INVESTIGATION OF THE KINETICS OF CRYSTALLIZATION OF SEVERAL HIGH TEMPERATURE GLASS SYSTEMS

J910939-2

by

James F. Bacon

JUNE 1, 1970

United Aircraft Research Laboratories

UNITED AIRCRAFT CORPORATION

EAST HARTFORD, CONNECTICUT

QUARTERLY STATUS REPORT NO. 2

CONTRACT NASW-2013

United Aircraft Research Laboratories

UNITED AIRCRAFT CORPORATION

EAST HARTFORD, CONNECTICUT

Report J910939-2

Investigation of the Kinetics of Crystallization of
Several High Temperature Glass Systems

Quarterly Status Report No. 2

Contract NASW-2013

REPORTED BY J. F. Bacon

APPROVED BY M. A. DeCrescente
M. A. DeCrescente, Chief
High Temperature Materials

DATE 6/1/70

NO. OF PAGES 34

COPY NO.

Investigation of the Kinetics of Crystallization of

Several High Temperature Glass Systems

TABLE OF CONTENTS

Investigation of the Kinetics of Crystallization of

Several High Temperature Glass Systems

Quarterly Status Report No. 2

February 1, 1970 through April 30, 1970

Contract NASW-2013

SUMMARY

Intensive investigation of glass fibers drawn from UARL glass composition 344 has shown that such fibers can be readily and continuously drawn at high rates of speed and restarted at will. Over forty million feet of these fibers have been drawn through an orifice of 0.038 in. dia at orifice temperatures from 1260°C to 1310°C, with leads of molten glass from 3/8 in. to 1 1/2 in., and at winding speeds of 4000 to 8000 ft/min (the top speed on our winder).

The UARL 344 glass fibers processed under these conditions show excellent properties. Diameters vary from 0.2 to 0.4 mil for these fibers which have a Young's modulus of 18.6 million psi, a specific modulus of 157 million inches and strengths which in twenty-two consecutive measurements averaged 772,000 psi and ranged from 600,000 to 1,000,000 after extreme values were discarded.

A limited evaluation of the UARL glass fibers in a resin matrix has been very encouraging and indicated a unidirectional longitudinal modulus as high as twelve million psi, shear strengths as high as 16,000 psi, and tensile strengths (unsized) of 270,000 psi. UARL scientists calculate for a 70 vol % glass fiber-resin matrix $\pm 45^\circ$ alignment, that the results will be:

Fiber	Density lbs/in.^{3}	Modulus million psi	Specific Modulus ten million inches
E	0.0776	3.27	4.21
S	0.0762	4.12	5.41
UARL 344	0.0951	6.08	6.39

In addition to the basic composition, a number of variants of UARL 344 glass have been prepared and eleven of these show higher specific moduli with three having higher absolute moduli as well.

While the study of the UARL glass composition and its potentialities has been the bigger half of the effort in the second quarter, research toward an improved non-toxic glass fiber to compete with or surpass the UARL 344 glass fiber has been resumed and recent results obtained are given in this report.

INTRODUCTION

This is the second quarterly report on the new contract between UARL and NASA Headquarters, namely NASW-2013, whose title is "Investigation of the Kinetics of Crystallization of Several High Temperature Glass Systems". This research follows directly from the former contract NASW-1301, "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems" under which sixteen quarterly reports were issued. It differs in the single very important respect that a sizable portion of the research effort deals with the selection of the two compositions most promising for glass fibers with outstanding properties and the investigation of those problems that arise when an effort is made to produce large quantities of these fibers, or to manufacture glass fiber-plastic resin composites, and to extensively study their properties not as yet measured. Because we have done relatively very little of this type of research, the first two quarters of the new contract represent a marked concentration of effort in these areas. The first part of the report is comprised, therefore, of the changes in bushing design necessary to produce more than forty million feet of the UARL 344 glass composition as monofilaments, an estimate of the cost per pound of the ingredients if the glass were to be produced in million pound lots, an assessment of the so-called virgin fiber strength, preparation of compositional variants, and the formation and evaluation of glass fiber-resin components.

Research of the type carried out under the first contract, namely, the origination and evaluation of new glasses was also resumed in this quarter and the report includes the compositions for new glasses UARL 433 through 454, as well as the preliminary evaluation of some of the properties of these new glasses together with a continuing study of the properties of the glass compositions originated in the two prior quarters. The aim of this research is to invent a non-toxic (no beryllia content) glass composition with properties at least equal to those of UARL 344 as well as to develop a still higher-modulus, higher-strength version of the beryllia containing glasses. Tables are included which gather up all of our pertinent experience believed to be suitable as guide posts for the directions in which to move to obtain the desired improved glass compositions.

RESEARCH PRIMARILY CONCERNED WITH UARL 344 GLASS AND ITS PROPERTIES

At the time of the start of the new contract, UARL 344 glass had been successfully fiberized only in the original UARL poor man's bushing. Five million feet of monofilament of this glass had been drawn through such bushings and its modulus was known to be almost invariable with a value of 18.6 million psi in fiber form. Nothing was yet known about the strength of this glass, the effect of varying composition on the properties of this glass, the viscosity-temperature relationship for this glass, nor even whether the glass could be successfully fiberized in a commercial-type single-hole bushing. The work of the first two quarters of the new contract has largely answered these questions although, of course, it has also raised some additional questions as yet unanswered.

Evolution Necessary In Commercial-Type Single Hole Bushing

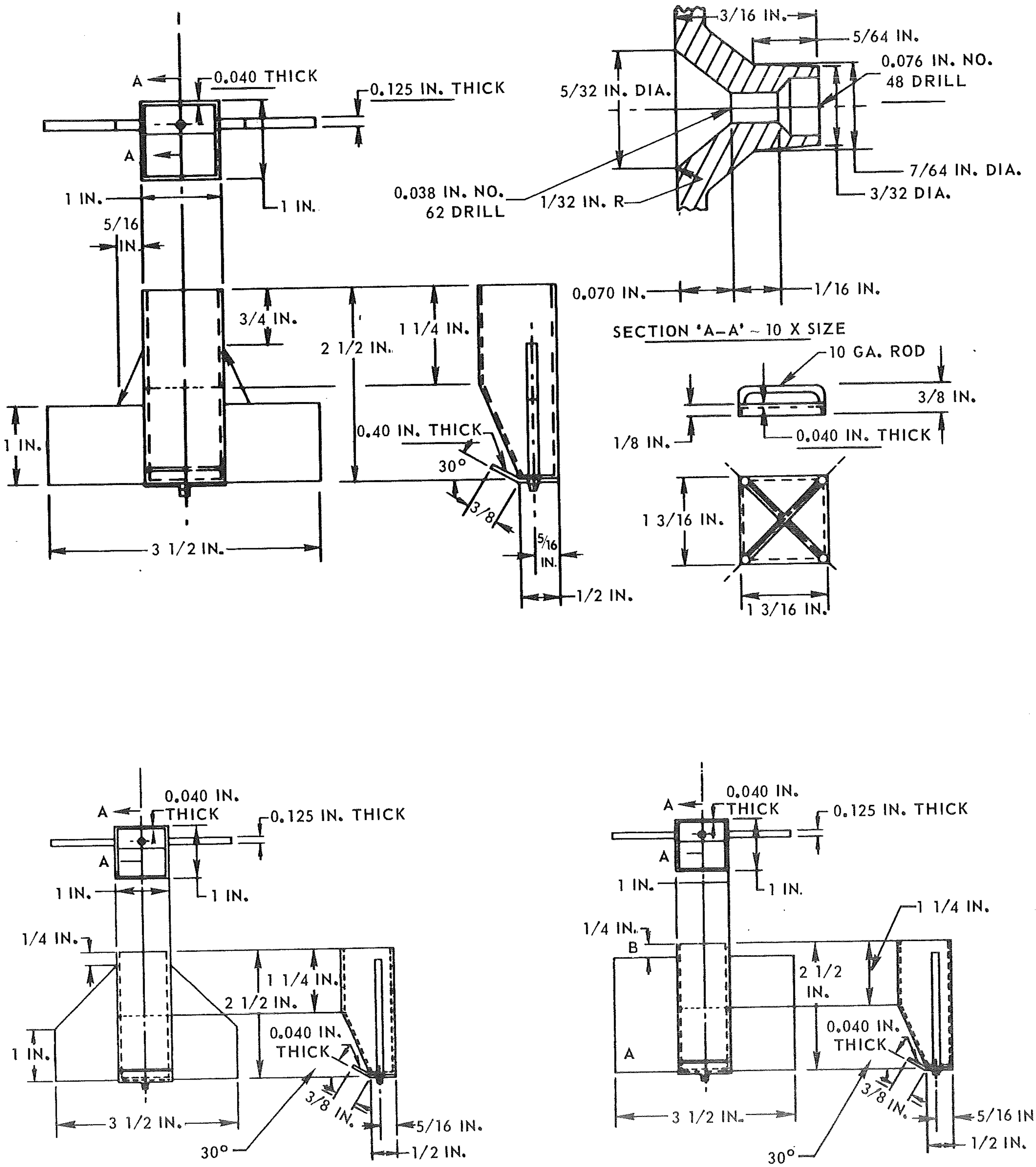
In attempting to form the UARL 344 glass fiber by means of a commercial type single-hole bushing, the glass itself was first remelted to form a shaped slug that would fit the platinum-rhodium single-hole bushing shown in the engineering sketch as IA. The bushing itself was insulated and heated by a massive current (1000 amperes at 1.3 volts, 60 cycle a.c.) supplied through water-cooled copper electrodes. Trouble quickly developed since with this original design bushing of Fig. 1a, the temperature at the top of the platinum bushing was approximately 350°C cooler than the temperature on the side of the bushing and just a quarter inch above the orifice. As a consequence of the lack of sufficient heat at the top of the bushing to prevent nucleation of UARL glass 344, the glass bridged across the top and interfered with the continuity of operation by making it impossible to charge a second shaped slug of glass. As a temporary expedient to alleviate this condition the installation of a gas-oxygen ring burner around the top of the bushing was suggested, but instead it seemed simpler to place a hollowed-out refractory brick carrying two silicon carbide heating element on top of the bushing with the platinum lid removed. This device proved satisfactory and allowed the necessary temperature distribution to be obtained, i.e. the top of the furnace approximately 45°C hotter than the bottom.

