INVESTIGATION OF THE KINETICS OF CRYSTALLIZATION OF MOLTEN BINARY AND TERNARY OXIDE SYSTEMS

G910373-10

by

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Molten Binary and Ternary Oxide Systems

Summary and Quarterly Status Report No. 10

Contract NASW-1301

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Contract No. NASW-1301

SUMMARY

This report is based on the work done in the last nine month period of Contract NASW-1301, June 1, 1967 through February 29, 1968. The contract commenced on September 1, 1965 and other summary reports similar to this report were issued September 30, 1966 and June 30, 1967 numbered UARL E910373-4 and UARL F910373-7, respectively.

In this nine month period one hundred and fifteen additional glass making compositions were prepared, melted, and partially characterized making the total of original glass formulations studied under this program two hundred and sixty-five. New glasses prepared may be thought of as belonging to one or another of five glass fields. Cordierite-rare earth compositions similar to those of our earlier reports form the first glass system but in our recent studies emphasis has been placed on lowering the silica content, the liquidus temperature and the density while increasing the working range without sacrificing the 16 to 18 million psi modulus previously achieved in this system. The second glass field investigated is that of the calcium-aluminate glasses of the type pioneered by the National Bureau of Standards and improved by the Bausch & Lomb Optical Company. These glasses are known to have moduli and the UARL contribution has been to substitute the very high-modulus factor rare earths where possible. The third glass system comprises the Morey-type optical glasses known to have the highest moduli of any known glass system and here emphasis has been placed on decreasing the density in order to achieve a useful specific modulus. Stevels "invert" glasses form the fourth region of our investigation. These glasses since they were developed for electrical characteristics are generally considered to be low moduli glasses but here we have been able to make rapid progress in increasing the modulus by adding ions with high-field strengths to these glasses in place of some of their usual constituents. The fifth area of glass composition research consisted of calcium aluminosilicate glasses lacking polarizable oxygen ions and which have, therefore, high moduli where we have concentrated on substituting other high-field strength ions to note the effect achieved.

An examination of the composition of most of the common glasses of commerce and antiquity would show that they usually have 64 or higher weight percent silica while the glasses of the five groups above have at the most twenty to forty weight percent silica and may even have no silica component in many cases. These experimental glasses, while still forming the brilliantly transparent material we think of as glass, have markedly different forming characteristics with sharply increased tendencies to devitrify or revert to crystalline masses. For this reason, the study of the kinetics of crystallization of molten oxides forms an essential

portion of this program. These studies carried out by direct microscopic observation of the molten glasses held in a microfurnace have shown that rare-earth additions such as lanthana, ceria and yttria impede and slow down devitrification confirming the basic reasoning of this program that the best criteria for the likelihood of glass formation in a given system is to treat it as a rate phenomenon as taught by R. W. Douglas.

An unexpected major gain of the necessity of adding rare-earths to the oxide systems to retard devitrification has been that these materials were found to make the highest contributions to Young's modulus per each mol percent added. For example, one mol percent of lanthana contributes 22.4 kilobars compared to 7.3 kilobars per mol percent contributed by silica while yttria contributes as much as 24.3 kilobars per mol percent even though crystalline yttrium oxide has a density less than twice as great as crystalline silica. Compositions based on these concepts have yielded glass fibers with a value of 16.8 million psi for Young's modulus when measured by mechanical testing or 18 million psi if evaluated by sonic techniques.

Since the measured value of Young's modulus has been proven to be very nearly independent of forming conditions, processing variables, and small inclusions in prior glass fiber research, such moduli measurements are used as the principal method of evaluating new glass compositions. In this period it was found that samples suitable for modulus determinations could be easily formed by drawing molten glass into fused silica tubes using a hypodermic syringe to supply controlled suction. This simplified technique greatly expedites comparative glass composition research while reducing expenses.

An equally important attribute of glass fibers is their strength. But in contrast to Young's modulus, the strength of a glass fiber is very strongly dependent on forming conditions and processing variables. The very greatly simplified fiber-pulling apparatus at UARL has proven hopelessly inadequate for meaningful strength evaluations and the only apparent solutions are the procurement of a standard commercial fiber bushing at an early date or alternately the evaluation of the UARL experimental glass compositions at a laboratory possessing such equipment.

INTRODUCTION

This is the tenth quarterly status report and the third summary report for Contract NASW-1301 named "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems". The tenth quarter started December 1, 1967 and ended February 29, 1968 and formed the third quarter of the second nine month extension to the contract, an extension running from June 1, 1967 through February 29, 1968 and for which the results are summarized in this report.

The primary objective of this contract is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the effect of anti-nucleating agents on the observed crystallization rate for systems which tend to form complex three-dimensional structures. The molten oxide systems selected for study, the reasons for their selection, and the methods used to prepare them form the first major section of this report.

Determination of the crystallization rate may be carried out by continuously monitoring the viscosity and electrical conductivity of the molten system as a function of time and temperature with checks of surface tension at selected temperatures. In this nine month period, however, crystallization rates were primarily determined by direct microscopic examination of samples in a micro-furnace as described in our latest summary report, UARL F910373-7. This work has largely confirmed the viewpoint that the probability of whether or not a glass will form is to be regarded as a rate phenomenon with the probability of glass formation greatly increased by employing cooling rates high enough to defeat the formation of the complex many-atom three dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis. The results of the microscopic observations form the second major section of this report.

Characterization of the experimental glasses produced as bulk specimens is the subject of the third large section of the report. Such characterization is largely achieved by measuring the density, studying the fiberization qualities, and determining Young's modulus for bulk samples of the experimental glasses. Prior to this report period specimens for measuring Young's modulus of bulk glass were made by first casting a glass slab and annealing it and then cutting rectangular bars from the slab by precision grinding equipment. This relatively elaborate, expensive, and time consuming procedure can now be supplanted by a new method of preparing modulus samples developed in this report period. In this new method it was found that samples suitable for modulus determinations could be readily formed by drawing molten glass into fused silica tubes using a hypodermic syringe to supply controlled suction to the molten glass. Description of this method and its use to evaluate the effect of annealing the glass is also included in the third report section.

C. J. Phillips (Ref. 1) has described a method for calculating Young's modulus from the composition of both simple and complex silicate glasses when the content of each oxide is expressed in mol percent. Each oxide is given a coefficient which may be typically 7.3, 12.1 and 12.6 kilobars per mol percent for SiO_2, Al_2O_3, and CaO respectively. The numerical value of the elastic constant is the sum of terms formed by multiplying the mol percentage of the constituent by its mol factor and agreement to within $\pm$ 0.3% between observed and measured moduli are obtained for thirty-five well defined glasses. Unfortunately, coefficients were not available for many of the components of the UARL experimental glasses. However, using the measured moduli for bulk specimens of these experimental glasses, the Phillips method has been extended to include oxides such as ceria, lanthana, and yttria and corrections have also been made to the Phillips factors for beryllia and zirconia while the factor for magnesia has been revised to include

the zero alkali content glasses of the present investigation. There is no reason apriori to assume that these calculations based on silicate glass systems can be readily extended to non-silica glasses such as the calcium aluminates. In fact, as is shown in the third section, the UARL attempts to extend such calculations to the calcium aluminates result in expecting a value for Young's modulus for these glasses which is considerably too high but since the differences between measured and experimental moduli is constant, it seems probable that with sufficient experimentation to provide complete new moduli factors for the constituents the calculation could be readily extended to this glass system as well.

The fourth large division of the report is concerned with the characterization of mechanically drawn glass fibers. Here it is shown that characterization of these fibers through measurement of their elastic modulus essentially presents no serious problem since such measurements are not drastically affected by forming conditions, process variables, inclusions except that these factors exaggerate the statistical error inherent in such measurements. The measurement of the strength of the virgin fiber is shown to be just the converse since all processing alterations, changes in forming procedures, and inclusions greatly alter the measured value of the strength.

SELECTION AND PREPARATION OF GLASS SYSTEMS FOR PRELIMINARY EVALUATION

One hundred and fifteen additional glass compositions were prepared, melted and partially characterized making the total of original glass formulations studied under this program two hundred and sixty-five. The new glasses prepared may be thought of for the most part as belonging to one of five glass fields.

The first of these glass fields is that of the cordierite glass system to which rare earths have been added as major constituents. Cordierite or $Mg_2Al_4Si_5O_{18}$ is a three dimensional ring former as discussed in earlier UARL reports (UARL E910373-4) and these glasses include major quantities of one of the rate earths such as lanthana, ceria, or yttria, which as shown in the following section, actively delay the onset of devitrification in these cordierite glasses while at the same time increasing their elastic modulus as shown in the third section of this report. These glasses occur throughout Table I while forming the whole of sub-tables Ia, Ib and Ik. It will be noted that other ingredients are added to lower the liquidus, the density and the silica content while increasing the working range and hopefully not lowering the elastic modulus of sixteen to eighteen million psi common to this system.

The second field of glass compositions melted may be called the calcium-aluminate series as developed by the National Bureau of Standards and the Research Laboratory of the Bausch & Lomb Optical Corporation. UARL has examined very few of these glasses at this time because of the extensive research by others in this area. As shown in Table I, glasses 217, 218, 219, 220, 221 have been prepared from compositions known to exist in this area so as to give UARL direct comparative information on this type of glass. These glasses are unique in that they

TABLE Ia

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	151	152	153	154	155
Silica	216.5	193.5	194.6	189.0	179.0
Alumina	45.2	40.6	40.6	39.9	43.4
Magnesia	107.3	95.9	96.3	93.6	88.85
Rare Earth Oxalate 381	---	---	---	---	---
Yttrium Oxalate	351.5	---	---	---	---
Lanthanum Oxalate	---	368.0	---	---	---
Cerium Oxalate	---	---	364.0	---	---
Samarium Oxalate	---	---	---	380.0	---
Tantalum Oxide	---	---	---	---	188.0
Chromium Oxide	---	---	---	---	---
Vanadium Oxide	---	---	---	---	---

	156	157	158	159	160
Silica	248.5	239.0	195.0	244.0	219.0
Alumina	103.3	57.75	27.45	47.75	42.75
Magnesia	123.2	118.4	96.75	80.0	71.85
Rare Earth Oxalate 381	---	---	---	---	---
Yttrium Oxalate	---	---	198.5	343.0	---
Lanthanum Oxalate	---	---	232.0	---	358.5
Cerium Oxalate	---	---	---	---	---
Samarium Oxalate	---	---	---	---	---
Tantalum Oxide	---	---	---	---	---
Chromium Oxide	25.45	---	---	---	---
Vanadium Oxide	---	85.0	---	---	---

	161	162	163	164	165
Silica	219.0	193.5	193.5	193.5	187.0
Alumina	42.75	40.6	81.2	---	43.2
Magnesia	71.85	95.9	95.9	95.9	31.8
Rare Earth Oxalate 381	368.0	368.0	185.0	600.0	---
Yttrium Oxalate	---	---	---	---	396.0
Lanthanum Oxalate	---	---	---	---	---
Cerium Oxalate	---	---	---	---	---
Samarium Oxalate	---	---	---	---	---
Tantalum Oxide	---	---	---	---	---
Chromium Oxide	---	---	---	---	---
Vanadium Oxide	---	---	---	---	---
Calcium Carbonate	---	---	---	---	78.7
Lithium Carbonate	---	---	---	---	27.5
TiO_2 (not rutile)	---	---	---	---	29.6

TABLE Ib

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredients	166	167	168	169	170
Silica	208.0	157.5	176.1	129.7	131.0
Alumina	157.0	82.3	92.6	100.5	21.6
Magnesia	49.5	32.35	36.15	38.35	31.3
Calcium Carbonate	---	---	---	---	---
Yttrium Oxalate	---	---	343.0	468.0	---
Lithium Carbonate	---	---	---	---	---
TiO_2 (not rutile)	---	---	---	---	---
Cerium Oxalate	---	359.0	---	---	597.0
Vanadium Pentoxide	85.35	60.0	67.0	56.6	38.5
Samarium Oxalate	---	---	---	---	---
Lanthanum Oxalate	---	---	---	---	---

	171	172	173	174	175
Silica	158.5	99.25	96.8	155.8	223.5
Alumina	26.05	64.75	63.2	85.8	31.3
Magnesia	37.25	25.25	24.7	29.8	49.6
Calcium Carbonate	---	---	---	---	---
Yttrium Oxalate	618.0	---	---	445.0	371.0
Lithium Carbonate	---	---	---	---	---
TiO_2 (not rutile)	---	---	---	---	---
Cerium Oxalate	---	452.0	---	---	---
Vanadium Pentoxide	46.4	46.85	45.6	62.2	55.9
Samarium Oxalate	---	---	575.0	---	---
Lanthanum Oxalate	---	---	---	---	---

	176	177	178	179	180	181
Silica	215.5	109.5	158.9	104.0	103.4	31.1
Alumina	23.6	47.3	57.0	45.0	56.45	105.5
Magnesia	34.0	54.1	62.9	47.8	22.35	---
Calcium Carbonate	---	---	---	---	166.2	259.5
Yttrium Oxalate	382.0	---	---	---	334.2	314.0
Lithium Carbonate	---	---	---	---	---	---
TiO_2 (not rutile)	---	---	---	---	---	---
Cerium Oxalate	---	---	39.4	62.2	38.9	36.65
Vanadium Pentoxide	34.5	46.95	56.5	44.6	80.6	84.9
Samarium Oxalate	---	---	---	---	---	---
Lanthanum Oxalate	---	525.0	317.0	498.0	---	---

TABLE Ic

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	182	183	184	185	186	187
Silica	148.0	145.8	128.0	130.0	128.7	125.9
Alumina	---	30.9	---	27.6	---	26.7
Magnesia	47.2	40.3	42.1	36.0	41.3	34.8
Calcium Carbonate	86.2	54.6	77.2	48.8	81.1	65.4
Yttrium Oxalate	372.0	367.0	---	---	---	---
Cerium Oxalate	43.5	42.8	38.8	38.7	37.9	37.1
Samarium Oxalate	---	---	---	---	401.0	391.0
Lanthanum Oxalate	---	---	389.0	382.0	---	---
Vanadium Pentoxide	56.0	55.2	50.0	49.2	48.9	47.6
Zirconium Carbonate	8.45	8.39	7.55	7.37	---	---
Titania	24.6	24.3	21.9	21.6	21.5	21.0
Lithium Carbonate	22.7	22.3	20.3	20.0	19.8	19.25
Rare Earth Oxalate	---	---	---	---	---	---

	188	189	190	191	192	193
Silica	193.5	174.3	170.7	174.4	174.3	173.0
Alumina	40.4	36.5	35.9	36.6	36.5	36.8
Magnesia	79.7	72.1	70.7	72.2	72.2	67.0
Calcium Carbonate	---	---	---	---	---	---
Yttrium Oxalate	313.0	---	---	---	---	175.8
Cerium Oxalate	---	332.0	---	---	---	---
Samarium Oxalate	---	---	343.0	---	---	---
Lanthanum Oxalate	---	---	---	330.0	---	204.7
Vanadium Pentoxide	70.75	64.0	62.8	64.0	64.0	63.5
Zirconium Carbonate	---	---	---	---	---	---
Titania	---	---	---	---	---	---
Lithium Carbonate	---	---	---	---	---	---
Rare Earth Oxalate	---	---	---	---	331.0	---

TABLE Id

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	194	195	196	197	198	199
Lanthanum Oxalate	222.5	268.5	---	---	---	---
Thoria	40.0	54.4	59.8	67.0	60.0	76.8
Barium Carbonate	57.5	75.5	82.0	92.8	77.2	89.7
Fused B_2O_3	110.0	143.8	156.3	177.0	150.0	174.0
Tantalum Pentoxide	65.0	76.2	82.7	---	90.0	---
Vanadium Pentoxide	---	43.9	47.7	54.0	---	---
Yttrium Oxalate	---	---	248.5	282.0	374.0	414.0
Zirconium Carbonate	---	---	---	28.65	---	28.8

