer, the physical optics of the laser could be considered relatively complex as compared to geometrical optics. The writer, for obvious reasons, will only refer to the geometrical optics. It is thought that this will serve to illustrate the optics of the present device.[4]

First, it is to be remarked that any light ray (or photon) which may be incident to and reflected from the plano-reflector in a direction normal to the mirror, (perpendicular to mirror surface), will necessarily make a double voyage in order to satisfy the requirement for an "identical rebound"(a phenomenon); and, too, the inherent optics of the tetrahedral reflector group will demonstrate successive (countless) identical rebounds of that same single ray or photon, thusly we have phenomena. (Quite plural!) Secondly, it is candidly pointed out that the right tetrahedral reflector group will furnish multiple-image reflection if its true geometry departs from the near-perfect. In this case, the laser beam is not only weakened (if present) but it becomes or divides into six closely positioned sub-laser beams, and will be observed to diverge from the laser beam normal direction more than the minimum theoretical divergence, or

$$\propto \frac{\text{wavelength (cm.)}}{\text{dia. aperture (cm.)}} \text{ radians.}^{5}$$

CONCLUSIONS

The optical arrangement in the gas laser tube system which has been described eliminates any requirement for critical adjustment of the two end-reflectors; it demonstrates that the optical components can successfully be self-contained in the laser tube plasma; and, it indicates definitely that the gas excitation can be an internal ionization mechanism, and take place within the gas laser tube plasma envelope. Finally, it would appear that the elimination of the critical end-reflector adjustments, plus the accommodation for stress, would allow one to declare that a gas laser tube of this type should prove most feasible for, say, certain space flight applications.

Thank you.

CREDITS

The writer wishes to express his appreciation for the splendid willingness to cooperate and to correct, as well as to suggest and criticize, on the part of several scientists at the Concord Radiance Laboratory, Bedford, Massachusetts. Special thanks are extended to Laboratory Chief, S. Stewart, Ph.D. Physics.

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WORLD OUTLOOK FOR GLASSBLOWING CHALLENGES OF THE FUTURE

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Good morning ladies and gentlemen.

When Karl Walther and Jules Benbenek first asked me to give you my views on the World Outlook for GlassBlowing, and the Challenges of the Future—one of my reactions was, "Where do I get the crystal ball?"

I don't have a crystal ball—though, if I had asked you to, I'm sure most of you could have made one to spec. However, I have been associated with this industry for some 30 years (all of them with Corning); and I've spent some of the last eight years visiting and observing operations in Corning's wholly owned and affiliated factories, as well as other glass shops, in England, France, Germany, The Netherlands, Belgium, Italy, Scandinavia, Japan, India and Mexico. And I'm planning to be working soon in some of the South American countries.

So I do have some feeling for what's going on in "the world of glassblowing" today and what some of the major trends for the future may be.

From my observations and experiences, I'm sure of one thing—that scientific glassblowers in the United States and Canada have the best opportunity to meet the demands of the future no matter what it may hold in store for all of us.

American glassblowers are first in skills and experience, Your present knowledge and your eagerness and ability to learn new skills and techniques is unsurpassed.

Without doubt—you have the best relationships with the scientists you work with—and you have the best working conditions in terms of physical envirnoment and equipment.

In addition, the professional recognition of American glassblowers is reflected by the fact that you get top salaries and fringe benefits. All of these things indicate to me that you have the best opportunities for the future.

Many of you may already have known this. But I did want to establish where you stand in comparison with foreign glassblowers.

Glassblowers in the highly developed countries produce very good apparatus. In fact, the German firm—Jena, and the English—QVF, have more experience, hence are better than we are in making large glass equipment for chemical process plants. Chalk this up to a chronic shortage of steel overseas. If you need proof of this, just attend the Achema Chemical Exposition in Frankfurt next June. At this show, which is held every three years, as many as 50,000 people a day view glass equipment 30 and 40 feet high. But enough of that. I'm not here to plug Achema.

The European capability in all forms of lab apparatus is good. Perhaps their standard varieties of apparatus are not as refined as that produced in the United States, but it is satisfactory and meets International Standards Organization's specifications. Most European companies are growing and have been growing for the last ten (10) years.

However, the underdeveloped countries don't have either the skills or the supplies needed for good glassblowing. In many areas, they are ignorant of proper mixtures of gas and oxygen. Their equipment is outmoded—burners, for instance, are much like those used in this country in the early 1900's.

Components, like joints and stopcocks, made in underdeveloped countries are generally poor—they are unable to hold vacuum and often won't even hold water.

This situation stems primarily from the past dependence of these countries on supplies of imported apparatus.

India, until recently, bought most of its supplies of borosilicate ware from England and other European countries. This ware was brought into the country either in finished form, or as tubing or blanks, for fabrication by Indian lampshops. This went on for years because India did not produce, even tho available, all of the raw material needed for glassmaking. However, as you no doubt know, India's financial picture is not bright. A year ago she rescinded import licenses to bring in borosilicate ware. As a consequence, India must now make its own borosilicate ware. There are three (3) Indian producers: Two pot melters—Skyrex and Sigcol--and Borosil, a company formed with Indian Nationals and Corning Glass Works. Borosil now has continuous melting units. They make hand blown flasks and beakers. Tubing is drawn automatically, as it is here. The ware is satisfactory (excellent for native production) and is getting better as they gain experience.

Pay scales and working conditions of glassblowers in many other countries simply do not compare with what we take for granted every day.

In India, a lampworker earns about half a rupee an hour. That's about 10 cents, or $4.00 for a 40 hour week. As his skill improves, he might get up to 15 or 20 cents an hour. That's $8.00 a week. In fact, one of the problems we've had in India has been to convince the glassworkers to sit at a bench where they can work more efficiently. They prefer to squat on the floor. Just try to get enough leverage to grind joints accurately in that position. Facetiously, you know, working in that position—with burners and grinding equipment—may account for the high percentages of male sopranos in India.

A typical skilled Japanese glassblower works in a wood-frame, paper-covered structure that would give a fire inspector fits. He makes about 50,000 Yen a month. That's about $138.

Japan, incidentally, is fairly well advanced—as far as lampworking skills go. However, they have no continuous melting units for scientific glass—everything is done in day tanks, or pot melting units.

Even in Europe, where production methods and skills more closely match those we know, wages are relatively low.

A skilled English glassblower earns about $35-$50 a week. The same is generally true in Germany and France.

Now, what about the availability of glassblowing supplies? Compared to glassblowers in foreign countries, your situation is a veritable Utopia. Here you order from distributors who generally carry a good stock of tubing, ground joints, and other lampshop supplies. And with our nationwide communications system, telephone lines—computer ordering, you can usually get what you want within a few days.

But, in other countries—particularly France and Germany—deliveries might take two to three months. England is somewhat better. And, because of the large number of melters and distributors in Japan, deliveries are usually made within a few days.

But, in Japan, even though delivery is not bad, glassblowers face another problem—the lack of uniformity of glass components.

Japan, for example, has 56 different glass melters supplying glasses with expansions which range from 36 to 70 and they are all sold as like items. As you can appreciate, such assortment of glass components can be very interesting to work with.

By comparison, here at home, the basic composition of Pyrex brand glassware has not changed significantly in more than 50 years. However, Corning has tightened specifications on tubing—such as, out-of-round, knots, stones and cord. They've improved glass distribution in flasks and beakers. They've set new standards in grinding joints and stopcocks. All these changes to give you a better product to work with.

To summarize the outlook for glassblowing in the underdeveloped nations: Except for India, the major needs for glass apparatus will continue to be supplied from external sources. They have, and will continue to have, a need for skilled glassblowers.

On a recent trip to India, I met an old friend—a man many of you know—Larry Ryan—of Ryan Velutto & Anderson, here in Boston. Larry is training glassblowers at the India Institute of Technology in Kanpur.

In case any of you are interested, The American University in Beirut, Lebanon, is looking for a retired (or soon-to-retire) glassblower who would like to spend a year or two in Beirut training one or two novice glassblowers for the University. They will pay about $7,000 a year, plus transportation over and back. Housing would be available in a University apartment. This is a nice opportunity for some for a year or two overseas—and Beirut is only a couple of hours, by air, from Athens and other scenic areas—and the outlook for revolutions, at the moment, is slight.

Have you ever wondered about how much we might expect the more advanced nations, such as the Europeans, to export apparatus into our domestic market?

Generally, the Europeans are pretty well committed to keeping up with their own rapid scientific growth and filling the demand at home. There seems to be little excess productive capacity in the manufacture of complex apparatus. Of course, they do have capacity to export blown beakers and flasks because they have essentially the same equipment as we. But, the costs of shipping, plus import duties, make it economically unfeasible. So, I don't think we'll have wholesale importation of scientific glassware right away, or at least not until the General Agreement on Tariffs and Trade is ratified.

And, similarly, there is a pressing demand for scientific equipment in the less advanced areas. Although standards are not as high as we require in this country, and although labor costs may be low, the total cost of some finished products can be higher than a comparable item here in the U.S. due to the high cost of raw materials. Raw materials for glass in India, for example, are about five times more expensive than in the United States.

Consequently, I think it is obvious that job security for glassblowers in the States is excellent, as far as the present and short-range outlook is concerned.

But, what of the future? What will you be required to do to keep up with changing technologies? Changing market demands over the long haul?

Today we see increased emphasis on speed and efficiency in lab and research operations—as is generally true of our modern society. There is a great pressure toward automating and simplifying lab operations, and this has brought about a rapid development and growth of instrumentation.

While standard lines of glass apparatus are not growing as fast as instrumentation, they are keeping pace with the growth in scientific education. There always will be a need for standard glassware in teaching because a scientist must still have a solid foundation in fundamentals. In other words, a chemist cannot very well work in advanced fields unless he understands thoroughly what the basics are all about.

Demand for intricate pieces of apparatus that are your specialty is growing at a very fast rate. Researchers depend on you to couple their ideas with your practical experience and create new apparatus. How many way-out types of apparatus (such as complex distillation equipment—heart-lung machines—or high vacuum pumps) could have been made without your skills? You know better than anyone else.

And the scientific community as a whole is continuing to grow. Authoritative sources place the rate of growth at eight percent a year. This is even higher than the growth rate of our booming national economy, which is about six percent.

The need for skilled glassblowers, of course, will grow also, to keep pace with the increasing demand for prototypes and specialized equipment.

Your skills are going to continue to become more and more complicated—just as they have in the past ten years. Just think for a moment —how far you've come in the last ten years. For example, I have here a program from the First ASGS Symposium, held June 8, 1956 in the Corning Glass Center, Corning, New York. Let me read the titles of a few papers given at that first meeting—just ten short years ago:

"Annealing and Strain Measurements in Glass"

"Glass Strength"

and here's a complicated one:

"Glass to Metal Seals"

And I might just note that the Welcome Address was given by yours truly.

Now, for comparison, consider some of the papers you are hearing at this meeting:

"The Glassblower and Optical Pumping of Lasers"

or

"Design Considerations for High Temperature Vacuum Systems Used in Gas Analysis"

and

"Accuracy in the Manufacturing of Image Tubes".

It seems readily apparent that the future for the American Scientific Glassblowers is indeed assured. The more skilled you become, the more the researcher will depend on you to make ever more intricate apparatus—probably for applications that today are not even imagined.

And from everything I've seen, you, in this country, are in the best position to take advantage of these opportunities and to keep up with the demands of the future.

Just by membership in the ASGS you have the tremendous advantage of sessions like this where you can meet periodically to exchange ideas, hear speakers discuss the latest scientific techniques and trends, and, generally, keep up with rapidly changing developments in the world of scientific glassblowing. In the same vein, your Journal provides an extremely informative tool in keeping you up-to-date, both in technology and in indicating the new areas where your skills will be called upon in the future.

In summary, let me just say—

That you men, sitting in this room, have glassblowing skills unequalled in the world.

You have professional recognition and the respect of the scientists with whom you work.

You're well paid. Have good working conditions.

But, most importantly, you have the right attitude—the eagerness and willingness to learn more that will let you take advantage of future opportunities.

It's a sincere privilege for me to be an Associate Member of ASGS—and I want to thank you for the opportunity of having talked with you today.

Thank you.

THERMAL ENERGY COATINGS FOR GLASS REFRACTORIES

Ace Glass Incorporated
Vineland, N. J.
Charles M. DeWoody

A thermal energy coating is one which emits infra-red energy when activated by a different kind of energy such as visible light, electricity, or magnetic field.

In the case of electricity, electrons migrating through the atomic maze of a conductor or semi-conducter encounter some opposition to movement, which results in the production of electro-magnetic waves of various frequencies. So long as the movement of electrons is via the outer atomic shell, or valence shell of the atoms, the frequencies generated will have wave lengths which lie in the invisible infra-red or heat wave, region of the spectrum. When the electron pressure becomes great enough to create a disturbance within the second atomic shell or orbit, visible is also created.

When magnetic field coupling is used, the so called free electrons present in the conductor are coerced into movement to convert the applied energy. Instead of having an unlimited number of electrons available to flow as in direct coupling, the captive electrons must be made to flow faster to produce the same amount of infra-red energy or even visible light. Now while this is inefficient, one of the very interesting things is that resonance can be produced with appropriate circuitry, as well as infra-red emission.

We have an intriguing picture when we consider some of the possibilities which could result from various combinations of energy sources and energy conversion films applied to glassware; however, the possibilities are not all practical, at least in the present economy.

For instance one could visualize a photo-electric or photo conductive film over a resistive film, and a light filter such as a dichroic film over the photo-electric film. The dichroic film selected will transmit only blue light and the amount of heat generated will not be proportional to the amount of blue light striking the film.

What can we do with such a system?

For one thing a heat sensitive plastic film or photographic film could be placed under the thermal film side and a quantitative record could be obtained of the amount of blue light, only, falling on the opposite side in a given time. On overcast days the amount of blue light reaching the earth is diminished, so another method is available for counting the number of clear days, partially clear days, and totally overcast days.

Plants grow best in bluish light so this composite film could be used to provide heat to the plant in proportion to the amount of bluish light supplied, and simultaneously to provide a record.

Here we have a basic product without a demonstrated need, hardly one on which capital would be expanded for extensive development.

There *are* practical uses to which thermal energy coatings have been applied.

In the flat glass field there are windshields, windows, and observation ports coated with electrically conductive tin oxide. This coating which is transparent, is commonly known as NESA coating or E.C. coating, and is a product with some interesting properties.

When electricity is passed thru it, heat waves are emitted predominantly in one direction normal to the major plane; and without electricity passing thru it, heat waves are reflected from it in the opposite direction normal to the plane. Some variation is experienced with varying film thickness and composition.

These windows, etc. can be used to prevent frosting or condensation, and being conductive, can also be used as a shield against static electricity or radio frequency noise. The infra-red reflection is put to use in steel mills to protect rolling mill operators and others from intense heat. Glass workers also find it useful as a face shield.

Such coatings can be applied by spraying solutions of tin salts on the hot ceramic surface which has been preheated to a temperature of 900°F. or more, usually up to 1250°F., which converts the salt to the oxide. Silver epoxy cements can be used for terminals. Many other metallic salts may be substituted for tin. Cadmium, indium, lead, magnesium, molybdenum and strontium may all be used to vary film attributes, notably electrical and chemical resistance, and hardness.

Electronic resistors so made are highly stable, practically noise free, and useful at high frequencies where other resistors are troublesome.

Desired patterns can be produced by several methods:

1. Airbrasive cutting. 2. Masking with bentonite clay mixtures before spraying and subsequently washing off the mask and 3. Chemical or electrochemical etching.

The choice of film type depends on intended use. When power needs go beyond 5 watts per sq. in. the metallic films are more suitable, providing transparency can be sacrificed. Metallic coatings also can be made more inductive and are more reflective. Metallic coatings can be employed advantageously as anodes in electron tubes with increased output and in special configurations such as electron guns and Geiger tubes.

Metallic films can be applied by sputtering and build-up by electrodeposition on the sputtered area, by decomposition of organo-metallic compounds and the application of metallic glazes, all of which are fired at one or more stages, or the coatings can be applied without firing to give a less stable system. The latter are commonly used on printed circuits and often consist of conductive material such as carbon or silver in an epoxy vehicle.

A composite coating of energized transparent oxide, a fluorescent sandwich and an energized metallic reflector is employed with A.C. current to create electro-luminescent signs and low current drain night lights. Here, as has been indicated, the metallic coating acts as a mirror or reflector, and one plate of a capacitor.

The use of films are legion, limited only by the fertility of one's imagination and background. Integrated circuits, field effect transistors and even lasers are within the realm of this science.

In the laboratory apparatus category thermal energy films applied to glass, quartz and porcelain provide high efficiency heating. Warm up times can be reduced to about 1/3 of mantle heating time and 1/2 of hot plate heating time. The films can be applied to just about any configuration and afford a time saving convenience.

First, there is no elusive mantle of the right size; *second,* the film is wholly in direct contact with the surface to be heated which provides multiple benefits:

(A) Heat can be directed precisely where it is required.

(B) Hot spot super-heating is eliminated; thermal decomposition is greatly reduced as well as side reactions.

(C) Efficiency is increased about 50%. This is a significant gain. It means that more work can be obtained from the present wiring system and at a 1/3 reduction in power cost, without including the reduced load on air conditioning systems. This may seem like a small item but consider what would happen with 1000 units saving 100 watts each.

(D) The system reacts almost instantly to changes in power input, so equilibrium is attained in a much shorter time. This is particularly useful in distillation work. The fact that there is no heat lag, discourages runaway reactions, but if such should happen, the whole unit can be plunged in a cooling bath, or cold water can be poured over the unit and heat reapplied when necessary. In one unusual application a vessel is first heated to 100°C. and then purposely dunked into liquid nitrogen.

Third the manipulation of hot vessels is no longer a chore. If you have ever wrapped a towel around a hot beaker or had a vessel slip out of the tongs, or have unzipped a hot mantle, you will immediately appreciate the presence of a clamp which supports and holds the vessel while it provides a handle, and also serves as an electrical connector.

Fourth it is advantageous to design the circuits for low voltage. Most equipment can be kept as safe as toy electric trains, but particular attention should be given to the controlled circuit. Auto-transformers are frequently used for voltage control and these can be dangerous if the thru-leg is connected to the hot lines of the mains. The sketch below (Fig. 1) shows the circuit from the pole transformer to the load of the auto-transformer.

When connected as shown the thru-leg "A" is always at a 120v potential to ground, no matter where the variable tap "B" is set. Even with "B" set at zero a person touching "A" and a water pipe or other ground would receive a 120v shock. If the thru-leg "A" is reversed at the mains (M) the transformer is safe from this hazard. A modified transformer which warns when danger exists, is available from Ace Glass Inc.

The auto-transformer has but a single winding; a double wound transformer isolates the load from the mains no matter which way it is connected. The maximum voltage can be fixed also, and kept at a relatively safe value.

Thermal energy films of the low voltage type are generally very sensitive to power changes. As the film heats its resistance changes and so

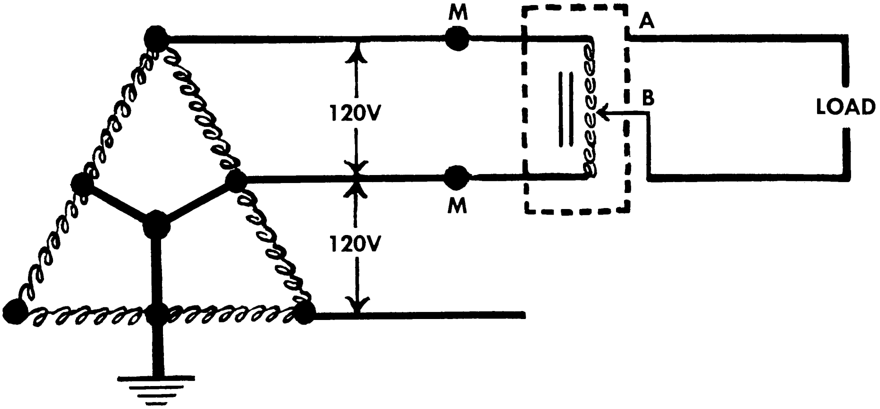

Figure I

does the current flowing through it, while the voltage across it remains practically constant, and it is obvious that an ammeter becomes valuable in maintaining constant power.

As you may know Ace Glass Inc. has pioneered the development of laboratory apparatus incorporating such films.

ADVANCES IN SOLDER GLASS TECHNOLOGY

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PART I.—CRYSTAL STUDIES (K. G. Lusher)

Devitrifying type solder glasses are characterized by their crystalline structure as opposed to the vitreous types which are amorphous or noncrystalline. Both types behave similarly during the early stage of heating, transforming from a powder to a glassy molten condition. At this point the behavior pattern begins to differ. Devitrifying types have, or develop, many small nucleii scattered throughout their mass, causing crystals to form and grow as heating continues. Time and temperature both play an important part in this crystal growth; specific time-temperature relationships exist for each solder glass. These are reflected in the recommended curing cycles.

The Differential Thermal Analysis, or DTA, Technique is an important tool in studying the crystal activity within a material during a heat cycle (Fig. 1). The Differential Thermal Analyzer detects small endothermic and exothermic reactions within a sample by measuring its temperature at a given instant and comparing it with the temperature of an inactive

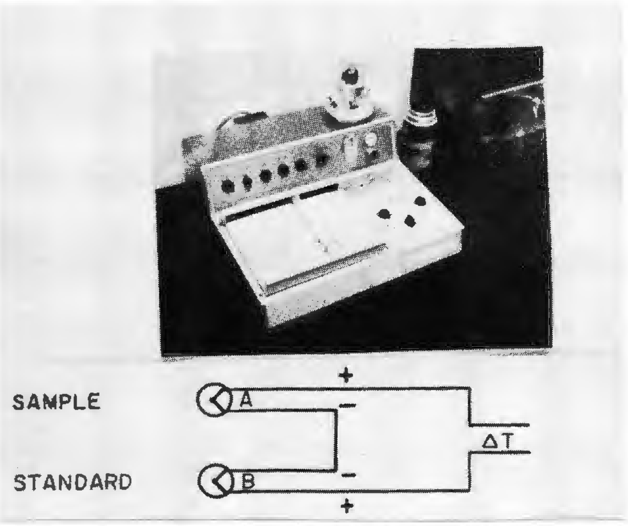

Figure 1

Differential thermal analyzer

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*Presented by W. E. Smith.

standard under identical conditions. Identical opposing thermocouples are placed in the sample and inactive standard; their "differential" is measured with a millivoltmeter. An exothermic reaction is indicated when the temperature of the sample is higher than the standard; current will flow in one direction. An endothermic reaction is indicated when the temperature is lower, and the voltmeter will deflect in the opposite direction. By plotting these reactions on a chart against temperature or time, a curve is produced which can be interpreted in terms of crystal activity. When materials melt, heat is absorbed and the reaction is endothermic. During periods of crystal formation and growth, heat is given off and the reaction is exothermic. The standard is always an inactive material which will neither melt nor crystallize, but remain at the ambient temperature.

Although DTA can determine the points of transformation and crystalline activities, it cannot provide data on the number, size or growth rates of the crystals. For this information the hot stage microscope is used. (Fig. 2) The equipment consists of a small controllable furnace mounted

Figure 2

Hot stage microscope

so that changes in the state of the material being fired can be viewed through a microscope. By incorporating a camera on the microscope, pictures can be taken periodically or continuously during the cycle.