Even with this auxiliary top heater, no glass fibers were made initially because the glass did not form the proper shape drop close enough to the orifice. At the suggestion of Dr. Otto, who was visiting UARL on other business, a water cooler was installed directly below the orifice to replace the argon jet cooling originally used and this worked satisfactorily. It was possible to carry out fiberization runs lasting several hours with this apparatus and more than five million feet of 0.4 mil fiber was prepared from the slugs of UARL 344. In the meantime, the original design of glass fiber bushing shown in Fig. 1a has been twice changed as may be seen from Figs. 1b and 1c. The resultant bushing appears as shown in the photograph of Fig. 2. Using this version of the bushing more than forty million feet of UARL glass fiber has been made without any serious interruptions or down time. Operating variables have included a variation in orifice temperature from 1260°C to 1310°C, a variation in the head of molten glass from 1 1/2 in. to 3/8 in., a variation in winding rates from 4000 to 8000 ft/min.

The mode of operation most successful with the single-hole bushing design sketched in Fig. 1c and photographed in Fig. 2 is to completely fill the bushing with a previously prepared glass slug, heat the mold to give the desired orifice temperature, allow the drop to form and fall to the 45° deflection plate near the winder with the winder running slowly and to gradually accelerate the winder until the desired winding rates are achieved. Glass is then added at the rate of about one 3/8 in. thick slug slice every hour. The winding can be continued indefinitely in this manner or started and stopped at will. Single lengths of several million feet in one piece can be obtained during the single working shift that we normally operate. No top heater is needed with this design.

FIG. 1

EVOLUTION OF UARL DESIGN FOR SINGLE-HOLE BUSHING



J910939-2

FINAL DESIGN UARL PLATINUM – RHODIUM BUSHING

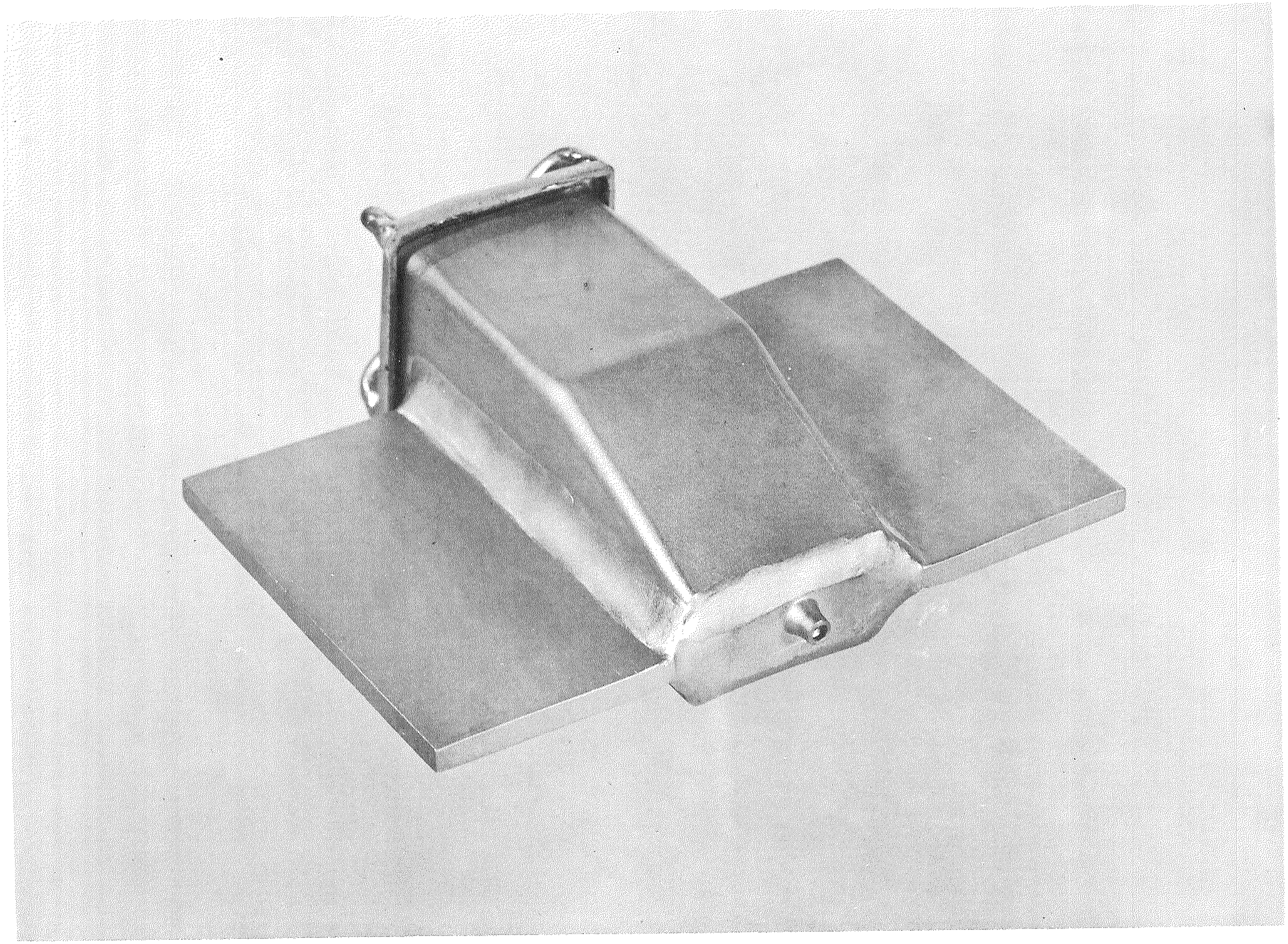


FIG. 2

The Measurement of the Viscosity-Temperature Curve for UARL 344 Glass

The device used to measure the viscosity of the UARL 344 glass at high temperature is the Brookfield Synchro-Electric Viscometer*. The device operates as follows. A cylinder or disc or spindle is rotated in the fluid under test by means of a beryllium-copper spring. The deflection of the spring is read on a dial. The dial reading resulting with the usual disc is multiplied by a simple constant to obtain the resulting viscosity at the particular rotational speed. When special design spindles are used, the device is calibrated through the use of oils of known viscosity. Measurements made at different speeds are used to describe the complete flow properties of the material at hand.