TABLE Ie

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	200	201	202	203	204	205
Silica	165.5	165.7	154.7	212.6	201.3	176.4
Alumina	78.2	78.1	73.0	---	---	---
Magnesia	66.1	66.0	61.7	101.2	97.6	83.7
Yttrium Oxalate	208.0	207.5	---	499.0	478.0	---
Lanthanum Oxalate	243.0	---	226.0	---	---	478.0
Cerium Oxalate	---	241.5	227.5	---	46.8	52.9
Calcium Carbonate	---	---	---	---	---	---
Barium Carbonate	---	---	---	---	---	---

	206	207	208	209	210
Silica	185.0	164.1	193.0	172.5	154.8
Alumina	83.9	80.8	87.8	81.9	73.2
Magnesia	---	68.3	74.1	69.2	61.8
Yttrium Oxalate	372.0	502.0	382.0	367.0	---
Lanthanum Oxalate	---	---	---	---	378.0
Cerium Oxalate	---	---	---	84.8	75.9
Calcium Carbonate	164.2	---	---	---	---
Barium Carbonate	---	---	---	---	---

TABLE If

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	211	212
Silica	381.0	321.0
Alumina	---	---
Magnesia	---	---
Yttrium Oxalate	---	---
Lanthanum Oxalate	---	---
Cerium Oxalate	---	---
Calcium Carbonate	---	---
Barium Carbonate	154.0	257.0

TABLE Ig

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	213	214
Silica	197.0	323.0
Alumina	13.6	55.0
Magnesia	---	123.0
Calcium Carbonate	---	---
Barium Carbonate	---	---
Lanthanum Oxalate	627.0	---
Cerium Oxalate	---	---
Yttrium Oxalate	---	---
Titania (not rutile)	---	---
Zirconium Carbonate	---	---

TABLE Ih

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	215	216	217	218
Silica	224.0	33.0	---	63.3
Alumina	---	173.0	178.5	156.3
Magnesia	22.6	---	---	---
Calcium Carbonate	287.0	515.0	528.0	458.0
Barium Carbonate	35.3	---	32.2	31.8
Lanthanum Oxalate	---	---	---	---
Cerium Oxalate	---	---	---	---
Yttrium Oxalate	---	---	---	---
Titania (not rutile)	73.0	---	---	---
Zirconium Carbonate	46.6	---	---	---

TABLE Ii

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	219	220	221
Sodium Carbonate	41.6	42.9	44.8
Potassium Carbonate	14.2	14.6	15.3
Calcium Carbonate	376.0	388.0	406.0
Alumina	186.0	192.3	201.5
Magnesia	13.0	13.4	14.0
Barium Carbonate	16.7	17.2	18.0
Lanthanum Oxalate	14.1	14.5	15.2
Ferric Oxide	6.5	6.7	1.75
Silica	32.4	16.8	---
Tantalum Oxide	---	---	---
Fused Boric Oxide	---	---	---
Thoria	---	---	---
Zirconium Carbonate	---	---	---
Titania (not rutile)	---	---	---
Lithium Nitrate	---	---	---
Yttrium Oxalate	---	---	---

TABLE Ij

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	222	223	224	225	226
Sodium Carbonate	---	---	---	---	---
Potassium Carbonate	---	---	---	---	---
Calcium Carbonate	---	---	---	---	---
Alumina	---	---	---	---	---
Magnesia	---	---	---	---	---
Barium Carbonate	---	---	---	---	---
Lanthanum Oxalate	361.0	---	302.0	---	458.0
Ferric Oxide	---	---	---	---	---
Silica	---	---	---	---	---
Tantalum Oxide	111.0	119.0	70.0	77.8	140.0
Fused Boric Oxide	167.0	174.2	100.0	111.1	---
Thoria	111.0	119.3	140.0	148.1	---
Zirconium Carbonate	---	---	---	---	33.8
Titania (not rutile)	---	---	---	---	60.0
Lithium Nitrate	---	---	50.0	55.6	---
Yttrium Oxalate	---	221.0	---	288.0	---

	227	228	229	230
Sodium Carbonate	---	---	---	---
Potassium Carbonate	---	---	---	---
Calcium Carbonate	---	---	---	---
Alumina	---	---	---	---
Magnesia	---	---	---	---
Barium Carbonate	---	---	---	---
Lanthanum Oxalate	---	---	---	361.0
Ferric Oxide	---	---	---	---
Silica	---	---	---	---
Tantalum Oxide	186.5	76.8	225.0	111.0
Fused Boric Oxide	---	---	---	167.0
Thoria	---	---	---	---
Zirconium Carbonate	45.2	---	84.4	111.0
Titania (not rutile)	79.9	423.3	200.0	---
Lithium Nitrate	---	---	---	---
Yttrium Oxalate	520.0	---	---	---

TABLE Ik

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	231	232	233	234	235
Silica	160.0	173.5	203.5	161.25	201.0
Alumina	94.65	81.85	91.9	59.5	68.1
Magnesia	96.35	69.15	77.8	70.6	80.9
Yttrium Oxalate	402.0	364.0	204.5	366.0	403.0
Cerium Oxalate	---	85.0	---	164.5	---
Vanadia	---	---	50.7	---	---
Lanthanum Oxalate	---	---	---	---	---
Cobaltous Carbonate	---	---	---	---	---
Calcium Carbonate	---	---	---	---	---
Lithium Carbonate	---	---	---	---	---
Zirconium Carbonate	---	---	---	---	---

	236	237	238	239	240
Silica	157.2	175.8	185.0	122.5	114.7
Alumina	92.9	99.4	104.6	138.5	126.7
Magnesia	73.4	78.6	82.7	117.7	110.2
Yttrium Oxalate	367.0	394.0	206.5	205.0	---
Cerium Oxalate	85.7	---	---	97.0	314.0
Vanadia	---	---	51.3	---	---
Lanthanum Oxalate	---	---	---	---	---
Cobaltous Carbonate	---	---	---	---	---
Calcium Carbonate	---	---	---	---	---
Lithium Carbonate	---	---	---	---	---
Zirconium Carbonate	---	---	---	---	---

	241	242	243
Silica	114.9	33.2	24.4
Alumina	129.9	156.2	123.5
Magnesia	110.3	---	8.2
Yttrium Oxalate	---	---	305.0
Cerium Oxalate	---	155.3	143.0
Vanadia	---	---	---
Lanthanum Oxalate	314.0	155.0	---
Cobaltous Carbonate	---	35.4	32.5
Calcium Carbonate	---	256.0	214.0
Lithium Carbonate	---	16.4	---
Zirconium Carbonate	---	---	28.1

TABLE I1

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredients	247	248	249	250	251	252
Silica	197.0	172.0	147.3	195.5	193.6	192.0
Alumina	100.2	108.4	116.5	99.35	98.6	97.5
Lithium Carbonate	72.6	78.3	84.2	48.0	23.6	35.6
Calcium Carbonate	98.7	106.5	114.0	97.5	96.5	144.0
Zinc Carbonate	122.5	133.5	143.0	122.0	121.0	121.3
Magnesia	39.7	42.9	46.0	52.35	64.8	38.7
Yttrium Oxalate	---	---	---	---	---	---
Lanthanum Oxalate	---	---	---	---	---	---
Calcium Fluoride	---	---	---	---	---	---

	253	254	255	256	257
Silica	97.6	158.1	136.6	147.7	128.5
Alumina	132.5	---	---	74.9	65.4
Lithium Carbonate	95.9	53.5	50.4	54.6	47.4
Calcium Carbonate	130.5	79.2	68.2	---	---
Zinc Carbonate	163.2	98.7	85.3	92.2	80.3
Magnesia	52.4	31.9	27.5	29.7	25.9
Yttrium Oxalate	---	476.0	---	446.0	442.0
Lanthanum Oxalate	---	---	479.0	---	---
Calcium Fluoride	---	---	---	---	---

TABLE Im

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	258	259
Silica	262.0	254.5
Alumina	112.0	109.0
Lithium Carbonate	---	---
Calcium Carbonate	81.2	---
Zinc Carbonate	---	---
Magnesia	60.5	59.0
Yttrium Oxalate	---	---
Lanthanum Oxalate	---	---
Calcium Fluoride	20.0	78.0
	Expected to melt in range	
	1080°C	1170°C

TABLE In

New Experimental Glass Batches
Actual Ingredients in Grams

Actual Ingredient	260	261
Silica	310.0	310.0
Alumina	75.0	92.5
Lithium Carbonate	---	---
Calcium Carbonate	206.0	89.2
Zinc Carbonate	---	---
Magnesia	---	47.5
Yttrium Oxalate	---	---
Lanthanum Oxalate	---	---
Calcium Fluoride	---	---
Expected Melting Temperature	1170°C	1222°C

contain little or no silica and their existence is usually explained by stating that in the $CaO-Al_2O_3$ in a small composition range around the composition: $12CaO.7Al_2O_3$ the liquidus temperature drops to approximately 1400°C, a temperature so low that it is stated that the energetics do not permit nucleation so that a glass results. This great lowering of the melting point is in stark contrast to the figure of 2072°C at which Al_2O_3 melts or 2614°C at which calcia melts and both of these latter figures are stated to be sufficiently high to permit nucleation so that neither member compound in a pure state is capable of glass formation. The calcium-aluminate glasses are known to have high moduli but also have very poor working characteristics and are difficultly fiberizable. UARL efforts in this area will include the addition of high modulus factor oxides to such melts together with materials to improve working properties.

The third area of glass compositions under investigation at this time are those of the Morey Eastman-Kodak optical glasses. These glasses cited in the patents of G. W. Morey, L. W. Eberlin, and P. F. DePaolis are known to have by far the highest Young's modulus although accompanied by high densities as well. They have not previously been evaluated in connection with glass fiber research. From the point of view of constitution, these glasses are stated by Weyl to be of fundamental importance because they are not based on a major constituent that can form a glass by itself. The UARL experience in this area is again limited at this time to learning to melt a few typical compositions such as those glasses shown in sub-tables Id and Ij as well as to investigate the problems in fiberizing such glasses. If we can handle these glasses successfully, obvious directions exist for markedly decreasing the density without adversely affecting the modulus so that high specific moduli may be achievable in this system. As of this time, however, the forming characteristics of these glasses are a formidable obstacle.

The fourth area of glass research is that of "invert" glasses using a concept developed by J. M. Stevels and his associates who found in 1954 that by proper combination of oxides, stable metasilicate glasses could be obtained. A typical example cited by Stevels is 50 mol % SiO_2 and 12.5 mol % of each of the following: Na_2O, K_2O, CaO, BaO. Dr. Stevels explains this "anomalous" case of glass formation by saying "choosing a batch with a great number of network modifiers the 'glue' between the chains is to irregular that crystallization is prevented" obviously by using a combination of alkali oxides and a combination of alkaline earth oxides, the liquidus temperature can be lowered and the field of glass formation can be increased.

Weyl states further that Trap & Stevels characterize the coherence of a silicate glass by a structural parameter Y, which denotes the average number of bridging ions per SiO_4 tetrahedron and is calculated from the expression

$$Y = 6 - \frac{200}{p} \quad \text{where } p = \text{mol \% } SiO_2$$

so that when p = 33-1/3, Y = 0 and the SiO_4 groups are isolated; when p = 40%, Y = 1 and on the average SiO_4 groups appear in pairs. Commercial silicate glasses have Y values between 3.0 and 3.5 in agreement with the Zachareisen rules

for stable glass formation that a stable silicate glass should consist of SiO_4 tetradedra sharing at least three of their corners with other SiO_4 tetradedra. On the other hand the "invert" glasses developed by Trap & Stevels have Y values lower than 2.0 in direct contradiction of the accepted rules for stable glass formation.

When the glass composition is changed to lower and lower SiO_2 concentrations, Trap & Stevels found that some properties go through maxima or minima such as the thermal expansion, the electrical deformation loss, and the viscosity which go through extreme values when the parameter Y passes the value of 2.0. It is the UARL feeling that the modulus of elasticity will likewise reach a decided maximum. UARL, however, has worked extensively with the "invert" glasses in the first eight quarters of this contract without achieving any marked change in modulus until the last two quarters when a sixty percent increase was achieved. Typical "invert" glasses studied are shown in sub-table Il.

The final class of glasses under investigation currently are calcia aluminosilicate glasses lacking polarizable oxygen ions. Such glasses are known to have high elastic moduli and high softening points and by incorporating additional high modulus-factor oxides such as lanthana and yttria in these glasses, significant improvements in modulus should be possible. Glasses 206 and 260 are typical examples. Typically, once a composition has been selected, 500 gram batches of raw materials are melted in high purity (99.9%) alumina crucibles in air using kilns with Super-Kanthal hair-pin electrical resistance elements. Starting materials used are 5 micron particle size, high purity silica, high purity alumina of 325 mesh, laboratory reagent grade magnesium oxide, 99.9% lanthanum oxalate, and other comparable materials such as reagent grade calcium carbonate or zinc carbonate. These materials customarily yield a water-white optical grade glass free of seed, stone, and bubbles when properly compounded and held at temperatures of 1450-1650°C for at least two hours. Less commonly glasses may be prepared in beryllia crucibles again in air and in the kiln or in platinum crucibles in air or in tungsten crucibles in purified argon or vacuum atmospheres. Alumina crucibles of even very slightly lower purity, i.e. 99.3 to 99.7% cannot be used successfully in melting these high temperature glasses.

USE OF THE MICROFURNACE FOR DIRECT OPTICAL OBSERVATION OF THE KINETICS OF CRYSTALLIZATION

The direct microscopic observation of the kinetics of crystallization of crystals originating in high temperature molten oxide systems are carried out on a microfurnace described in our last summary report, F910373-7. In this period this equipment was used for rate determinations for cordierite glass batches containing the rare-earth additive lanthanum and soda-lime aluminosilicate glasses. The results obtained are as follows.

The rate of growth of cordierite was measured in glass batch No. 62. The composition of this glass, as determined by chemical analysis, is 53.41 wt % SiO_2, 25.06 wt % Al_2O_3, 15.36 wt % MgO, and 5.63 wt % Ce_2O_3. The oxidation state of the cerium ion in this glass was not determined, but is reported here as Ce_2O_3. The crystal growth-rate data obtained for this glass are listed in Table II and are plotted in Fig. 1. It can be seen from Fig. 1 that the maximum rate of growth of cordierite in this glass is about 115 microns per minute; that appreciable rates of crystal growth begin at about 1000°C, and that the liquidus temperature is 1370 ± 5°C. The maximum growth rate of 115 microns per minute is about one-fourth that measured for batch 1 (485 microns per minute), but is approximately twice that of batch 63 (66 microns per minute) which contains 5.6 wt % La_2O_3. This glass becomes less transparent at higher temperatures, which may be due to a change in the oxidation state of the cerium ion. Upon cooling to lower temperatures, the glass becomes more transparent again. This change in transparency is not so great as to impede the crystal growth measurements. The cordierite which was grown in this glass was nucleated with seed crystals of cordierite, just as in our preceding work. The devitrification product in this glass was determined to be cordierite by means of powder X-ray diffraction.

Another feature of interest which can be observed in Fig. 1 is that the high temperature end of the curve approaches the liquidus temperature asymptotically just as in our other growth-rate curves for cordierite. This means, of course, that the rate of growth is not continuous with the rate of solution as the curve passes through the liquidus temperature, but that instead there is a more or less pronounced change in slope. This conflicts with the data of Swift (Ref. 2), which were obtained on soda-lime-aluminosilicate glasses. His measurements were made by two different methods, but essentially consisted of heating the glass for certain periods of time, then removing it from the furnace and measuring the changes in crystal length microscopically by using a micrometer ocular. Because of the discrepancy between our results and those of Swift, it was decided to attempt to reproduce the data of Swift by using the same glass composition as used in his work, but by using our microfurnace, with our methods of measurement. Accordingly, a soda-lime-aluminosilicate glass was prepared in a 60 gram batch. This glass was melted in a platinum crucible at approximately 1300°C for 30 min, then removed from the furnace and stirred with a platinum-20% rhodium stirring rod until the glass became too viscous for further stirring. The glass was reheated and stirred in this manner four more times. The stirring rod remained in the crucible during the reheating and stirring operations, so that no glass was removed from the crucible during the mixing procedure. The composition of Swift's glass was 69 wt % SiO_2, 17 wt % Na_2O, 12 wt % CaO and 2 wt % Al_2O_3. A chemical analysis of a portion of our glass gave a composition of 69.46 wt % SiO_2, 16.78 wt % Na_2O, 11.48 wt % CaO, and 2.14 wt % Al_2O_3. The measurements of the rate of crystal growth were measured in our usual manner, the crystals being nucleated with seed crystals of devitrite. The devitrification product was identified as devitrite by powder X-ray diffraction. The sample for the X-ray diffraction analysis was obtained by allowing glass contained in a micro-crucible to crystallize for 14 hrs at 925°C, a temperature near which the highest crystal growth rate occurs. A rather weak diffraction pattern was obtained for this sample, but the pattern contained all of the diffraction lines for devitrite ($Na_2Ca_3Si_6O_{18}$) except for a few of the less intense lines. Some of the intensities on our pattern do not match those from the ASTM card; this may be due in part to the difficulty in estimating the intensities of our rather weak pattern. Because of this discrepancy in intensities, the X-ray diffraction data are presented in Table III.