The DTA and hot stage microscope studies were made on a typical glass-sealing solder glass. Other devitrifying solder glasses exhibit similar, although not identical, behavior to this one. (Fig. 3) To demonstrate the importance of temperature on crystal formation, a series of DTA tests were made at selected temperatures below, at, and above the recommended sealing temperature. Heating rates in these tests were 8° Centi-

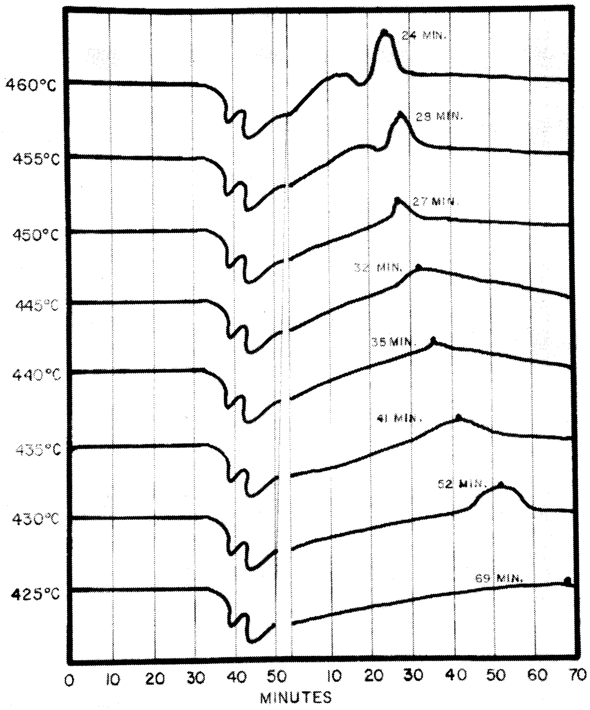

Figure 3

DTA Curves: For various firing cycles
(Typical devit. solder glass)

grade per minute, with hold times at these selected temperatures maintained until all crystal activity apparently had ceased. Results showed crystals forming and growing faster at the higher temperatures than at the lower temperatures. At 425°C., 69 minutes were required to reach maximum crystal activity. At 440°C. this time was reduced to 35 minutes, and at 445°C., to 28 minutes.

These DTA results agreed well with corresponding hot stage microscope studies. (Fig. 4) At 375°C. some coalescence can be observed, indicating melting is occurring. This is reflected in the endothermic slope of the DTA curve. (Fig. 5) At about 425°C. some nucleii and growth of very small crystals can be detected, and there is a corresponding exothermic slope of the DTA curve at this temperature. At the start of the holding cycle at 440°C., many small crystals in early growth stages are observable. As this isothermic cycle continues, crystal growth continues, reaching a maximum in activity after about 32 minutes. After about 50 minutes at 440°C., crystallization has essentially been completed, with minimal or no activity thereafter.

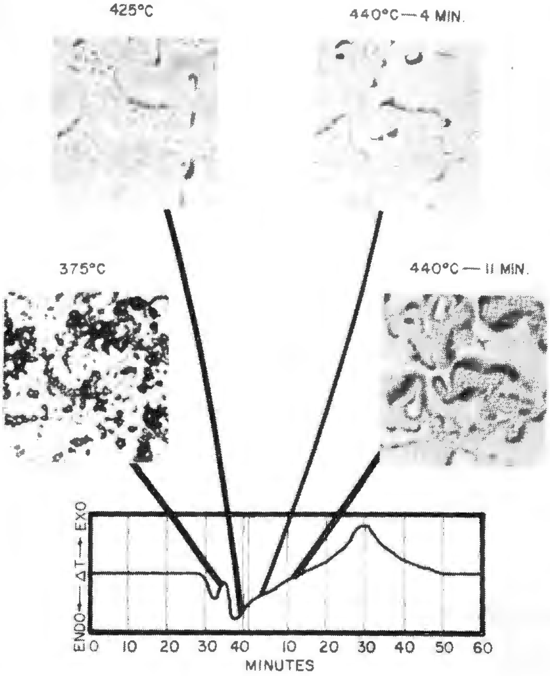

Figure 4

Hot stage microscope studies (I.)

The DTA curves for other Owens-Illinois solder glasses are similar. The CV-97 solder glass shows crystallization peaks after 12 minutes and 44 minutes at 450°C. The CV-101 peaks after 11 minutes and 25.5 minutes at 425°C. The CV-137 solder glass has crystallization peaks after 13 minutes and 29 minutes at 425°C. Examination of the crystal structures within all these solder glasses has shown several types of crystals present. Each type forms and grows at different points during the heat cycle, and probably contributes to the two peaks shown in each DTA curve. Crystallization is considered essentially completed after the DTA curve returns to the base line late in the isothermal cycle. Even at this point a small amount of vitreous matrix remains surrounding the crystals.

Properly crystallized solder glasses have certain advantages over the vitreous types and partially crystallized types. The crystals contribute to the overall strength of the product, acting as reinforcing to produce a stronger product. Another factor to be considered is thermal expansion. Normally the glassy phase of these solder glasses has a higher expansion than the devitrified phase. To obtain the proper thermal expansion, a high degree of crystallization is required. Consideration should be given to the heat stability of the cured product, particularly if further heat cycling

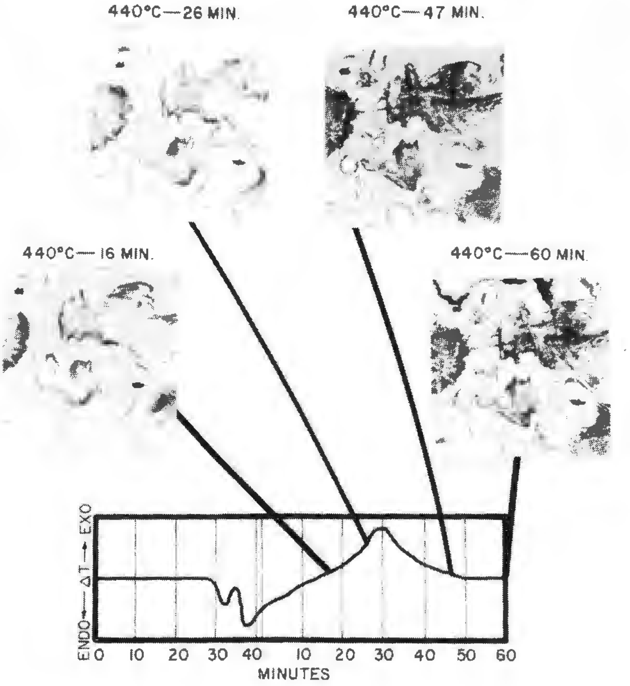

Figure 5

Hot stage microscope studies (2.)

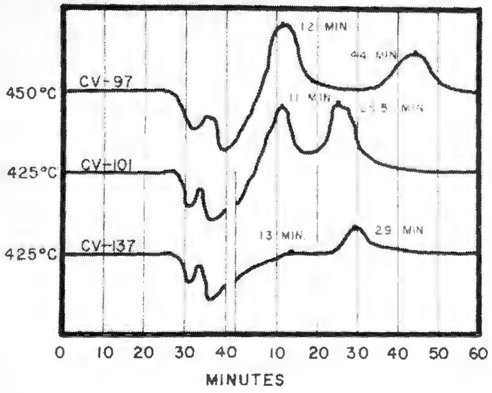

Figure 6

DTA Curves: CV-97, CV-101, CV-137
Solder glasses

is anticipated. Partially crystallized glasses continue to change during further heat cycles, causing property changes and other effects which could be undesirable.

These DTA and hot stage microscope studies were conducted to explore and further understand the crystallization processes in solder glasses. They have been extremely helpful in showing the relationship between time and temperature during the curing cycle, and have reflected the importance of a complete cure. As this technology advances, other new tools and instrumental techniques will be employed which will make our studies of crystallization processes even more complete.

PART II.—LOW EXPANSION GLASSES FOR SEALING TO FUSED SILICA (W. E. Smith)

About a year and a half ago, Dr. Trygve Baak and others working in the Fundamental Research Section of Owens-Illinois made a scientific breakthrough in the field of Glass Technology. This breakthrough involved the discovery of a family of glass compositions which maintain the structural integrity of fused silica, hence we have virtually zero thermal expansion, but which can be melted at temperatures several hundred degrees lower than can pure silica.

Research on these glasses has continued since that time in order to characterize them more fully and determine areas of potential maximum utility.

The combination of low melting temperatures and low thermal expansion along with their ability to wet fused silica has led to their application as solder glasses for fused silica. It is believed that these materials offer possibilities for fabrication of objects heretofore impossible or made only with greatest difficulty. It is hoped that these comments will stimulate new ideas and questions on your part, since you are most familiar with the needs in this area.

Most conventional solder glasses are based on the properties of lead oxide. These new glasses are based primarily on the properties of oxides of copper. Actually, the compositions and physical properties can be varied over a wide range without affecting the thermal expansion appreciably. Properties which are affected, however, are glass melting temperature and viscosity. Table I refers to two representative glasses and their

TABLE I

PHYSICAL PROPERTIES COPPER GLASS

	Fused Silica	*RZ-1*	*RZ-2*
Melting Temperature	>1800°C.	1625°C.	1575°C.
Softening Temperature	1665°C.	800°C.	750°C.
Annealing Point	1140°C.	640°C.	570°C.
Strain Point	1070°C.	590°C.	520°C.
Thermal Expansion 0-38°C.	3.5-5.0 x 10^{-7}	...	1.0 x 10^{-7}
Thermal Expansion 0-300°C.	5.5 x 10^{-7}	5.0 x 10^{-7}	5.0 x 10^{-7}

respective properties compared to fused silica. It can be seen that in the case of RZ-2, the annealing temperature is about half that of fused silica, while the thermal expansion remains nearly identical.

The maximum use temperature for objects in which these glasses are incorporated is limited by the transformation range of the solder glass. In other words, RZ-2 with an annealing temperature of about 575°C. could not be used at temperatures much above that. Actual tests have shown that seals made with this glass begin to deform under load at about 750°C. (Table II) Under high vacuum conditions, outgassing with evolution of oxygen will occur at this same temperature. With prolonged holding at this temperature, devitrification will occur with seal failure caused by a difference in thermal expansion between the solder glass matrix and the crystalline products. RZ-1, with annealing point 70°C. higher than RZ-2, is useful at temperatures about 70° higher. Consequently, it requires higher processing temperatures and initial melting temperatures. Further steps in these directions are possible.

TABLE II

MAXIMUM USE CONDITION:

	Fused Silica	*RZ-1*	*RZ-2*
Maximum Use Temperature— Self-loaded Deformation (log 11.6) . .	1310°C.	800°C.	750°C.
Devitrification Begins at	1100°C.	800°C.	750°C.
Outgassing	Permeable He & H_2	800°C.	750°C.

With the discovery that glasses of moderate fusion characteristics and low thermal expansion can be made using copper oxides, we have produced *altered* properties by crossing these series with more conventional recognized glass series. By this procedure, graded seals between fused silica and higher expansion materials can be made.

So far we have described the properties of these sealing glasses without discussing the act of sealing itself. The seals are not easy to make. They require particular attention to detail and technique, because of their complex reactions with ambient surroundings. Most of the problems are caused by the fact that the element copper can exist in three different oxidation states and at high temperatures can change from one state to another with comparative ease. The copper in the glass is predominantly cuprous or in the monovalent state.

The effects of oxidizing or reducing atmosphere upon these glasses produces the expected property changes—an alteration of surface properties, melting characteristics, sealability, etc. There are, of course, desirable sealing techniques which we will now discuss.

In furnace sealing where powdered copper glass with very large surface area is used, the seals must be made in a neutral atmosphere such as helium, argon or nitrogen, with nitrogen preferred for simple economic reasons. Care must be used also in selecting a binder which volatilizes completely without charring to a carbonaceous residue. At high temperatures such a residue would serve as a reducing agent for copper oxide in the glass surface layers. Water alone can be used as a binder, but a mixture of amyl acetate and nitro-cellulose serves better.

In flame or torch sealing, care must be used to keep the fire oxidizing to avoid formation of free copper on the surface. The combination of heat input and comparatively small exposed surface area minimizes the amount of copper oxidized to the cupric state under these conditions.

Seals can be made rapidly and efficiently using these techniques. Because of the low thermal expansion, little stress is present in the seals even in the unannealed state, permitting fabrication of small parts without annealing. Large pieces should be annealed, however, as seal stresses as high as 2000 psi may develop. Hermetic seals can be made, but great care must be used in making them, particularly in preparing the fused silica surface and in laying on the solder glass bead.

In summary, then, these new solder glasses offer the possibility of sealing fused silica parts together at temperatures which assure that even the finest optical members will not warp. Low stress hermetic seals can be made which are useful at least to the annealing temperature of the solder glass.

Demonstrations of flame sealing and furnace sealing with an RF generator as heat source will be carried out during the work shop sessions.

NEW DEVELOPMENTS IN GLASS TECHNOLOGY

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The highly technological age that we live in continually presents any material manufacturer with challenges and opportunities to exercise his ingenuity. In the case of glass, some of the new types being developed possess capabilities that were formerly not believed possible. As our knowledge of the fundamental nature of glass improves, we are able to manipulate its properties in new and different ways.

Photosensitive glass is a good example of an unusual material. Possibly it should not be listed as a new development since it is nearly 20 years old. However, continual development work since the glass was first produced has improved it to the point where it is uniquely suited to two products that are new within the past few years—fluid amplifiers and masters for flexographic printing plates.

When this glass is exposed to ultraviolet then heat treated, it turns from transparent to opal. Put a negative in front of the glass during exposure and the pattern of the negative is reproduced in the glass. Detail as fine as 350 lines per inch may be reproduced in this glass. Images produced in this manner are permanent. (Fig. 1)

This can be the end product if you want an opal pattern in clear glass. Or it can be the beginning if you want to take advantage of another property of this glass. The exposed areas will dissolve in hydrofluoric acid approximately 15 times as rapidly as the unexposed areas. This allows the exposed areas to be etched away either completely to form holes, or partially to form passages. Dimensions of these holes and passages can be controlled as closely as 0.001 inch.

Another heat treatment will convert the glass to a crystalline ceramic material trademarked Fotoceram. The process here is similar to the conversion process used to produce Pyroceram brand materials. In fact, Fotoceram was the original glass-ceramic material. After conversion the crystalline material is approximately four times as strong as when it was a glass. There is 1 - 2% shrinkage during conversion that must be taken into account when designing the original piece. This shrinkage is predictable and finished parts can be held to close tolerances as long as the original part is properly designed.

Flexographic printing plates made from photosensitive glass produce sharp impressions and permit reproduction of fine detail. These plates are made by pressing raw rubber against the glass master and vulcanizing the rubber while it is held against the master. These plates are used to print on soft materials such as plastic bags.

Fluid amplifiers, or fluidic elements as they are also called, represent a promising new field of activity. Fluidic circuits perform many functions that are performed by electronic or electro-mechanical circuits. They do

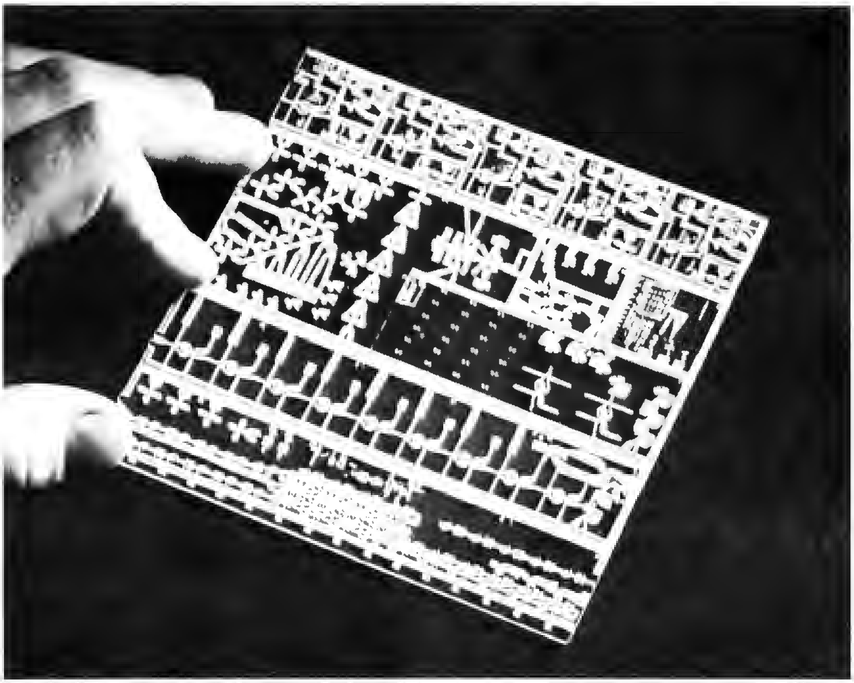

Figure 1

To produce the patterns in this sheet of photosensitive glass, the patterns were first produced in a photographic negative. Then the glass was exposed through this negative, using an ultraviolet lamp. Heat treatment developed the image. The white areas received exposure; the clear areas were protected from exposure by the negative.

so by controlling and directing the flow of air through precisely formed passages of rather involved shapes. Photosensitive glass permits forming these passages quickly and economically. To machine them or form them by other means would be considerably more difficult. (Fig. 2)

Fluid amplifiers are coming into use to control machine tools, operate production equipment such as glass presses, control production processes. These fluidic circuits can operate under conditions of heat, vibration, and radiation that would damage electronic circuits. Since there are no moving parts in a fluid circuit, maintenance is almost non-existent.

Photochromic glass also responds to light but in a different manner. To produce an image in photosensitive glass, both exposure and development are required and the resulting image is permanent. Only exposure to long ultraviolet is required to produce an image in photochromic glass, but the image is not permanent; it will fade on exposure to either visible light or infrared (heat). Eye glasses made of photochromic glass will darken in the sunlight and fade a few minutes after the sunlight is removed. (Fig. 3)

Photochromic glass darkens to various degrees, depending on the composition. A particular composition will darken to a certain level and

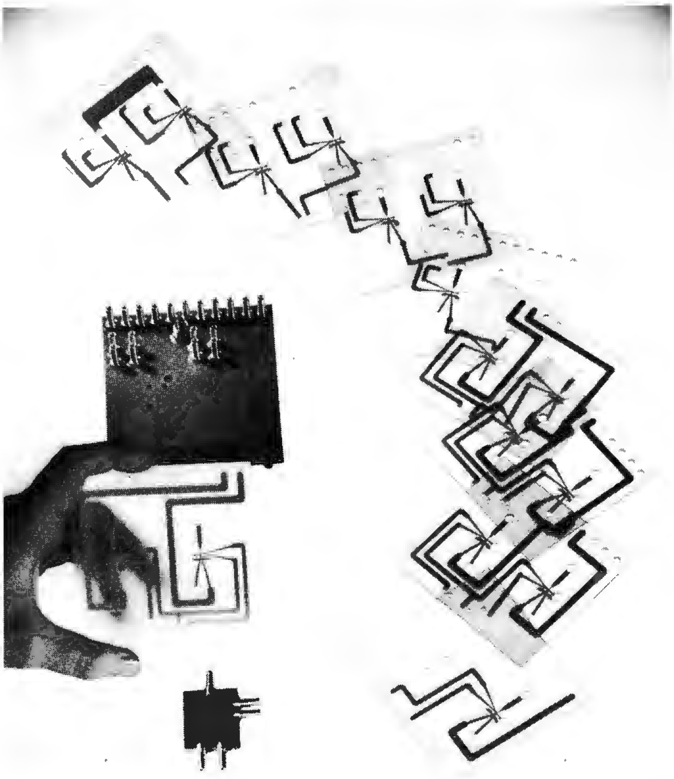

Figure 2

Fluid binary-to-decimal converter (dark device above hand) uses 17 NOR gates in 11 layers of circuits etched in photosensitive glass. Fluid channels in layers (top and bottom layer not shown) were hermetically enclosed and glass converted to stronger, higher temperature glass-ceramic by heat.

remain there as long as exposure to ultraviolet continues. Some compositions remain dark as long as a week after exposure and will not fade until exposed to light or heat. Others will begin to fade immediately when the ultraviolet is removed. Generally speaking, the darker the saturation level, the slower the rate of darkening and fading.

Glass has the unusual mechanical property of always breaking from a tensile stress, never from compression. Because of this behavior, glass can be strengthened by prestressing. When all surfaces are put in compression, any applied load must first overcome this built-in compression before the surface can be put in tension—the type of stress necessary to cause breakage. (Fig. 4)

Prestressing is most often done by tempering. In this process the glass is heated to just below its softening point, then quenched with either a blast of cold air or in a molten salt bath. However, other methods of prestressing have been developed recently that produce even greater

Figure 3

New ophthalmic glass made by Corning Glass Works for prescription eyeglasses darkens on exposure to sunlight and then becomes clear again indoors or after sundown.

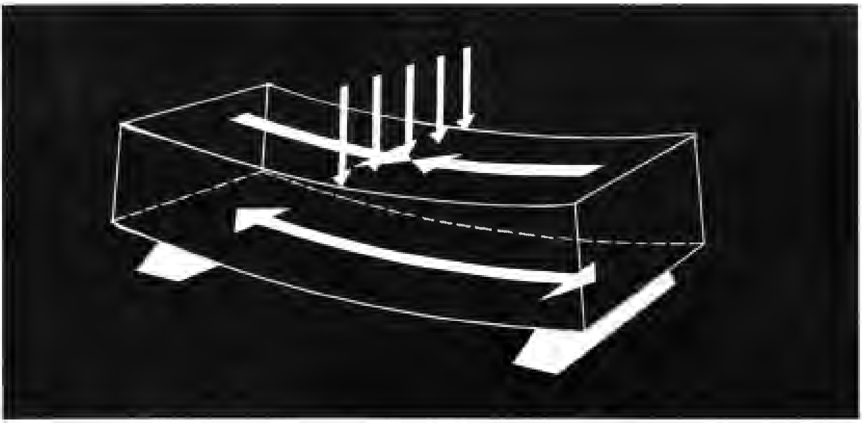

Figure 4a

Typical sample used for measuring strength of glass. The bending load applied to the middle of the bar produces tension in the lower surface and compression in the upper surface. If the load is high enough, the bar will break. When it does the break will start in the lower surface because glass always breaks from tension, never compression.

strengthening than is possible with tempering. These methods involve a chemical treatment of the surface. Tempering can produce strengths up to four times annealed; chemical strengthening is currently producing strengths of 10 times annealed with still greater values possible.

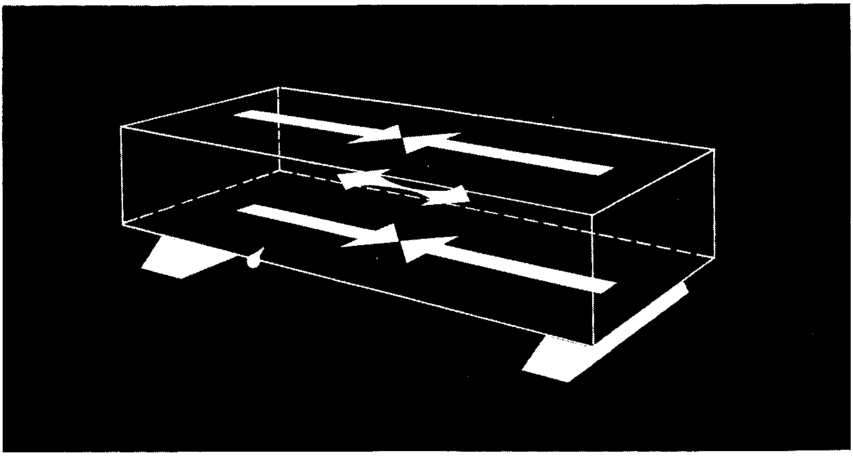

Figure 4b

Pre-stressed bar has compression in all surfaces. The reactive tension, which is equal to the amount of compression, is buried within the bar. Pre-stressing may be done by tempering or by chemical treatment.

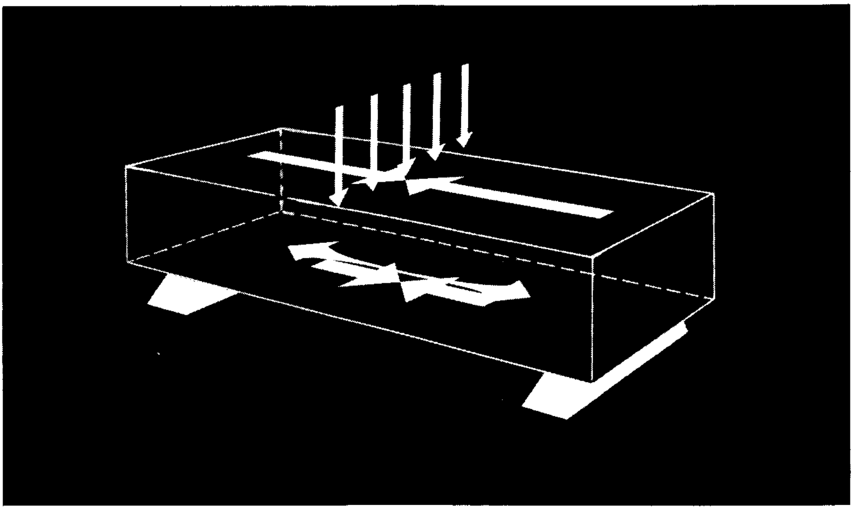

Figure 4c

A bending load applied to a pre-stressed bar must first overcome the built-in compression before the surface can be put in tension. Thus the pre-stressed bar is stronger by the amount of compression built into the surface.