The Brookfield viscometer had never been used before at temperatures as high as those likely to occur in this contract. However, this merely meant that the device must be equipped with a long shaft entering the furnace and with a spindle of suitable high temperature material. Single-crystal tungsten was selected as the spindle material since it can easily be machined and does not rely for its machinability on the usual adulterants nickel and copper added to normal tungsten to make it workable. This material is known from previous research to be compatible with all the molten oxide systems investigated to date. The shaft is a good grade of commercial tungsten. The tungsten assembly and the Brookfield viscometer were then calibrated using the National Bureau of Standards standard viscosity oil "P" and substituting an exact silica replica for the tungsten crucible later to be employed at high temperatures. The entire oil filled crucible is held at a temperature of $\pm 0.005^{\circ}C$ by use of a constant temperature bath and the temperature varied from $-5^{\circ}C$ to $+100^{\circ}C$.

Once calibrated the Brookfield viscometer and the tungsten assembly are installed in and on the tungsten resistance furnace as shown in Fig. 3 and through the use of this equipment the viscosity-temperature curve for UARL 344 glass sketched in Fig. 4 is obtained. While the working range of the UARL glass is not as great as that of Owens-Corning "E" glass sketched in the same figure, although with a different temperature scale, it appears more than sufficient since it is approximately $100^{\circ}C$. And, indeed, it has proven possible by a variation of operating parameters to draw good quality fibers from the UARL 344 composition at high rates of speed over a very considerable temperature range.

Chemical Composition and Cost of Ingredients in Large Quantities

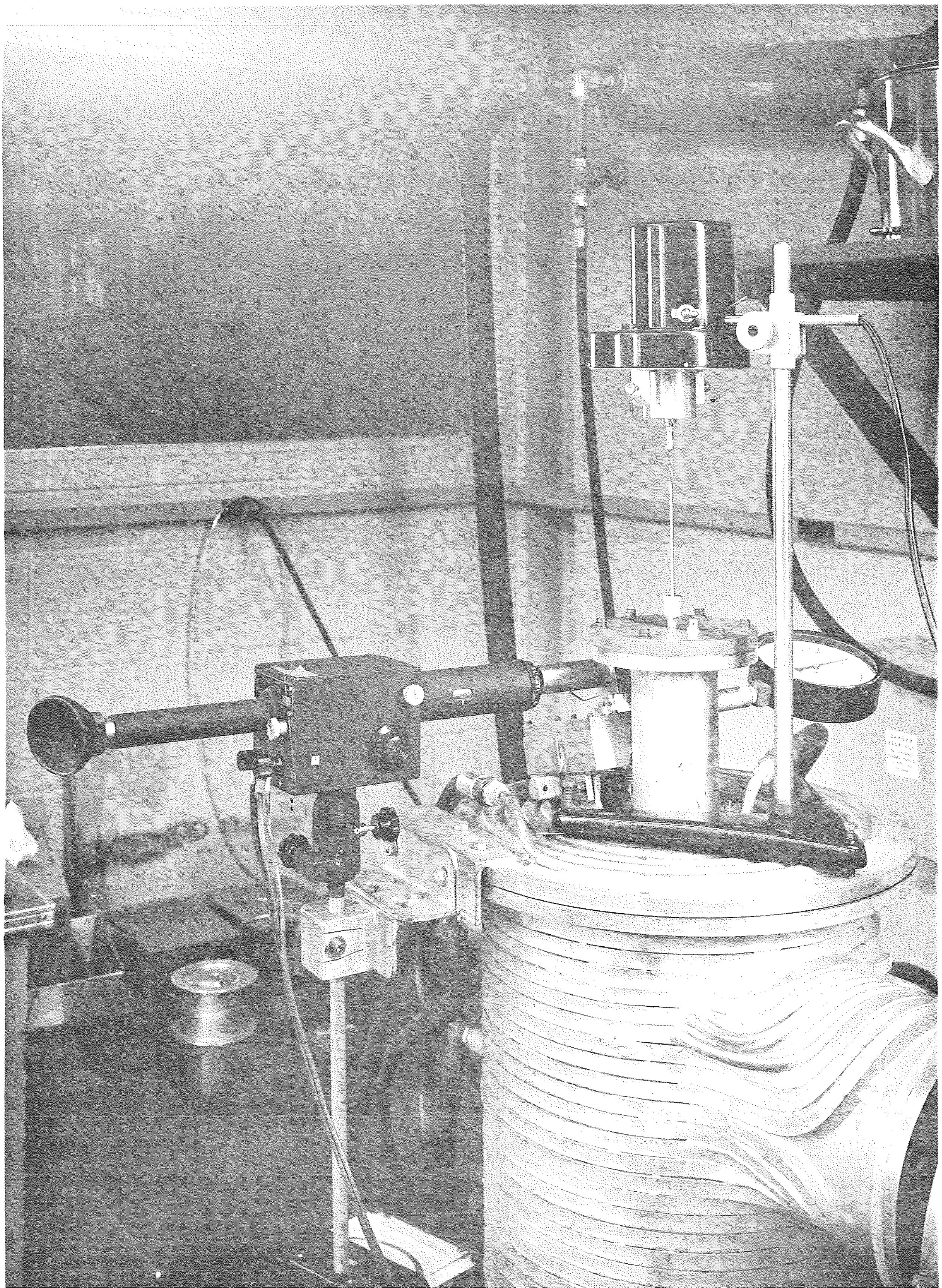
The chemical composition of the UARL 344 glass is shown in Table I in terms of the actual ingredients used in forming the glass. The copious evolution of gas from these ingredients is sufficient to completely fire the glass when the