Table II

Growth Data for Cordierite in Batch 62

No.	Temp.	Rate	No.	Temp.	Rate
1	1309 ± 2	16.1	11	1256 ± 3	114
2	1369 ± 5	0 in 60 min	12	1300 ± 4	48
3	1372 ± 3	-2.5	13	1210 ± 4	115
4	1172 ± 4	100	14	1107 ± 3	40
5	1285 ± 3	59	15	1143 ± 2	74
6	1344 ± 2	2.5	16	1053 ± 2	15
7	1363 ± 3	1	17	1291 ± 3	59.7
8	1328 ± 3	8.5	18	1238 ± 3	117
9	1270 ± 2	101	19	1069 ± 4	26
10	974 ± 4	2			

FIG. 1

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH
OF CORDIERITE IN BATCH 62

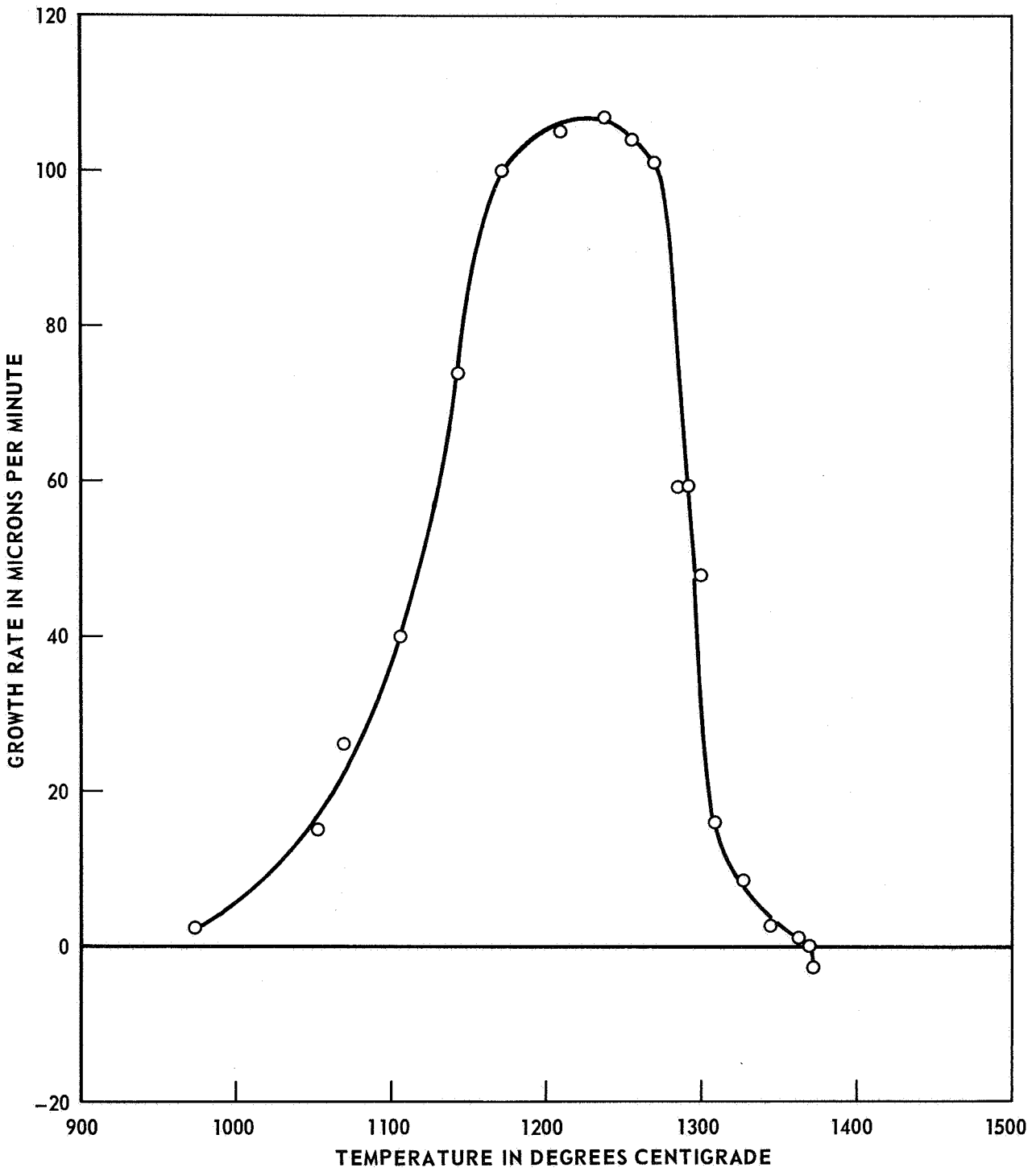


Table III

X-Ray Diffraction Data for Devitrites

$Na_2Ca_3Si_6O_{16}$ (ASTM)		Devitrification Product		$Na_2Ca_3Si_6O_{16}$ (ASTM)		Devitrification Product	
d	I	d	I	d	I	d	I
9.88	14			2.390	6		
4.76	25	4.75	M	2.316	14	2.32	W=
4.16	20	4.15	M+	2.251	8	2.25	W=
3.82	25	3.83	W	2.225	8		
3.30	60	3.30	S	2.159	8	2.16	W=
3.23	30	3.23	W+	2.138	6		
3.09	55	3.08	W	2.063	12	2.06	W=
2.983	45	2.97	S	2.030	14	2.03	W=
2.915	25	2.91	W-	2.004	6		
2.836	8	2.84	W-	1.968	4		
2.773	100	2.76	M-	1.951	4		
2.664	12	2.65	W-	1.930	4		
2.554	10	2.55	W-	1.881	18	1.88	W-
2.509	6			1.842	14	1.84	W-
2.473	6	2.48	W-	1.809	18	1.80	S-

The crystal growth-rate data for our soda-lime-aluminosilica glass are presented in Fig. 2 and are listed in Table IV. Also shown in Fig. 2 is the growth-rate data of Swift for a glass of the same composition and the data of Milne (Ref. 3) for a glass of nearly the same composition, the main difference being that silica is substituted for the alumina, so that Milne's glass contains 72 wt % SiO_2, 16 wt % Na_2O, and 12 wt % CaO. Our data, and that of Swift and Milne (when extrapolated) give very nearly the same liquidus temperature, and it appears that the data would also agree if extrapolated to the temperature (about 750°C) where measurable crystal growth begins. Our rate of solution measurements are also in very close agreement with those of Swift. The most important differences are that different maximum rates of growth are obtained, and that our rate of growth curve is not continuous with the rate of solution curve through the liquidus temperature but instead exhibits a change in slope in this region. The high temperature end of our growth-rate curve and that of Milne (which is presumably for the rate of growth of devitrite) can be fitted to a straight line in this temperature region, but since no rate of solution measurements were plotted by Milne, no further comparison is possible regarding the shape of the rate of devitrification curve. A further examination of devitrification curves as obtained by Swift and replotted here is possible by reference to Fig. 3, which includes data for 3 glasses with 0, 2, and 4 wt % Al_2O_3 substituted for silica. The glass with 2 wt % Al_2O_3 is the same as that shown in Fig. 2. It can be observed in Fig. 3 that the data used to draw the curves are fewer in number than those obtained in our work and by Milne. It should also be noticed that the low temperature end of the curve for the 2 wt % Al_2O_3 glass is concave upward, while any such curvature for the 0 and 4 wt % Al_2O_3 glasses is much less pronounced. All of our observations indicate that there may be at least two types of devitrification curves, one exemplified by our results on the soda-lime-aluminosilica glass. and the other by the data obtained on the cordierite-composition based glasses. In the former, the high temperature end of the curve can be fitted to a straight line, which may have a more or less pronounced change in slope as the curve passes through the liquidus temperature. In the other type of curve, the high temperature end of the curve is not linear with temperature, and there is an asymptotic approach to the liquidus temperature. The data obtained for these cordierite composition based glasses contain much more scatter than do the data obtained on the soda-lime-aluminosilica glasses, which were taken at much lower temperatures. The difference in the liquidus temperatures is 350 to 400°C.

These soda-lime-aluminosilicate glasses have maximum growth rates for devitrite of 11 to about 18 microns per minute. This is about one-fourth of the growth rate observed for cordierite in batch 63 (66 microns per minute) and much smaller than that measured in batch 62 (115 microns per minute). This rather large difference is probably due to the much higher silica content in the soda-lime-aluminosilica glasses. A comparison of more importance can be made between the growth rates for batches 63 and 62, which have the same content of SiO_2. The difference in the growth rates in these glasses appears to be inversely proportional to the difference in the ionic size of the rare-earth ion which is added to the other components in the glass. Thus, lanthanum (in batch 63) gives a much slower devitrification rate than does cerium (in batch 62) when present in these glasses in equal amounts. This correlation could be better examined if the oxidation state of the cerium ion were determined.

FIG. 2

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH OF DEVITRITE

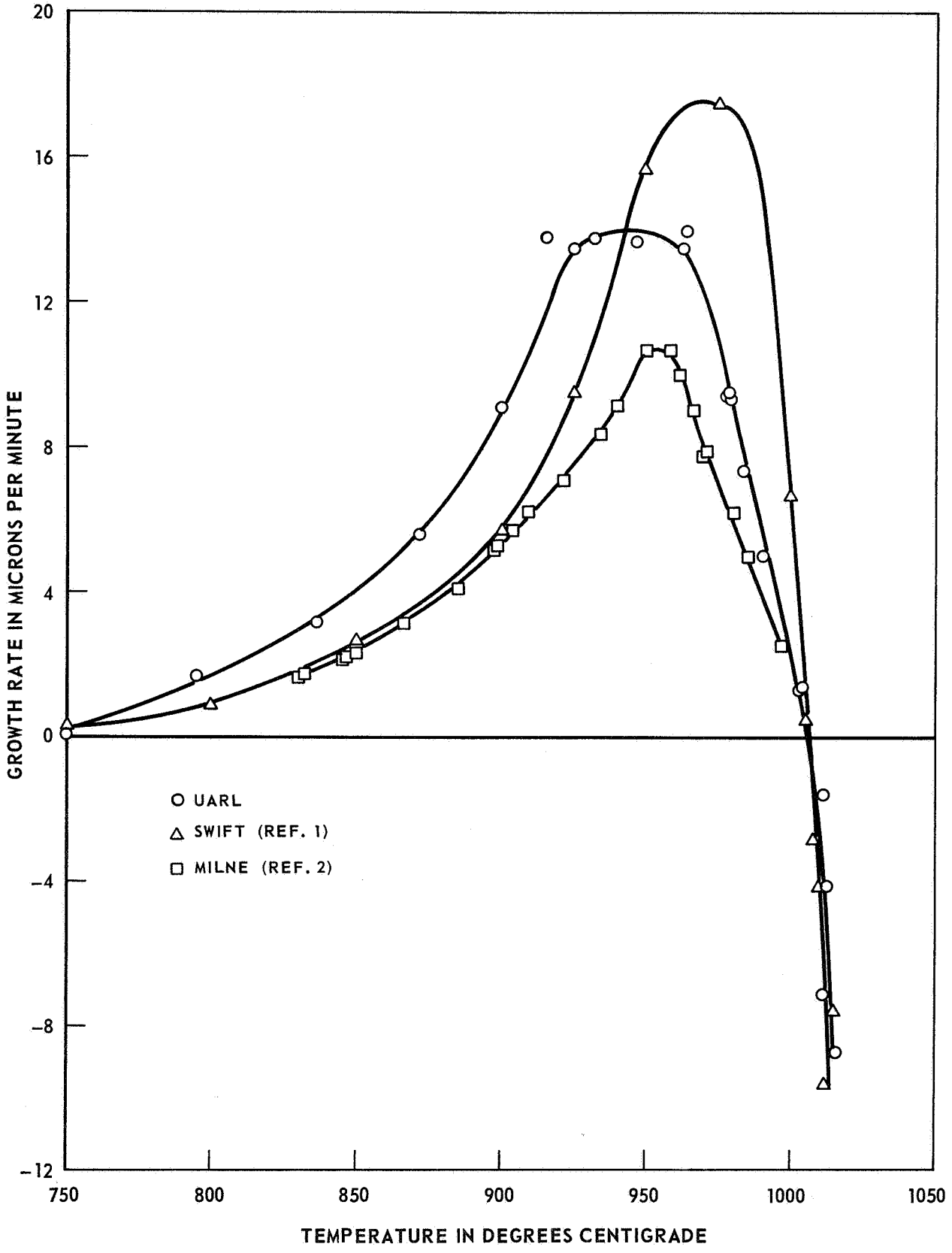


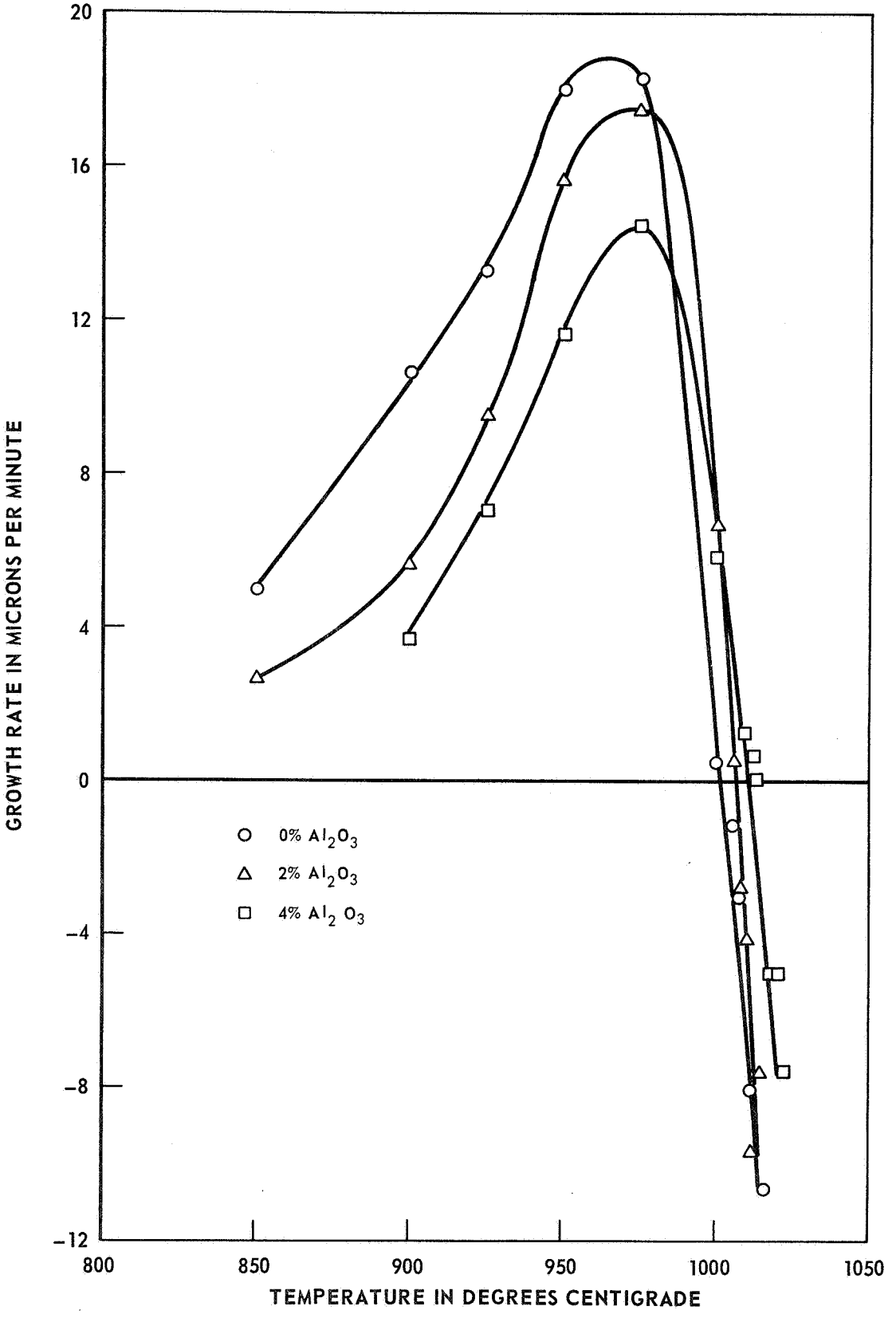
Table IV

Growth Rate Data for Devitrite in Soda-Lime-Aluminosilicate glass

No.	Temp.	Rate	No.	Temp.	Rate
1	964 ± 5	14.0	13	748 ± 4	0 in 41 min
2	900 ± 5	9.1	14	963 ± 2	13.5
3	872 ± 4	5.6	15	916 ± 3	13.8
4	794 ± 3	1.66	16	978 ± 2	9.4
5	1004 ± 4	1.41	17	978 ± 3	9.5
6	990 ± 3	5.0	18	932 ± 4	13.8
7	947 ± 4	13.7	19	925 ± 2	13.5
8	836 ± 3	3.1	20	1014 ± 2	-20.0
9	1003 ± 3	1.3	21	983 ± 4	7.36
10	979 ± 3	9.3	22	1011 ± 3	-1.6
11	1026 ± 2	-29	23	1012 ± 2	-4.1
12	1016 ± 2	-8.7	24	1011 ± 2	-7.1

FIG. 3

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH OF DEVITRITE AFTER SWIFT (REF. 1)



CHARACTERIZATION OF UARL EXPERIMENTAL GLASSES FROM BULK SPECIMENS

Many of the experimental glasses prepared were characterized by measuring the density and Young's modulus on bulk samples of these glasses and by investigating their annealing and fiberizability characteristics.