One chemical strengthening method consists of immersing the formed glass article in a molten salt bath and allowing an exchange of ions to take place. In a typical exchange, potassium ions from the salt bath will be forced into the glass surface where they replace the sodium ions. (Fig. 5)

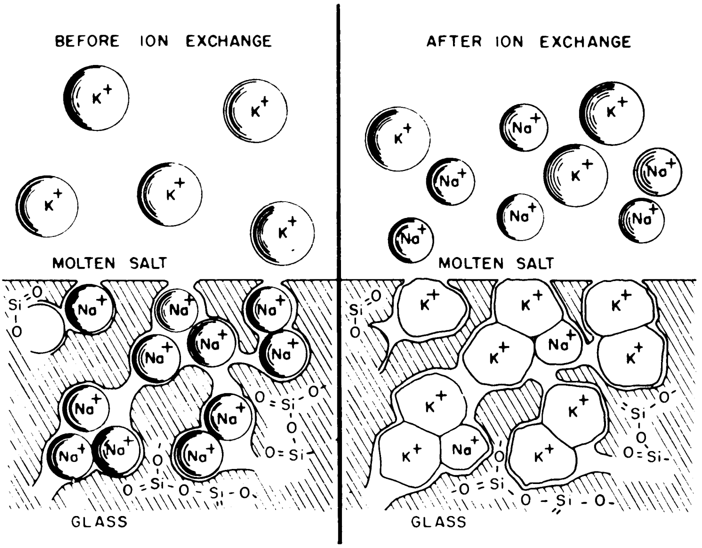

Figure 5
Crowding from low-temperature exchange of K^+ for Na^+.

Since the potassium ions are larger than the sodium ions, the surface is crowded or compressed after exchange is completed. Surface compression can be as high as 100,000 psi; tempering under the best possible conditions can produce 40,000 psi. Tempered glass is the same composition throughout as it was before tempering. However, chemically strengthened glass is a sandwich with the surfaces a different composition from the interior.

Prestressed glass, whether tempered or chemically strengthened, cannot be cut, ground, or drilled after prestressing. Once the tool penetrates the compressed surface, the balance between the surface compression and interior tension will be upset and the glass breaks. When the stress is sufficiently high, the glass breaks into many small pieces suddenly. The limit of stress required for this type of break is called the dicing limit. The resulting pieces do not have sharp edges and can be safely handled. (Fig. 6A & B)

Tempering can be applied to soda-lime, borosilicate, and aluminosilicate glasses. The most favorable composition for chemical strengthening is soda-aluminosilicate. Tempering is limited to thicknesses above 0.100 inch and relatively simple shapes; chemical strengthening can be used down to thinner cross sections and complex shapes. Tempered aluminosilicate can be used at temperatures up to 450°C.; chemically strengthened glass is limited to 200°C. - 300°C., depending on composition.

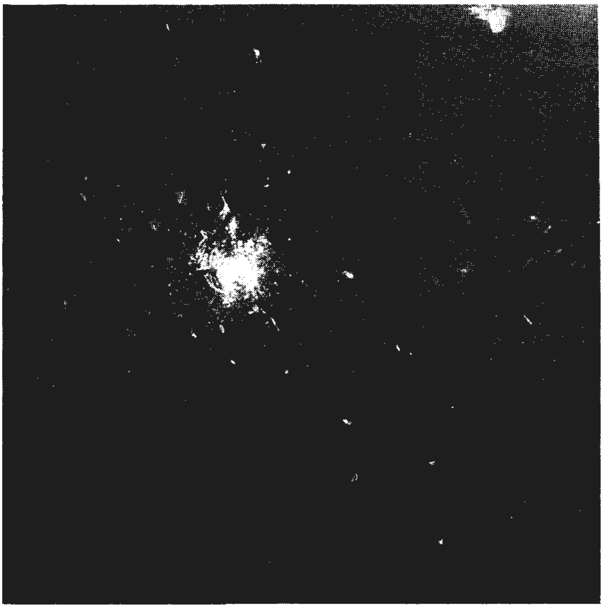

Figure 6a
Typical break pattern in annealed sheet glass.

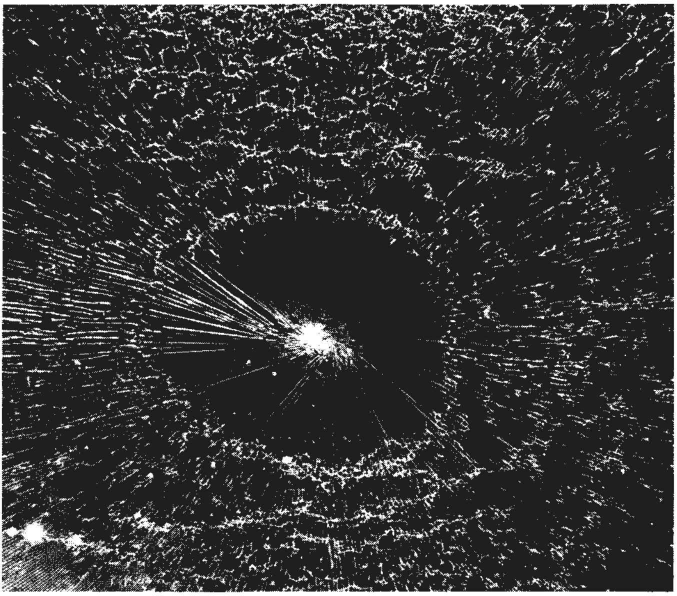

Figure 6b
Typical break pattern in sheet glass pre-stressed above the dicing limit.

New developments are not confined to new compositions or new glass types. Fabrication techniques continue to improve and to widen the variety of sizes and shapes into which glass can be formed. In the field of undersea research we find two interesting examples. A cylindrical shell 16 inches in diameter and 58 inches long was made for sonar research by forming short, ribbed sections then sealing them together. Width of the seal face was as large as 1¼ inches. This cylinder was equipped with metal end caps and loaded with instruments. (Fig. 7)

Glass spheres are used in a number of applications under the sea. They may serve as floats to counteract the weight of a cable or to return samples of the ocean bottom to the surface. Sometimes a flashing light is enclosed in a sphere so it can be spotted after it arrives at the surface.

Figure 7

This transparent glass tube, nearly five feet long and 16 inches in diameter, is designed to carry recording instruments 20,000 feet beneath the sea in a U.S. Navy research program. Glass was specified because of its great strength and buoyancy. The capsule has aluminum end plates.

These spheres are made in several sizes. The latest in this family is 44 inches in diameter. Two hemispheres are formed, then sealed together. Each hemisphere weighs approximately 500 pounds. This is the largest lathe sealing job yet, (Fig. 8) but an even larger one is on the way. The next sphere will be 56 inches in diameter. The day of the glass submarine may be closer than you think. Glass spheres are now operating to depths of 20,000 feet.

Figure 8
This 44-inch diameter hemisphere will be used in undersea research. Hemispheres such as this may be sealed to a larger vessel to function as observation domes. Or they may be fusion sealed in pairs to form spheres to carry instruments.

Another submersible, called Benthos, is made from a glass-ceramic; the same material used for nose cones. Benthos is approximately 8 feet long and a foot in diameter and is designed to explore the depths of the ocean below 30,000 feet. Glass-ceramic turns out to be an ideal material for this submersible because of its corrosion resistance; it is not affected by sea water. And its favorable strength-to-weight ratio allows walls to be relatively thin, leaving capacity for the maximum amount of pay load. Pay load in Benthos is all instruments; it is a tight fit for a live crew. (Fig. 9)

All these submersibles benefit from the high strength of glass and glass-ceramic in compression. As long as the shell is designed so that the load from water pressure produces only compression in the glass (or glass-ceramic), the shell can descend to great depths with no fear of breakage. In fact, the compression produced by water pressure makes the shells stronger at operating depths than they are at the surface. This has been confirmed in laboratory tests where spheres were held under high water pressure and impacted with a sharp tool. Resistance to chipping and spalling increased as water pressure increased.

These few examples were chosen to give some idea of the growing world of glass and glass-ceramics and the novel uses to which these materials are being put. Of course still newer developments are in the laboratory stage and when some of these are perfected, they may make those listed in this paper seem unspectacular.

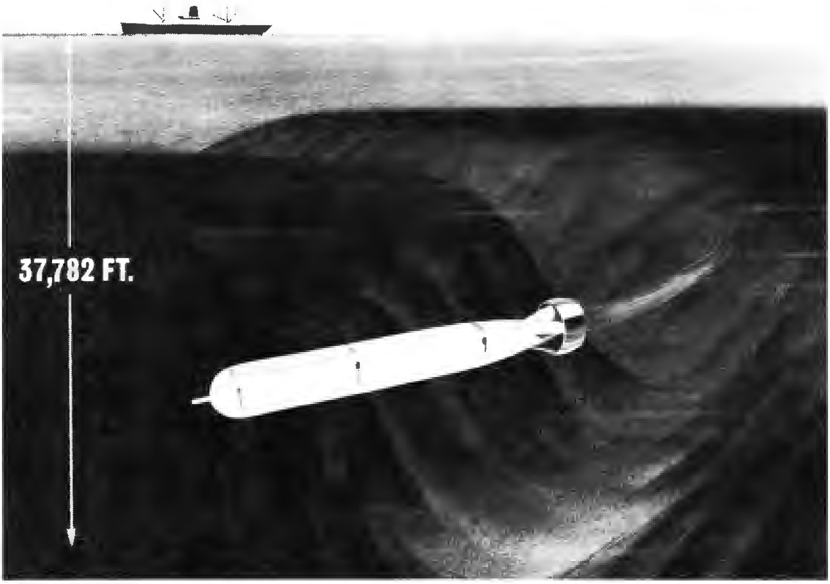

Figure 9
A glass-ceramic submersible 8 feet long and one foot in diameter designed to explore depths of the ocean. Shown here is the Mindanao trench east of the Philippines.

A TECHNIQUE FOR EVALUATING AND CONTROLLING THE SEALING CHARACTERISTICS OF GLASSES

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INTRODUCTION

For almost two decades the Kimble Glass Company* determined and controlled the sealing characteristics of its production glasses by determining the stress in a seal between a known and unknown glass. The technique is simple, fast, and provides seal stress data which are more accurate than estimates made from expansion measurements. This seal method has been used in production, as well as research work, and in recent years has been extended into the field of glass-to-metal seals. It has been termed the "butt-type" seal in contrast to the "bead seal" configuration (ASTM Designation F14).

This report covers the method of making seal measurements. Some of the details of our experience with this procedure are included to give a better understanding of the method. The technique is ideal for rapidly checking the sealing characteristics of glass.

For making such tests, one of the necessities is a supply of known or reference glass, preferably in the form of canes or rods of approximately 1/4 inch diameter. Anyone wishing to use this technique should obtain a uniform supply of 1/4″ canes made all during one production run for a reference glass. In order to avoid conflicting data and to expedite standardization we have found it advisable to assign an identifying serial number to each cane of glass as it is produced. The glass reference selected need not have identical physical properties to the ideal or "target" for a particular glass, if the glass is reasonably uniform as to properties and homogeneity; the reference standard can give results that are comparable to those obtained by using a target glass. Owens-Illinois can make small quantities of reference standard sealing glasses available through the R. D. and E. Laboratories, Consumer and Technical Products Division, Owens-Illinois, Inc.

A step-by-step procedure for making seals and calculating stress has been included in this report so that the details of making glass-to-glass seals may be followed easily. Some duplication between sections of this report was necessary in order to make different sections suitable for separate publication. It is intended that the material in this report be available for use in the standardizing activities of such industry comimttees as ASTM Committee F-1, Subcommittee V on Metallic-to-Nonmetallic Seals, and ASTM Committee C-14 on Glass and Glass Products.

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†Presented by H. E. Powell

*Now the Consumer and Technical Products Division of Owens-Illinois, Inc.

CONSIDERATIONS ARISING IN CONNECTION WITH PRODUCTION OF SEALING GLASS IN A LARGE TANK

When making glass to be used for sealing to other glasses or to metals, the glass maker has a need for very accurate control of properties. If the glass is melted in a large tank, slight but significant changes in thermal expansion and other properties must be detected quickly so that proper adjustment in batch can be made. It is necessary to know the trend of the properties of the glass that is being melted, because in a large glass tank it may take several days for a batch change to become effective. Therefore, knowing the trend of thermal expansion or other properties is extremely important so that the glass composition does not get out of control; this requires measurements of high accuracy. To meet this need in the past, the fused silica dilatometer method[1] has been used for thermal expansion; variations in density have been followed by the fast, accurate "sink-float" method. Periodic chemical analyses were carried out. However, tests for chemical analysis and for thermal properties required many hours to complete in order to provide adequate data for comparison. When results were not always consistent and when data for batch changes were needed within a few hours after the glass was used in the forming operation, the practice was adopted wherein a sample and a reference glass were sealed together and the stress between the two glasses was measured photoelastically. This method for checking two glasses for difference in thermal expansion has been suggested by Wright;[2] A. A. Padmos[3] and others have discussed glass-to-glass and glass-to-metal sealing techniques. The fused silica dilatometer test was used to provide elongation *vs.* temperature data which we have termed *"thermal expansion"* for the temperature range of 0°-300°C. upon heating and *"thermal contraction"* for the range of annealing point to room temperature upon cooling (*i.e.*, A.P. — 25°C.).

When two glasses produced in a tank and undergoing normal production variations are sealed together, the glass with the higher thermal contraction will generally, during cooling, contract more and induce a compressive strain in the lower contraction glass, while at the same time the higher contraction glass will have tensile strain. Photoelastic or polariscopic examination will show, therefore, which glass has the higher thermal contraction and give quantitative measurements. In the following discussion the term *"expansion"* will be used to include both the heating and cooling properties of glass.

In correlating properties by the glass-to-glass seal technique, it was found, rather frequently, that expansion measurements were not as precise as needed. The expansion equipment was improved and considerable care was exercised in its use, but still showed that expansion measurements could not always be correlated with seal stress data. For example, two glasses which had the same linear thermal expansion coefficients (0°-300°C.) as measured with a dilatometer might have a stress of more than 100 p.s.i. when sealed together. It was realized after making check seals that the seals were not necessarily in error; that is, if glass *A* had a tension stress when sealed to glass *B*, then glass *A* must have a higher thermal contraction than glass *B*. The expansion from 0° to 300°C. may remain virtually the same but variation in the annealing point and the contraction from the annealing range can affect the seal stress to a considerable extent. However, in considering sealing characteristics, the information that is of prime importance is the observed stress between two glasses, coupled with knowledge of the thermal conditions following sealing, rather than merely the expansion relationship.

Since it has been possible to measure the stress in a seal to an accuracy of between 20 and 40 p.s.i., the seal method gave an accuracy at least five times better than the expansion equipment. We have found that a seal could be made more quickly, with minimum equipment and by properly trained technicians. In fact, it is comparatively easy for an experienced technician to make a seal and have the results in less than two hours, including the annealing time.

BRIEF DESCRIPTION OF THE SEAL TEST

In Appendix I are listed items of equipment which should be assembled in order to make seals and measure their stress. To make these glass-to-glass seals, one end of each of the ¼ inch glass canes to be sealed is ground flat on a fine grinding wheel (see Appendix II). The ends of the samples are heated in a blast burner or gas-oxygen flame and sealed together. For identification purposes, the known or reference glass is burned or rounded off with a flame while the unknown sample is broken (flat) as shown in Figure I. This seal is then annealed at a temperature of 25° ±5°C. above the annealing point for at least 30 minutes and cooled at not more than about 4° to 5°C. per minute. Samples may be removed from the furnace at any temperature under 300°F. After grinding opposite surfaces flat and parallel (see Figure 1), the retardation in millimicrons of the seal at the interface is measured by use of a polarimeter.[4] The detailed procedure for making these measurements is described in Appendix IV.

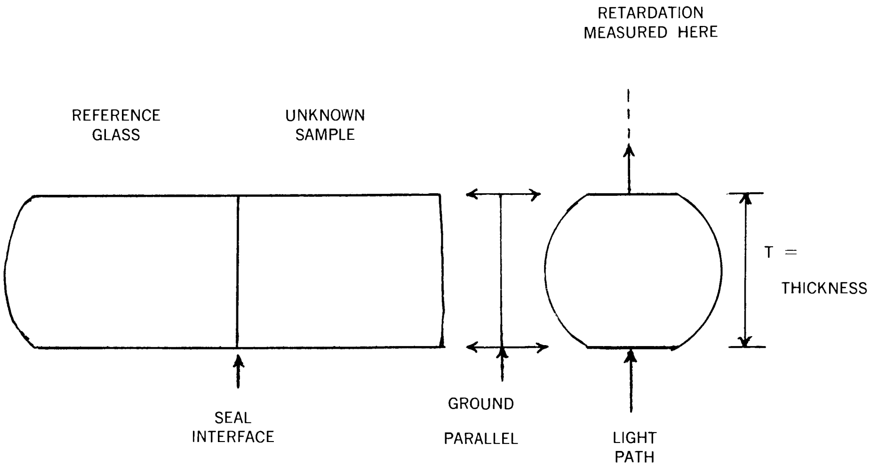


Figure I
Typical seal configuration.

THEORY AND INTERPRETATION OF RESULTS

The stress in a glass seal may be calculated from the retardation and thickness by the following:

$$S = \frac{R}{T \times C}$$

Nomenclature and Units

S = Stress in kg/cm^2

R = Retardation in millimicrons

T = Thickness in cm of glass through which the retardation was measured

C = Stress-Optical Coefficient of the glass in mμ/cm/kg/cm^2—This is the relation between retardation per unit thickness and the strain produced by a known stress.

Converting to a form involving stress and thickness in English engineering units, this relation becomes:

$$s = \frac{5.6}{C} \times \frac{R}{t}$$

s = stress in p.s.i.

t = thickness in inches

Since $\frac{5.6}{C}$ is a constant for a particular glass, it may be replaced by a factor K_{in}. Thus, the relation becomes:

$$s = K_{in} \frac{R}{t}$$

K_{in} = Stress factor when glass thickness is measured in inches

The factors, K_{in}, for various Kimble glasses are listed in Table I. A similar conversion allowing the use of metric units throughout to yield stress in p.s.i. is also given on Table I.

With a little practice, it is possible to measure the retardation with the polarimeter to within 3 to 4 millimicrons. After some experience, it is possible to make these measurements within 2 millimicrons. Using ¼″ cane, 1 millimicron is equivalent to about 10 p.s.i. Measurements have shown that the stress data obtained by this type of glass-to-glass seal are not significantly affected by using seal diameters in the range of 0.20″ to 0.40″, but for greatest accuracy a range of, say, 0.20″ to 0.30″ is preferable.

Polarimeters[5] have been devised which will measure retardation more accurately than the polarimeter used for this work. Thus, it is possible to get even greater accuracy from this glass seal technique, if necessary. Of course, when properly used, the polarimeter differentiates between tension and compression and so it is possible to determine rather readily which glass has the higher thermal contraction, this being the glass in tension.

TABLE I

TYPICAL STRESS-OPTICAL COEFFICIENTS OF KIMBLE GLASSES

(With Multiplying Stress Factors for Calculating Seal Stress)

Glass	*Stress-Optical Coefficient C (annealed glass)* ($m\mu/cm/kg/cm^2$)	*(Metric) Multiplying Stress Factor* K_{cm} *(for R/T in mμ/cm)* (p.s.i./mμ/cm)	*(English) Multiplying Stress Factor* K_{in} *(for R/t in mμ/in)* (p.s.i./mμ/in.)
A 3008	2.7	5.3	2.1
Amber 45	3.1	4.6	1.9
Amber 60	3.1	4.6	1.9
Amber 203	3.4	4.2	1.7
EE - 2	2.6	5.6	2.2
EE - 4	2.6	5.5	2.2
EF - 9	3.1	4.6	1.8
EG - 3	0.8	17.2	6.8
EK - 3	2.9	5.0	2.0
EN - 1	3.8	3.7	1.5
EN - 4	2.7	5.2	2.0
EN - 5	2.6	5.6	2.2
ER - 3	4.2	3.4	1.3
ES - 1	5.0	2.8	1.1
EU - 2	2.5	5.7	2.2
EU - 3	2.4	5.9	2.3
EZ - 1	2.7	5.3	2.1
IA - 1	2.9	4.9	1.9
IA - 9	2.8	5.2	2.0
II - 1	1.2	12.0	4.7
IN - 3	3.4	4.1	1.6
IR - 1	3.2	4.4	1.7
IS - 5	3.7	3.9	1.5
KG - 1	2.9	5.0	2.0
KG - 12	2.9	5.0	2.0
KG - 30	2.7	5.2	2.1
KG - 33	3.9	3.7	1.5
KG - 34	3.5	4.1	1.6
K - 650	3.9	3.7	1.5
K - 704	3.8	3.8	1.5
K - 705	3.8	3.8	1.5
K - 772	3.6	4.0	1.6
N - 10	3.1	4.6	1.8
N - 51A	3.3	4.4	1.7
RP - 3	3.2	4.5	1.8
TH - 10	2.6	5.4	2.1
TL - 2	2.6	5.5	2.1
TM - 5	2.9	5.0	2.0

Seal stress in p.s.i.: $s = K_{cm} R/T$ for T = Thickness in centimeters.
$s = K_{in} R/t$ for t = thickness in inches.
R = Retardation in millimicrons.

CONSIDERATIONS IN SELECTION OF REFERENCE GLASS AND USE OF GLASS SEALS FOR PRODUCTION CONTROL

Because control of glass by making seals offered so many advantages, procedures were set up for using the seal method as a production control. A prime necessity was to select a standard glass which had uniform, desired expansion and other physical characteristics. This glass would be used to seal to everyday production samples taken from a glass furnace so that data could be reported on a standard basis. However, it was difficult to obtain a supply of "standard" glass which had the exact desired sealing characteristics. To get around this problem, any production of seal reference cane which had uniform properties near the target was selected. Then the difference in properties between the glass selected and the target was taken care of by applying a correction factor. For example, the target linear thermal expansion coefficient (0°C. to 300°C.) of a glass might be $90 \times 10^{-7}/°C.$ while the known reference glass might have a thermal expansion coefficient greater than the target by $0.6 \times 10^{-7}/°C.$ Since this reference glass had a higher thermal expansion, seals made to it should not have as high a tension stress (or as low a compression stress) as if they had been sealed to the target glass. Again, if an unknown daily production sample of glass had a thermal expansion coefficient of $90.6 \times 10^{-7}/°C.$, the seal should be neutral, whereas the unknown glass would have been in tension had it been sealed to the target glass. To adjust for this, a correction factor in terms of stress(p.s.i.) was added to the stress observed between the known glass and the unknown glass. This correction factor enabled all data for production glasses to be compared over an extended time and provided a consistent basis for making batch adjustments on a day-to-day schedule, if necessary.

An example may show how this has been done. The standard (or target) properties of KG-12 published in Kimble technical bulletins were 433°C. for the annealing point and $90 \times 10^{-7}/°C.$ for the linear thermal expansion coefficient. The diagram on the lower half of Data Sheet I shows the stresses developed when two production glasses are sealed to a reference glass. As pointed out above, the reference glass was selected as having properties near the target glass. The unknown or production glass No. 1, when sealed to the reference glass, results in 130 p.s.i. *C* (compression) in the unknown glass (130 p.s.i. tension in the reference glass). However, the reference glass is known to have a stress of 130 p.s.i. *T* (tension) against the target glass. By adding to the 130 p.s.i. *C* observed in the unknown glass the 130 p.s.i. *T* between the target and the known reference glass, the stress, zero p.s.i., is obtained that would result if the unknown glass had been sealed to the *target*. This 130 p.s.i. *T* is called the correction factor and is characteristic of the particular reference glass. In this case the unknown or production glass No. 1 was right on target and would have made an ideal seal reference material.