*Trademark, Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

J910939-2

FIG. 3

BROOKFIELD VISCOMETER INSTALLED ON TUNGSTEN FURNACE FOR HIGH TEMPERATIRE VISCOSITY MEASUREMENTS



RL-66-69-D

VISCOSITY-TEMPERATURE CURVES FOR OWENS-CORNING "E" GLASS COMPARED TO UARL 344 GLASS

J910939-2

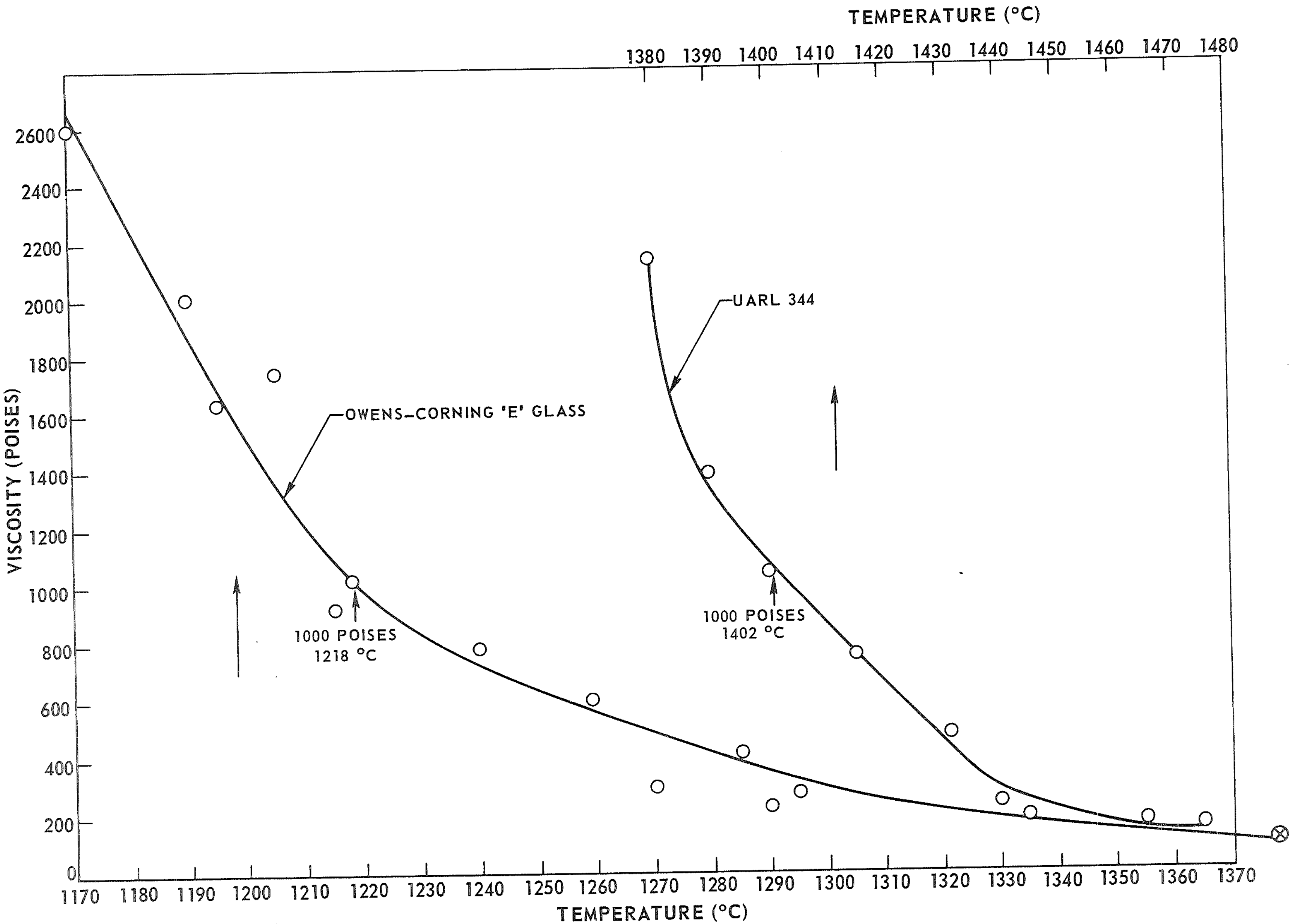


FIG. 4

Table I

Chemical Composition of UARL-344 High Modulus Glass

	Weight Percentage	
	Glass Composition	Raw Material Composition
SiO_2	36.2	22.6
Al_2O_3	20.4	12.8
MgO	8.1	5.1
BeO	5.0	9.0 (as the carbonate)
Y_2O_3	30.2	50.6 (as the oxalate)

molten mixture is held at temperatures of 1450°C to 1520°C for periods of two hours. The molten glass is then poured into a heated graphite mold to form the slug used to load the single-hole bushing for fiber preparation.

The actual cost of the ingredients used to form the glass are shown in Table II based on the prices quoted to us for the preparation of this glass in million pound lots. It must be noticed that these prices do not include any processing charges or profit.

Assessment of Strength

The strength of the glass in fiber form is perhaps the second most important parameter necessary in evaluating the usefulness for the UARL 344 glass composition. The equipment used to study the strength is shown in detail in Figs. 5 and 6.

In Fig. 5, the tensile strength and tensile modulus tester is shown unencumbered by the usual associated equipment. This tester is equipped with interchangeable load cells, which can apply full scale loads of 10 grams to 200 pounds. The fiber to be tested is held in place by sealing wax which is softened by nichrome wire heaters embedded in the two heads of the test fixture. For a very strong fiber where the sealing wax cannot hold the fiber, epoxy can be used in place of sealing wax. A constant load is applied to the fiber by a synchronous motor and a drive screw. The output of the load cell can be plotted on a chart.

In Fig. 6, the tensile strength tester together with its usual associated equipment is shown. The movable jaw to which the fiber is attached is designated by the letter A and the load cell platform to which the other end of the fiber is attached is lettered B. These jaws hold embedded heaters to melt the sealing wax used for attaching the fiber. Jaw A is then driven at a constant rate of 0.03 in./min by a synchronous motor, lettered C, and a drive screw, D. The load cell output in microamperes is calibrated in terms of microamps/gram load on the fiber. The fiber diameter of the break is determined microscopically and the breaking stress is then calculated.

Because of the sensitivity of glass fiber to surface damage that can result from winding it on a drum or any similar contact, and by exposure to uncontrolled atmosphere for even very short times, it has become the practice to report so-called "virgin strength" of freshly drawn glass fiber. This is accomplished by capturing a sample of the fiber between the bushing and the winding drum (see Fig. 7), and measuring the tensile strength as quickly as possible before any obvious damage has occurred. In capturing the test specimen, a paper tab fiber mounting system has proven desirable because such a system provides a degree of self-alignment for the tensile specimens, and the paper mounts help absorb the energy of the fiber whiplash thus damping fly-out. Further, such a system makes possible the preparation of several tensile specimens from each captured fiber. The capture device is made long enough to engage eighteen inch lengths of fiber between the bushing and the take-up spool. 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 fiber paper mounting tabs,

Table II

Cost of Raw Materials for Preparation of UARL 344

Batch Materials

	grams required	pounds required
Silica	181	0.3990
Alumina	102.3	0.2255
Magnesia	40.5	0.0893
Yttrium Oxalate	405	0.8929
Beryllium Carbonate	71.8	0.1583
		1.7659 lbs → 500 grams
		or 1.1023 lb finished glass

Cost in Million Pound Lots

	Raw Material pounds/1.1023	Cost per 100 pound drum	Cost per pound in million pound
Silica (sand)	0.36197	0.90	0.00326
Alumina	0.20457	1.64	0.00335
Magnesia	0.08101	4.84	0.00391
Yttrium Oxalate	0.81003	75.00	0.60752
Beryllium Carbonate	0.14361	425.00	0.61034
			$1.22838