Density

The density of the experimental glasses has been determined for UARL by the Glass Testing Laboratory of the Hartford Division of the Emhart Corporation. For samples with densities less than 3.00 gms/cm^3 they employed the heavy-liquid of known density comparator method while for samples with densities greater than 3.00 gms/cm^3 the Archimedean procedure was followed. The results of all density measurements made to date are shown in Table V. As may be seen the observed densities range from 2.57 to 5.22 gms/cm^3.

Young's Modulus for Bulk Samples of UARL Experimental Glasses

Modulus measurements on bulk specimens of the various experimental glasses prepared in this laboratory were made by preparing an annealed patty, slab, or cylinder of the experimental glass and then cutting rectangular rods from the glass by means of a diamond wheel and diamond grinding the rods to finished dimensions. Samples prepared in this manner averaged 2 in. in length by 1/8 in. by 1/8 in. This procedure was followed up to the tenth or last quarter of the report period. In this quarter a much simpler and very much less expensive technique was evolved consisting of drawing samples directly from the crucibles of molten glass into fused silica tubes by the use of a hypodermic syringe to supply controlled suction. Since the rods drawn in this manner represent a glass of higher fictive temperature than the rods cut from annealed glass slabs, the results are given in separate tables. For both types of samples, the actual modulus measurement is carried out by the sonic method described in detail in our last summary report, F910373-7.

Measured Values of Young's Modulus for Rectangular Rod Bulk Samples

All measurements made to date on rectangular rod samples are shown in Table VI. Highest results, i.e. results of approximately 16.5 million pounds/square inch are obtained for the Young's modulus of the rare-earth cordierite glasses 114, 117, and 138 while the calcium aluminate glass 96 with additions of magnesia, zirconia, yttria and silica has a value of 16.30 million pounds/square inch and a lower density.

TABLE V

Summary of Density Results Obtained on UARL Glasses on Bulk Specimens

Glass No.	Density	Glass No.	Density	Glass No.	Density
25	2.5672	113	3.5298	173	4.525
40-3	2.9574	114	3.2237	174	3.472
56	2.4368	125	2.7818	175	3.189
62-3	2.7036	126	3.4634	176	3.151
63-1	2.6847	127	3.2553	177	4.196
64-1	2.6818	129	3.3105	178	3.613
65-1	2.7197	131	3.1200	179	4.331
66	2.6112	134	3.0671	188	3.2548
66-1	2.6784	135	2.6303	194	4.479
67-3	2.6535	136	2.8035	195-2	4.167
68-2	2.6295	137	3.0834	200	3.584
69	2.5910	138	3.5498	201	3.550
70-1	2.7526	140	3.678	202	3.769
71	2.6627	151	3.2541	203	3.490
72-2	2.8877	155	3.5452	205	4.0576
73-2	3.0152	157	2.6962	212	3.0360
74	2.9983	159	3.2216	215	3.1277
75	2.6342	160	3.2211	222	
82-3	2.5875	161	3.4523	223	5.2235
83	2.8376	162	3.6150	224	5.1584
93	3.1167	163	3.1876	225	4.6850
96	2.9676	164	4.0593	231	3.4337
97	2.8426	165	3.3088	232	3.5892
98	2.9168	166	2.6295	233	3.0314
99	3.186	167	3.4085	234	3.7081
102	2.9188	168	3.2047	235	3.3261
103	2.9089	169	3.6355	244	3.63
106	3.6859	170	4.202	247	2.9870
107	3.3799	171	3.810	248	3.0906
108	3.1107	172	3.934	249	3.0114
110	2.6128				

TABLE VI

Measured Values of Young's Modulus for Bulk Samples of UARL Glasses
(Sonic measurements using ground rectangular rods)

Glass No.	Average Modulus ($\times 10^{-6}$ psi)	Glass No.	Average Modulus ($\times 10^{-6}$ psi)
1	14.86	64	15.57
4	14.94	64 (repeat)	14.78
14	15.07	65	15.20
24	10.67	66	15.14
26	10.18	68	15.36
27	11.53	70	15.23
29	14.02	72-2	15.15
41	10.83	72-3	15.14
42	10.82	73-2	15.13
43	10.27	76	11.51
45	11.08	77	12.16
46B	10.40	93	15.72
47	11.07	96	16.30
47B	11.62	97	10.86
48B	11.28	98	10.62
49B	10.77	99	11.37
50	11.10	114	16.5
50B	10.83	117	16.54
51	11.75	138	16.53
52	10.87	191	15.35
63	14.71	192	14.05

Measured Values of Young's Modulus for Circular Rods Directly from Melt

In the usual method of preparing specimens of bulk glass for Young's modulus determinations, a glass slab is first cast and annealed. Rectangular bars are then cut from the slab, and re-annealed to remove stresses imposed by the cutting operation. Young's modulus of the bar may then be obtained by static or sonic methods. This technique has been used in the current research program, but was found to be time consuming and relatively expensive; consequently, a simplified technique for preparing sonic test specimens was sought. It was found that samples satisfactory for modulus determinations could be easily cast by drawing molten glass up into fused silica tubes using a syringe to apply suction to the tubes. A light dusting of MgO powder inside the silica tubes was used at first to prevent the glass from adhering to the walls of the tubing, but was found to be unnecessary. The fact that most glasses have higher thermal expansion coefficients than does fused silica results in the shrinking of the cast bar away from the silica tube on cooling to room temperature, thus facilitating easy removal of the rods. After the rods are removed, the ends are trimmed off square with a cut-off wheel. The rod casting syringe and representative glass rod samples are shown in Fig. 4. Young's moduli were determined for a number of experimental glass rods prepared in this fashion using sonic equipment described previously. Correction factors for the radius of gyration: length ratios were taken from the data of Pickett (Ref. 4), assuming a value of Poisson's ratio of 1/6.

Measurements made in the last quarter by this technique are shown in Table VII. Some of the same glasses occur in both Table VI (rectangular rods) and VIII and it will be seen that the agreement between the two methods involving as they do glasses with different effective fictive temperatures is fair with an average variation of $\pm$ 6%. The cordierite-rare earth glasses 114, 126, 129, and 159 are again outstanding and show values for Young's modulus greater than 16 million psi. However, glass 83 prepared from Owens-Corning patent U.S. 3,122,277 issued to R. L. Tiede which contains the toxic ingredient beryllia and glass 96, the UARL modified calcium aluminate have the highest specific moduli.

The glass rods were then annealed by heating at 850°C for 4 hrs and cooling to room temperature over a 12 hr cycle. Young's moduli were then determined on the annealed rods. Modulus values for as cast and annealed rods are given in Table VIIa. The average increase on annealing is 1.8% and in no instance was more than 2.5%. Thus, for comparative purposes, the use of as-cast bars is deemed satisfactory.

Calculation of Young's Modulus from Compositional Factors

In an outstanding paper entitled "Calculation of Young's Modulus of Elasticity from Composition of Simple and Complex Silicate Glasses" (Ref. 1) C. J. Phillips describes a method for calculating Young's modulus of elasticity for some 44 glasses by expressing the content of each oxide in mol percent and multiplying it by a modulus factor peculiar to that oxide. Coefficients are derived, however,

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FIG. 4

ROD CASTING SYRINGE AND EXAMPLES OF GLASS RODS

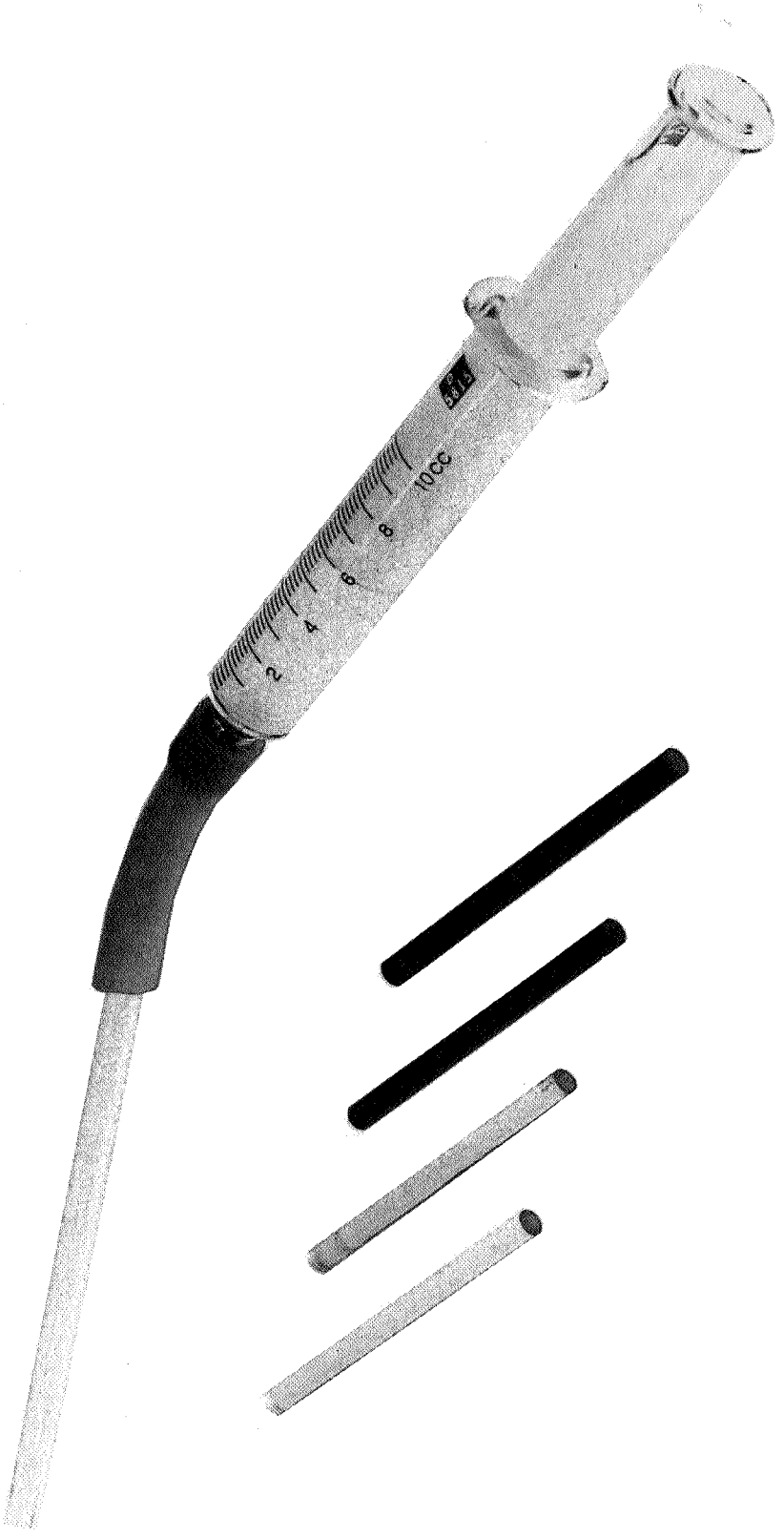

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TABLE VII

Measured Values of Young's Modulus for UARL Glasses
(Sonic measurements using circular rods formed directly from melt)

Glass Number	Measured Modulus x 10^{-6} psi	Glass Number	Measured Modulus x 10^{-6} psi
40	15.5	135	14.3
68	14.1	136	14.4
72	14.0	137	14.8
83	16.0	138	15.3
96	15.7	140	15.6
99	10.5	155	15.7
114	16.7	157	13.3
126	16.8	159	16.2
129	16.5	179	14.9
134	15.4		

TABLE VIIa

Comparison of Young's Modulus of As-Cast and Annealed Glass Bars

Glass	E x 10^{-6} psi as-cast	E x 10^{-6} psi annealed	Percent Increased
68	14.4	14.7	2.1
	13.7	14.0	2.2
	13.8	14.1	2.2
	14.5	14.5	0
114	16.3	16.5	1.2
	16.6	17.0	2.4
	16.6	17.0	2.3
126	16.7	17.0	1.2
	16.9	17.3	2.4
129	16.9	17.0	0.6
	16.3	16.6	1.8
	16.5	16.2	1.8
135	14.3	14.6	2.1
	14.4	14.7	2.1
	14.3	14.5	0.7
	14.4	14.7	2.1
136	14.6	14.8	1.4
	14.3	14.5	1.4
	14.3	14.6	2.1
138	15.2	15.4	1.3
	15.4	14.8	2.5
	15.2	15.6	1.9

TABLE VIII

Calculation of Young's Modulus Factors by C. J. Phillips' Method

A. Using Known Silica, Alumina, Zirconia Values to Derive New Magnesia Value

1. The Basic Glass (1,4,14)

Actual batch for this glass 198 gms SiO_2, 120 gms Al_2O_3, 180 gms basic magnesium carbonate [$MgCO_3.Mg(OH)_2.3H_2O$] with a conversion factor to MgO of 2.44.

	Actual Batch	Batch on Oxide Basis	Weight %	Atomic Weight	Mols	Mol %
SiO_2	198	198	50.7	60.09	0.845	52.4
Al_2O_3	120	120	30.5	101.94	0.299	18.6
MgO	180	73.7	18.85	40.31	0.468	29.0

Constituent	Mol %	Kilobars/mol	Contribution
SiO_2	52.4	7.3	383
Al_2O_3	18.6	12.1	225
MgO	29.0	X	29X
			608+29X

But average exp. value for 1,4,14 = 14.96 x 10^6 lbs/in.^{2} = 10.52 x 10^5 kg/cm^2 = 1031 kilobars

∴ MgO contribution = 1031-608/29 ≅ 14.7 kilobars/mol %

2. Using Glass 66

Constituent	Mol %	Kilobars/Mol %	Contribution
SiO_2	53.7	7.3	392
Al_2O_3	15.3	12.1	185
MgO	28.3	X	28.3X
ZrO_2	2.56	18.9	47.4
			624+28.3X

But average exp. value for 66 = 15.14 x 10^6 lbs/in.^{2} = 10.64 x 10^5 kg/cm^2 = 1043 kilobars

MgO contribution = 1043-624/28.3 = 14.8 kilobars/mol %

for only certain oxides likely to be present in the usual glasses; namely, SiO_2, Na_2O, K_2O, Li_2O, B_2O_3, Al_2O_3, CaO, MgO, PbO, BaO, ZnO and BeO. The numerical value of the elastic constant is then the sum of the terms $C_1p_1 + C_2p_2 + \ldots C_np_n$ where $C_1 \ldots C_n$ are the molal coefficients and $p_1 \ldots p_n$ are the molar percentages of the corresponding oxides. Agreement between calculated and observed values is better than $\pm$ 0.3% for 35 well defined glasses.