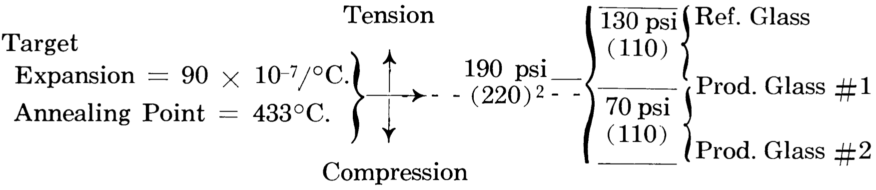
Another sample, production glass No. 2, sealed to the reference glass with 190 p.s.i. *C* in the production glass. Again the 130 p.s.i. *T* correction factor would be added algebraically to obtain a figure of 60 p.s.i. *C*. This latter figure is the stress that would have been obtained if the production glass No. 2 had been sealed to the target glass.

DATA SHEET I

A COMPARISON OF SEAL AND THERMAL CONTRACTION DATA FOR KG-12 GLASSES

Temperature °C.	Relative Elongation — $\frac{\Delta L}{L}$ ($\times 10^{-5}$) *Production Glass #1*	*Reference Glass*	*Production Glass #2*
25	0	0	0
100	64.0	64.5	63.5
200	154.0	154.0	154.5
300	250.0	252.0	250.5
400	362.0	364.0	361.0
418	389.0	391.5	386.5
425	400.5	403.5	397.5
433	415.5	419.5	412.5
438			422.5
Expansion (0°-300°C.)[1]	90.0×10^{-7}/°C.	90.6	90.1
Annealing Point (°C.)	433.	433.	438.
Observed Seal Stress (p.s.i.)	130 *C*		190 *C*
Corrected Seal Stress (p.s.i.)	0		60 *CC*

SEALS:



1. The coefficient has been calculated to three significant figures although it is not this accurate.
2. Figures in parentheses are calculated from the contraction data at 418°C.

Also shown on the figure is the stress—70 p.s.i.—actually measured when production glasses No. 1 and No. 2 were sealed together. This agreement within 10 p.s.i. is very good. Checking three glasses of the same composition in this manner has been done many times and agreement within 20-40 p.s.i. is usually obtained.

By following the above procedure of applying correction factors, it is possible to change from one reference glass to another and still keep the seal data consistent. For example, production glass No. 1 was actually used for a reference glass after all the first reference glass was used. Of course, the correction factor for the production glass No. 1 was *zero,* since it was right on target for both expansion and annealing point. Thus, production glass No. 2 gave seal results of 60 p.s.i. *C* corrected when the first reference glass was used and 70 p.s.i. *C* corrected when the production glass No. 1 was used as a reference. The notation 60 *CC* is used which means 60 p.s.i. Compression Corrected. In this manner, the seal data are kept on a comparable basis in going from one reference glass to another.

It was experimentally determined that with KG-12 glass, a difference in thermal expansion coefficient of $1 \times 10^{-7}/°C.$ over the temperature range of 0°-300°C. was equivalent to about 200 p.s.i. in seal stress (tension in the glass having the higher expansion). Also, it has been estimated that each 1°C. difference in annealing point is equivalent to about 15 p.s.i. (compression in the glass have the higher annealing point). These empirical factors are difficult to obtain because of the problems of obtaining accurate physical and chemical property data, but they have been of value in associating seal data with other properties. The relation between stress and difference in thermal expansion coefficient (0°-300°C.) varies from one glass composition to another. This relationship depends largely upon the annealing point and the inflection in the thermal contraction curve. In general, the higher the annealing point, the greater the number of p.s.i. seal stress per unit difference in thermal expansion (measured from 0°-300°C.). The annealing point factor may be related to variation in the thermal contraction which accompanies variation in annealing point, as is pointed out in Section 7.

The correction factors are calculated by using the above factors and correlating them with the results obtained by sealing new reference glasses to old references glasses. It should be understood that these factors apply only to samples of the same or closely similar glass. When dissimilar glasses are sealed it is quite possible for the glass with *lower* thermal *expansion* (0°-300°C.) to be in tension.

TOLERANCE IN SEAL STRESS

Experience with production items has shown that for most applications a stress of 800 p.s.i. between two glasses may be tolerated. By this it is meant that there may be 800 p.s.i. tension in one glass and 800 p.s.i. compression in the other glass. However, in order to minimize breakage when different glasses are sealed together it is customary to control production glass seal stresses within a range of 500 p.s.i. or less.

EFFECT OF ANNEALING POINT VARIATIONS ON SEAL STRESS

The information listed on Data Sheet I is plotted on the thermal contraction curve. (See Figure 2.) This curve shows the effect of an annealing point variation on the stress developed when two glasses are sealed together. Whereas the contraction data at 300°C. or less do not indicate great differences between production glasses No. 1 and No. 2, the data above 400°C. show a greater divergence from the reference on the part of No. 2 glass. This greater divergence may occur because the annealing point of production glass No. 2 is slightly higher (438°C.) than that of the other glasses (433°C.), so that the inflection in the contraction curve probably occurs at a slightly higher temperature. This inflection region, or rapid change in the slope of the contraction curve, is related to the viscosity of the glass and its thermal history preceding the thermal expansion test. It can also be seen on Data Sheet I that, although the two production glasses have about the same thermal expansion up to 300°C., their thermal contraction data are different above 300°C. Therefore, they do not seal to the reference with the same stress. It may be concluded that a glass may have a lower annealing point than the reference, with a slightly lower thermal expansion (0°-300°C.). and still tend to give a neutral seal.

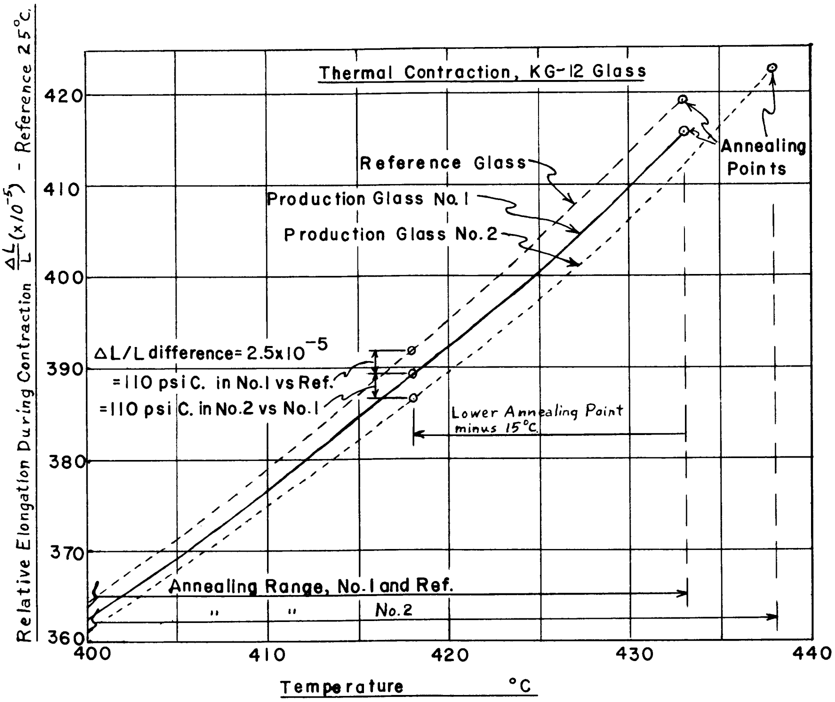


Figure 2

SEAL STRESS ESTIMATION FROM THERMAL CONTRACTION DATA

The seal stresses between two glasses can be calculated or estimated from the thermal contraction curves. Past experience has indicated that the glass "sets up" somewhere in its "annealing range," or the region between strain point and annealing point. This *setting temperature* is a function of the cooling rate and viscous properties of the glass, and has been estimated as occurring from 5°C. above the strain point to 15°C. below the annealing point. If the difference between two glasses in $\frac{\Delta L}{L}$ (change in length per unit length) at a temperature near to 15°C. below the annealing point of the glass with the lower annealing point is obtained from the contraction curves or the data, the seal stress may be estimated from this difference by the following expression, for glasses A and B sealed together:

$$\text{Stress in p.s.i.} = 0.5 \times (\text{Young's Modulus}) \times \left[\left(\frac{\Delta L}{L}\right)_A - \left(\frac{\Delta L}{L}\right)_B \right]_{(\text{A.P.}^* - 15^\circ\text{C.})}$$

Young's Modulus for KG-12 glass is 8.7 × 10^6 p.s.i. On the data sheet the estimated stress for the reference and the two production glasses is listed in parentheses. The differences in $\frac{\Delta L}{L}$ for the two production and reference glass seals are indicated on the contraction curves of Figure 2, at a temperature of 418°C., or 15°C. below the lower annealing point (433°C.). For production glass No. 1, the difference in $\frac{\Delta L}{L}$ is 2.5×10^{-5} at 418°C. which yields a calculated stress of 110 p.s.i. Compression in No. 1 glass *vs.* an observed value of 130 p.s.i. *C.* In all three seals the calculated values of seal stress come rather close to the measured values. Good correlation is not always the case as pointed out above. In order to calculate seal stresses in this manner, so many measurements have to be made that the accuracy of such estimations from thermal contraction data is in question as compared with the direct method of measuring seal stresses. In some cases the seal stress corresponds to a $\frac{\Delta L}{L}$ difference nearer to the strain point.

The observed stress in a seal may be reconciled with thermal contraction data by determining the elongation difference required by the stress, by:

$$\begin{matrix}\text{Elongation Difference} \\ \text{at Setting Temp. T°C.}\end{matrix} \left[\left(\frac{\Delta L}{L}\right)_A - \left(\frac{\Delta L}{L}\right)_B \right]_{(\text{T °C})} = \frac{2 \times \text{Stress}}{\text{Young's Modulus}}$$

then tabulating the $\frac{\Delta L}{L}$ differences from the contraction data for the two

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*The *lower* A. P. temperature of A or B.

glasses, and calculating the temperature at which the elongation difference should have occurred during contraction. For example, the observed seal stress for production glass No. 2 of 190 p.s.i. *C vs.* the reference indicates that the elongation difference should be $(2 \times 190$ p.s.i$)/8.7 \times 10^6$ p.s.i. $= 4.4 \times 10^{-5}$. The tabulated differences for No. 2 *vs.* the reference would be -3.0×10^{-5} at 400°C. and -5.0×10^{-5} at 418°C., which indicates a setting temperature of about 413°C., or 20°C. below the annealing point of the reference glass.

SUMMARY

In the past, it has been common practice to examine expansion data only in order to determine whether two glasses can be sealed together. A more careful analysis is necessary to prevent breakage when production items of two glasses are sealed together over a period of time. Since the probability of breakage can depend upon the actual seal stress level it is more appropriate to measure the seal stress.

In evaluating and controlling the sealing properties of glasses to be sealed to other glasses or to metals, the most effective method is to make a glass-to-glass seal with a known reference glass. The sealing characteristics and other properties of the known glass should be thoroughly and carefully tested, including seals to previous references, thermal contraction data, and viscosity points, such as annealing and strain points.

With this method glass in nearly any shape can be used merely by lampworking it into short canes about 1/4″ in diameter. Equipment and methods for making glass-to-glass seals and measuring the stress between the reference glass and the unknown sample, are found in Appendix I, Appendix II, and Appendix IV. In Appendix III is found a description of a suitable polarimeter.

The authors wish to express their sincere appreciation to Mr. R. R. Miller and Mr. E. L. Burns for their contributions to the formulation of this paper, and to Dr. H. H. Holscher for his valuable assistance in reviewing this paper for publication.

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APPENDIX I

EQUIPMENT FOR MAKING SEALS AND FOR MEASURING STRESS IN GLASS

1. *Equipment for Making Seals.*

1.1. Gas-Oxygen burner and supplies for operating.

(a) Source: Eberbach & Son, Company, P. O. Box 63, Ann Arbor, Michigan 48107.

Materials: #9-364 Blast Burner—air or oxygen, and gas M.I.T. or #9280 Blast Burner with #9-154 gas-oxygen tips.
Tips: #OX—2 (small) and #OX—4 (large).

(b) Source: Bethlehem Apparatus Company, Inc., Hellertown, Penna.

Material: Tygon Twin Tubing, Standard, 25 ft. length (3/8″ O.D. × 1/4″ I.D.)

(c) Source: Central Scientific Company, 1700 Irving Park Road, Chicago 13, Illinois.

Material: #13-910 Oxygen Tank Regulator, constant pressure.

1.2. Small electric furnace with temperature control for annealing.

(a) Source: Marshall Products Co., P. O. Box 4857, Sta. B., Columbus 2, Ohio.

Material: Marshall Tensile Testing Furnace, Spec. Sheet #804-B 2½″ I.D. × 7″ O.D. × 16″ long (max. temp. 1800°F.)

(b) Source Leeds & Northrup Co., 18240 James Couzen Hwy., Detroit 35, Michigan.

Material: Cat. No. 1-901-051-001-5-000-3-1 L & N Speedomax "H" Temperature Controller—Model R—110 V.A.C., 50 cycle, 0°-2000°F. Scale—Chromel-Alumel Thermocouples.

(c) Source: Lumenite Electronic Co., 407 S. Dearborn St., Chicago 5, Ill.

Material: M60 Series MF-2111A Lumenite Interval Timer with Switch—0-60 minutes—115 v, 60 cycle, 10 amp.

1.3. Small cut-off saw, #180 carborundum blade for cutting and polishing cane.

(a) Source: Sommer & Maca Glass Machine Co., 5501 W. Ogden Ave., Chicago, Illinois.

(b) Material: Cat. No. NM-8-BM13 Notching and cut-off machine, without diamond wheel.

2. *Equipment for Assembling Polarimeter for Measuring Stress in Glass.*

(a) Source: Fisher Scientific Co., 1458 N. Lamon Ave., Chicago 51, Ill. 60651

Materials:

- Cat. No. 4-732 Optical Cell (50 mm cubical)
- Kodak No. 65 Wratten Filter, 2 in. square in "B" glass.
- Cat. No. 14-666-10 Flexaframe Rod.
- Cat. No. 14-666-25 Flexaframe Foot.

(b) Source: Eberbach & Son, Co., P. O. Box 63, Ann Arbor, Mich., 48107

Material: Cat. No. 72-096 Polaroid Film, 2 in. square.

(c) Source: Central Scientific Co., 1700 Irving Park Road, Chicago 13, Ill.

Materials:

- Cat. No. 87604-1 Polaroid Mounting
- Cat. No. 19086 Cenco-Lerner Micro Lab Jack
- Cat. No. 66175 Microscope Illuminator
- Cat. No. 66177 Lamp Bulb, 6½ volt (spare)

(d) Source: Bausch & Lomb Optical Co., Inc., 20200 Outer Dr., Dearborn, Michigan.

Materials: #31-29-10 Microscope (10x), Wide Field Tube

(e) Source: Polarizing Instrument Co., Irvington-on-the-Hudson, New York, N.Y.

Material:

- No. 310 Polaroid
- No. 340 Quarter-wave Plate

APPENDIX II

Procedure for Making Glass-to-Glass Seals

1. Select the sample or unknown cane ¼″ in diameter or slightly larger.
2. Select a reference cane of about the same diameter as the sample.
3. Cut the ends of both canes flat and at right angles to the axis of the cane. Use a diamond or carborundum wheel to cut the canes. Partially polish the cut ends by working against a grinding wheel of about 180 grit, eliminating all cutting chips or checks and edge defects. Wash.
4. Heat the ground ends of both canes slowly and evenly, holding one cane in each hand and alternately inserting the ends of the canes in an oxygen-gas flame. A reducing flame will spoil the visibility through the seal of a lead glass; too rapid heating may do the same thing by causing reboil.
5. Continue the heating until the ground ends of the canes become fire-polished, but not hot enough to distort the flat surfaces severely. (If necessary, the ends may be mechanically polished instead of fire-polished.)
6. Press the treated ends of both canes together lightly, being careful to align them axially. Continue heating until the two canes are fused together, producing the cross-section shown in Fig. A II-1.

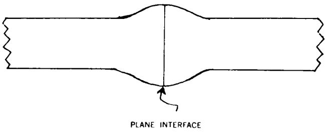


Figure A II-1

7. Allow the seal to cool slightly, then melt off the reference cane about 1″ from the seal. Identify the sample cane, marking it with a diamond pencil close to the seal.
8. Scratch the sample cane with a file and break the cane about 1″ back from the seal.
9. Anneal the seal, holding the glass at a temperature 25° ±5°C. above the higher annealing point of the two glasses for about 30 minutes, cooling at a rate not to exceed about 5°C./min. to near 300°F. or below.

   Precautions to be observed—

   Select a portion of cane that is free of stones, blisters, seeds and cord. Do not heat the glass too hot either before or after sealing. The seal faces should remain flat and parpendicular to the axis of the canes. This procedure is followed in order to make sure that the glass interface is flat. The seal should be well annealed, with clear visibility through the interface when viewed at a slight angle.

APPENDIX III

POLARIMETER FOR MEASURING STRESS IN GLASS

Introduction:

Qualitative measurements of retardation resulting from stress in glass can be of considerable help in evaluating the degree of annealing of a particular glass item after experience with its performance has been obtained. Also, glass-to-glass and glass-to-metal seals can be analyzed. Goranson and Adams* have dealt thoroughly with the theory behind a polarimeter for measuring retardation usually expressed in millimicrons. For measuring stresses in various glass items, a modification of their equipment has been found very useful. Their device consists of a monochromatic light source, a polarizer, a quarter-wave plate, and an analyzer mounted in an eyepiece which can be rotated. With no sample in place, extinction can be obtained by rotating the eyepiece to the proper zero position. If a glass sample exhibiting birefringence is put in place, the observer can see light. Extinction of the light can be obtained by rotation of the analyzer. The amount of rotation determines whether a net compression or tension exists in the glass at the point examined.

The arrangement here described is essentially a Goranson and Adams polarimeter with the exception that a white light source is used. Instead of obtaining complete extinction, however, a dark blue color is reached which indicates that the analyzer has been rotated the proper amount.

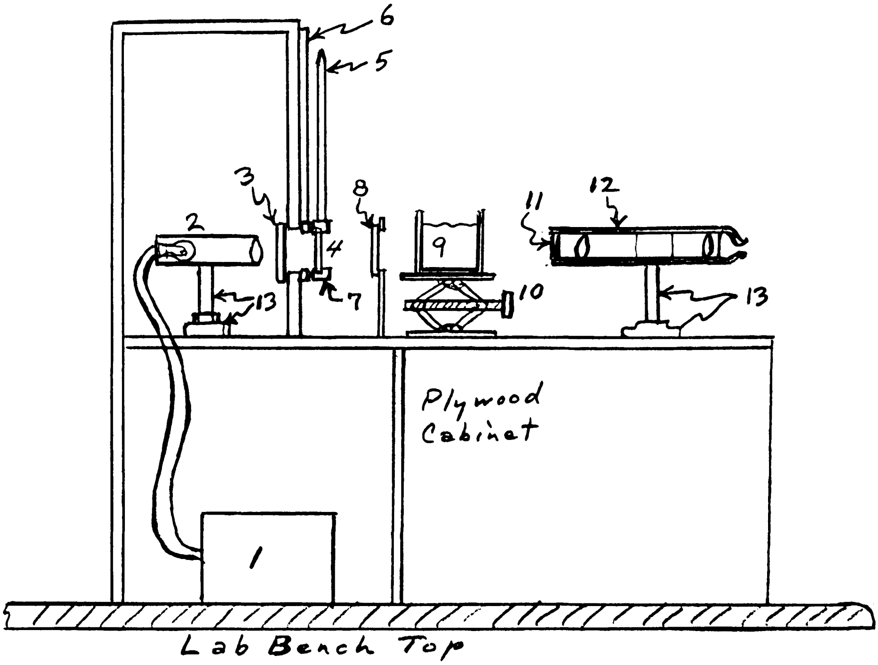
Equipment:

A polarimeter can be set up in several ways. It is quite easy to set up the arrangement in an optical bench, essentially as shown in Figure A III-1 The equipment listed in Appendix I is needed to make this seal polarimeter. Other optics are, of course possible.

The various optical parts must be lined up properly. This alignment can be done quite easily. The polarizer should be at 45° with respect to the north-south direction, as shown in Figure A III-2.

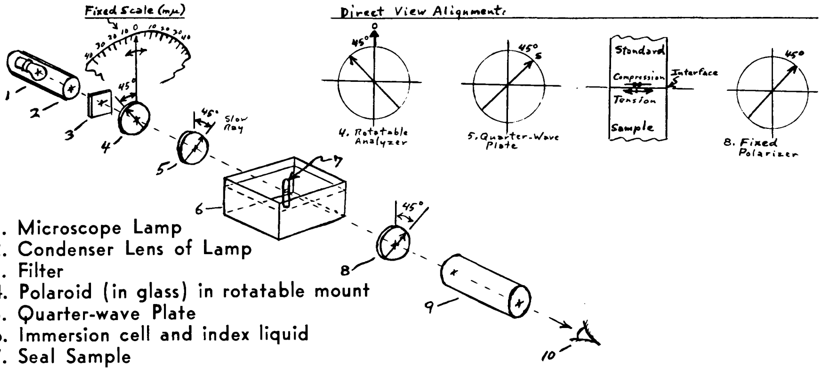
The quarter-wave plate is removed from the system and the pointer is set at zero. Then the analyzer is rotated until extinction exists. The analyzing polaroid is fixed in this position with regard to the pointer (while pointer is at zero). Next, the quarter-wave plate is placed in the system and rotated until extinction exists. If the slow ray of the quarter-wave plate is parallel to the polarizing axis of the fixed polarizer, then counter-clockwise movement of the analyzer will indicate compression in the glass samples when the compression is in the vertical direction. The quarter-wave plate is fixed in this position. The polarimeter is now ready for use. In using the polarimeter for measuring stress, it is necessary to periodically check the zero position. Before examining the glass seal specimen in the tank of monochlorobenzene (or optical cell containing a suitable index liquid), the pointer is rotated until the least amount of light is seen in the eyepiece. If the pointer is not at the zero position, the instrument should be realigned as described above, or a correction must be applied to all seals measured in that particular set-up.

Journal of the Franklin Institute, v. 216, p. 475, 1933



1. Transformer, Microscope Lamp
2. Microscope Lamp with Condenser Lens
3. Filter
4. Polaroid (in glass)
5. Pointer
6. Scale (3 mμ per degree rotation)
7. Rotatable Analyzer Mount
8. Quarter-Wave Plate
9. Immersion Sample Cell
10. Lab Jack
11. Polaroid Film (Fixed Polarizer)
12. Telemicroscope
13. Flexaframe Supports

Figure A III-1
Polarimeter for Measuring Stress in Glass.



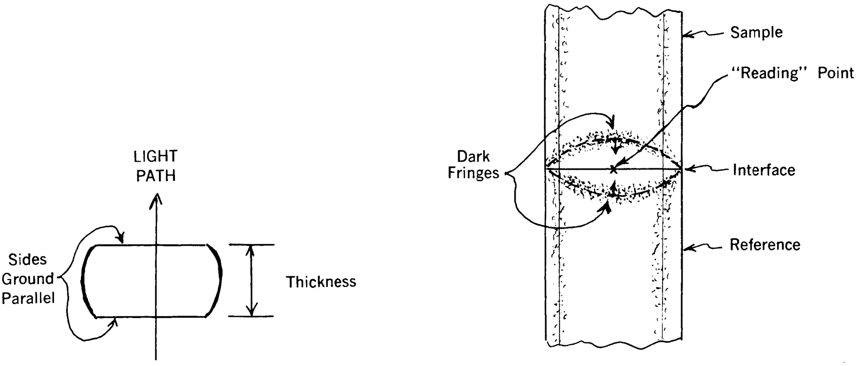
1. Microscope Lamp
2. Condenser Lens of Lamp
3. Filter
4. Polaroid (in glass) in rotatable mount
5. Quarter-wave Plate
6. Immersion cell and index liquid
7. Seal Sample
8. Fixed Polaroid
9. Telemicroscope
10. Eye

Figure A-III-2
Alignment of Optical Parts.