Approx. $1.25 per pound in million pound lots

TENSILE STRENGTH TESTER

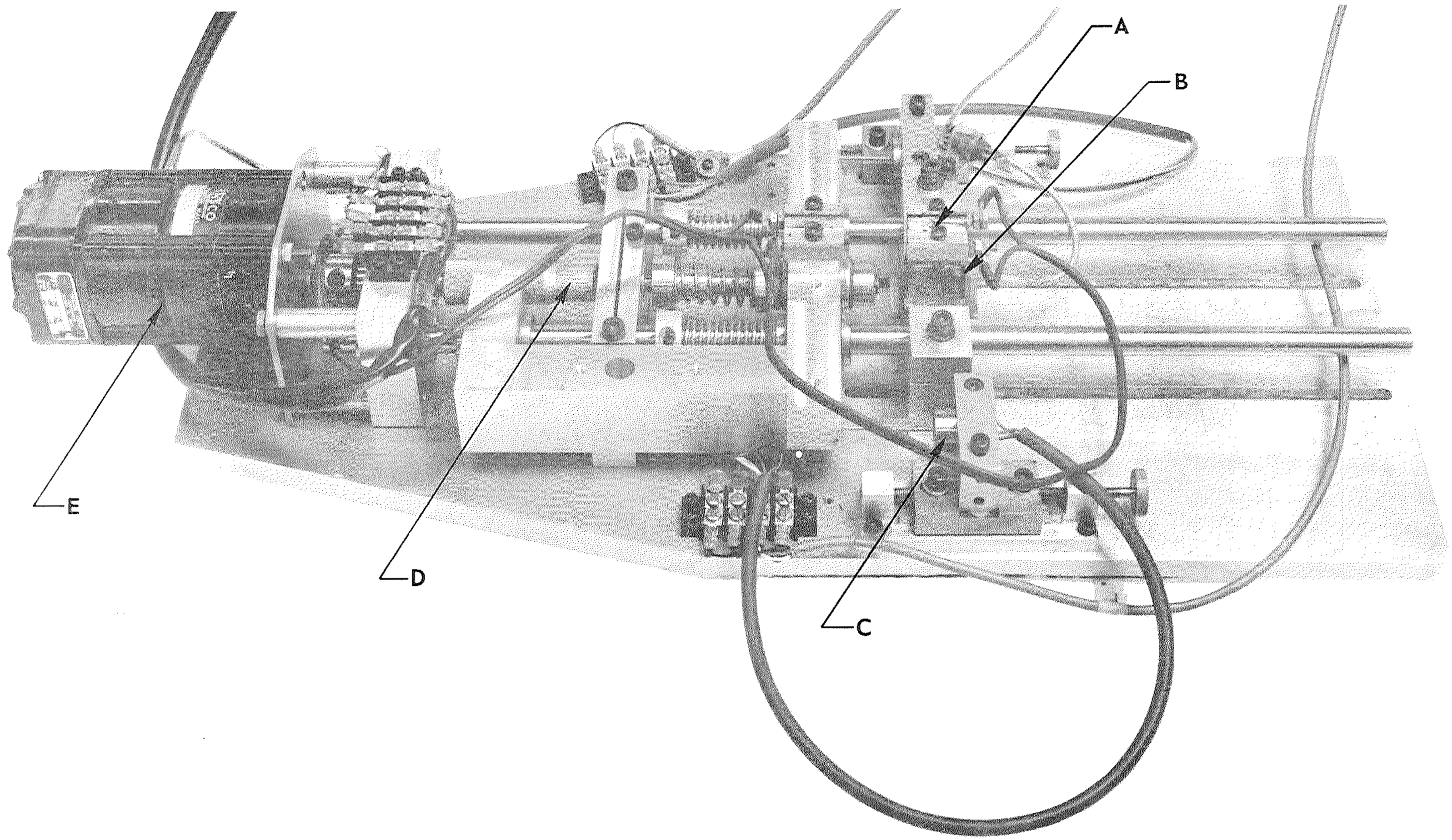


FIG. 5

TENSILE TESTER

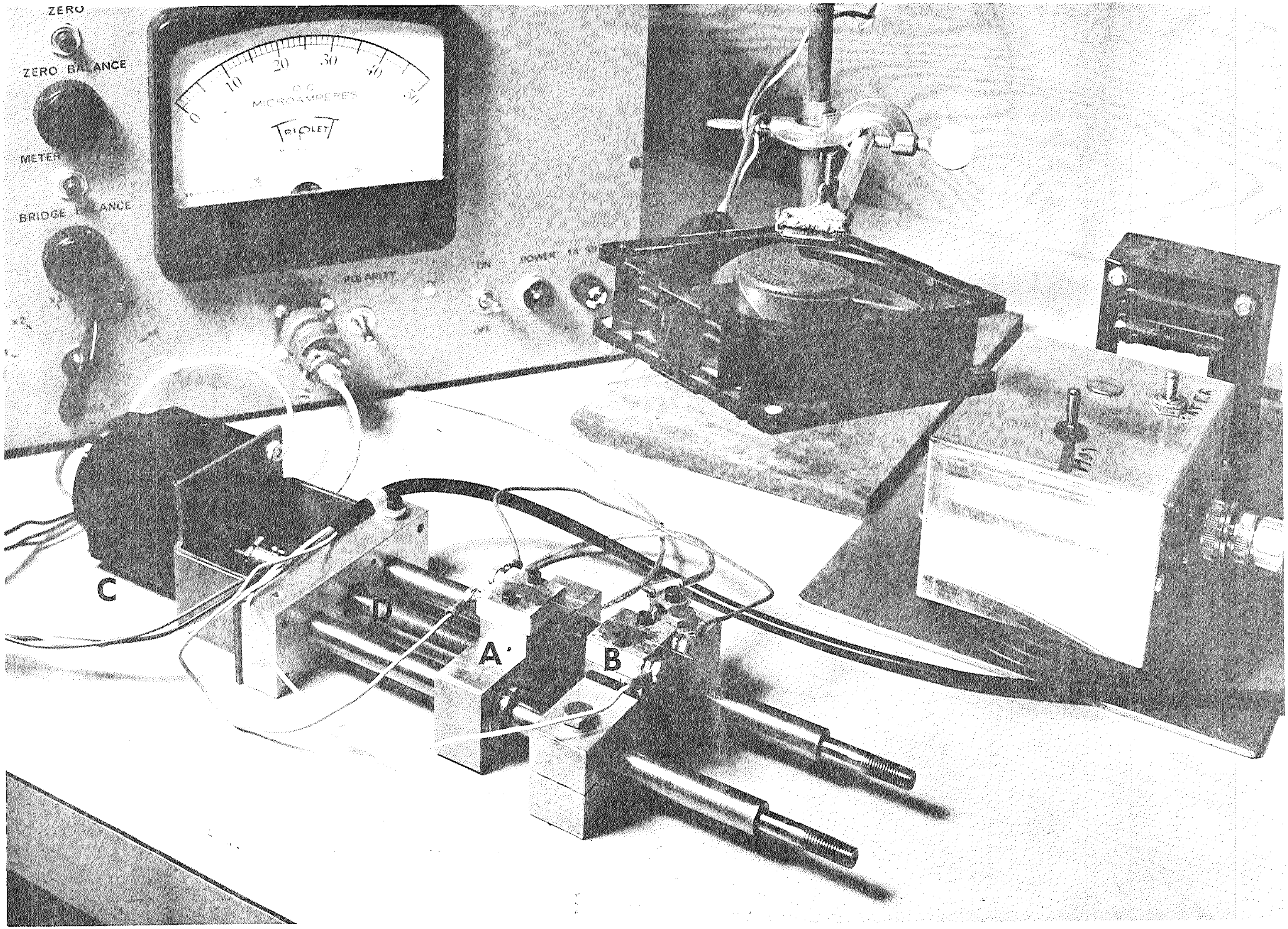
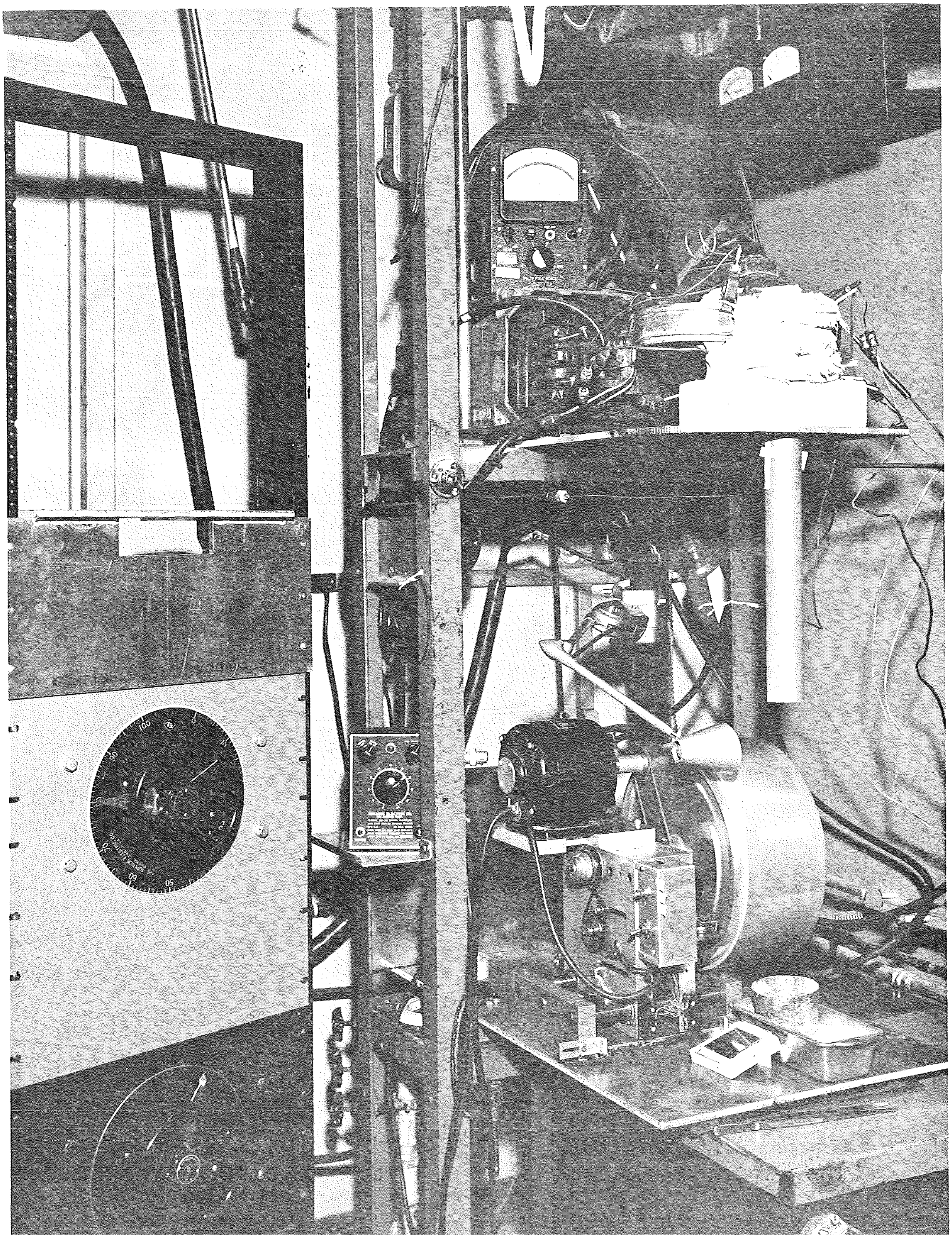


FIG. 6

FIG. 7

COMPLETE ASSEMBLY OF MONOFILAMENT WINDING EQUIPMENT



and then attached to the tabs using Banker's wax (a hard red sealing wax) applied with a pencil-sized soldering iron. The tensile specimen is then cut from the tape and mounted on the testing machine (see Fig. 8).