In one of our earlier summary reports, E910373-4, we showed that Phillips through a juxtaposition of the composition of his glass 73 had inadvertently obtained an incorrect value for the beryllia molar coefficient and in this same report we recalculated this BeO coefficient from published data on two Owens-Corning glass fiber compositions and found it to be 19.0 kilobars/mol %. In this same summary report, E910373-4, we also calculated the molal coefficient for zirconia from Loewenstein's glass Z_1^1 (Ref. 5) and found it to be an unbelievably high value of 28.6 kilobars per mol%.

At this stage in our research we have derived sufficient data from the UARL experimental glass compositions to permit the extension of the calculations of C. J. Phillips to glasses containing rare earth oxides such as yttria, lanthana, and ceria. These experimental UARL glasses like Loewenstein's glass Z_1^1 are alkali free and it appears that in such alkali-free glasses the molar coefficient of magnesia is 14.8 kilobars per mol percent. According to Weyl (Ref. 6) in alkali-free glasses, MgO_6 groups form in place of the MgO_4 groups of alkali-alkaline earth silicates and this formation of MgO_6 groups resulting from the lower polarizability of O^{2-} ions in alkali-free glasses causes the average coordination of the O^{2-} ions to increase, the structure to become more compact, and the value of the E modulus to increase. Using this value for magnesia, the value of the zirconia coefficient is recalculated from Loewenstein's Glass Z_1^1 and a very much more reasonable result of 18.9 kilobars per mol % is obtained for ZrO_2.

Table VIII gives in detail the calculations for the Young's modulus molar factor for magnesia. It will be noted that two different computations of two very different glasses give respectively values of 14.7 and 14.8 kilobars per mol percent for MgO when the new value of 18.9 kilobars per mol % for ZrO_2 is employed.

In Table IX, Phillips type calculations are extended to yttria containing glasses and the very high molar contributions of 22.2, 25.5, and 25.2 kilobars per mol % yttria are found. This high modulus factor for yttria is particularly significant since earlier direct microscopic observations of the rate of crystallization of yttria containing glass has shown that this material successfully slows down the formation of cordierite crystals.

Table X extends the calculation of Young's modulus based on compositional factors to glasses containing lanthana and ceria with results of 22.4 kilobars per mol % lanthana and 18.6 kilobars per mol % ceria (calculated Ce_2O_3). Again, these values like the yttria value are an unexpected gain from our primary concept of adding such rare-earth materials to slow the kinetics of crystallization.

TABLE IX

Calculation of Young's Modulus from the Composition
by C. J. Phillips' Method

B. Using Known Alumina, Silica Values Plus New Magnesia Value to Derive Factor for Yttria

1. Using Glass 70

Constituent	Mol %	Kilobars/mol %	Contribution
SiO_2	55.3	7.3	404
Al_2O_3	12.6	12.1	152
MgO	29.3	14.7	431
Y_2O_3	2.83	X	2.83X
			987+2.83X

But #70 experimentally = 15.23×10^6 lbs/in.^{2} = 1050 kilobars

$\therefore$ Y_2O_3 contribution = 1050-987/2.83 = 22.2 kilobars/mol %

2. Using Glass 114

Constituent	Mol %	Kilobars/mol %	Contribution
SiO_2	51.7	7.3	377
Al_2O_3	22.5	12.1	272
MgO	15.8	14.7	232
Y_2O_3	10.0	X	10X
			881+10X

But #114 experimentally = 16.5×10^6 lbs/in.^{2} = 1136 kilobars

$\therefore$ Y_2O_3 contribution = 1136-881/10 = 25.5 kilobars/mol %

3. Using Glass 64

Constituent	Mol %	Kilobars/mol %	Contribution
SiO_2	54.6	7.3	399
Al_2O_3	15.5	12.1	188
MgO	28.8	14.7	422
Y_2O_3	1.39	X	1.39X
			1009+1.39X

But #64 experimentally = 15.14×10^6 lbs/in.^{2} = 1044 kilobars (on average)

$\therefore$ Y_2O_3 contribution = 1044-1009/1.39 = 25.2 kilobars/mol %

TABLE X

Calculation of Young's Modulus from the Composition
by C. J. Phillips' Method

C. Using Known Silica, Alumina Factors and New Magnesia Factor to Derive Lanthana and Ceria Factors

1. Based on Glass 138

Constituent	Mol %	Kilobars/mol %	Contribution
SiO_2	47.3	7.3	345
Al_2O_3	15.6	12.1	189
MgO	28.9	14.7	425
La_2O_3	8.0	X	8.0X
			959+8.0X

Experimentally 138 = 16.5 x 10^6 lbs/in.^{2} = 1138 kilobars

La_2O_3 contribution = 1138-959/8 = 22.4 kilobars/mol %

2. Based on Glass 117

Constituent	Mol %	Kilobars/mol %	Contribution
SiO_2	51.67	7.3	377
Al_2O_3	10.0	12.1	121
MgO	18.33	14.7	269
Ce_2O_3	20.0	Y	20.0Y
			767+20Y

Experimentally 117 = 16.54 x 10^6 lbs/in.^{2} = 11.64 kg/cm^2 = 1138 kilobars

$\therefore$ contribution of ceria = 1138-767/20 = 371/20 = 18.6 kilobars/mol %

In Table XI an attempt is made to extend the Phillips type of calculation based on simple and complex silicate glasses to the totally unallied calcium aluminate glass system. As is to be expected the calculations fail to yield a correct result and instead give a result 20% too high. However, the calculations for both glasses give the same amount of discrepancy indicating that this type of calculation can be extended to the calcium aluminate glass system if one wishes to carry out sufficient experimentation to rederive molal coefficients appropriate for this very different structure. The alarming fact that the factors for the calcium aluminate system are going to be smaller than for the silica and complex silicate systems must indicate a more open structure for this type of glass system and a corresponding lower bond energy and ultimately achievable Young's modulus.

Table XII summarizes the new Phillips compositional factors for Young's modulus available from the UARL data on the experimental glasses evaluated to date. It is particularly noteworthy that the oxides possessing unusually high modular contributions now include yttria, lanthana, ceria, and zirconia in addition to beryllia and also that magnesia is 20% more effective in alkali-free glasses than in those glasses containing alkali.

Alternate Calculation of Young's Modulus from Composition by Method of S. D. Brown

S. D. Brown, et al (Ref. 7) have suggested an alternate method of calculating Young's modulus from composition factors peculiar to each oxide present. In contrast to Phillips method as presented above, he bases his calculation of Young's modulus on "packing efficiency" of the discrete ions present. This packing efficiency was measured by a parameter called "the true ionic volume fraction" (f). The parameter is then defined as follows. It is assumed that every ion in the material has a definite spherical volume as determined by radii values given by Pauling (Ref. 8). The summation of these spherical volumes for all ions divided by the total macroscopic volume of the aggregate is the true ionic volume fraction and is calculated by

$$f = \frac{N\rho}{M} \sum_i n_i v_i$$

where i designates a given ionic species, M is the molar formula weight of the material, ρ is its density, v_i is the volume of ionic species i, n_i is the number of ions of species i per molar formula of material and N is Avogadro's number.

For convenience, instead of considering individual ions, it can be assumed that the material is composte of j component oxides (e.g. Al_2O_3, SiO_2, etc.). Then in terms of weight fractions, x_j, of component j in the material the f factor is given by

$$f = \rho \sum_i x_j \frac{N v_j}{M_j} = \rho \sum x_j g_j$$

TABLE XI

Discrepancies Resulting When Young's Modulus for Calcium Aluminate Glasses are Calculated by C. J. Phillips' Factors Derived from Silica Glass Systems

Glass 96	Constituent	Gms	Weight %	Molecular Weight	Mols	Mol %	Kilobars Mol %	Contribution
	CaO	165.3	36.7	56.08	0.654	45.9	12.6	462
	Al_2O_3	185.0	41.2	101.94	0.463	28.3	12.1	498
	MgO	25.0	5.6	40.31	0.139	9.8	14.7	144
	ZrO_2	24.9	5.5	123.22	0.045	3.2	18.9	61
	SiO_2	50.0	11.1	60.09	0.185	12.9	7.3	94
								1259

But actual exp. value = 16.30×10^6 psi = 1148 kg/cm^2 = 1125 kilobars

∴ Have a large discrepancy indicating that factors for calcium aluminate glasses are appreciably lower

Glass 93	Constituent	Gms	Weight %	Molecular Weight	Mols	Mol %	Kilobars Mol %	Contribution
	CaO	140.0	28.0	56.08	0.498	38.0	12.6	478
	Al_2O_3	210.0	42.0	101.94	0.412	31.4	12.1	380
	MgO	25.0	5.0	40.31	0.124	9.5	14.7	140
	ZrO_2	24.9	5.0	123.22	0.046	3.5	18.9	66
	SiO_2	50.0	10.0	60.09	0.166	12.6	7.3	92
	BaO	50.7	10.0	153.3	0.065	5.0	11.35	57
					1.311			1213

But actual experimental value = 15.72×10^6 psi = 11.05×10^5 kg/cm^2 = 1083 kilobars

∴ Again have a large discrepancy indicating that factors for calcium aluminate glasses are appreciably lower. Discrepancy for 93 = 130 kilobars; for 96 = 134 kilobars

Since these values are consistent, this mode of calculation is probably just as valid for calcium-aluminate glasses as for silica glasses once the proper molar values are known.

TABLE XII

Some Additional Molal Factors for the Calculation of Young's Modulus from Composition by Method of C. J. Phillips as Derived from UARL Experimental Glass Data

A. Factors Used by C. J. Phillips in his Original Publication

Oxide	Contribution Per Each Mol % in Kiolbars
SiO_2	7.3 and constant
Al_2O_3	12.1 and constant
CaO	12.6 and constant
Na_2O	3.4
K_2O	1.8
Li_2O	7.0
BaO	11.35 and falling with increasing R_2O
B_2O_3	7.2
ZnO	1.75 and rising with increasing R_2O
TiO_2	13.3

B. New Factors Based on UARL Experimental Glass Evaluations

Oxide	Contribution Per Each Mol % in Kilobars
BeO	19.0
ZrO_2	18.9
MgO	12.0 & rising with decreasing R_2O and SiO_2 to 14.8
Ce_2O_3	18.6
Y_2O_3	24.3
La_2O_3	22.4

Typical g_j factors for various oxide components computed in this manner are 0.298 for B_2O_3, 0.280 for BeO, 0.267 for Li_2O, 0.233 for SiO_2, 0.189 for MgO, 0.183 for TiO_2, 0.166 for CaO, and 0.123 for ZrO_2. It will be noted immediately that these factors place even greater emphasis on low atomic number materials than do those of C. J. Phillips. It is also immediately apparent that in some cases these factors directly contradict those of Phillips; for example, the g_j factors for BeO and B_2O_3 are virtually identical while Phillips finds a molal contribution of only 7.3 kilobars/mol % contrasted to 19.8 kilobars/mol % for BeO.

Table XIII shows the computation for two calcium aluminate glasses using S. D. Brown's coefficients. Unfortunately, the calculated results are not in concordance with the experimental results also taken from S. D. Brown's report. Because the experimental modular data of Brown are based on hand-drawn fibers, one cannot say with any degree of assurance whether the method of calculation has failed. However, the method of Phillips seems to be the better choice for calculating Young's modulus from compositional factors at this time.

Evaluation of Glass Forming Characteristics and Fiberizability on UARL Experimental Glasses

The oxide materials previously melted in the kiln using the procedures described earlier in this report furnish the starting materials used in this phase of our research. From the previous firing in the kiln they have emerged either as fully melted and fined glasses, glass and interpenetrating crystalline masses, or materials that appear similar to clinkers or cinders. One chooses a sufficient amount of this material to fill a 15 milliliter platinum crucible and this material is then crushed or ground to approximately 10 mesh size and placed in the platinum crucible. The platinum crucible then is placed on the motor-driven platform of the Super-Kanthal hair-pin furnace and this furnace platform is raised until the crucible is in the center of this furnace, whose temperature is already at the desired value. The crucible is held at this temperature for a time varying from one-half hour to two hours dependent on the original condition of the charge and is then lowered as rapidly as possible. As soon as the crucible emerges from the furnace, one man grasps it in his tongs and a second man dips a twenty mil platinum wire into the molten glass and runs away from the crucible as rapidly as possible. Usually in this manner it is possible to hand draw a glass fiber, 2 to 5 mils in diameter and thirty to forty feet long, if the glass is to be termed readily fiberizable. The Super-Kanthal hair-pin kiln used in this experiment readily obtains a temperature of 1800°C in air.

In the simple fashion described above or by attempting to form buttons by pouring glass out of the crucible it is usually possible to obtain some crude idea concerning the working characteristics of the experimental glass. Indeed, tables of such working characteristics for various glasses were included in our two previous summary reports, E910373-4 and F910373-7. As our experience in mechanically drawing fibers continues to accumulate we find, however, that crude tests of this type are insufficiently selective to assure the production of high quality fiber by our simple mechanical drawing procedures. Much more informative

TABLE XIII

Discrepancies Resulting When Calcium Aluminate Glasses are Calculated by Packing Efficiency Considerations of S. D. Brown

1. Calcium Aluminate Glass with Measured ρ = 3.19 gms/cm^3 and E = 16.7 x 10^6 psi

Oxide	Weight %	g_j	$x_j g_j$
CaO	19.4	0.166	0.03224
MgO	2.3	0.189	0.00435
BaO	8.8	0.086	0.00755
Na_2O	2.4	0.181	0.00328
Al_2O_3	48.8	0.209	0.10180
TiO_2	4.6	0.183	0.00842
ZrO_2	11.8	0.123	0.01453
K_2O	1.8	0.199	0.00358
			0.17575

$\rho \Sigma x_j g_j$ = 0.5606
= Ionic Volume Fraction

Calculated E
= (59.5)(0.561)-20.4
= 33.38 - 20.4
= 13.0 x 10^6 psi

2. S. D. Brown's R-105 Glass Has a Measured ρ = 2.90 gms/cm^3 and E = 16.0 x 10^6 psi Measured on Hand-Drawn Fibers

Oxide	Weight %	g_j	$x_j g_j$
Al_2O_3	44.0	0.209	0.0920
SiO_2	3.5	0.233	0.0082
CaO	48.8	0.166	0.0810
MgO	3.5	0.189	0.0066
			0.1878

$\rho \Sigma x_j g_j$ = 0.545
Calculated E
= (59.5)(0.545)-20.4
= 32.43 - 20.4
= 12.4 x 10^6 psi

In comparison with Table IX where similar calculations are made by method of C. J. Phillips, the discrepancies calculated by the packing efficiency method are much larger as well as too low in place of too high. The consistency of the differences again indicates hope that the method can be made to work for calcium aluminate glasses when the correct factors have been determined.

are direct microfurnace observations of liquidus temperature and rates of devitrification. Also equally helpful are studies involving the pouring and controlled annealing of large glass patties, 3 to 4 in. in dia and 3/8 to 5/8 in. thick. The results of a typical study of this kind conducted for us by the Glass Testing Laboratory of the Hartford Division of the Emhart Corporation are shown in Table XIV. The superior working characteristics of glasses containing either ceria or lanthana are evident.

CHARACTERIZATION OF GLASS FIBERS MECHANICALLY DRAWN FROM EXPERIMENTAL GLASSES

Originally, it was felt that the hand-drawn fibers produced in the fiberizability tests of bulk glasses could be used for the evaluation of the properties of the glass fiber. It quickly became evident, however, that no matter how carefully hand-drawn fibers were prepared, they tended to show a distorted elliptical cross-section to such a degree that it was impossible to obtain a meaningful value for the cross-section of such fibers. Therefore, values of Young's modulus deduced by dead-weight mechanical testing procedures are extremely untrustworthy for hand-drawn fibers since this type of measurement is dependent on an accurate value for the average fiber cross-sectional area.