APPENDIX IV

Method of Reading Stresses in Glass-to-Glass Seals

1. Remove the seal from the annealing furnace at about 300°F. and allow about five minutes for the seal to cool to room temperature.
2. Opposite sides of the seal are ground flat and parallel, in planes perpendicular to the seal interface. Only a slight amount of grinding is done. This procedure makes it possible to see the seal interface more clearly and allows an accurate glass thickness measurement to be made. (See Figure A IV-1.) If the seal is highly stressed, *do not grind.*



TOP VIEW

FRONT VIEW

(A small holder may also be made to cradle the seal while it is being measured.)
Figure A IV-1

3. Measure the seal thickness from flat to flat at or near the center of cross-section at the interface. Turn on the polarimeter lamp and check the zero reading for the immersion cell to be used with the seal sample. The index of refraction of the immersion liquid should be similar to that of the glass. Monocholorobenzene is a good index liquid for many ordinary glasses, of index refraction near 1.52. Liquids for other index ranges are available commercially.
4. Holding the seal by the standard end, immerse the seal in the liquid until the interface can be seen in the field of view. Adjust position of cane manually until clearly in focus and with interface horizontal as shown in Figure A IV-1, looking through the cane in the direction in which its thickness was measured. (If the polarimeter eyepiece is equipped with a calibrated scale, measurement of the cane thickness may be made while the cane is immersed.)
5. With the polarimeter[1] set at extinction (zero millimicrons) the seal should appear as in Figure A IV-1 if there is stress* present. If no stress* is observed, the seal is neutral, with no apparent dark fringes near the interface.

6. Rotate the polarimeter indicator until the *center* of the dark line or fringe of the sample cane moves into the interface position. Read the stress* indicated in millimicrons. Repeat once or twice as a check. Rotate the indicator in the other direction until the center of the dark line of the standard cane moves into the interface position. Read this stress,* repeating once or twice as a check.
7. In the polarimeter arrangement usually employed, settings clockwise from zero indicate compression in a horizontal direction, while counterclockwise settings indicate horizontal tension. These would apply to the interfacial stress for seals positioned as shown in Figure A IV-1.
8. Both readings, in sample and standard, should be equal in magnitude and opposite in sense if both canes are of the same glass (same stress-optical coefficient). If not equal, three conditions may be found:

   The zero setting may be off—check by removing the seal and setting the indicator to extinction with the immersion cell in place.

   The seal may be cordy—this will be evident as streaks of inhomogeneities parallel to the axis of the sample cane running perpendicular to the interface, which move in position if the cane is rotated about its axis. Only an approximate stress* may be read for this condition.

   The seal may be poorly annealed—the magnitude of stress* remaining from annealing may be determined by reading the residual stress* at least one cane diameter away from the interface and at the center of the cross section.
9. If poor annealing is found, reanneal the seal. In general, it must be reannealed if the sample stress* reading is more than 10 millimicrons different from the standard, for the same glass. For differences of 10 millimicrons or less, the approximate seal stress* may be found by averaging the two readings; *e.g.*, sample 20 mμ compression, standard 12 mμ tension, seal stress* in sample is 16 mμ compression.
10. Calculate the seal stress in the sample by the following relation:

$$s = K_{in} \frac{R}{t}$$

s = Stress in p.s.i.

K_{in} = Stress factor when glass thickness is measured in inches—see attached Table I

R = Retardation in millimicrons measured with the polarimeter (stress*)

t = Thickness of sample in inches

OR

$$s = K_{cm} \frac{R}{T}$$

K_{cm} = Stress factor when glass thickness is measured in centimeters

T = Thickness of sample in centimeters

For example, with TM-5 glass the stress in p.s.i. is found by multiplying the number of millimicrons by K_{cm} (5.0) and dividing by the seal diameter in *centimeters,* or by multiplying the number of millimicrons by K_{in} (2.0) and dividing by the seal diameter in *inches*.

---

1. See Appendix III on polarimeter. (*One degree* analyzer rotation $\simeq$ 3 mμ retardation.)

*Stress = Summation of "strain-differences" causing *retardation.*

NOTES

The retardation caused by the stress condition at the interface of glass-to-glass or glass-to-metal seals is determined in millimicrons by use of a suitable polarimeter. For polarimeters reading in degrees, where 180° rotation is equal to one wavelength retardation for the light used, the conversion factor is 3.27 millimicrons per degree for sodium light, $\lambda = 589\ \text{m}\mu$, or 3.03 millimicrons per degree for mercury green light, $\lambda = 546\ \text{m}\mu$. The seal diameter or path length traversed by the light at the seal interface may be measured either in centimeters or inches.

In Table I are listed the stress-optical coefficients and stress factors for Kimble glasses.

TIN OXIDE: WHAT CAN WE DO WITH IT?

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INTRODUCTION

It may seem strange for me, representing an electrical manufacturer, to talk to you about a product which we do not manufacture, especially since there are present, representatives of glass manufacturers who do make and sell tin oxide films on glass as a product. Thus, I may fit in the category of "fools enter where angels fear to tread". Nevertheless, I have found tin oxide films on glass substrates an extremely useful tool for many experiments which I conducted in the past. In the course of this work we have performed measurements on the films of tin oxide which I wish to report to you this morning.

PREPARATION OF FILMS

There are two methods used for applying thin films of tin oxide which have developed through the years.

(a) SPRAY PROCESS

Some of the early experiments done with spraying tin oxide in General Electric were by Dr. K. Blodgett in 1943. The method of spraying presently used was described by her in 1951 and consists of the following:

(1) 10 grams $SnCl_4 \times 5H_2O$ (stannic chloride) in 50 cc denatured alcohol.

(2) 5 grams Sb_2O_3 in 20 grams HCl. Allow it to settle for 12 hours before use. Small percentage of red precipitate. Pour off nearly clear solution.

(3) Use 1% Sb_2O_3 solution (0.5 g) in the $SnCl_4$ solution when ready to spray. The temperature of the substrate should be between 500 and 550°C. while spraying.

(4) Resistance of the film may be usually lowered by heating in H_2 at 330°C. for 10 minutes.

The Center glass shop uses a DeVilbiss spray gun model TGA-551 and a vented furnace for application of the tin oxide films. Figure 1 shows the spraying operation. The carrier gas for the spray gun is nitrogen or dry air.

The vaporized $SnCl_4$ reacts on the hot substrate surface with water vapor from the air to form a SnO_2 film and HCl gas. The production of HCl gas is the reason for the vented furnace. The reaction with dry air proceeds but at a greatly reduced rate.

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl\ g$$

The addition of Sb_2O_3 as a dopant lowers the resistance of a film by a factor of 10.

Figure 1
Picture of technician spraying tin oxide coating in vented furnace.

Figure 2
Technician mounting Hall sample in Hall rig.

(*b*) LIQUID PROCESS

Liquid techniques have been worked on successfully, and the process consists of adding the $SnCl_4 \times 5H_2O$ salt to an acetate base and dipping the material to be coated. The substrate is then fired at 500°C. to complete the chemical reaction. High resistance films generally are produced by this method, thus limiting their usefulness for heating devices.

The surface condition of the material to be coated is important. The spray process requires a smooth surface, free of sharp pits and edges such as are produced by coarse sandblasting. However, the ripples found on the surface of glass before polishing do not interfere with the coating.

ELECTRICAL PROPERTIES

In order to study the electrical properties of these films we used a Hall measuring apparatus such as is shown in Figure 2. A technician is shown mounting a sample on a copper block, the temperature of which is very accurately controlled. This apparatus allows us to take a sample from 300°C. down to −269°C.

Figure 3 (Hall sample) shows the detail of a Hall sample. Wires are attached to the electrodes and a known current is passed along the length of the sample as shown by the arrow. We then measure the voltage drop across the voltage electrodes and knowing the dimensions of the material we can calculate the resistivity of the material by the formula

$$\rho = \left(\frac{E}{I}\right)\left(\frac{\text{Area}}{\text{Length}}\right)$$

Next we apply a magnetic field as shown in Figure 3 by the arrow labelled H. This field exerts a force on the electrons traveling through the sample and creates a higher density of electrons on the left side of the sample. This makes that electrode relatively more negative than the one opposite, giving a voltage difference which we can measure. Once again we go to another equation for the Hall coefficient

$$R_H = K\left(\frac{\text{Thickness}}{\text{Field}}\right)\left(\frac{2V_H}{\text{Current}}\right)$$

Now we have all the necessary data to get some basic numbers which will characterize the material. The mobility of electrons in the material is obtained by dividing the Hall coefficient by the resistivity, and the number of electrons per cubic centimeter is obtained by dividing a constant by the Hall coefficient. (Figure 4)

From the above type of measurements, tin oxide has been identified as a degenerate n-type semiconductor, band gap 3.54 eV, with a room temperature mobility of ~ 15 cm²/volt sec and carrier concentrations of 1 to 6×10^{20} carriers/cm³, by Groth, Kauer and Linden(1) and verified at our Center. A resistivity of 10^{-4} ohm cm has been realized in thin films. By varying thickness and doping, films with a resistance of from 10 to 10^6 ohms per square can be made. Figure 5 shows Hall data for a 2μ thick sample from 3000°K. to −80°K.

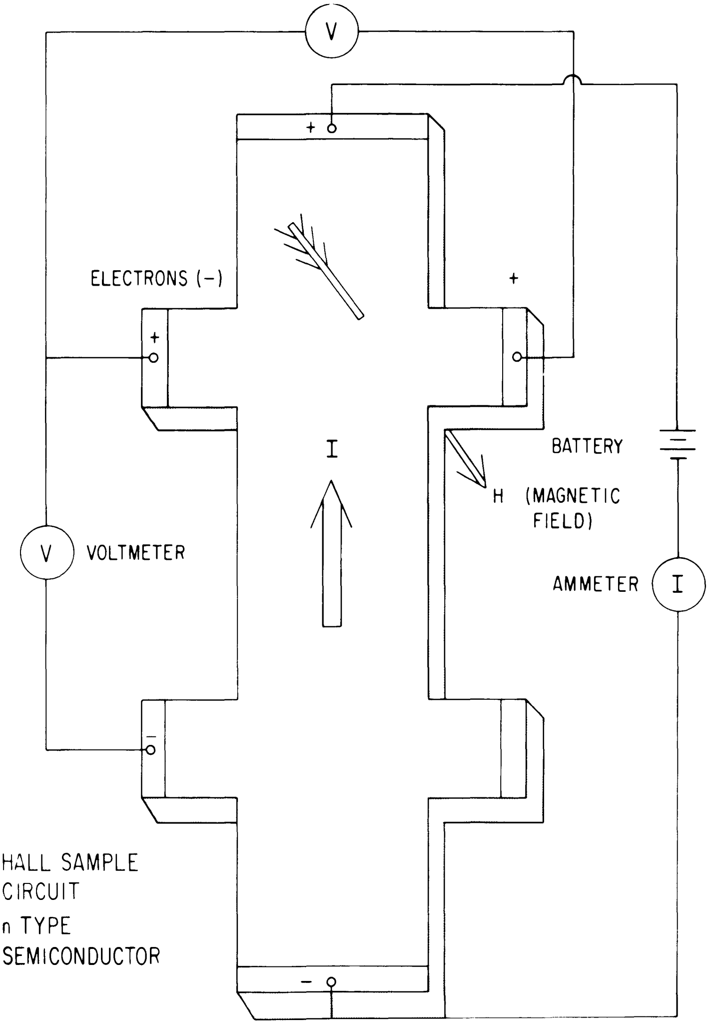

Figure 3
Schematic of Hall sample.

$$\text{MOBILITY} = \mu \quad \frac{\text{HALL COEFFICIENT}}{\text{RESISTIVITY}} = \frac{R_H}{\rho}$$

$$\text{NUMBER OF CARRIERS} = \frac{\text{CONSTANT}}{\text{HALL COEFFICIENT}} = \frac{6.24 \times 10^{18}}{R_H}$$

Figure 4
Hall data equations.

Undoped films can be made with resistance as low as 100 ohms/square. The addition of antimony as a dopant reduces the resistance an order of magnitude. Lytle(2) introduces hydrazine to lower resistance but is not sure of its function. Lytle(3) also reports the addition of fluorine as

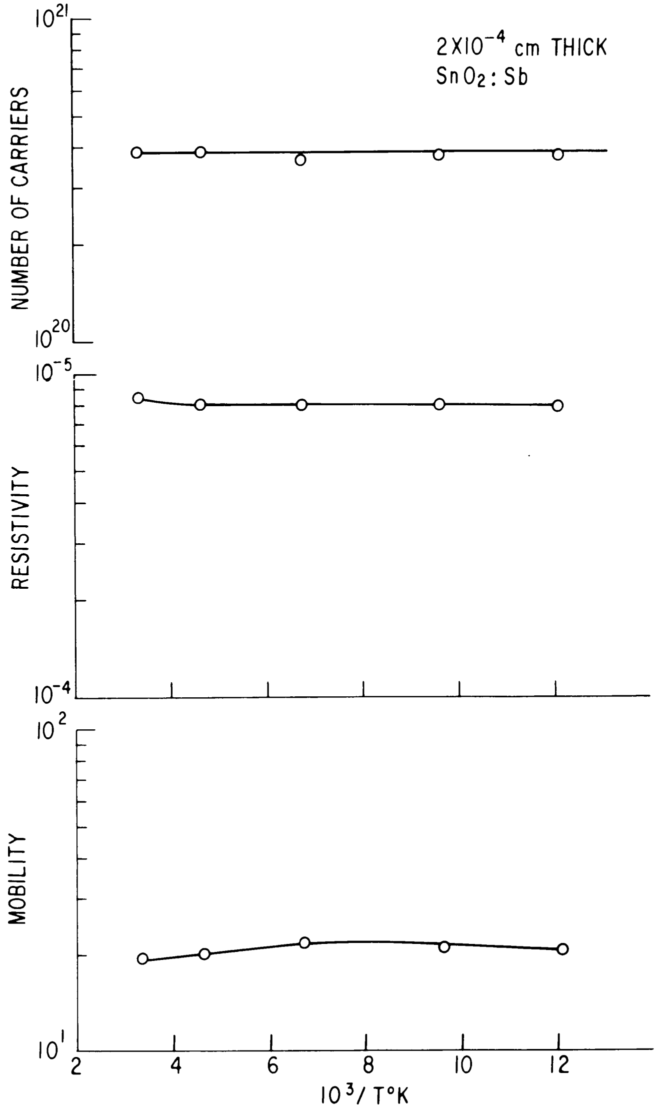

Figure 5
Hall data.

a dopant and notes that it counteracts the presence of antimony. Mochel(4) described the use of antimony as a dopant in SnO_2.

One would expect other group V elements to substitute for tin and serve the same doping function as Sb. Similarly, group VII elements other than fluorine should reduce resistivity by substituting for oxygen. Some workers in the field explain the conductivity of unintentionally-doped tin oxide by suggesting that chlorine from the $SnCl_4$ is incorporated into the lattice substitutionally at an oxygen site. Others explain that the conductivity is due to oxygen vacancies, and I tend to favor this latter explanation. The observations by Lytle on the simultaneous addition of fluorine and antimony tend to contradict the above explanation unless, in the presence of fluorine, antimony substitutes for oxygen, thus neutralizing the charge carriers locally. Recently reports of research on crystalline SnO_2 have appeared in the literature. Additional research could well be done on this compound to answer some of the remaining questions.

The most successful method for application of electrodes found here is described below:

(1) One-half the area of electrode is masked, closest to SnO_2 coating area, and the other is lightly sandblasted with a S. S. White Pencil Blast.

(2) Tin oxide is applied over the entire surface including sandblasted area.

(3) Bake-on Du Pont Silver Paste is applied to entire electrode area.

The roughening of the surface provides a surface more conducive to bonding.

OPTICAL PROPERTIES

The optical properties of SnO_2 films have been described by Groth, Kauer, and Linden.(1) Their data on the reflection of light incident on thin SnO_2 films are quite similar to data obtained at our Center in 1960 for SnO_2 films on sapphire. Figure 6 shows the transmission and reflection of our films which were considerably thicker than in the Groth studies. The bump between 9 and 10μ on their samples is also present in ours even though we worked on sapphire. Thus, I question their assumption that it is due to the Reststrahlen bands in the glass substrates.

Generally speaking, the high transmission in the visible decreases as one makes thicker films to obtain lower resistance. This is shown by comparing Figure 6 with Figure 7. The oscillations in the visible range are due to the interference effects of the thin film.

The use of tin oxide films as infrared reflections has some interesting possibilities. Figure 7 shows 70% reflection of incident radiation from 3 to 14 microns. This particular film was not designed to be a reflector. Thus, its reflectivity is somewhat lower than the 85% by Groth, Kauer, and Linden. The high reflectivity in the infrared, plus high transmission in the visible could be used to make unique reflectors for heat lamp installations, where the source temperature is lower than 2000°C.

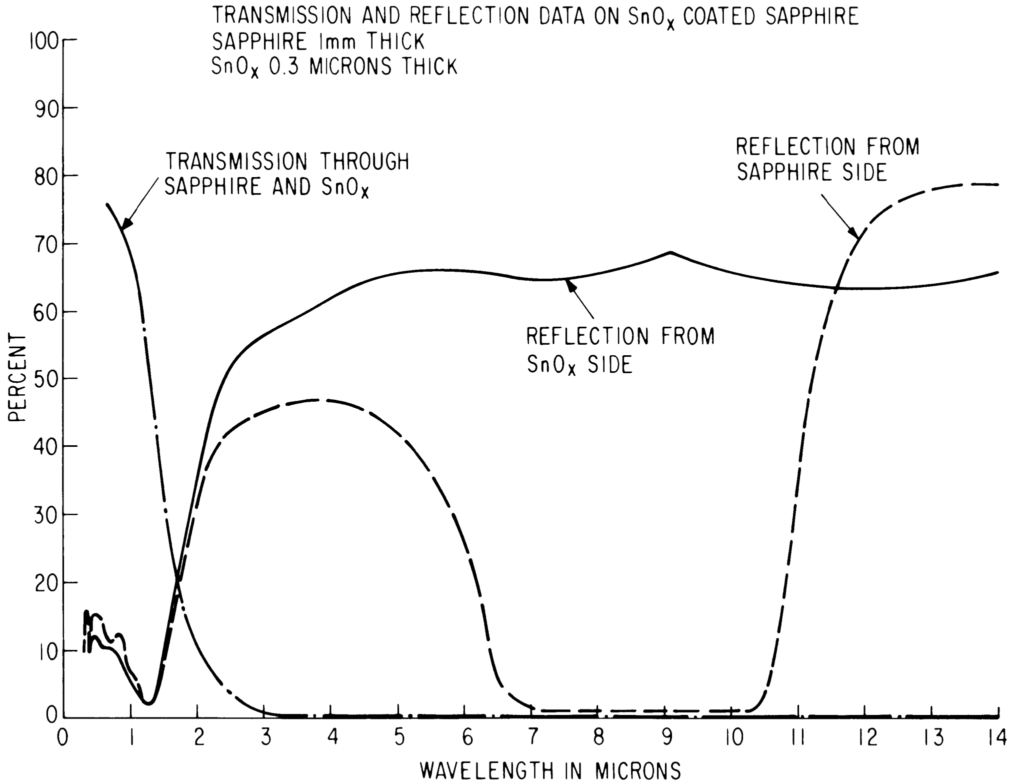

Figure 6

Transmission and reflection from 0.3 micron thick sample.

PHYSICAL PROPERTIES

Films of tin oxide range from clear, with interference colors, to dull gray on thick low resistance films. They are highly resistant to attack by acids and bases. Films on Pyrex® in boiling concentrated HCl or NaOH for an hour has no measurable effect. Three-day exposures in KOH or NaOH at room temperature produce no change either.

The films bond extremely well to clean substrates ranging from low temperature soda lime glass to high temperature quartz, sapphire and Lucalox. We have not had any peeling problem resulting from differences in coefficients of expansion between film and substrate.

The films will take any physical punishment which the glass can take. Rubbing with steel wool and similar materials have little, if any effect; however, rubbing with coarse sandpaper or emery cloth causes scratches which become hot spots and failure centers.

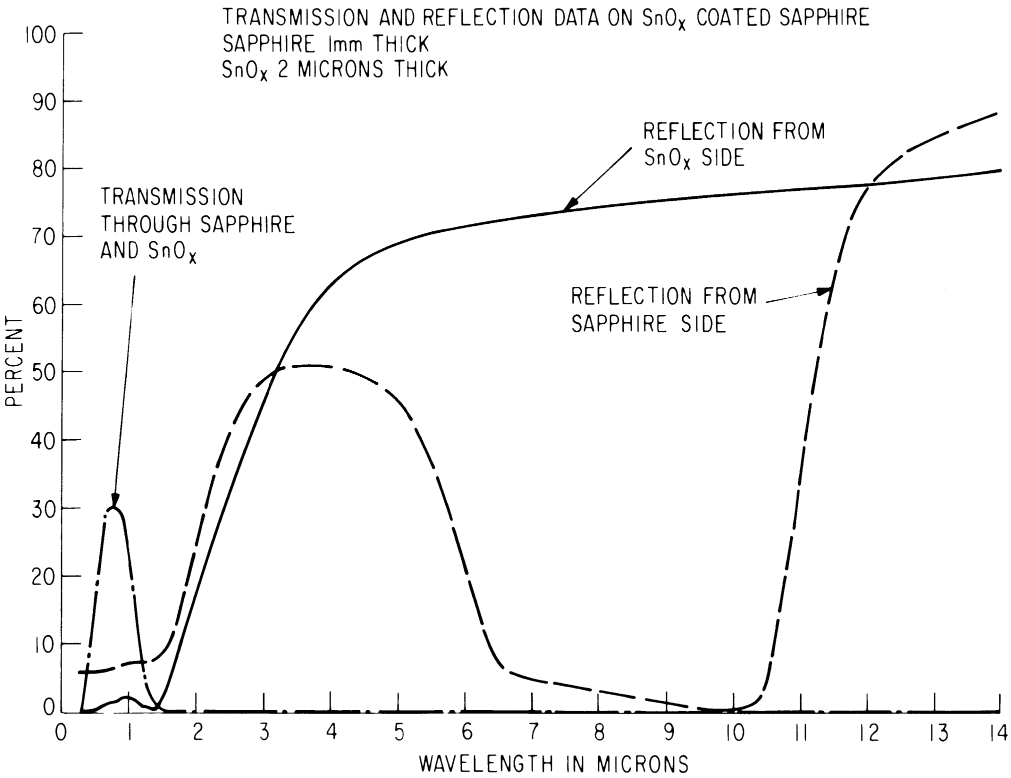

Figure 7
Transmission and reflection from 2 micron thick sample.

FAILURE MECHANISMS ON GLASS SUBSTRATES

There appear to be two completely different failure mechanisms which apply to tin oxide, depending on the temperature stability of the substrate material.

The first method is when tin oxide is applied to glasses, such as Pyrex,® which have a relatively low softening temperature of 600°C. The failure of heating devices centers around imperfections in the tin oxide coating which tend to be hot spots. These local hot spots seem to produce a thin layer of fluid glass in contact with the tin oxide, which breaks the film. This hot spot then propagates across the film as an arc running perpendicular to the direction of current flow.

The second method occurs on high temperature substrates such as quartz. Here, the substrate remains intact, but the tin oxide fails by increasing in resistance. It is thought that this increase in resistance is due to the re-oxidation of the reduced tin oxide. Our experience indicates that the tin oxide is stable at 650-700°C. with little if any change in resistance with time up to 4,000 hours when tests were terminated. At 750°C., a noticeable drop in useful life has occurred such that heaters are good for only several hundred hours. Above 800°C. the useful life has decreased to about 10 hours.

USES AND POSSIBLE APPLICATIONS

There is the obvious application of tin oxide films as heating elements where large area coverage is desired. In this field one must compete with well-established devices such as calrod units. I believe that the secret to becoming competitive lies in the cost of the substrate material for the tin oxide film.