Using these procedures, the strength measurements shown in Table III were obtained. The twenty-two consecutive measurements listed in this table gave an average tensile strength of 772,000 pounds per square inch and discarding the three lowest and three highest values the values range from 600,000 $lbs/in.^2$ to 1,000,000 psi. It will be noted also that there is a considerable variation in diameter. The range in strength values may be due to gas trapped in the glass or local lack of uniformity in chemical composition or variation in orifice temperature or in the level of molten glass present in the bushing. Until the effects of such variables are understood and eliminated, we cannot say with certainty what the strength of the UARL 344 glass actually is and the average value of 772,000 psi obtained should be regarded as the lower limit of strength likely to be obtained.

Preparation of Compositional Variants of UARL 344

In Table IV we have listed the several compositional variants of the UARL 344 glass prepared to date together with the properties obtained for these glasses. It will be noted that eleven of these show higher specific moduli and three of them have higher absolute moduli as well. The fiberizing qualities of these variant compositions are now under investigation together with the determination of viscosity-temperature curves for the most improved composition.

Incorporation of UARL 344 Glass Fibers in Plastic Matrices

The UARL glass fibers have been successfully added to several plastic matrix composites. The results of the evaluation of these composites is shown in Table V. It will be noted that the epoxy-resin composite with UARL glass fiber shows a modulus forty percent higher than that achievable with the most common type of competitive glass fiber, and twenty percent higher than that obtainable with the best available grade of competitive fiber. Specimens have been subjected to flexural stresses as high as 277,000 psi at which point shear failure occurred. Composite tensile strengths in excess of 300,000 psi appear likely with the UARL 344 glass fiber. Even further increases in composite strength may be realized by applying a surface finish during the preparation of the fiber although this investigation is still in the preliminary stage. Shear strengths are greater than 16,000 psi. A picture of a typical UARL fiber glass plastic composite is shown in Fig. 9.

Calculations by Mr. R. Novak of this laboratory of the modulus of a 70 vol % glass fiber epoxy resin composition with a layup $\pm 45°$ shows the marked advantage of UARL 344 glass fibers in modulus limited applications:

PAPER TAB FIBER MOUNTING SYSTEM

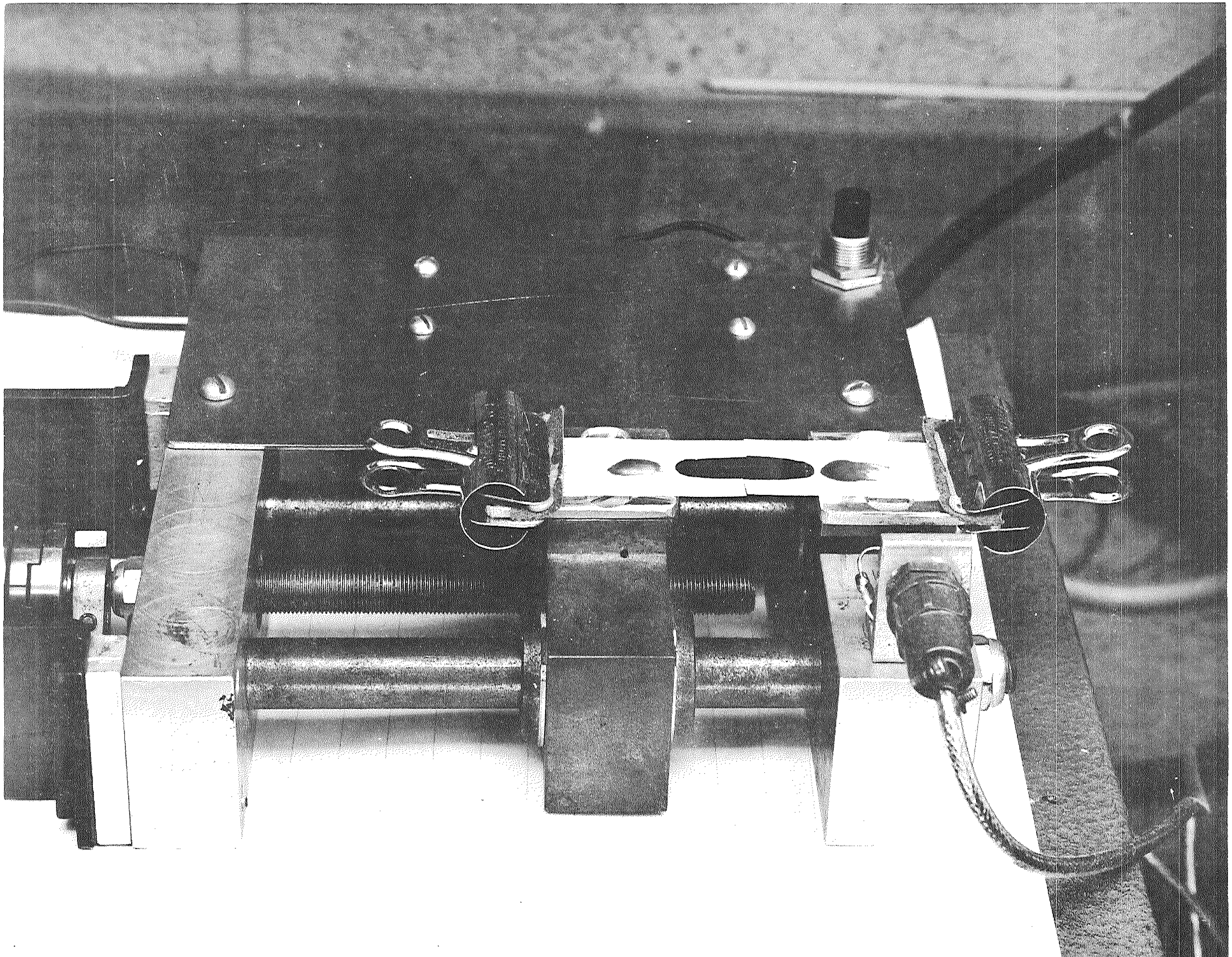


FIG. 8

Table III

Assessment of Strength of UARL 344 Glass Fiber

Diameter (mils)	Area (square mils)	Breaking Load (pounds)	UTS (#/in.^{2})
0.202	0.032	0.02381	743,000
0.302	0.072	0.04938	689,000
0.199	0.031	0.03748	1,205,000
0.265	0.055	0.03307	600,000
0.190	0.028	0.03086	1,089,000
0.262	0.054	0.03307	613,000
0.226	0.040	0.03307	824,000
0.223	0.039	0.03086	790,000
0.181	0.026	0.01543	600,000
0.160	0.020	0.01984	987,000
0.199	0.031	0.02205	709,000
0.175	0.024	0.02425	1,008,000
0.199	0.031	0.01543	496,000
0.163	0.021	0.01984	951,000
0.154	0.019	0.01984	1,065,000
0.320	0.080	0.04321	537,000
0.280	0.062	0.05115	831,000
0.335	0.088	0.05379	610,000
0.323	0.082	0.04321	527,000
0.247	0.048	0.04057	847,000
0.247	0.048	0.02910	607,000
0.253	0.050	0.03263	649,000

Mean UTS 771,730 $\pm$ 204,000 lbs/in.^{2}

Table IV

Compositional Variations Based on Composition of UARL 344 Glass

Glass No.	Compositions in Mol Percent										Young's Modulus		
	SiO_2	Al_2O_3	MgO	Li_2O	CaO	ZnO	La_2O_3	BeO	Y_2O_3	Re_2O_3	Bulk Glass 10^6 psi	Specific for Bulk Glass 10^6 psi	Fiber 10^6 psi
344	45	15	15					15	10		20.3	170	18.6
345	45	15						30	10		21.1	175	
408	45	10				10	10	25			18.3	131	16.6
410	45	15	15	3				15		10	18.23	139	16.7
411	45	15	15				10	15			18.0	135	16.5
416	45	12	15	3				15	10		19.61	164	18.6
417	45	15	15	3				15	7		19.4	173	17.5
418	45	15	12	3				18	7		19.4	172	18.0
419	42	15	15	3				15	10		20.2	170	18.4
420	42	12	15	3		3		15	10		19.5	161	17.8
421	42	10	20	3				15	10		20.4	169	
422	40	9	18	5				18	10		20.6	171	
423	40	9		2	18	3		18	10		20.7	165	