The problems encountered in attempting to obtain a reliable value for Young's modulus on hand-drawn fibers made it obvious that it was time to switch to mechanical drawing of fibers from the experimental glasses in question. Normally, this is done by purchasing massive platinum-rhodium bushings of proven design. But in our case several such bushings would be necessary since the experimental glass compositions vary so widely that the lifetime of such a bushing might be very limited. Several such bushings would represent an expenditure for materials three to four times as great as the program material cost to date. Fortunately, as described in our last summary report, F910373-7, it has proven possible to substitute "a poor man's bushing" for much of our work by using a 20 cc platinum crucible with reinforced bottom and a central hole as a bushing. This crucible is shaped by starting with a normal platinum crucible and welding several thicknesses of platinum foil to the crucible until a bottom thickness of 3/16 in. is obtained and then taper reaming a central orifice 0.088 in. at top, 0.063 in. at bottom and 3/16 in. long in the bottom of the crucible. The crucible is then filled with glass and introduced into the platform furnace with Super-Kanthal heating elements together with a ring orifice providing water cooling immediately below the crucible as well as a second ring orifice for cooling the fiber as it forms with helium jets. The equipment has now been extensively used and has proven satisfactory for the production of very nearly circular glass fiber having approximately one mil diameter at pulling rates of 4000 ft/min.

The mechanically drawn experimental glass fibers produced in this apparatus have proven very satisfactory for modulus measurements as we have shown in our previous reports F910373-7, F910373-8, F910373-9 and indeed again in this report in Tables XVI and XVII of a later section. The ability to obtain satisfactory modulus values from fiber produced in such a crude bushing is dependent on the fact that the modulus of a glass fiber is largely insensitive to stones, seed, microscopic inhomogeneities, etc. occurring in the fiber.

TABLE XIV

Glass Forming Characteristics of Selected Rare-Earth and Cordierite Based Glasses and Two Calcium-Silica Glasses

Glass Number	Components	Remarks
200	La_2O_3, Y_2O_3, MgO, Al_2O_3, SiO_2	Melted at 1500°C. Annealed at 850°C.
203	Y_2O_3, MgO, SiO_2	Melted above 1500°C. Devitrified in pouring, liquidus probably 1500°C, annealed at 900°C.
205	CeO_2, La_2O_3, MgO, SiO_2	Same as 203 but a little less prone to devitrify & possibly a little lower viscosity at 1500°C. Devitrified at 850°C to form a yellow opal.
206	Y_2O_3, CaO, Al_2O_3, SiO_2	Did not melt at 1500°C, only sintered. Top portion of melt at higher temperatures was a clear glass but bottom half opaque.
207	Y_2O_3, MgO, Al_2O_3, SiO_2	Devitrified on pouring. Very fluid at 1500°C. Annealing satisfactory at 850°C.
208	Y_2O_3, MgO, Al_2O_3, SiO_2	Melted easily at 1500°C to form a stable glass, quite fluid at 1500°C, annealed at 780°C.
209	CeO_2, Y_2O_3, MgO, Al_2O_3, SiO_2	Same as 208 but more fluid at 1500°C.
210	CeO_2, Ka_2O_3, MgO, Al_2O_3, SiO_2	Same as 208 & 209 but even more fluid at 1500°C. Much less prone to devitrify. Annealed at 750°C.
214	MgO, Al_2O_3, SiO_2	Melted at 1500°C. Fairly stiff at melting. Turns to opal on cooling. Annealed at 800°C.
215	ZrO_2, TiO_2, BaO, CaO, MgO, SiO_2	Glass almost watery at 1500°C. Most stable glass in series with respect to devitrification. Has longer working range. Annealed at 700°C.
219	Fe_2O_3, La_2O_3, BaO, CaO, MgO, Al_2O_3, SiO_2	Melted at 1500°C. Quite fluid but devitrified rapidly on slight cooling. Annealed at 800°C. Pots are semi-crystalline.

An equally important characteristic of glass fibers, however, is the strength of the virgin fiber and in direct contrast to modulus measurements any assessment of strength values for glass fibers is strongly dependent on defects present in the fiber as we show in the next section.

Attempted Strength Evaluations Using Mechanically Drawn Fibers Produced in a Simplified Bushing

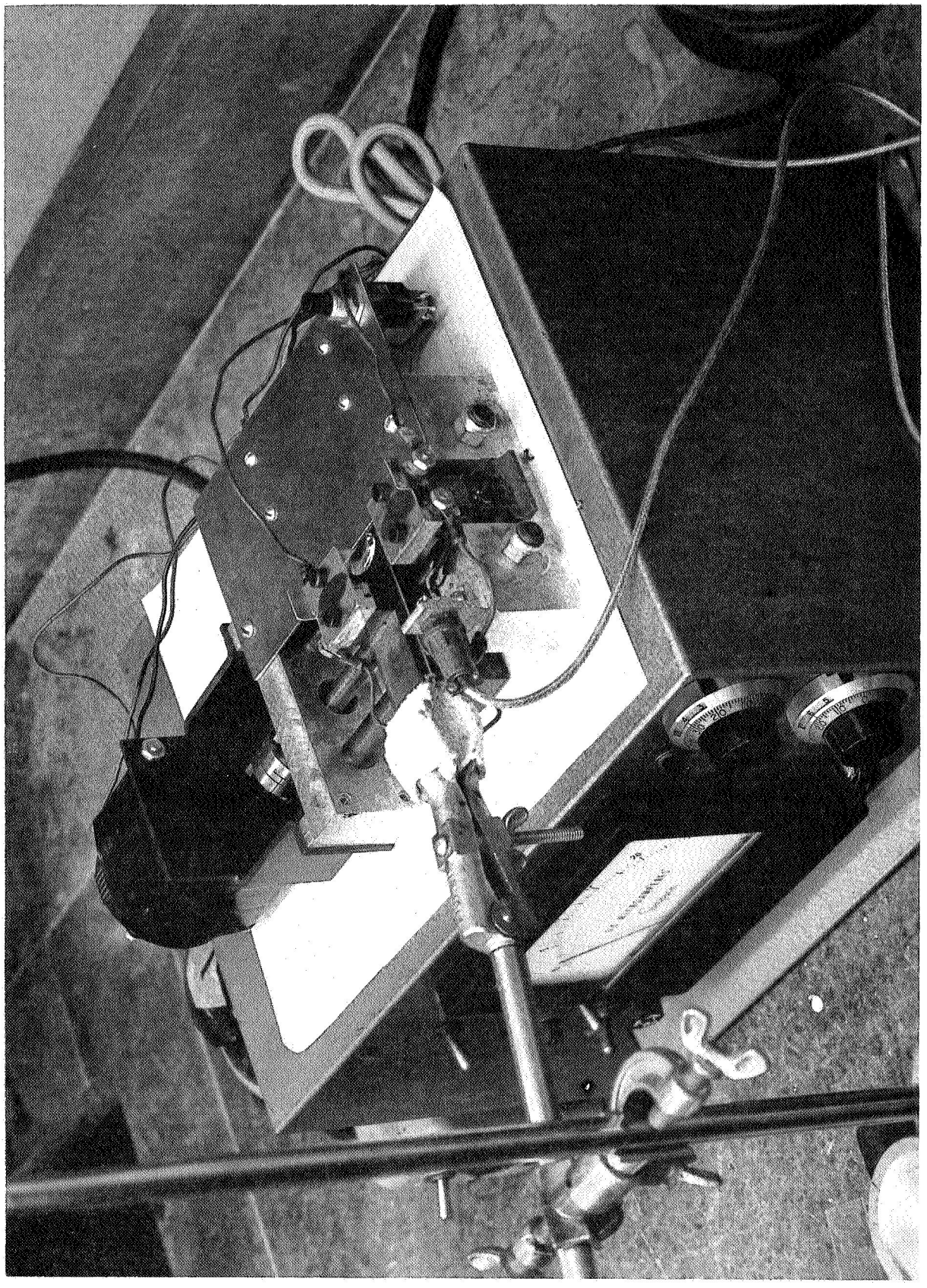
Possible sources of scatter and low strength values for E glass fibers tested as described in the previous progress report have been investigated. Considerable uncertainty as to the validity of a given strength measurement exists when the fiber failed in the "fly-out" mode described previously. This is because of the impossibility of measuring the fiber diameter at the point of failure, and because it is not possible to assess whether initial failure was in the guage length. In order to assess the prevalence of grip failures occurring with fly-out, a series of E glass specimens were taken from a spool and tested. Alternate specimens were tested in air, or damped with oil in order to prevent fly-out. The method of accomplishing the damping is shown in Fig. 5. A microscope slide is positioned just below the mounted fiber, and a drop of oil is placed on the slide so as to cover the fiber over most of the guage length. Of ten samples broken without damping, five failures were fly-out, four were normal (i.e. a single fracture within the guage length) and one was a grip failure. Of eleven samples broken with oil damping, none were fly-outs, five were normal failures and six were grip failures, i.e. fracture occurred immediately adjacent to the wax, or under the wax. Thus, about half of undamped tests were fly-out, and where fly-out was prevented it was disclosed that about half the failures were grip failures and cannot be considered as valid data.

Consider now the strength data for virgin E glass fibers presented in the previous progress report. This data is replotted as a histogram in Fig. 6a. The mode of failure in all instances was fly-out. A bimodal distribution of strength values is observed. It seems reasonable that the low strength values centered around 300 to 350 x 10^3 psi represent grip failures possibly resulting from misalignment, and that high values centered around 450 x 10^3 psi are valid guage length failures.

Based on these observations, it was decided to change to a paper tab fiber mounting system for tensile specimens, because such a system would provide a degree of self-alignment for the tensile specimens, and because it was thought that the paper mounts would absorb energy from fiber whiplash thus tending to damp fly-out. Also, because several tensile specimens can be prepared simultaneously from a captured fiber, testing can be speeded up. The capture device was modified so as to capture eighteen inch lengths of fiber between the bushing and the take-up spool. The modified capture device, mounted on the fiberization furnace, is shown in Fig. 7. The captured fiber is picked off the capture device using a bent wire frame to which the fiber is temporarily glued, and transferred to a precut paper tape consisting of five (5) paper mounting tabs. The fiber is attached to the tabs with de Khotinsky cement applied with a pencil type

FIG. 5

METHOD OF DAMPING TENSILE TEST SPECIMEN



RL-68-74-A

FIG. 6

G910373-10

STRENGTH OF VIRGIN E GLASS FIBERS

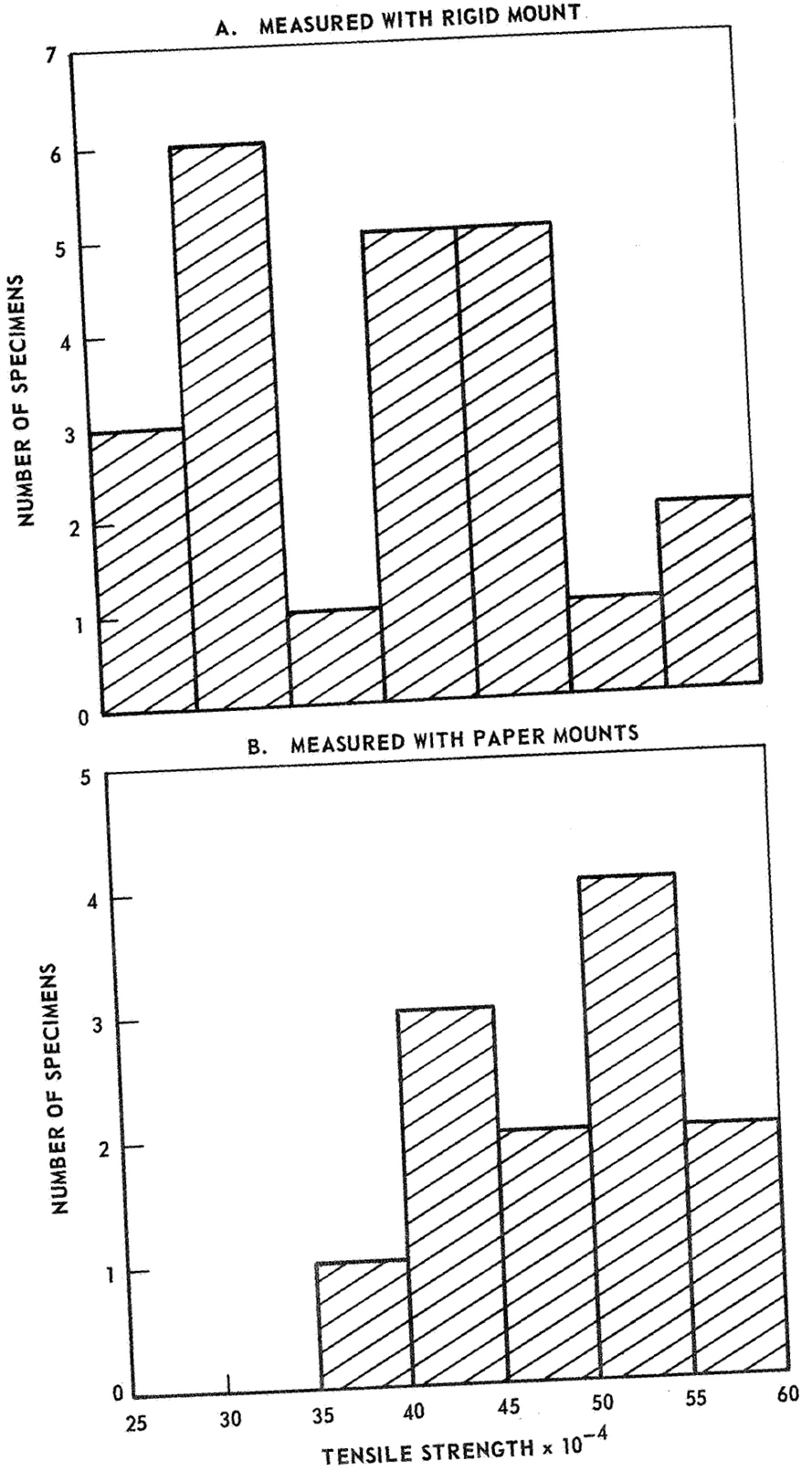
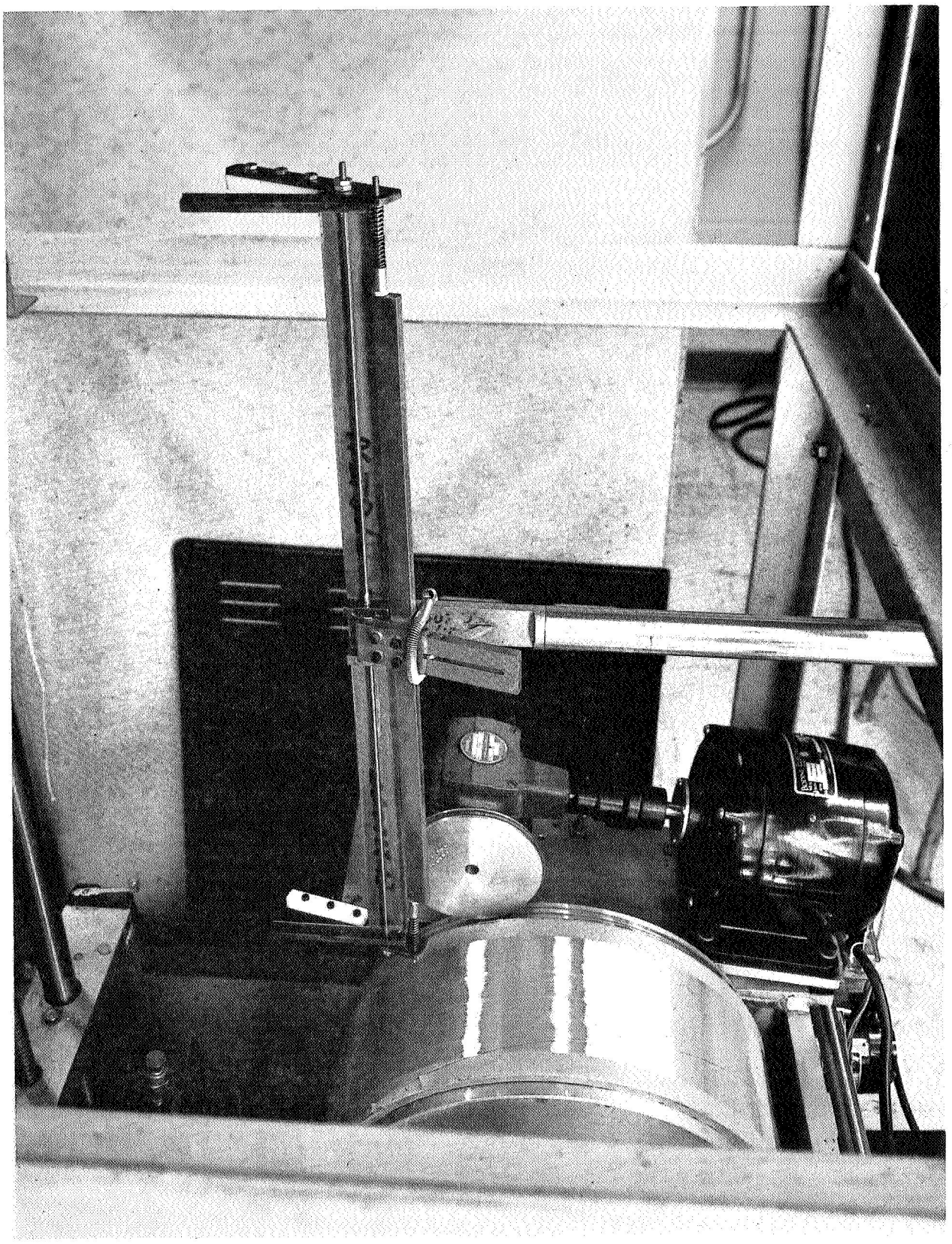


FIG. 7

FIBER CAPTURE DEVICE



RL-68-74-B

soldering iron. A tensile specimen is then cut from the tape, mounted on the testing machine with spring clips, and the mounting tab cut so as to permit loading the fiber. A tensile specimen mounted on the testing machine in this fashion is shown in Fig. 8.