For high temperature applications above 400°C., one can coat Vycor,® quartz, or ceramics such as Pyroceram. Figure 8 shows a 2½" diameter by 12 inch long quartz see-through evaporation chamber. The tin oxide is on the outside and heated by the passage of current between silver paste electrodes. We have run this assembly up to 800°C. Figure 9 shows an infrared photograph of a Vycor plate running at 650°C. The white areas are the electrodes which were masked during printing so that they could be seen. This plate has been run for 4,000 hours. It is important to note that due to the poor emissivity of tin oxide, only one-fourth of the heat energy

Figure 8
Infrared photograph of Vycor plate.

is emitted from the tin oxide surface, while three-fourths of the energy is emitted from the side of the substrate which is uncoated.

Another application which is open is that of thin film resistors for microcircuitry. Hence SnO_x is desirable because of its low coefficient resistance with temperature.

CONCLUSIONS

In my opinion, tin oxide, even though it has been around for a long time, has never attained commercial significance as a heating device. The major reason for this has been its relatively high cost compared with other heating devices. The high cost is due primarily to the substrate materials and probably not the application of the films. Experiments indicate that the coefficient of expansion is not important in this material when the films are less than 5 microns thick.

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1. R. Groth, E. Kauer, and P. C. v. d. Linden, *Z. Naturforsch.* **17a**, 789 (1962).
2. W. O. Lytle, U.S. Patent No. 2,614,944.
3. W. O. Lytle, U.S. Patent No. 2,566,346.
4. J. M. Mochel, U.S. Patent No. 2,564,706.

ELECTRONICALLY CONDUCTING GLASSES

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INTRODUCTION

The properties of oxide glasses have been studied for a very long time but it wasn't until the early nineteen fifties that it was recognized that some glasses could be made to conduct electricity by means of moving electrons rather than ions. Since that time, a great number of glasses conducting in this way have been made. The practical consequences of this discovery have, up to the present, been almost zero. The reason for this is probably the fact that the resistivity of these glasses is still rather high so they cannot replace metals as conductors, but they do have other unique properties associated with the way they conduct which could possibly be taken advantage of in special applications. The making of an electronically conducting glass has been reduced to a set of rules for combining ingredients. The logic behind these rules will become clear if we start with a discussion of ionic conductivity.

STRUCTURE AND IONIC CONDUCTIVITY

For the sake of concreteness, let us talk about glasses based on the silica molecule, SiO_2. In the crystalline forms of silica, quartz and crystobalite for instance, we know that each silicon atom is surrounded by four oxygen atoms in a very precise tetrahedral arrangement and that these silicon-oxygen tetrahedra are stacked and bonded together in a regular geometrical manner to make the crystal. The bonding is through the oxygens, each of which is attached to two silicon atoms. We think of fused quartz glass as being composed of the same basic tetrahedra, but now they are slightly distorted and arranged in a random manner with respect to each other. This kind of packing of tetrahedra is fairly open since in going from quartz to fused quartz there is a 20% increase in volume, implying the existence of appreciable empty space.

Although open, this arrangement is still strong as evidenced by the fact that fused quartz is mechanically strong and has a high softening temperature. It is also highly resistive. The glass is weakened, and thus made more workable by introducing so-called glass modifiers; sodium oxide, potassium oxide and calcium oxide for instance. The metal atoms in these compounds attach themselves to oxygen atoms and break up the bonding between the silicon-oxygen tetrahedra. These ions are quite large and tend to be located in the open spaces of the glass structure. Because they are loosely bound, they can move around in the glass, the singly valent ones, such as sodium, potassium and lithium, being especially mobile.

If a voltage is applied across a sample of such a glass, current is conducted through it by means of the mobile ions. It is apparent that if the current persists for any time, the composition of the glass will change because current carrying ions are constantly being depleted from one side of the sample while at the other side their concentration is increasing. This gives rise to two effects; the first is an increase in resistance with time arising from the fact that current carriers are constantly being removed from the glass at one electrode without being replaced at the other; the second is called "polarization" and refers to the fact that a voltage, opposite to the applied voltage, is measured across the sample when the applied voltage is removed. This polarization voltage develops because there are more current carrying ions on one side of the sample than on the other. It decays slowly upon removal of the applied voltage as the ion concentration smooths out by diffusion.

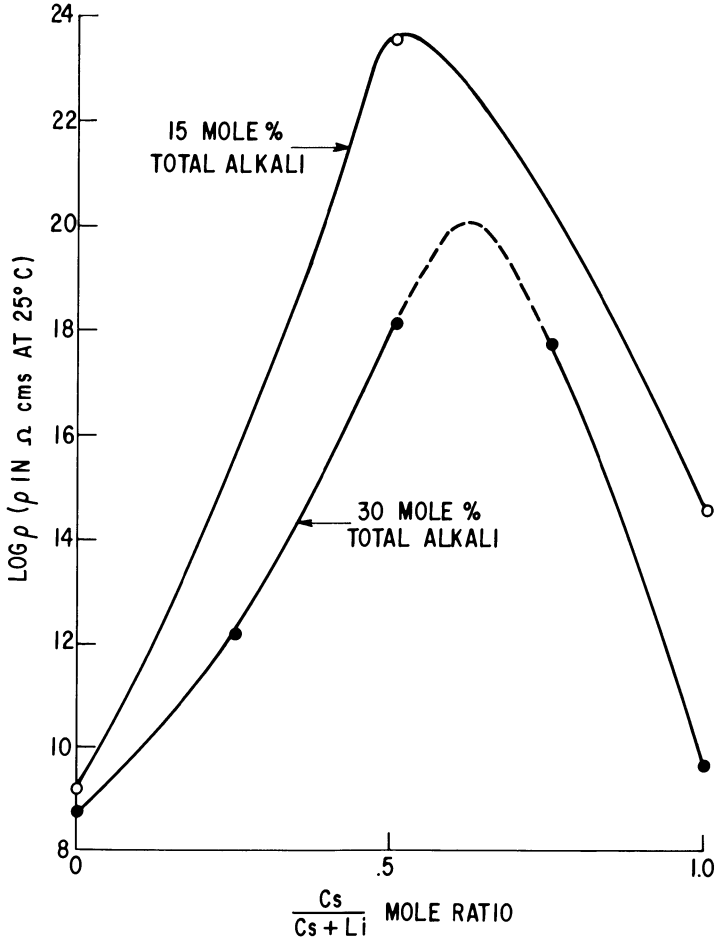

Figure 1
Room temperature resistivity versus mole ratio of cesium to lithium oxides in silica glass.

In order to make glasses that conduct by some other mechanism we must start with ones that are already very highly resistive. Such glasses are usually free of mobile alkali ions such as sodium or lithium, but sometimes we may be able to increase the resistivity of an alkali containing glass, thus making it suitable, by adding another alkali to it. This phenomenon of a glass containing a mixture of two different ions having a higher resistivity than one containing either alone is called the "mixed alkali effect" and an illustration of it is shown in Figure 1, which is a plot of some data taken by Dr. R. J. Charles of the General Electric Research and Development Center.

The curves represent the resistivity of fused quartz containing either 15 or 30 total mole percentage of lithium and cesium oxides as a function of the relative proportion of each. The end points give the resistivity when only one of the alkali metal oxides is present in the given concentration. It is apparent that a tremendous increase in resistivity is realized by splitting up the total alkali concentration between the two oxides. The reason for this effect is not completely understood. In this particular case, it may be due to the formation of two intimately mixed liquids in the melt with one being rich in alkali ions and having low resistivity but occurring in the form of very small spheres completely surrounded by high resistivity material(.1) On the other hand, adding divalent alkaline earth ions of low mobility such as calcium or barium may reduce conductivity by impeding motion of the faster ions such as sodium and potassium.

ELECTRONIC CONDUCTIVITY

However it is made, a highly resistive glass can be rendered electronically conducting by adding transition metal oxides, either singly or in combination, to it.(2,3) The oxides of iron, vanadium, nickel, cobalt, manganese and titanium have all been tried and found to work. The quantities used can be very great, up to 25 mole per cent vanadium pentoxide has been used for instance; the general rule being the lower the resistivity desired the more transition metal oxide that must be added. The resistivity limit for a given base glass is reached at those concentrations that cause the melt to crystallize on cooling instead of forming a glass. Resistivities as low as 10^4 ohm-cm at room temperature have been measured in certain vanadium borate glasses. The main reasons for believing that conductivity in such glasses does not occur by means of the movement of ions are that their resistance does not change with time as they conduct and because they do not polarize.

Table I gives a partial listing of oxide combinations that have been made into electronically conducting glasses.

One sees that each glass composition includes one of the glass forming oxides P_2O_5, SiO_2 or B_2O_3, one or more transition metal oxides and sometimes one or more glass modifying oxides. It should be apparent that, because of the wide variety of compositions that exhibit electronic conductivity, there is a good possibility of tailoring such a glass to have any softening point, viscosity, corrosion resistance, etc. that may be necessary in a specific application.

TABLE I

OXIDE COMBINATIONS THAT HAVE PRODUCED ELECTRONICALLY CONDUCTING GLASSES

$V_2O_5 — P_2O_5$
$V_2O_5 — P_2O_5 — Na_2O — BaO$
$V_2O_5 — B_2O_3 — CaO$
$V_2O_5 — Fe_3O_4 — CaO — B_2O_3$
$MnO — Al_2O_3 — SiO_2$
$CoO — Al_2O_3 — SiO_2$
$FeO — Al_2O_3 — SiO_2$
$Fe_3O_4 — P_2O_5 — CaO$
$TiO_2 — B_2O_3—BaO$
$Fe_2O_3 — B_2O_3 — SiO_2 — Al_2O_3 — CaO — Na_2O$

The details of the conduction mechanism in these glasses is not well understood but the general idea is that conduction is due to electrons hopping from one transition metal ion to another in a manner similar to that which occurs in some crystalline substances such as nickel oxide. Figure 2 is a schematic diagram of a hypothetical crystalline oxide that conducts in this way. The large circles represent oxygen ions and the small ones, metal ions. If such an oxide is made to give up oxygen by heating it in a vacuum, hydrogen or other reducing atmosphere, each oxygen on escaping from the crystal leaves behind two electrons which attach themselves to two metal ions, changing their valence from +2 to +1. These electrons need not stay on ions in the immediate vicinity of the missing oxygen but may wander around through the crystal by hopping from one metal ion to another. If a voltage is applied to the crystal, the electrons all tend to hop in the same direction and this constitutes the electric current. The same thing is believed to be happening in an electronically conducting glass. As might be expected, the number of current carrying electrons, and thus the resistivity of the glass, is strongly dependent on the number of

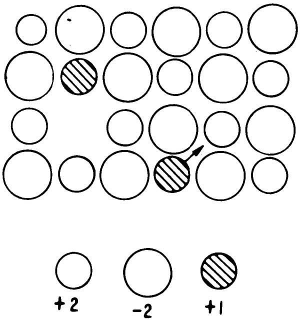

Figure 2
Schematic diagram of a hypothetical metal oxide structure containing an oxygen vacancy.

missing oxygens hence on the atmosphere in which the glass is melted and annealed. This is the explanation of the fact that the least resistive glasses of the same composition are produced in strongly reducing atmospheres. Atmosphere control during melting can also be used as a method for adjusting resistivity.

An important requirement for this type of conduction is that the metal ion in question give up or take on another electron fairly easily. This is exactly the characteristic that distinguishes the transition metals, all of which occur in at least two oxide forms. Vanadium, for instance, whose usual valence state is +5 as in V_2O_5 can also occur in valences of +4, +3 and +2.

IMAGE ORTHICON

One application in which the non-polarizing, constant resistivity characteristics of electronically conducting glass have been put to use is in the target of an image orthicon television camera tube.(4) Such a tube is shown

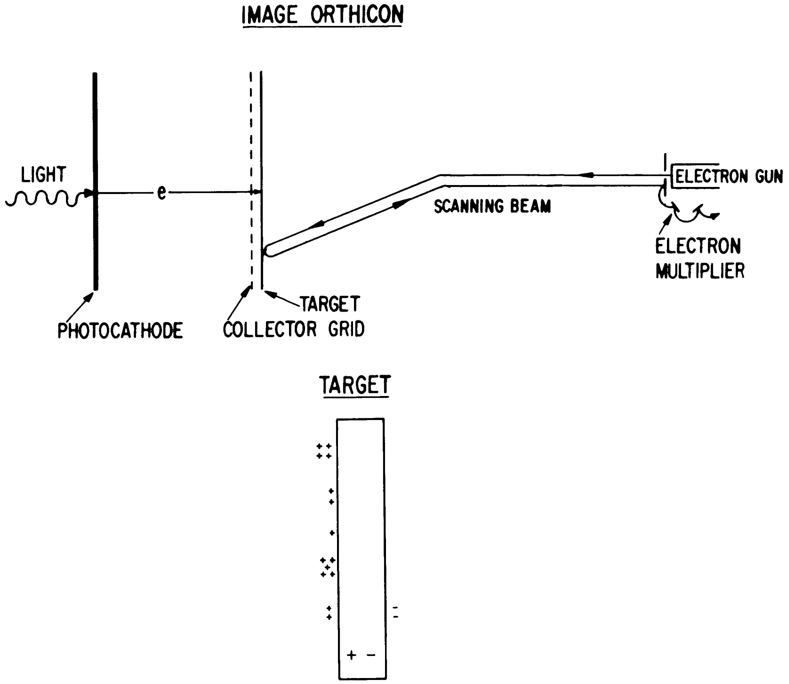

Figure 3
Schematic of an image orthicon television camera tube and blow-up of target showing charge pattern.

schematically in Figure 3. Its operation is as follows: light from the scene strikes the photocathode liberating electrons which are accelerated and strike the target. Each electron knocks off several other electrons that are collected on a grid and carried away. This process leaves a pattern of positive charges on one side of the target as shown in the blow-up, the number of charges at a given location being proportional to the amount of light coming from a part of the scene. A scanning beam of electrons is swept over the other side of the target so that it passes over each part of it 30 times a second. This beam deposits a number of electrons on each part of the target just equal to the positive charges on the other side. The return beam current is amplified and the variations due to varying numbers of electrons deposited constitutes the video signal.

The target normally is a film of soda-lime glass about a ten-thousandth inch thick and two inches in diameter. Conduction through it is by means of sodium ions so the positive charges on the photocathode side represent sodium ions that must move through the target to the electrons on the gun side to be discharged. Constant flow of ions in one direction changes the resistivity characteristics of the target so that after about 600 hours it is no longer usable because a general lack of ions on the photocathode side makes the target too highly resistive.

By making the target of an electronically conducting glass, tube life has been greatly extended. The reason for this being that there is never any lack of current carriers since the electrons knocked off on the photocathode side are constantly replaced by the scanning beam and it is they, rather than sodium ions, that move through the target.

CONCLUSION

Without going into too much detail we have attempted to give a picture of the nature of electrical conduction in glass and, in particular, to describe the general method of making an electronically conducting glass. Our main point is that if there is need for a non-polarizing glass in an electrical application when the room temperature resistivity is to be in the range 10^6 to 10^{12} ohm-cm and not change, then a basic glass having these properties can be put together easily. Also, since these properties may not be much affected by the addition of other components to the glass either singly or in combination, other properties such as thermal expansion and softening point may possibly be adjusted by such additions.

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SEALING GASES AT HIGH PRESSURES INTO STANDARD WALL GLASS TUBING

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In recent years it has become desirable in certain fields of low temperature and NMR rsearch, to seal samples of various gases into capsules of standard wall borosilicate glass tubing, at pressures ranging up to 1500 lbs./sq. in. A search of the literature produced little information regarding bursting strengths of such tubing. A testing programme was instituted in this laboratory, which was designed to indicate the pressure required to burst tubing of diameters from 6 mm. o.d. to 51 mm. o.d. Tests were also carried out on three sizes of boiling flasks.

The variations in pressures needed to burst several samples of each size of tubing were less than expected, while the average bursting pressure for each individual size was much higher than was anticipated. This paper describes the pressure testing techniques employed, and gives values for bursting pressures of a wide range of sizes of glass tubing. Details are also given of the manner in which such high pressure samples are used, and of methods of filling. A description of a novel method in sealing helium gas at 1100 p.si. into glass sample tubes is given in some detail.

The high pressures needed for the tests mentioned above were produced by a hand-operated hydraulic press, fitted with a pressure gauge reading up to 3000 p.s.i. Test samples were connected to the press by means of a 1/4″ glass pipe flange joined to each sample. These flanges were bolted to a matching brass fitting on the outlet of the press, with a neoprene gasket between the flanges. During each test run, the sample was covered by a stout wooden box as a safety precaution against flying splinters. A number of samples of each size were tested in the following set sequences:

1. The pressure was raised steadily until the tube burst.
2. The pressure was raised in the second sample to 200 p.s.i. less than that at which the first sample burst, then lowered to zero. This process was repeated three times, after which the pressure was raised until the tube burst.
3. The pressure was raised in the third sample as quickly as possible to the bursting point.

With a few exceptions, the above procedure was followed throughout these tests.

In the case of tubing up to 20 mm. in diameter, the sample almost filled with oil before bursting. Larger tubing tended to burst while still containing an appreciable amount of air. This produced a rather more violent explosion than was desirable. We overcame this problem by filling the larger samples and the boiling flasks with water, which was held in the sample by a small cork loosely fitted in the bore of the glass pipe. In

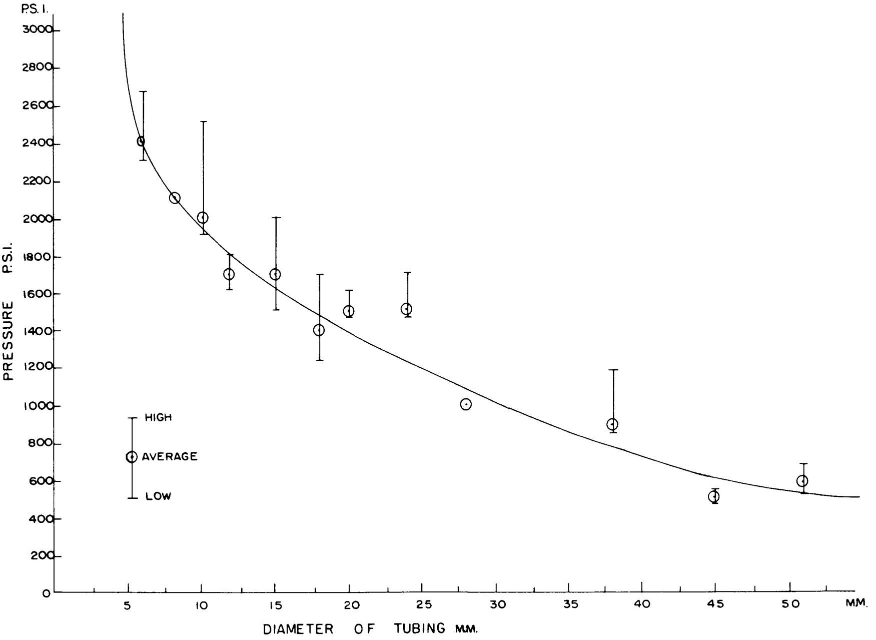

Figure 1
Results of pressure tests on tubing showing high, low, and average, values.

this manner, we economized on hydraulic oil, and also preserved the arrangement of the lab furniture.

The results of this series of tests is given in Fig. 1 where diameter of tubing is plotted against bursting pressure. The three points indicated are the average bursting pressure, and the high and low in each case. It will be noticed that the average is not necessarily midway between high and low, and that in some cases, there is a considerable variation in results. The majority of test pieces were flame annealed only, but an identical series was run with oven annealed samples, which to our surprise showed no significant difference in results. The average bursting pressures for tubing and boiling flasks are shown in Fig. 2. It must be strongly emphasized that these values do not represent pressures below which it is safe to use glass tubing as a container. The variations in results show that individual pieces of standard wall tubing vary considerably in strength. We never allow less than 100% tolerance, and take considerable precautions in handling and storing what we refer to as our "stockpile" (of bombs).

(The values given for boiling flasks should be taken as merely indicative of strength, as the variations of flask wall thickness are very much greater than those of tubing. Before performing these tests we had been very concerned about putting even 20 p.s.i. into a 500 ml. flask, and we still worry, but not quite so much.)

Dia. of Tubing M.M.	Average Bursting Pressure in P.S.I.	Dia. of Tubing M.M.	Average Bursting Pressure in P.S.I.
6	2600	20	1500
8	2100	24	1500
10	2000	28	1000
12	1700	38	950
15	1700	45	500
18	1400	51	600

Vol. of Flask in ML.	Bursting Press. P.S.I.
300	500
500	200
1000	220

Figure 2
Average values of bursting pressures for tubing and flasks.

An interesting feature of our test programme was the manner in which the tubing broke. Almost every sample broke into longitudinal strips with the cracks spiralling slightly from end to end. This gave the odd appearance of being curved from end to end, as if the tube had expanded slightly, like a balloon before bursting. Fortunately, examination showed this to be only an illusion.

The main purpose of this test series was to determine whether certain hydrocarbons could be sealed into glass capsules at pressures which would maintain the sample in liquid form at room temperature. Such gases as ethane, methane, etc. were successfully sealed into capsules in this manner and used in relaxation measurements in NMR research.

In this type of work, it was necessary to remove all oxygen from the gases being investigated. A system was developed (Sandhu, Lees & Bloom), of using a misch metal getter for this purpose. A convenient filling system was designed, shown in Fig. 3 whereby a number of capsules and a "condensing tube" were attached to a litre flask, with provision for coating the inside of the flask with a layer of misch metal, and the whole assembly then sealed to a high vacum system. The system was exhausted to a pressure of approximately 10^{-6} mm, the getter was fired, and gas introduced to slightly less than atmospheric pressure. Liquid nitrogen was used to condense the gas into the condensing tube, and the assembly then

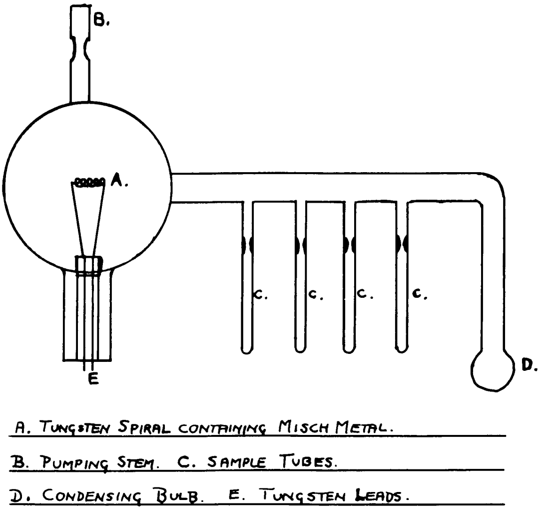

Figure 3
Apparatus used for filling capsules with hydrocarbons.

sealed off from the system. After a period of some 24 hours to allow the getter to remove the oxygen from the sample, each capsule in turn was filled to an extent previously calculated to produce the desired pressure at room temperature. It was necessary to manipulate two liquid nitrogen containers rather carefully in order to get the right amount of sample into each capsule. The process involved filling the capsule with condensed liquid till it was almost to the right level, then quickly applying liquid nitrogen to the condensing tube. This process is tricky, but with practice we were able to fill some capsules with an amount of liquid ethane, for example, which, on warming up to room temperature, completely filled the capsule.

Many different gases and liquids have been treated in this manner. On one occasion we attempted to improve our filling technique of mixtures of very volatile liquids, by weighing the amounts to be placed in the capsules, with great accuracy. We used a very accurate balance, and proceeded with much painstaking care, only to find that the evaporation rate from our sample was such that our measurements were completely invalid. We returned to our previous system of pipetting the liquids with some embarrassment.