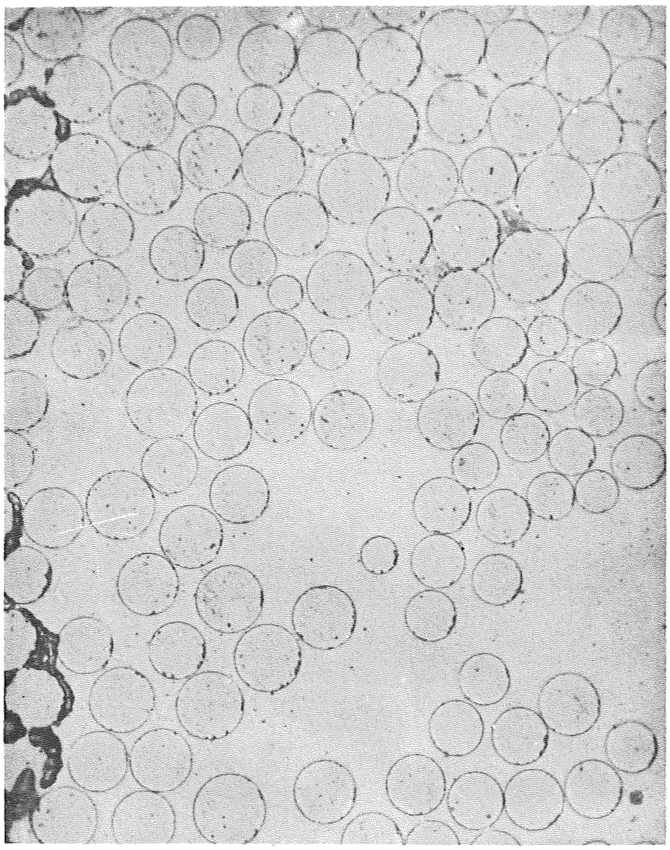
Table V

Glass Fiber-2256-0820 Epoxy Resin Composites

UARL 344 Glass	Surface Treatment	% Void	Fiber Volume %	Density g/cc	Shear Strength psi	Flexural Properties Strength 10^3 psi	Flexural Properties Modulus 10^6 psi	Flexural Properties Norm. to 50 Vol % Fiber Strength 10^3 psi	Flexural Properties Norm. to 50 Vol % Fiber Modulus 10^6 psi
344-0	none	---	51	2.32	---	127[a]	8.67	125	8.50
344-1	none	---	74	2.61	12,000	---	12.1	---	8.20
344-C7	1% A-1100	---	64	2.52	12,475	245	10.4	192	8.1
612	A-1100 + wetting agent	4.0	54	2.34	4,600 4,055[b]				
625	none	3.7	73	2.75	11,710	192	11.9	131	8.2
636	none	2.6	59	2.41	14,800	264	11.6	225	9.85
638	none	5.5	63	2.52	16,070	241	10.8	192	8.60
678	235B	6.5	69.8	2.57	10,000	140[a]	11.8	100	8.50
679	231A + 2313	6.4	70.4	2.67	9,500	126[a]	12.2	113	11.0
689	237A + 231B-2	2.1	55.6	2.10	13,000				
690[c]	235D + 231B-1	3.5	64	2.56	13,930				
S-glass									
456 A	HTS	---		1.99	10,330	---	----		
SG-1	HTS	---	77	2.16	5,990 5,310[b]	141	10.1	91.5	6.5
634	HTS	0.6	67	2.07	13,920	---	----	---	---
635	HTS	0.6	59	1.96	15,200	150	7.5	124	6.35
637	HTS	2.9	53	1.86	14,950	150	7.4	148	7.0
SG-2[d]	HTS	<1.0	63	2.03	---	---	----		

[a] failed in shear, S/D = 20/1; other flex tests run at S/D = 32/1
[b] after 2 hrs in boiling water
[c] tensile property, strength 250 x 10^3 psi, modulus 10.9 x 10^6 psi
[d] tensile property, strength 266 x 10^3 psi

HIGH MODULUS GLASS REINFORCED POLYIMIDE COMPOSITE



500X

Fiber	Density lbs/in.^{3}	Modulus million psi	Specific Modulus ten million inches
E	0.0776	3.27	4.21
S	0.0762	4.12	5.41
UARL 344	0.0951	6.08	6.39

PROGRESS ON NEWER GLASS COMPOSITIONS

This division of the report is primarily concerned with the resumption of activities in originating and evaluating new glass compositions and in reviewing all of our available data as a guide for the directions in which we should move if we want non-toxic glass compositions that are the equal or better than the beryllia-containing UARL 344 composition whose properties were reviewed in the previous section.

New Compositions Prepared in the Second Quarter

Table VI states in terms of grams of actual ingredients all of the new compositions originated in this period. As has been usual with our recent research in this area, the new glasses developed are either those of the cordierite-beryl glass system to which rare earths have been added in major amounts or are "invert" analog types of glasses with rare earth additions. This quarter also features a more determined effort of reducing the density of these glasses and improving their fiberizability while retaining their inherently superior moduli. For these purposes it will be noted that many of the glasses contain lithia or boria and many have zinc oxide and reduced magnesia contents or calcia and reduced alumina contents. Since these glasses are still under investigation no definite conclusions can be drawn at this time except to say that glasses 445, 447, 448, and 449 appear to be much the least promising while 442, 443, and 446 seem the most hopeful.

Moduli of Recent Glasses in Bulk Form

The values for Young's modulus measured on bulk specimens of glass are brought up to date in Table VII. As is usual, these values are measured by our improved ultrasonic technique described in earlier reports.

Young's Moduli As Determined On Glass Fibers

Table VIII lists all the values of moduli obtained recently on glass fibers. These values are measured both at Panametrics using their thin-line ultrasonic technique and at Lowell Institute of Technology using an Instron Test Machine with air-actuated grips. The agreement between the two sources is excellent.

Table VI

New Glass Compositions
Actual Ingredients in Grams

Actual Ingredient	407	408	409	410	411	412	413
Silica (SiO_2)	190.8	164.8	129.3	159.4	159.8	122.8	213.9
Alumina (Al_2O_3)	54.0	58.9	67.4	90.2	90.3	78.1	60.5
Zinc Carbonate	66.3	73.5	82.7	---	---	---	74.2
Magnesia (MgO)	---	---	---	35.7	35.7	30.9	---
Lanthanum Oxalate	---	412	465	---	415	539	---
Beryllium Carbonate	143.6	132.5	124.3	80.0	80.0	69.3	161.0
Rare Earth Oxalate	372	---	---	417	---	---	---
Yttrium Oxalate	---	---	---	---	---	---	358

	414	415	416	417	418	419	420
Silica (SiO_2)	146.2	158.2	186.0	197.2	194.5	171.0	172.8
Alumina (Al_2O_3)	61.9	---	84.2	111.1	109.8	103.7	83.7
Lithium Carbonate	---	62.9	15.3	16.1	15.9	14.8	15.2
Calcium Carbonate	---	85.3	---	---	---	---	---
Zinc Carbonate	76.1	---	---	---	---	---	25.8
Magnesia (MgO)	---	34.3	41.6	43.9	43.5	41.0	41.4
Lanthanum Oxalate	428	---	---	---	---	---	---
Beryllium Carbonate	165.3	153.5	88.2	93.2	110.1	86.7	53.5
Yttrium Oxalate	---	518	410	308	304	409	414

	421	422	423	424	425	426	427
Silica (SiO_2)	178.4	173.9	170.4	158	262	67.9	86.0
Alumina (Al_2O_3)	72.0	66.4	65.0	10.5	71.5	115.0	65.6
Lithium Carbonate	15.7	26.6	10.5	---	---	50.9	58.2
Calcium Carbonate	---	---	---	142.1	---	113.0	101.0
Zinc Carbonate	---	---	26.6	---	---	---	---
Magnesia (MgO)	56.9	52.5	51.5	52.5	104.5	45.6	28.8
Fused Boric Acid	---	---	---	---	---	---	88.7
Zirconium Acetate	---	---	---	139.2	---	---	---
Beryllium Carbonate	87.4	111.0	109.0	179.9	212	102.1	103.5
Yttrium Oxalate	427	437	438	---	---	427	432

Table VI (Cont'd)