Virgin E glass fibers were captured and tensile strength measured using the above procedure. These strength data are shown in Fig. 6b. Comparison with the strength data obtained using the original mounting system indicates that a major source of low strength values has been eliminated. However, samples still failed with fly-out making accurate diameter measurements at points of fracture impossible. Diameters used in strength calculations are therefore averages of values measured some distance from the point of fracture. Variations in diameter along a captured eighteen inch length of fiber were found to be as high as twenty percent. Thus, uncertainty in diameter is possibly the greatest remaining source of scatter in the virgin strength data measured for E glass. Further effort should thus be directed toward producing defect-free fiber of uniform diameter.

Testing Experimental Fibers

Representative glass compositions that had previously been fiberized in the UAC apparatus and for which modulus data had been obtained were selected, and virgin strength measured by the method described. These data are recorded on Fig. 9. The values fall roughly on a single curve of strength versus diameter. Such behavior is typical of fibers containing flaws and probably indicates that the fiberization process variables which control the quality of the fiber rather than any variation in glass composition are determining the strength. Fibers of these experimental glasses were examined under the microscope, and in all instances were found to contain crystalline inclusions, examples of which are shown in Fig. 10. The lowest strength values were seldom accompanied by fly-out and so the point of fracture could be observed. This was found frequently to be at such inclusions.

In order to assess qualitatively the possibility of continuously pulling good quality fibers of a short-working range high modulus glasses such as UAC-114, 135, 6, 7, 8, 126, 129 etc., the behavior of 126 glass was examined in the microfurnace. The liquidus temperature was found to be approximately 1460°C. A qualitative measure of the viscosity could be obtained by microscopic observation of the flow of glass as the thermocouple was withdrawn from the glass surface. By correlating observations on UAC 126 glass and E glass it was concluded that in the temperature range 1200-1250°C, viscosity was in the proper range to permit fiber drawing. This is in agreement with previous experience in fiberizing this composition. However, after being held at 1200°C for several minutes, crystals could be discerned growing in the glass at an appreciable rate. After 10 min the sample in the microfurnace was filled with crystalline material.

In order to confirm that these results were indeed characteristic of 126 glass in bulk and not specific to the particular environment and high relative surface conditions of the microfurnace the following experiments were performed. A 50 ml platinum crucible was charged with 126 glass buttons, and a thermocouple arranged so as to be immersed when the glass became liquid. The crucible was

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FIG. 8

PAPER TAB FIBER MOUNTING SYSTEM

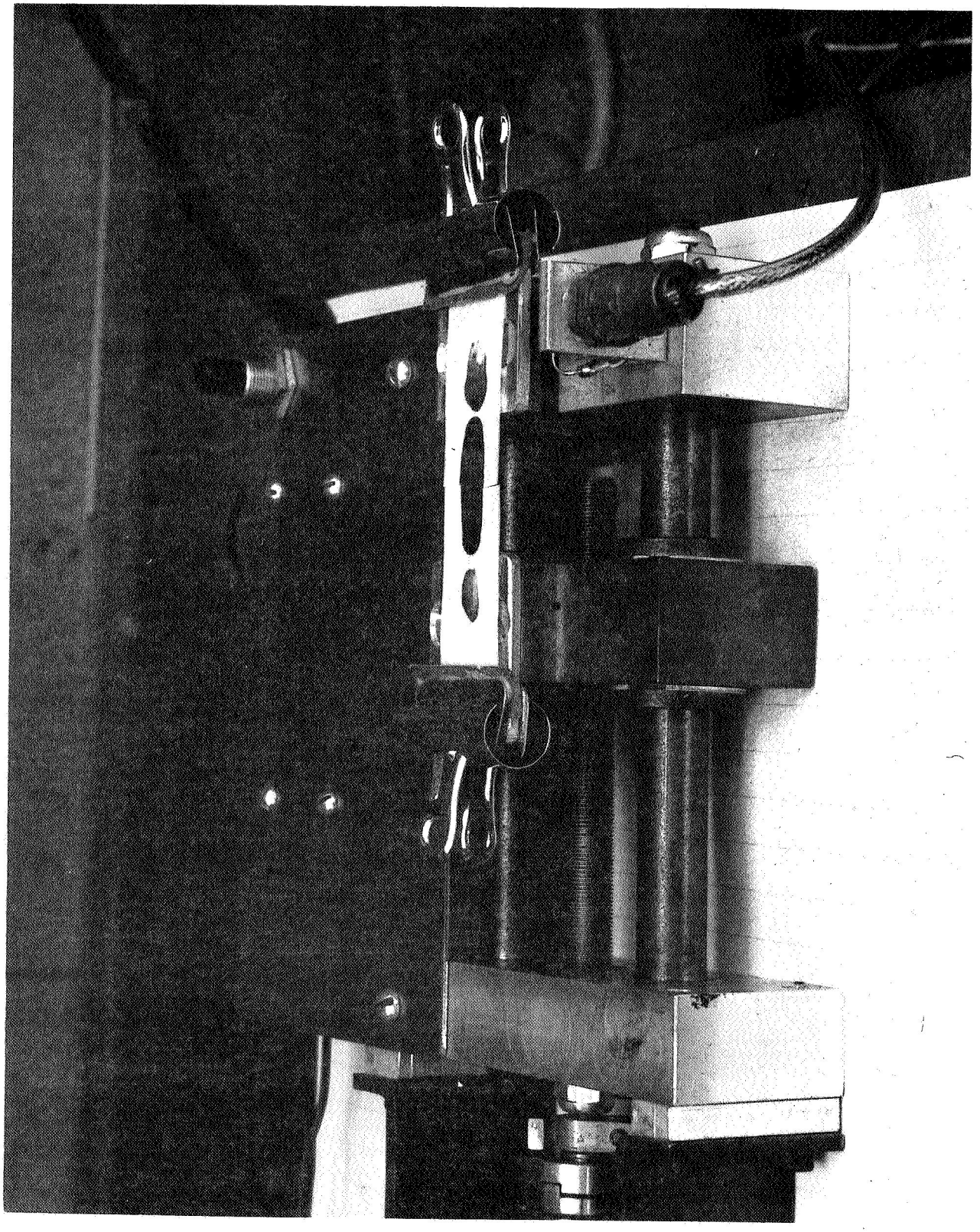

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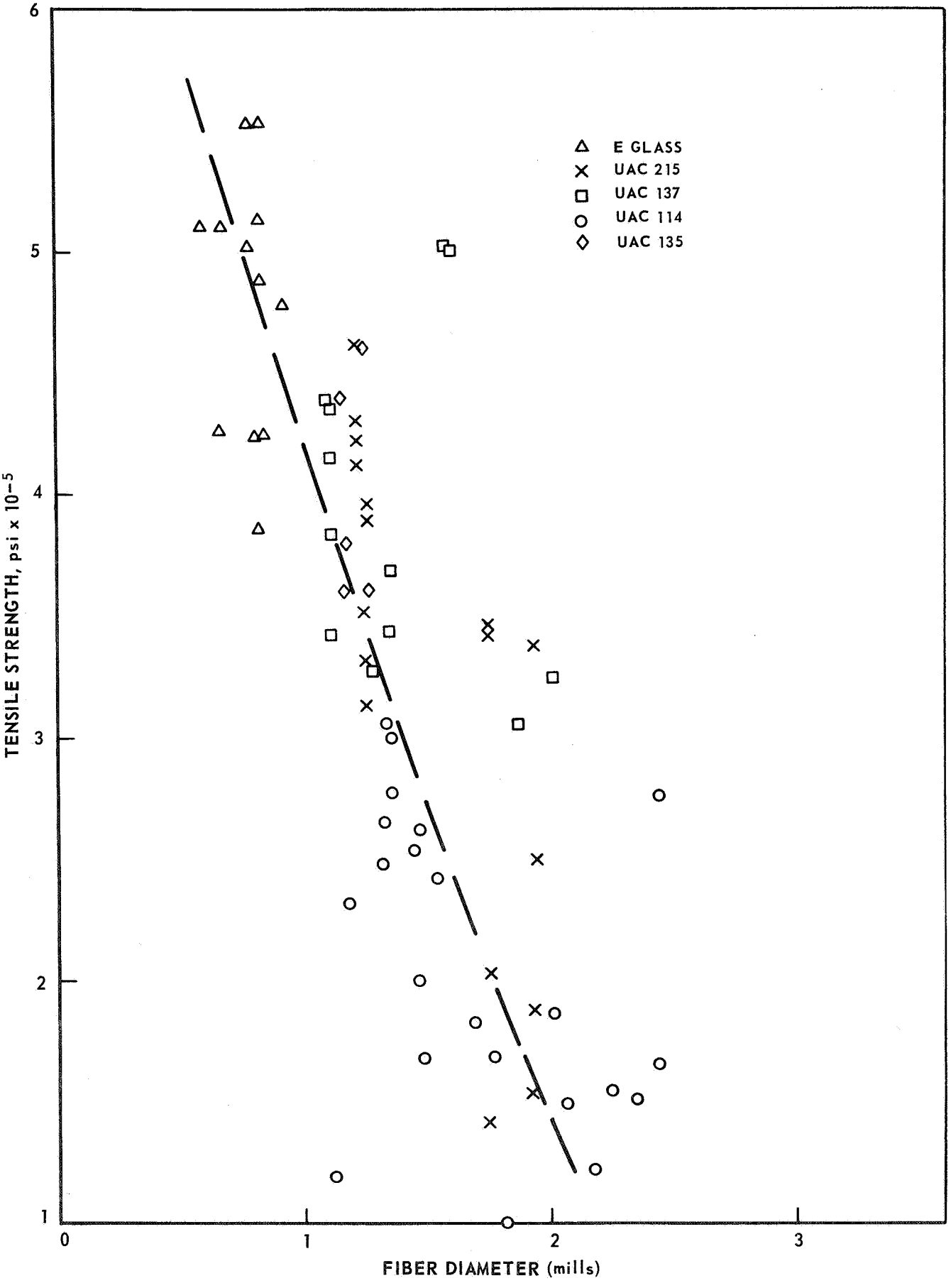
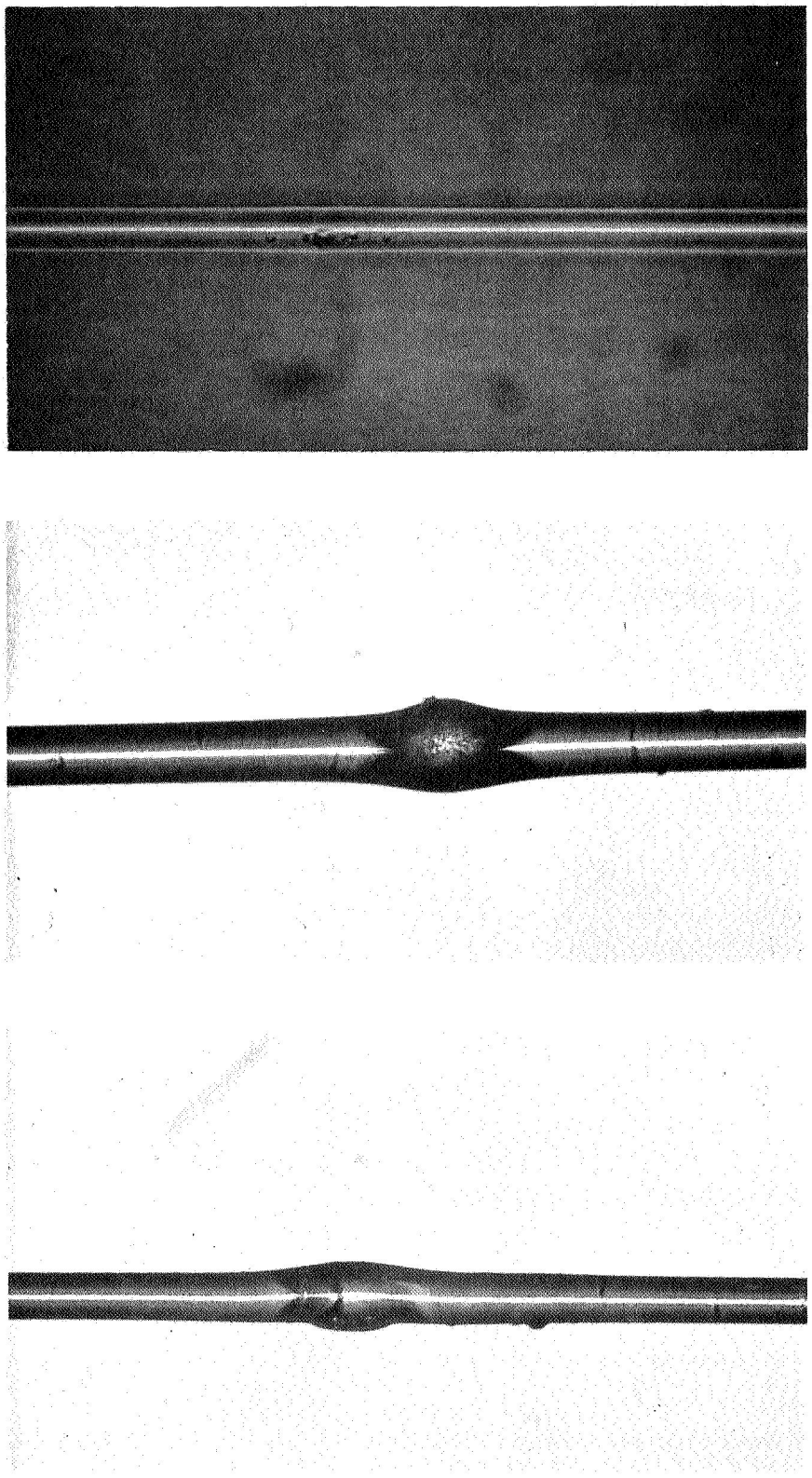
FIG. 9

STRENGTH OF EXPERIMENTAL GLASS FIBERS



TYPICAL INCLUSIONS IN FIBERS



heated to 1560°C, i.e. 100°C above the liquidus, for one hour, then removed from the furnace and cooled to room temperature. No crystalline material was observed in the glass. The crucible was returned to 1560°C for an hour then moved to a cooler portion of the furnace where the temperature fell to 1200°C in about 5 min. The glass was maintained at this temperature an additional twenty minutes, then removed from the furnace. It was found that a considerable amount of crystalline material had formed as shown in Fig. 11. It can be concluded that, at least for this glass, microfurnace observations can be considered to apply to bulk conditions as well. Assuming that microfurance observations on other glass could equally well be translated to bulk conditions, glasses 144, 129, 136 and 138 were examined in the microfurnace. Qualitative observation of crystal growth rate at temperatures in the fiberization range are given in Table XV.