An interesting problem arose in our Low Temperature laboratories some time ago. An experiment on film flow of helium was planned in which visual measurements were to be made of liquid helium levels. In previous experiments, a heat leak to room temperature had been present in the apparatus. To eliminate this, it was necessary to contain a measurable amount of liquid helium in a beaker contained in a sealed glass capsule. This entailed sealing helium gas into the capsule at room tem-

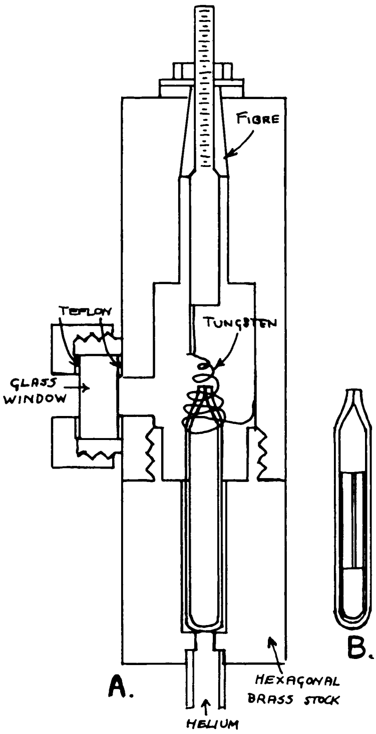

Figure 4
High Pressure chamber used for sealing helium into glass capsules at 110 p.s.i.

perature at a pressure of 1100 p.s.i. Subsequently it was possible to reduce the required pressure to 750 p.s.i. by means of a change in the container design.

The glass capsule contained a certain amount of manganous ammonium sulphate for adiabatic cooling, and a closely fitted capillary tube to act as a beaker for the actual measurements. 8 mm standard wall tubing was used for the capsule. One end was closed, then the salt and capillary tube were packed in. The open end of the tube was drawn down until the bore was approximately .2 mm, then cut to the appropriate length. The process of sealing helium into the capsule had to be carried out with the minimum of heat, in order to prevent loss of water of crystallization from the salt. Several methods were tried without success, then the apparatus shown in Fig. 4 was constructed. The capsule was contained in a brass chamber with provision for holding it centrally, and an arrangement for a small adjustment for height. Helium was introduced at 1100 p.s.i. pressure, then current was fed to the tungsten coil until the end of the capsule melted and sealed. The timing of this process was very critical, and it was found to be essential to have a window through which to watch the process carefully throughout the operation. On removal from the chamber, the capsule was placed in a strong plastic container, and normally kept therein when not in use.

There were several interesting developments during this programme. For example, we found that if the capsule made good contact with the tungsten coil at any point, this resulted in the tube opening becoming wider, rather than closing. The strength of the sealed capsule seemed to depend greatly on the symmetry of the seal. We tried a number of "blanks", of which a fair number turned out to be duds, either not properly sealed at all, or poorly sealed and eventually exploding. We had explosions ranging from 10 mins. to six hours after sealing. Consequently, the capsules used in experiments were kept for several days after sealing, before being used. Another interesting fact emerged when some of our early efforts proved conclusively that nichrome will melt very readily in helium at 1440°C.

We made some attempts to reseal some of the duds, and found that a second heating produced masses of bubbles in the sealing area. A few experiments indicated that high pressure helium had diffiused into the glass during the first sealing attempt, and reheating caused this to expand and "boil" out. This phenomenon caused us to speculate on the possibility of using this effect to introduce small amounts of specific gases into systems by impregnating glass rods with the gas under high pressure, then boiling it out into a closed system when desired. This could be said to be the opposite process to gettering.

Safety measures are very necessary in work dealing with high pressures. Plastic face masks and leather gloves, should be worn when handling capsules. When not in use, capsules should always be stored in stout separate containers. Great care should be taken to see that capsules are not inadvertently left lying around the lab, and indeed, there should be some sort of register kept of all capsules in the lab and their whereabouts. All containers should be clearly marked with warning signs. In particular, capsules no longer needed should be destroyed. Such warnings may seem trite and obvious, but are the result of long experience.

The lack of readily available information regarding the bursting strength of glass tubing is in itself a safety measure. In any batch of glass tubing, it is always possible that variations and imperfections may be found which could cause great differences in strength from one piece to another. Published figures tend to be taken at face value, without regard for variations from the average. I would like finally, therefore, to stress once more that the values given in this paper should be taken only as an indication of the strength of standard wall borosilicate glass tubing without imperfections, and not as absolute values to be relied on in all circumstances.

ACKNOWLEDGMENT

I would like to acknowledge the cheerful and able assistance of Mr. Ernest Williams in the preparation of samples and the conducting of the test programmes.

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ALKALI-FREE GLASSES

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There has long been the suspicion that alkalis, especially sodium, evolved from the surfaces of glasses containing alkalis. Until recently, almost all glasses contained alkalis. In 1955 Dr. J. Francel and Mr. J. S. Loguidice from Owens-Illinois conducted numerous tests to derive an evolution curve of sodium from a glass. Figure 1 shows this curve. It reveals a relatively low sodium evolution until the temperature reaches 950°F. (510°C.) where the evolution becomes much greater. Dr. J.

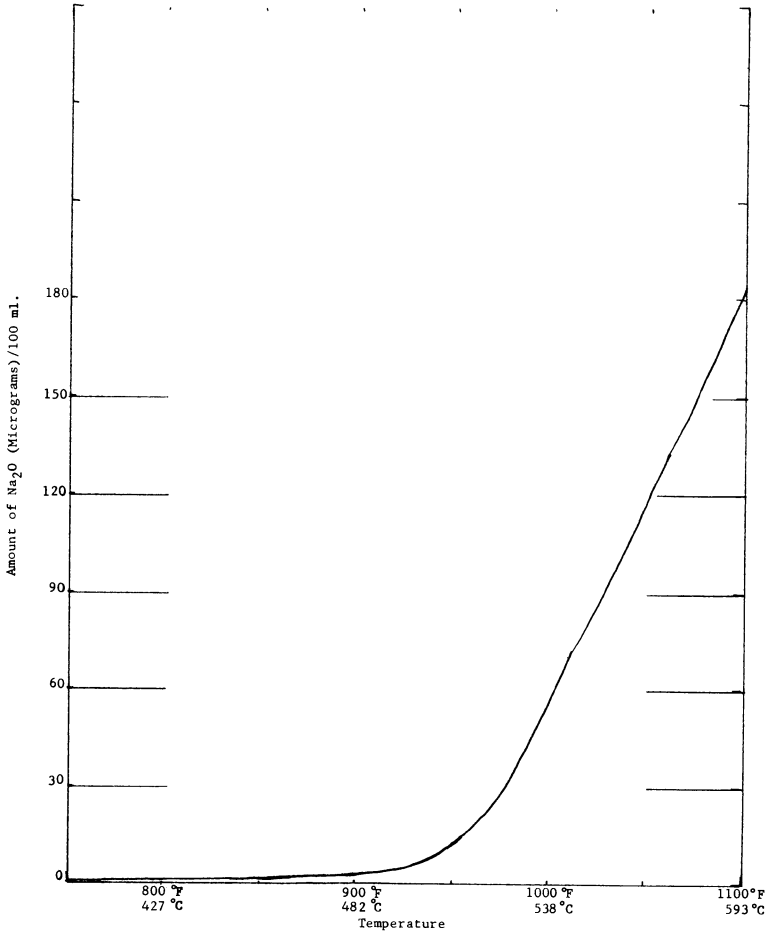

Figure 1

Francel and Mr. J. S. Loguidice covered this subject in a paper which they presented before the American Ceramic Society at their fall meeting at Bedford Springs in 1955.

As part of an alumina-silicate glass development program in the early 1950's, the alkali-free glasses EE-2, EE-4, EE-5 and EE-6 were developed by Owens-Illinois. Table I shows the properties of these glasses.

TABLE I

PROPERTIES OF EE-2, EE-4, EE-5, EE-6

OWENS-ILLINOIS ALUMINA SILICATE GLASSES

		EE-2	*EE-4*	*EE-5*	*EE-6*
Working Point, °C.		1210	...	...	...
Fiber Softening Point, °C.		955	960	1070	859
Annealing Point, °C.		755	765	820	666
Strain Point, °C.		720	730	787	634
Coefficient of Expansion (0-300°C.)		43	42	31	51
Contraction Coefficient		...	...	40	...
Density		2.59	2.58	2.57	2.60
Refractive Index		1.55	1.55	1.53	1.55
Volume Resistivity	250°C.	13.2	13.7	...	...
	350°C.	11.7	11.6	...	...
Dielectric Prop.:					
60 Cycles	K	6.3	...	6.0	6.6
	Δ%	.1	...	.66	.3
	Loss Factor %	.6	...	4.0	1.9
1 Megacycle	K	6.2	...	5.9	...
	Δ%	.2	...	.25	...
	Loss Factor %	1.2	...	1.5	...
USP XVI Durability		.9	.64	.2	1.0
Seals to		Moly	Moly	Silicon	Kover®
Glass Type		Alumino-Silicate	Alumino-Silicate	Alumino-Silicate	Alumino-Silicate
Special Note		Alkali & Boron Free	EE-2 + Cerium	Alkali & Boron Free	Contains Lithium

They cannot be produced by normal production processes. New developments in drawing processes are needed before these glasses can be marketed. Widespread interest in these glasses has created the need for developments to circumvent these production problems, which will eventually be overcome.

In 1961 and 1962 the Kimble Division of Owen's Illinois undertook the development of an alkali-free glass which could be sealed to the Iron-Nickel-Cobalt (Kovar,® etc.) type of metal. It was not believed that lithium would be a problem. A completely alkali-free glass, which Owens-Illinois had available in 1961, (61-434E) was believed to be satisfactory because it had a low stress when sealed to Kovar. A melt in tubing form was made and seals could not be made to Kovar without cracking. When the expansion curves of the glass and Kovar were compared, it was determined that a high temporary stress developed during the cooling (annealing) of the seals. The temporary stress was estimated to be around 4000 psi. Figure 2 shows these expansion curves. The first experimental seal apparently did not crack and the resultant low final seal stress looked satisfactory. It was therefore necessary to return to the drawing board and develop several lithium-containing glasses which make a good seal to Kovar. A lithium-containing glass for sealing to Molybdenum was also developed. These glasses were marketed under the codes EN-4 and EN-5, respectively. Table II shows the properties of these glasses, and EN-1, the glass developed for Kovar sealing for the electronics industry. There is no advantage to the lithium-containing glasses over EN-1, however, because our postulate that lithium would not be detrimental was incorrect. EN-1 is a better glass because of durability and availability. For some time after this project, activity on the alkali-free glasses was at a low level.

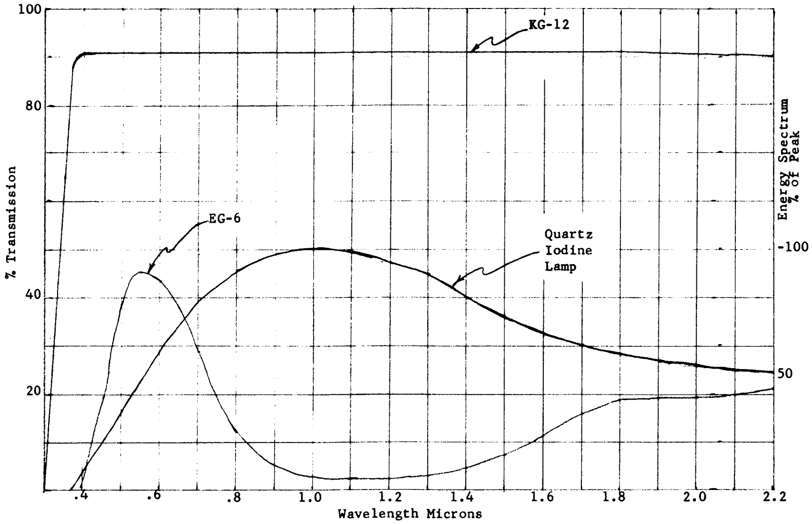

Figure 2

Recently the desirability of alkali-free glasses has again become evident. In 1964 Mr. R. T. Borawski of Bell Telephone Laboratories at Allentown, Pennsylvania presented a paper that was abstracted in the Electrochemical Society Journal III (1964). In this abstract, Mr. Borawski provided evidence by both x-ray and mass spectrometric techniques that sodium, potassium, etc. were detrimental, degradating the silica of silica pro-

TABLE II

PROPERTIES OF EN-5, EN-4, EN-1

OWENS-ILLINOIS GLASSES

		EN-1	*EN-4*	*EN-5*
Working Point, °C.		1115	957	1024
Fiber Softening Point, °C.		710	709	772
Annealing Point, °C.		480	552	592
Strain Point, °C.		445	528	562
Coefficient of Expansion		47	51	43
Contraction Coefficient		61	. . .	. . .
Density		2.28	2.50	2.53
Refractive Index		1.48	1.54	1.55
Volume Resistivity	250°C.	9.0	8.1	8.2
	350°C.	7.2	6.5	6.6
Dielectric Prop.:				
60 Cycles	K	5.1	6.6	6.7
	△%	.7	1.2	1.2
	Loss Factor %	3.8	8.1	7.9
1 Megacycle	K	5.1	6.3	6.4
	△%	.26	.4	.4
	Loss Factor %	1.3	2.5	2.7
USP XVI Durability		2.8	1.4	. . .
Seals to		Kovar®	Kovar®	Moly
Glass Type		Borosilicate	Aluminoborosilicate	Aluminoborosilicate
Special Note		Contains Alkali	Contains Lithium	Contains Lithium

tected silicon bodies. Other investigations corroborated this, leading to a more intensive search for alkali-free glasses. These investigations are still underway. Considerable effort on modifying EG-3 (a medium expansion high lead glass) was successful in producing alkali-free glasses that made fair seals to Dumet and #4 Alloy. However, we encountered some potential production problems and have not as yet released these glasses. Table III shows the properties of EG-3 and some modifications. The properties of KG-12 and EG-6 are also shown on this table for comparison purposes. EG-6 is an infra-red absorbing modification of KG-12.

For several years we have been selling the two alkali-free vitreous solder glasses SG-7 and SG-67. These lead-zinc-borate glasses were developed in the mid-50's for sealing color TV bulbs before the advent of the crystallizing types of solder glasses. SG-7 seals to Kovar and is also a glaze for alumina. SG-67 seals to 90 expansion materials. Table IV shows the properties of these glasses, and SG-68 (a companion glass).

TABLE III

PROPERTIES OF EG-3, G-3118, EG-6 AND KG-12

OWENS-ILLINOIS GLASSES

		EG-3	*G-3118*	*KG-12*	*EG-6*
Working Point, °C.		...	...	980	970
Fiber Softening Point, °C.		557	...	632	625
Annealing Point, °C.		448	425	433	435
Strain Point, °C.		...	398	400	395
Coefficient of Expansion (0-300°C.)		79	88	90	90
Contraction Coefficient		...	...	102	109
Density		...	...	3.05	3.08
Refractive Index		...	...	1.56	1.58
Volume Resistivity	250°C.	...	...	9.9	9.9
	350°C.	...	...	7.8	7.9
Dielectric Prop.:					
60 Cycles	K	...	...	6.8	...
	Δ%	...	...	.2	...
	Loss Factor %	...	...	1.4	...
1 Megacycle	K	...	...	6.7	...
	Δ%	...	...	.15	...
	Loss Factor %	...	...	1.0	...
Seals to			#4 Alloy Dumet	#4 Alloy Dumet #52 Alloy	#52 Alloy #4 Alloy, etc.
Glass Type		Lead	Lead	Lead	Lead & Iron
Special Note					Green Color IR Absorbing

Our latest endeavor in the alkali-free glass area has produced the low expansion copper glasses. These glasses make excellent seals with fused silica and with low expansion CER-VIT® materials. They will be discussed in other papers.

Late last year some evidence was obtained by several researchers outside Owens-Illinois that the alkalis may not be as big a problem as originally interpreted. We are working with several organizations on these new approaches.

We do not know where investigations of the alkali-free glasses will take us. A paper by Dr. B. Sunners and Mr. B. Narken of IBM entitled "Preparation of Alkali-Free Silicate Glasses" points out the many difficulties encountered in melting high purity alkali-free glasses. This paper was published in the *American Ceramic Society Bulletin,* Vol. 44, No. 8, on August 7, 1965. The surface passivation techniques for silicon developed within the last few years may eventually negate the need for alkali-free materials in electronic devices.

TABLE IV

PROPERTIES OF SG-7, SG-67 AND SG-68 OWENS-ILLINOIS SOLDER GLASSES

		SG-7	*SG-67*	*SG-68*
Working Point, °C.		. . .	485	485
Fiber Softening Point, °C.		572	441	416
Annealing Point, °C.		471	366	354
Strain Point, °C.		443	346	334
Coefficient of Expansion (0-300°)		46	82	90
Contraction Coefficient		56	107	115
Density		4.07	5.38	5.89
Volume Resistivity	250°C.	11.3	11.1	10.6
	350°C.	9.3	. . .	. . .
Dielectric Prop.:				
1 Megacycle	K	8.2	12.5	14.8
	Δ%	.8	.15	.16
	Loss Factor %	6.6	1.9	2.4
Glass Type		Kovar® Alumina	90 Exp. Materials	
Seals to		Lead-Zinc-Borate	Lead-Zinc-Borate	Lead-Zinc-Borate

PROTECTIVE VALVE FOR GLASSBLOWERS*

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In two instances the glassblower is not allowed to blow directly into his glasswork during fabrication—first, where the glassblower must be protected from radioactive or toxic material in the glassware which may reach his mouth or lungs through his mounthpiece and secondly, where the glass work itself must be protected from the moisture and oxygen content of the glassblower's breath in the fabrication of his glass apparatus.

Several types of valves have been designed in recent years for glassblowers, but most of these valve designs have inherent disadvantages. One such valve, for example, is hand operated and thus deprives the glassblower of the use of one of his hands.[1] Another is operated with the glassblower's breath pressure; the pressure inside his glasswork, however, is not proportional to the pressure being applied to the mouthpiece[2]—because of this the glassblower loses some control over his work. Furthermore, most valves that have been developed do not allow the glassblower to apply suction or negative pressure to his glasswork.[3]

The valve to be described here overcomes these disadvantages and gives the glassblower the same precise control in applying positive and negative pressures that he would have if he were applying these pressures directly to his glasswork; at the same time he is safely separated from his glasswork since his breath is replaced by an inert or reducing gas. This valve design has been used successfully by several glassblowers in laboratories at Wright-Patterson Air Force Base since 1965. The glass apparatus fabricated with the aid of this valve is not contaminated, and the metal parts are not oxidized. A patent is pending on this device.

Figure 1 gives a cross section of the valve. A soft rubber bellows (1) and a sliding valve (2,3) are mounted inside a leakproof container (4). Three tubes (5,6,7) are connected to the valve cylinder (2) at different heights so that when the valve piston (3) is moved up and down, only one tube at a time is open through the hollow piston to the container (4). The glasswork is signified by the bubble (10); however, during actual operation, a flexible hose is provided between tubulation (9) and the glasswork.

When the valve is being operated, the glassblower connects his mouthpiece with flexible tubing to hosepiece (8); tubulation (7) is connected to a pressure regulator which is set to a few psi. Any inert gas such as nitrogen or forming gas may be used. Tubulations (5) and (6) are left open to the atmosphere or, if necessary, connected to an exhaust. If the glassblower wishes to work with negative pressure, tubulation (6) must be

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*Information contained in this paper is the result of research performed within the Electronic Research Branch, Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio. U.S. Air Force Office of Aerospace Research Project 4152 is the programming authority for this work.

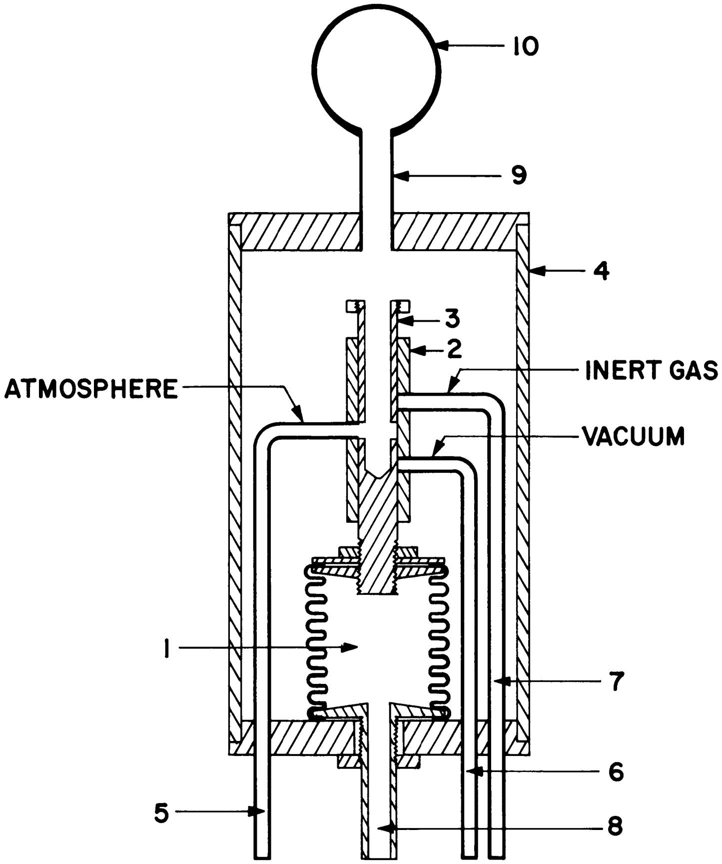

Figure 1
Cross Section of Valve

connected to a suction pump. If no positive or negative pressure is applied to tubulation (8), the bellows (1) and valve piston (3) remain in their initial position (indicated in Fig. 1), and the pressure inside housing (4) and the glasswork (10) will be equal to the pressure of the outside air.

If the glassblower wishes to expand the bubble, he blows into his mouthpiece with the same pressure he would normally use. The bellows expands, and the piston moves upward. Tubulation (5) is now closed, and tubulation (7) is opened to the chamber. Inert gas enters the chamber, and the bubble expands. When the pressure in the chamber reaches the pressure in the bellows, the bellows moves back a little and the piston closes tubulation (7) cutting off the gas flow. If the glassblower wishes to reduce the pressure in the bubble, he releases some air from his mouthpiece in the usual way. Then the pressure in the chamber is greater than the pressure in the bellows; the bellows is compressed further, the piston assumes its initial position, and gas from the chamber escapes through tubulation (5) until the pressure in the chamber equals the pressure inside the bellows. In this way the pressure in the chamber and also in the bubble will always be equal to the pressure in the bellows.

This holds also for negative pressure. When the glassblower sucks on his mouthpiece, the bellows is compressed by the gas in the chamber. The piston closes tubulation (5) and then opens tubulation (6) which is connected to a suction pump. The pressure is reduced in the chamber and in the bubble until it equals the pressure inside the bellows. Should the pressure in the chamber become lower than that in the bellows, the bellows will expand and close tubulation (6) again.

If the valve is operated with a suction pump, tubulation (5) cannot be left open to the atmosphere. It may be connected, for example, to a plastic bag partially filled with the inert gas. This bag should have a relief valve to allow the excess gas to escape when the bag is full.

Both the valve and the glass apparatus being fabricated must be flushed with the inert gas before the glass parts are heated. If a constant flow of the inert gas is desired, a small needle valve can be incorporated easily within the housing (4); this will allow some gas from tubulation (7) to leak into container (4). An easier way to achieve this small constant flow of gas is to fit the valve piston (3) with an additional small clearance inside valve cylinder (2). The pressure in both cases will be only a fraction of an inch of water since tubulation (5) allows excess gas to escape.

This valve also facilitates the fabrication of large-volume apparatus since the glassblower must give only a positive or negative pressure signal to the valve instead of controlling the pressure within the large vessel with his breath pressure.

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1. Bartl, K., U.S. Pat. 1,556,985.
2. Clarke, C. M., U.S. Pat. 900,914.
3. Rudolph, P. S., *Rev. Sci. Instr.* **35**, 1237 (1964).

A GLASS LASER COUPLING REFLECTOR

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INTRODUCTION

In the course of designing laser equipment, it becomes necessary to design and fabricate a glass laser reflector to be used as a coupling between light source and laser crystal. This reflector consists of a double walled jacket made with two concentric glass tubes and side ports sealed through to the interior for coolant fluid forming a closed body with a cooling chamber at the center. With a suitable solid material in the jacket, this assembly was found superior to other laser coupling reflectors.

In the fabrication of the glass coupling reflector, the inner jacket is made of precision bore glass tubing sized to admit a xenon flash lamp and a laser rod assembly. The assembly, which houses the lamp and rod in a fixed position, is supported by two end plugs which are machined to fit the inner glass jacket and to form a closed chamber. The ring seal for the side ports also serve to join the inner and outer tube forming the jacket and keep these tubes concentric.