Table XV

Qualitative Observations on the Crystallization of Experimental Glasses

Glass	Approximate Liquidus	Approximate Fiberization Range	Relative Crystallization Rate
114	1375	1200-1250	rapid
126	1460	1200-1250	rapid
129	1355	1200-1250	relatively slowly
136	1315	1200-1250	relatively slowly
138	1325	1200-1250	quite slowly

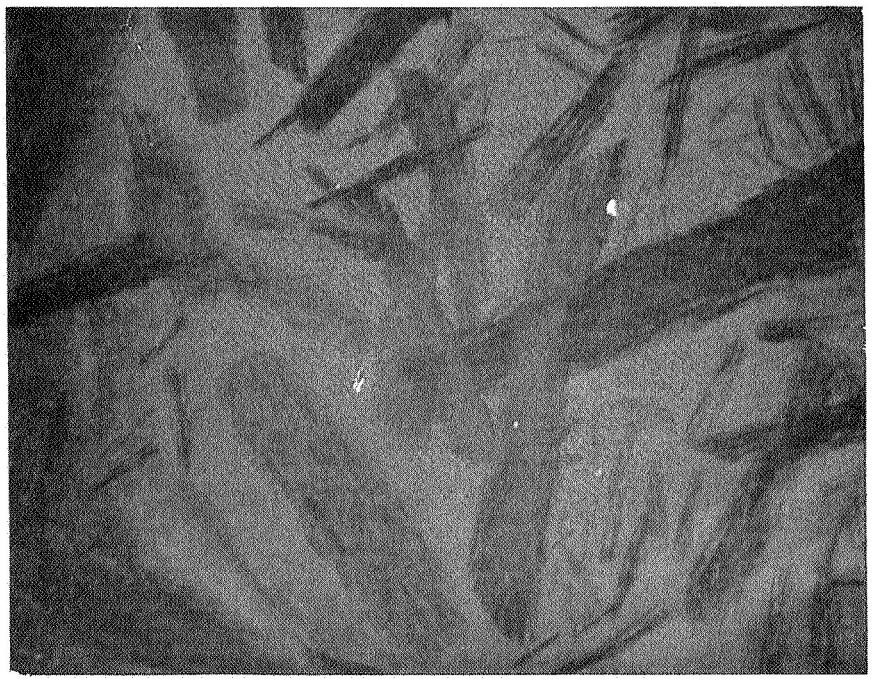
These qualitative observations are in agreement with quantitative kinetic studies which showed the greater effectiveness of La_2O_3 (glasses 136 and 138) in reducing the crystallization rate of cordierite in similar glasses compared to Y_2O_3 (glasses 114, 126, 129). The La_2O_3 bearing glass compositions should be more adaptable to a continuous fiberization process.

Young's Modulus for Mechanically Drawn Experimental Glass Fibers as Measured with Sonic Equipment

Table XVI lists the values for Young's modulus for some of the glasses which have been drawn successfully by mechanical means. Glass melt 82-2 was made from the teachings of U.S. Patent 3,044,888 and melt 83-1 from the doctrine of example 4 of U.S. 3,127,277 in order to provide samples of two of the most outstanding glasses found in the literature. Glass 83-1 contains 11.0% beryllia by weight. All of the other glasses shown in this table are original with UARL. All the glasses of the table were prepared, drawn into fibers, and tested in identical manner so that the comparative data of the table should be reliable even though the absolute numbers assigned to the values of Young's modulus may be in error by a constant multiple. Tests marked FAB were carried out at Fabric Research

FIG. 11

CRYSTAL GROWN IN UAC 126 GLASS AT 1200 °C FOR 20 MINUTES



MAGNIFICATION 50x

TABLE XVI

Measured Values for Young's Modulus on Mechanically Drawn Fibers of UARL Experimental Glasses as Determined by Sonic Tests

Batch	Density (ρ) gms/cm^3	Velocity (C) cm/sec x 10^{-5}	Young's Modulus kg/cm^2 x 10^{-5}	Young's Modulus psi x 10^{-6}	Tested At
40-3	2.9574	5.72	9.72	13.80	FAB
56-1	2.4368	5.79	8.16	11.60	FAB
62-3	2.7036	6.31	10.75	15.30	UARL
63-2	2.6847	6.43	11.10	15.78	FAB
64	2.6818	5.99	9.63	13.67	UARL, Morgan
65	2.7197	6.375	11.07	15.75	FAB, UARL
66	2.6112	6.63	11.69	16.63	UARL
67-3	2.6535	6.58	11.47	16.33	FAB, UARL
68-2	2.6295	6.55	11.27	16.05	FAB, UARL, Morgan
69	2.5910	6.45	10.4	14.80	FAB, UARL
70	2.7526	6.44	11.42	16.25	Morgan
71	2.6627	6.85	12.48	17.75	UARL
72-4	2.8877	6.08	10.69	15.20	FAB, UARL
73	3.0152	6.09	11.02	15.70	FAB, Morgan
74	2.9983	5.92	10.5	14.95	UARL
75	2.6342	5.69	8.53	12.12	UARL
76		5.64			UARL
77		5.66			UARL
82-2*	2.5875	6.61	11.30	16.08	FAB, UARL
83-1**	2.8376	6.512	12.03	17.11	FAB, UARL
102	2.9188	4.82	6.79	9.66	UARL
114	3.2237	6.28	12.72	18.10	FAB, UARL, Morgan
126	3.4634	6.00	12.44	17.72	FAB
127	3.2553	6.075	12.62	17.12	FAB, UARL
129	3.3105	6.195	12.70	18.08	FAB, UARL
131	3.1200	5.87	10.73	15.28	FAB, UARL
135	2.6303	6.16	9.98	14.19	FAB
136	2.8035	6.08	10.37	14.75	FAB
137	3.0834	6.08	11.4	16.22	FAB
138	3.5498	5.66	11.36	16.15	FAB
140	3.678	5.64			UARL

* 82 - Houze Glass - U.S. 3,044,888
** 83 - Owens-Corning - U.S. 3,122,277 (BeO)

Laboratories by their personnel and those marked UARL were carried out here by our personnel on different sets of identical equipment; namely, Dynamic Modulus Tester PPM-5R manufactured by H. M. Morgan Co., Inc., Cambridge, Mass. This apparatus functions by measuring the velocity of a longitudinal sound wave in a lightly loaded fiber sample and is a widely sold and distributed device which has been used to measure the elastic modulus of various synthetic fibers and yarns, inorganic and refractory fibers and yarns, wires, polymer fibers, hair, felts, and other extensively varied types of fibers. This method of testing possesses the great advantage that it is independent of the measurement of the fiber diameter and depends only on the longitudinal sound velocity and density which are much simpler measurements.

Figure 12 shows the progress in glass fiber research over a span of time of three decades where the sonic measurement of modulus is used as the criterion of such progress.

Young's Modulus for Mechanically Drawn Experimental Glass Fibers as Evaluated by Mechanical Testing

The results of the measurement of Young's modulus by mechanical tests conducted for UARL by the Lowell Institute of Technology are shown in Table XVII. These tests were conducted by Lowell Institute of Technology using an Instron CRE tester operated with a machine speed of 0.2 in. per minute, a chart speed of 20 in. per minute, a gage length of 5 in., and a full scale capacity of 1.0 pound. The specimens were held in air actuated clamps with flat rubber coated faces.

For each fiber listed in the table, a minimum of 20 specimens were taken from approximately the center portion of each spool. The specimens were 8 in. long with about one yard of fiber being discarded between each specimen. It was not always possible to select fibers in exactly this manner because many of the spools had discontinuous odd lengths of fiber, but in general, the specimens selected represent the middle 20 yards of the fiber supplied for testing. Three fiber diameter measurements were made in the middle three-inch portion of each eight-inch specimen. These measurements were made using a monocular microscope equipped with an eye piece reticule and operated with a magnification of 774 (18 x eye piece, 43 x objective). Each reticule division was equal to 0.092 mils.

The average of twenty determinations for each fiber is shown in Table XVII together with the maximum and minimum value of the modulus. As shown in our earlier report F910373-8, this data has a standard deviation of 1.82 million psi for example, for glass 126 so that one can say with 99% probability the value for glass 126 tabulated at 16.4 million psi actually lies between 15.2 and 17.6 million psi.

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FIG.12

THREE DECADES OF PROGRESS IN FIBER GLASS RESEARCH

SONIC MEASUREMENTS ON MECHANICALLY DRAWN FIBERS

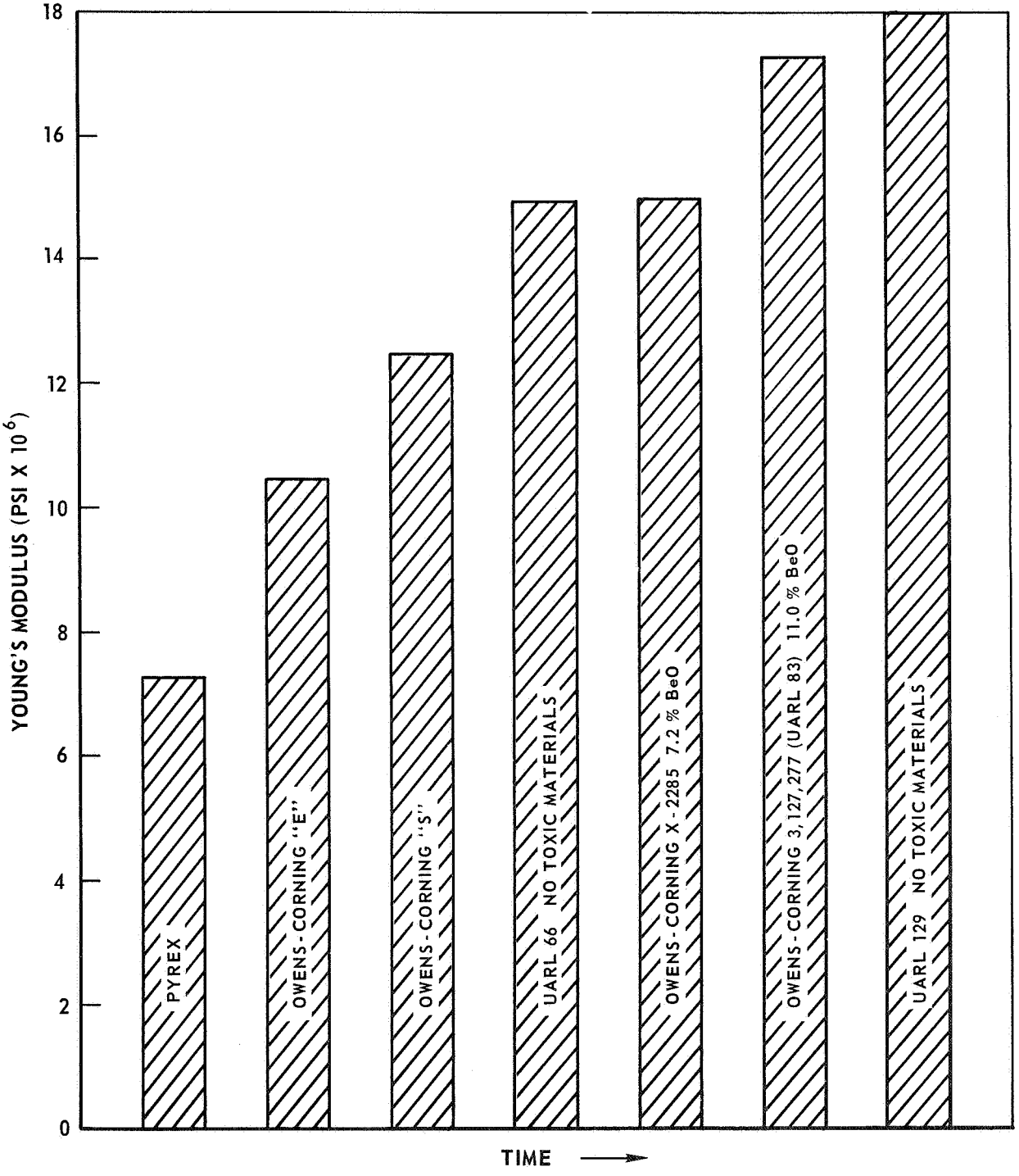

TABLE XVII

Values for Young's Modulus on Mechanically Drawn Fibers of UARL Experimental Glasses as Determined by Measurements on Tensile Test Equipment

Glass Number	Measured Modulus x 10^{-6} psi	Glass Number	Measured Modulus x 10^{-6} psi
25	12.3	97	10.4
40	16.2	98	10.8
56	10.7	102	13.3
62	14.0	108	12.5
63	13.0	110	13.8
64	14.7	114	15.1
65	13.8	126	16.15
66	14.6	127	15.2
67	12.7	129	16.7
68	13.7	131	12.5
69	13.6	135	13.3
70	13.4	136	13.5
71	13.7	137	13.9
72	12.5	138	12.2
73	15.1	140	15.0
74	13.8	155	14.7
75	9.8	157	13.1
76	10.4	159	15.7
77	11.0	160	14.6
82*	13.3	161	14.3
83**	15.35	166	13.6

* 82 - Houze Glass - U.S. 3,044,888
** 83 - Owens-Corning - U.S. 3,122,277 (BeO)

All tabulated moduli values are the average of twenty observations except that the results for 40, 83, 126, 129 are the average of sixty observations and the result for 70 is the average of forty.

Comparison of Table XVI listed the sonically determined values for Young's modulus with Table XVII listing the mechanically determined Young's modulus for some of the same experimental glasses shows that these two methods of measuring elastic moduli fail to yield concordant results. This is true not only for this laboratory but also, in general, for all other laboratories using both methods and is believed to be due to the fact that the sonic method more nearly measures an instantaneous value of the modulus than does the stress-strain machine type of testing. Since the ability of a glass to respond to a given mechanical load is itself dependent on the composition of the glass, the sonic moduli vary with respect to the mechanical moduli in an unpredictable manner. Many of the likely applications for new high moduli glass fibers are dependent on the long-term properties of the fiber and may be more closely correlated with the mechanical method of testing so that this method will be used whenever possible for future measurements. As can be seen from either table, several of the UARL experimental glass compositions yield values for Young's modulus superior to the two competitive glasses prepared for comparison and which were melted, fiberized and tested in procedures identical with those throughout.

CONCLUSIONS

1. The rare-earth additives such as lanthana, ceria, and yttria used to slow down crystallization in the UARL program of controlling the kinetics of crystallization of molten oxides likely to form complex three-dimensional molecules function effectively in this capacity. Further, such additives markedly increase the Young's modulus obtainable in this glass system.

2. Further research concentrated on improving the working characteristics and lowering the density is needed before glass fiber production from rare-earth cordierite glasses will be practical.

3. Useful strength data on virgin glass fibers of the UARL experimental glasses will result only when these glasses are processed using a conventional glass fiber bushing either here at UARL or elsewhere.

4. The marked increase in modulus obtainable in the last quarter from very limited research on "invert" glass compositions suggests that a large part of our future research effort should be concentrated in this area.

PERSONNEL ACTIVE ON PROGRAM

Personnel active on the program throughout the last nine month period have been J. F. Bacon, Principal Investigator, and Norman J. Chamberlain, senior experimental technician. In the first six months of the period, Robert B. Graf carried out the optical studies of crystallization kinetics and in the last six months Geroge Layden set up the program for investigating the strength of virgin

glass fibers and originated and applied the method of obtaining circular glass rods directly from the melt. Liaison throughout the program has been carried out by Peter A. Stranges of the UARL Washington Office. Throughout the program all of the UARL personnel have reported progress to and received advice from James Gangler of NASA Washington Headquarters.

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