The inner tube is also used as a coolant carrier for the xenon flash lamp. The sealed port holes are made of standard wall glass tubing. Coolant can be delivered at a rapid rate so that the flash lamp can be used in in a rapid fire manner. Magnesium oxide is packed in the space between the inner and outer tubes to serve as a reflective material.

FABRICATION OF THE REFLECTOR

A sketch of the glass reflector body is shown in Fig. 1. In construction of the inner glass tube of the jacket, (cooling chamber), precision bore glass tubing (.0750 ±.002 in.) was used. The tubing was cut oversize (7 - 8 in.) in order to provide a holding area while fabricating the two ports. The ports are located in the tube wall by measuring from one end of the tubing to a starting point and then to the other location, the openings being 4¼ in. from one another center to center.

The ports were made intentionally small (⅛ in. diameter) in order to prevent distortion of the tube wall, which would cause difficulty in the insertion of the xenon flash lamp and laser rod assembly. The tube was then placed in a "tee" jig (Fig. 2) and the ends of the ports were flared to about ¼ in. by means of a ⅛ in. carbon rod pointed at one end. With the tube rotating, the rod was placed against the edge of the hole as soon as the glass was heated sufficiently. Flaring of the hole prevents distortion and gives a lip edge to use while sealing to the inner surface of the outer tube. The height of the flare must be carefully adjusted because of the necessity of fitting the inner tube into the outer and to prevent cracking

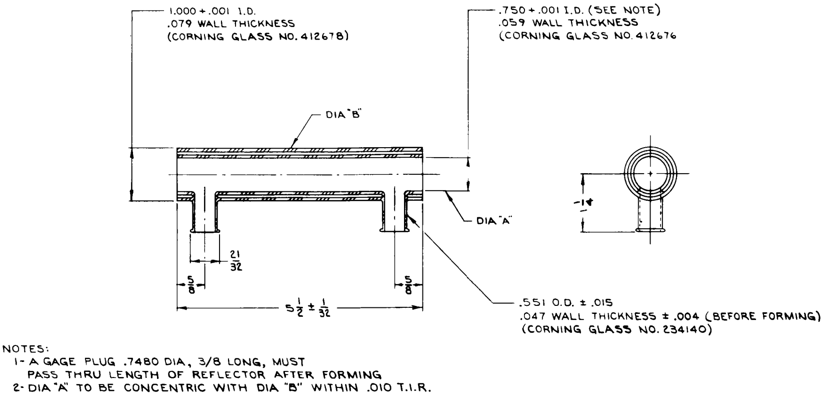

Figure 1
Glass laser reflector body.

while the ports are being sealed to the outer tube. The tube was then cut and ground on both ends to obtain a distance of ⅝ in. from either end to the center of the nearer porthole.

Next, it was necessary to fasten lengths of glass tubing to the flared holes. Five to six inch lengths of 14 mm (outer diameter) were used. The

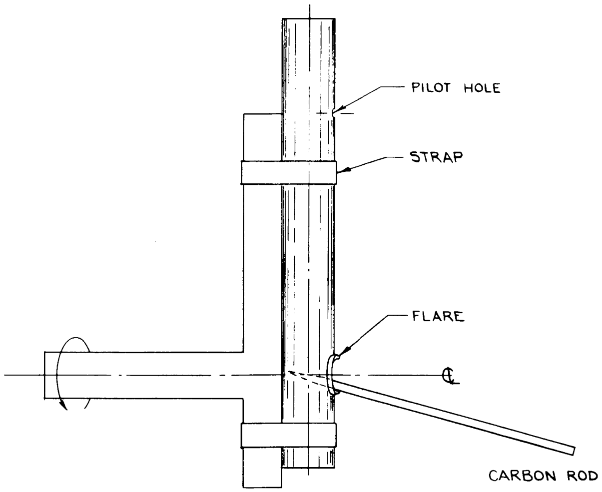

Figure 2
Tee jig.

tubes were heated at one end and, with a pointed carbon rod, were flared to 16 mm. This was done in order to surround and seal the ports at each end of the flared holes by means of a ring seal.

A piece of precision bore tubing for the outer tube jacket was cut oversize. This piece of tubing is approximately 8 inches long and 1 inch in diameter. This tube must slide over the inner tube and flared ports with a precise clearance between the two tubes of 2 mm within .010 T.I.R. (Total Indicated Reading). This 2 mm clearance is maintained by a graphite spacer until the apparatus is assembled. This spacer was made from a 1 in. diameter graphite rod and held to tolerance as shown in Fig. 3. (Note: The hole in the center of the graphite spacer was used for blowing air into the inner jacket to make the ring seal at the flares. Three flats were cut on the edge of the graphite plug to allow air to pass into the space between the two tubes.

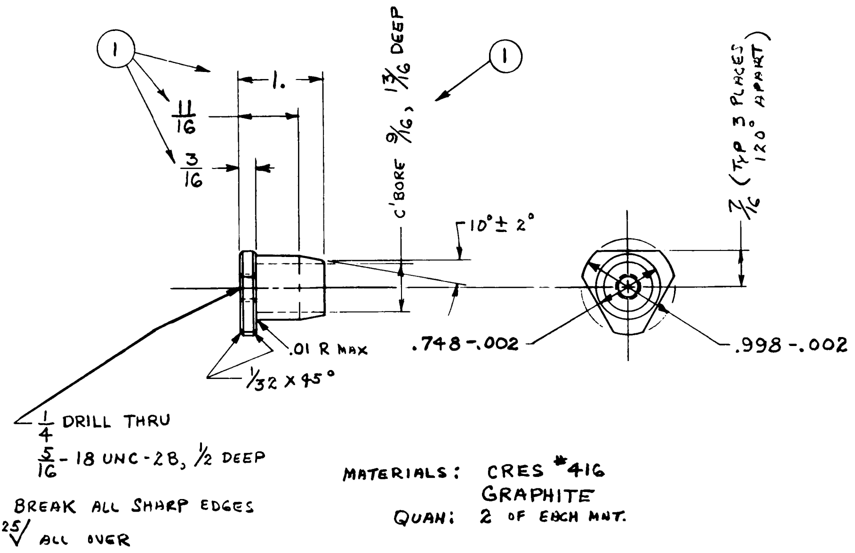

Figure 3
Graphite plug.

A jig was fabricated from a block of wood 1½ in. × 2 in. × 5½ in. (Fig. 4). Two holes were drilled through the 1½ in. side. A center hole was drilled to the opposite side of the two ¼ in. holes. The center hole was ⅛ in. in diameter while the other two were 4½ in. apart and had a diameter of 14 mm. The block was then cut through the holes producing two grooved halves. The use of a ⅛ in. nut and bolt made this an easily usable jig for holding the 14 mm glass tubing in position for fabrication.

Collars and stoppers at the ends of the outer jacket were used to make the seals for glassblowing. A collar was made from .030 in. thick asbestos

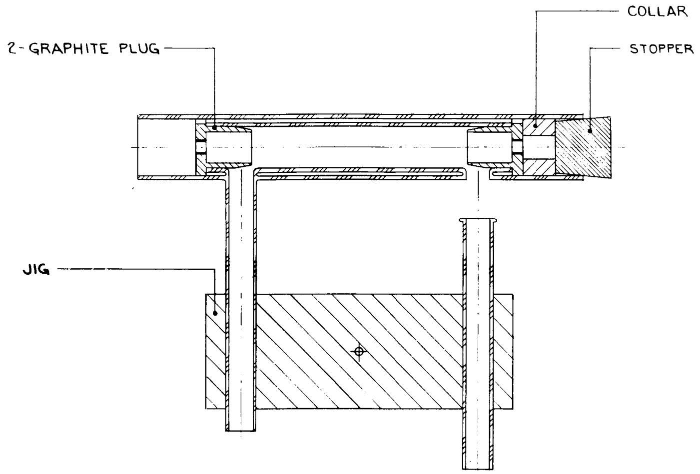

Figure 4
Glass laser reflector body jig assembly.

paper and was cut to fit in front of the rubber or cork stopper and the two were inserted into the end of the tube together. The jig glass assembly, graphite plug, collar and stopper, are shown in Fig. 4. The paper must not touch the inner jacket or it might produce stresses and strains during glass blowing and produce cracking during cooling.

Next, the inner jacket was inserted into the outer glass jacket and the graphite plugs were put into one end. The collar and stopper were placed in the same end to hold the inner jacket in a fixed position. Then heat was applied to make a seal at the point where the flare on the inner jacket rested against the inner surface of the outer jacket. The flare was worked in and out while hot in order to make a positive seal. After sealing, the piece was kept warm and, with a hotter flame applied at the outer surface where the seal was made, a hole was blown through the outer jacket.

While still keeping the area hot, a previously prepared (flared) piece of glass tubing was preheated, brought up to the same temperature as the port area, and was applied to the hole in the outer jacket. The temperature of both was increased and a seal made, providing an opening through the tubing and the outer wall into the inner wall. The flame was then lowered and the area was kept at a lower temperature for a while in order to reduce stresses and strains set up by making the ring seal.

The next step was to keep the piece warm while the other collar and stopper were put in place, and the assembly mounted on the wooden jig (about 2 in. clearance between jacket and wood) with the sealed tube through one of the 14 mm holes and the flare hole in the jacket above the other 14 mm hole (See Fig. 4). The whole outer jacket was warmed slowly. The second set of seals was made like the first except that in this case, the blowing was done through the first port rather than through an end opening.

After these seals were made, all supporting structures were removed and the piece was put into an annealing oven which was preheated to 350°F. and set to reach the annealing temperature of 1050°F. slowly. The double walled glass reflector was removed after annealing and a cap gauge inserted to check for error. The cap gauge was inserted into each end and rotated to assure that the 2 mm clearance was true. Then the space between the inner and outer walls was packed with MgO powder.

This reflector with the double glass wall is considered outstanding for the following reasons:

a. Dielectric properties of the glass are more suitable to high voltage (30KV) xenon flash lamp than other reflector materials.

b. The cooling is physically isolated from the reflector material.

c. Material compatibility problems are eliminated. Glass is unreactive especially retaining optical properties at glass-fluid interface over long periods of time. There is no corrosion.

d. Low thermal expansion coefficient results in greater environmental stability (tolerances).

e. The design permits a leakproof seal for the MgO powder (ends sealed with elastomer).

f. Glass is amenable to optical cleanliness requirements.

g. The assembly is less expensive than other reflector designs when long range stability and maintenance problems are taken into account.

Figures 5 and 6 show the unassembled and assembled laser with reflector.

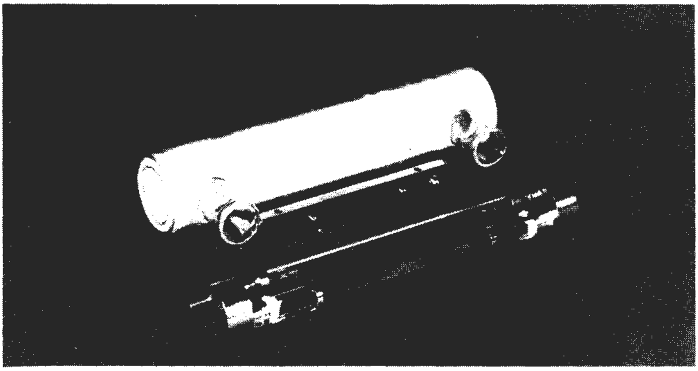

Figure 5

Laser and reflector body unassembled showing flash tube and laser crystal.

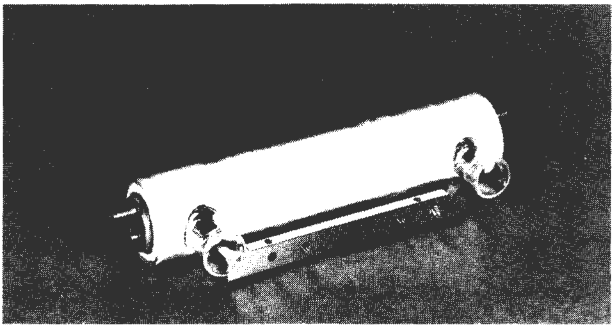

Figure 6
Laser assembled.

CENTRIFUGING GLASS TUBING

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INTRODUCTION

The discovery of centrifuging glass tubing was first revealed at the Second Symposium of the British Society of Scientific Glassblowers, during the discussion period at a lecture, given by Heathway Engineering Company on glass working lathes.

Long before this, most prominent glassblowers realized that tubing of large diameters, (above 4″) had a tendency to increase in diameter, whilst it was being turned on their lathes, but only a few had thought about adopting this technique to form shapes, and indeed opinions were expressed as to what might happen if one were to throw hot glass about at high revolutions. However, four known glassblowers set about this challenge to control glass and adopt a new technique of centrifuging.

At present, no known figures have been written up on this subject. Being one of the few who have achieved some results and compiled some data, I wish now to present such data to this Symposium. The details being presented will, it is hoped, further the knowledge of the scientific glassblower and benefit the glassblowing world as a whole. In addition, it introduces the principle used to obtain and form pre-determined shapes in glass tubing with methods that are both repetitive and time saving.

Figs. 1 and 2 help to present a picture of what speeds, tools, machinery and flames were required to ascertain the information and the details now available.

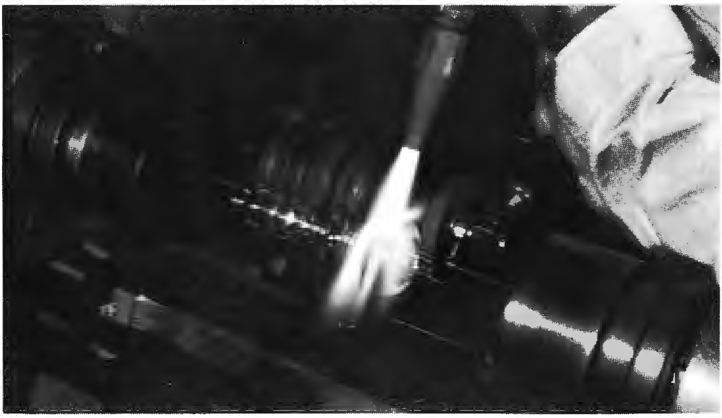

Figure 1

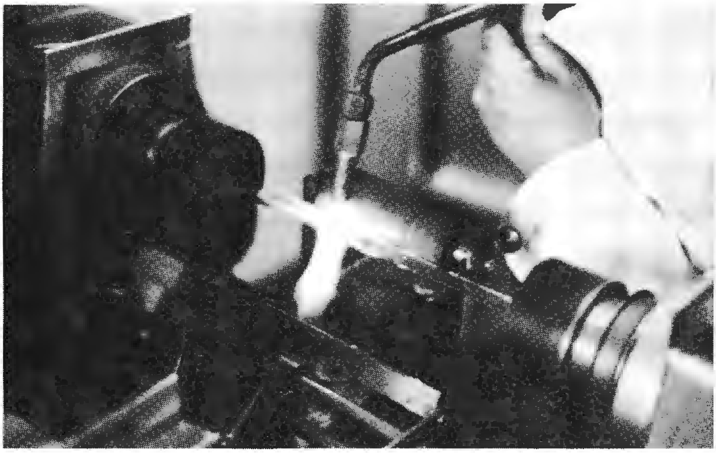

Figure 2

The graph (Fig. 3) gives an indication of centrifuging speeds required to throw varying diameters of tubing into shapes.

PRINCIPLE OF OPERATION

To form pre-determined shapes in glass tubing (without the aid of blowing) by revolving it at very high speeds, which, when heated, will be centrifuged in an outward direction, to be controlled by and conform to the shape of the machined carbon roller.

METHOD AND PROCEDURE

The glass tubing to be shaped is placed between the head and tail stocks of the lathe, the appropriate carbon roller being selected and placed in carriage in the required position.

The lathe is revolved at low speed to allow pre-heating of glass and to align the tube if necessary. The speed is then raised to the centrifuging speed of the glass diameter. (See graph). A hot softening flame is then applied at one end of the tube. The glass on becoming soft will then centrifuge on to the carbon which will rotate on contact with the glass. The flame is then run along the length required to complete the shape. Care must be taken that the glass does not become overheated as this leads to the overlapping of glass and uneven wall thickness.

Most satisfactory results were obtained by only one application of heat, attempts to reform by reheating resulted in disturbance of and uneven wall inside, although the outside surface remained reasonably true.

MACHINE AND TOOL DETAILS

The lathe being used in my department has been modified from an old engineering lathe to a glass working lathe, by adding a tail stock and

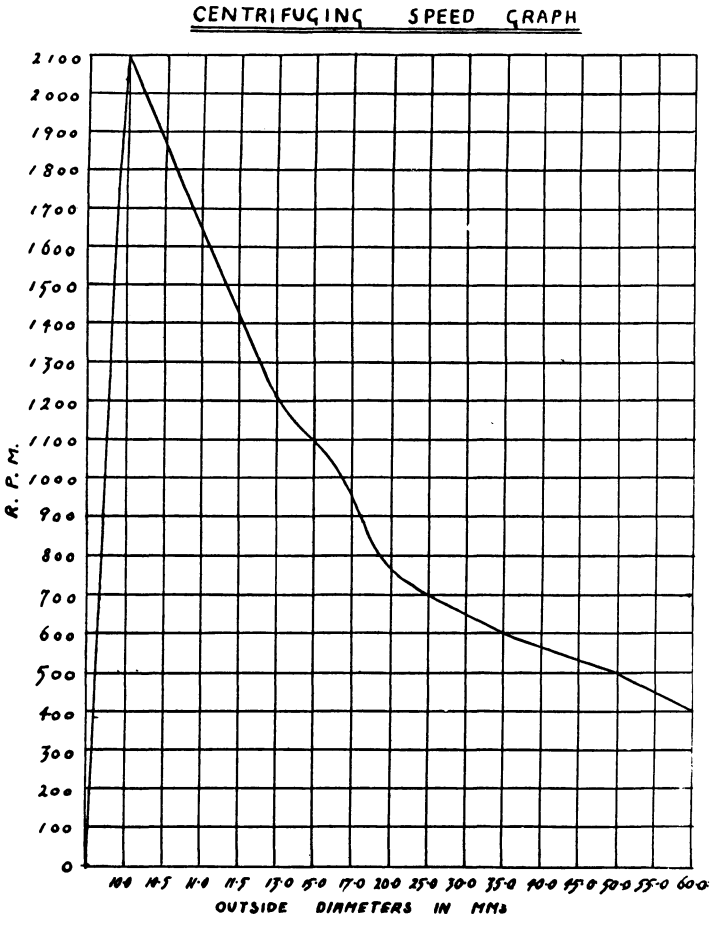

Figure 3

drive. A Kopp Variator was introduced between the drive motor and centre shaft to enable variation in speeds. Details of the modification can be given to anyone requiring them.

The lathe I have here for demonstration purposes has been specifically manufactured by Heathway Engineering Company, who are well known throughout the world. It has been designed for high speed, precision work, and has a speed range of 60 - 2000 r.p.m. with a 2″ maximum through head and tail stock.

The carbons which are high grade CY 9 have been drilled and fitted with bearings, which have been "doctored", by running them in with fine grinding paste for 10 minutes. This is to allow for expansion of the races; to prevent them seizing up on becoming hot.

The burner used is a Jet 7 surface mix type, using butane at 12 lb./sq. in. and oxygen at 25 lb./sq. in. approximate temperature of flame 2,100°C.

EXPERIMENTS AND RESULTS

It has been found that tubing under 10 mm in diameter tends to constrict, no centrifuging takes place up to 2,100 r.p.m., it is generally thought that much higher speeds would be required, but lathe prevented this. However, on 10 mm tubing a humped-back effect took place which indicated that this was the minimum diameter which could be moved at 2,100 r.p.m.

TABLE I

CENTRIFUGING SPEED TABLE

Tubing diameter m/ms	*Speed r.p.m.*
10.0	2100
10.5	1875
11.0	1650
11.5	1450
13.0	1200
14.0	1150
15.0	1100
17.0	950
20.0	750
25.0	700
30.0	650
35.0	600
40.0	575
45.0	525
50.0	500
55.0	450
60.0	400

Experiments quickly established that the larger the diameter of tubing the less revolutions were required for centrifuging, although no set pattern was arrived at (see graph).

Practically any shape applied to the carbon could be formed on the glass, but it must be appreciated that the further the glass is extended outwards the less the wall thickness becomes.

Attempts to thicken the wall by the conventional method of bench hand glass working, resulted in uneven wall thickness on the finished products, but in most cases the outside wall was formed true. It is better to calculate the necessary requirements and use a heavier walled glass, than try and thicken up during the operation.

EXAMPLES

1. A piece of 17 mm Pyrex tubing was placed in chucks, carbon roller locked in position 4 mm away, the glass pre-heated at low speed, r.p.m. increased to 900, hot flame applied, glass centrifuged to meet roller, the flame was moved along the glass for 5″ to produce an expanded tube of 25 mm diameter, test showed a tolerance of 0.05 mm.
2. A more ambitious attempt was then made to produce skirted cones. To do this, carbon roller was machined to correspond to two B19 extended cones—end to end. Using 17 mm tubing preheating etc., was carried out, but before centrifuging, the centre of the tube was drawn to a lower diameter to facilitate the shaping of the skirted section.

   The roller was then correctly positioned against the shanks to rotate the carbon. At 900 r.p.m. the flame was applied, starting at one end and carrying along until both cones and skirts were centrifuged. Excellent results were obtained, with close tolerances. After parting, the cones were ground with one grade of carborundum only. This was a finishing grade of 450 mesh.

   Two cones were completed from start to finish in 2 minutes 10 seconds including grinding. No rocking was visible with or without lubricant. The operation is repeatable. Other items produced included syringe barrels, side arms (double), bulbs of varying sizes (pear, round, etc.) buttons, square sections and tapers.
3. Threading glass tubing presented a small problem of overlapping which was overcome by using an opposing thread to the one required, an experiment took place on these lines: a piece of 54 mm tubing was placed in chucks and pre-heated, a carbon roller of 54 mm diameter with a left hand thread 3 mm deep and 4 turns to 25.4 mm was placed in carriage, speed at 500 r.p.m. glass centrifuged giving right hand thread of equal dimensions. Little or no distortion. For threading, carbon and glass diameters must be equal.

TABLE II

By centrifuging lathe	*Time*	*Results*	*By Hand*	*Time Reduction*
Double side arm	60 secs	Good Constant	240 secs	180 secs 75%
Tapered bulb and round bulb	51.5 secs	Good Constant	480 secs	428.5 secs 89%
3 buttons and 3 increasing diameter bulbs	61.5 secs	Very good Perfectly true	480 secs	418.5 secs 87%
5″ expanded cylinder true outside diameter to 0.50 mm	37 secs	Very good Constant	No time difficult under present conditions	100%
Syringe plungers	36 secs	Very Good Constant	No time difficult under present conditions	100%
Screw thread 4 turns × 25.4 mm	84 secs	Excellent Constant	No time difficult under present conditions	100%
Double B19 extended cones	79.5 secs	Very good Constant	300 secs	220.5 secs 73%

Obvious allowances for expansion of glass and carbon have to be made before setting up to do a run of jobs.

Carbon rollers have to be kept accurate, it is plain that for repetitive work it is advisable to have more than one set of rollers.

It is found that a great deal depends on the operator, but as the technique can easily be acquired, semi-skilled operators can be trained for the work.

Centrifuging glass has a challenging potential throughout the industry and lends itself to many applications previously lengthy and not completely repetitive. It has tremendous possibilities, which, I am sure, will be widely explored in future and it is hoped that the information presented will contribute towards the further development and application of this new technique.

The Author wishes to acknowledge his colleagues, Mr. K. B. Hughes and Mr. G. Hepburn, for the invaluable suggestions that they have contributed; Mr. A. A. Ross for the construction of the original lathe and carbons; Mr. M. B. Payne for the slides; Heathway Engineering Co. Ltd., for supplying the newly designed precision lathe; Fisons Pest Control Limited for permission to present and publish this paper.

IN ATTENDANCE

The following are on record as having attended the Eleventh Symposium on the Art of Glassblowing held at the Statler Hilton Hotel, Boston, Massachusetts, June 8, 9, 10, 1966. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

In addition to the names listed herein, 39 persons registered by Day Card, and 129 to attend the Exhibit only.

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