Actual Ingredient	428	429	430	431	432	433	434
Silica (SiO_2)	62.1	63.6	123.2	127.2	159.4	159.4	159.4
Alumina (Al_2O_3)	67.8	69.3	41.8	43.2	54.1	54.1	54.1
Lithium Carbonate	71.1	55.8	---	---	---	---	---
Calcium Carbonate	118.2	113.5	---	---	---	---	---
Zinc Carbonate	---	---	51.4	---	---	---	---
Magnesia (MgO)	47.6	30.5	---	17.1	38.6	38.6	38.6
Fused Boric Acid	56.8	56.2	---	---	---	---	---
Lanthanum Oxalate	---	---	288.3	298.3	37.3	373	373
Beryllium Carbonate	107.0	177.0	111.3	115	143.5	143.5	143.5
Yttrium Oxalate	444	455	---	---	---	---	---
Neodymium Oxalate	---	---	293	302	75.8	37.9	18.95

	435	436	437	438	439	440	441
Silica (SiO_2)	159.3	160	161.5	117.5	165.7	163.3	157.4
Alumina (Al_2O_3)	69.1	69.5	70.1	68.7	71.9	70.9	109.3
Lithium Carbonate	30.1	30.8	30.4	29.8	31.2	30.8	29.7
Calcium Carbonate	13.6	13.6	13.7	13.5	14.1	56.8	13.4
Zinc Carbonate	51.2	51.5	51.8	50.6	---	---	---
Magnesia (MgO)	27.4	27.5	27.8	27.2	45.5	28.1	27.1
Fused Boric Acid	---	---	---	83.4	---	---	---
Copper Oxide	10.8	---	---	10.7	11.2	11.1	10.7
Titanium Oxide (not rutile)	---	10.5	---	---	---	---	---
Beryllium Carbonate	88.6	92.6	92.6	91.6	95.8	94.4	90.9
Ferric Oxide	---	---	22.0	---	---	---	---
Yttrium Oxalate	409	412	414	407	425	420	404

	442	443	444	445	446	447	448
Silica (SiO_2)	170	167.8	155.4	156.4	165.3	98.0	97.1
Alumina (Al_2O_3)	---	---	67.8	68.1	43.2	---	---
Lithium Carbonate	32.1	30.4	29.4	29.5	31.3	49.5	33.4
Calcium Carbonate	14.5	57.3	66.5	13.4	14.1	97.9	97
Zinc Carbonate	91.2	89.7	66.5	50.3	53.1	81.7	64.9
Magnesia (MgO)	46.9	28.9	---	---	39.8	40.0	39.1
Fused Boric Acid	---	---	---	---	---	105.0	103.8
Copper Oxide	11.6	11.4	10.6	10.6	11.2	---	10.3
Titanium Oxide (not rutile)	---	---	---	---	---	---	10.35
Beryllium Carbonate	98.6	97.1	90.2	30.2	95.6	---	---
Yttrium Oxalate	439	433	402	404	427	473	468

Table VI (Cont'd)

Actual Ingredient	449	450	451	452	453	454
Silica (SiO_2)	97.5	94.4	155.8	151.2	153.6	148.4
Alumina (Al_2O_3)	---	38.4	---	---	---	38.1
Lithium Carbonate	33.6	32.3	48.3	46.8	31.4	30.3
Calcium Carbonate	97.5	56.4	97.0	95.3	96.5	56.1
Zinc Carbonate	32.7	31.6	82.1	63.6	32.6	31.3
Magnesia (MgO)	52.4	50.6	39.5	38.4	53.7	50.7
Fused Boric Acid	104.2	100.8	---	---	---	---
Copper Oxide	10.3	10.0	---	10.1	13.0	12.6
Titanium Oxide (not rutile)	15.6	15.2	---	15.2	19.6	18.9
Yttrium Oxalate	470	457	473	472	467	451

Table VII

All Values for Young's Modulus Measured on Circular Rods
Formed Directly from Melt, Melts 360 et seq.

Glass No.	Density gms/cm^3	Density $lbs/in.^3$	Young's Modulus millions, psi	Specific Modulus 10^7 in.
356A	3.3158	0.1193	13.9	11.63
360	3.5183	0.1269	18.5	14.6
361	3.4989	0.1260	18.6	14.8
362	3.4997	0.1260	18.0	14.3
363	3.5680	0.1289	19.26	14.9
364	3.0985	0.1120	16.70	14.9
365	3.5453	0.1281	19.04	14.9
366	3.4697	0.1255	16.19	12.9
367	3.5310	0.1277	19.03	14.9
368	3.6229	0.1320	19.08	14.4
369	3.5272	0.1277	17.78	13.9
370	3.6285	0.1320	18.59	14.15
371	3.5664	0.1289	18.54	14.4
372	4.0747	0.1473	17.34	11.8
373	3.4937	0.1262	19.00	15.05
373A	3.4937	0.1262	22.0	17.35
374	3.4276	0.1238	19.00	15.45
374A	3.4276	0.1238	19.15	15.5
375	3.6819	0.1333	16.58	12.42
375A	3.6819	0.1333	15.73	11.8
376	3.6820	0.1334	15.80	11.85
376R	3.6820	0.1334	15.75	11.79
377	3.6108	0.1304	15.62	11.96
377R	3.6108	0.1304	15.02	11.53
378	3.2971	0.1192	---	---
378A	3.1701	0.1147	14.4	12.55
379	3.1448	0.1137	17.3	15.22
380	3.7107	----	15.7	---
381	2.9591	0.1063	15.87	14.9
382	3.0054	0.1082	17.7	16.32
383	3.1418	0.1136	22.75	20.02
384	3.8927	0.1407	18.62	13.23
385	2.8006	0.1011	---	---
386	3.3705	0.1218	---	---
387	3.2777	0.1183	17.85	15.08

Table VII (Cont'd)

Glass No.	Density gms/cm^3	Density lbs/in.^{3}	Young's Modulus millions, psi	Specific Modulus 10^7 in.
388	3.5767	0.1293	17.28	13.38
389	3.4540	0.1247	17.2	13.80
390B	3.3462	0.1210	16.80	13.88
391A	3.3062	0.1193	17.38	14.57
392	3.5920	0.1298	16.24	12.52
393	3.6019	0.1303	16.46	12.63
394	3.3024	0.1195	16.59	13.87
395	3.7273	0.1348	16.00	11.86
396	3.2443	0.1175	15.15	12.87
398	3.2622	0.1182	16.30	13.78
399	3.3742	0.1219	16.89	13.85
400	3.3266	0.1204	15.78	13.11
401	3.3031	0.1196	16.76	14.04
402	3.3063	0.1198	17.77	14.85
403	3.3728	0.1220	17.17	14.05
404	3.5661	0.1292	18.13	14.04
405	3.7262	0.1350	19.74	14.63
406	4.3956	0.1590	17.69	11.12
407	3.6398	0.1312	18.10	13.86
408	3.8661	0.1393	18.32	13.13
409	4.0420	0.1457	19.16	13.16
410	3.6381	0.1311	18.23	13.87
411	3.7073	0.1340	18.00	13.45
412	4.0954	0.1477	17.92	12.13
413	3.4375	0.1239	19.13	15.43
414	3.8764	0.1402	18.73	13.37
415	3.2899	0.1186	20.57	17.35
416	3.2877	0.1193	19.61	16.4
417	3.0915	0.1121	19.35	17.25
418	3.0884	0.1121	19.31	17.18
419	3.2665	0.1185	20.15	17.0
420	3.3605	0.1220	19.50	16.13
421-Spe	3.3370	0.1208	20.72	17.15
421	3.3356	0.1208	20.37	16.85
422	3.3222	0.1207	20.58	17.05
423	3.4505	0.1252	20.68	16.47
424	3.0401	0.1103	19.51	17.7
425	2.7355	0.0990	19.51	19.7
426	3.4378	0.1248	20.56	16.45
427	3.1550	0.1146	15.69	13.72

Table VII (Cont'd)

Glass No.	Density gms/cm^3	Density lbs/in.^{3}	Young's Modulus millions, psi	Specific Modulus 10^7 in.
428	3.2284	0.1164	18.20	15.64
429	3.2496	0.1172	---	---
430	4.3482	0.1570	19.34	12.33
431	4.2720	0.1540	19.65	12.76
432	3.7345	0.1345	19.28	14.35
267A	2.7322	0.0976	16.50	---
433	3.6325	0.1308	18.38	14.08
434	3.5304	0.1273	18.44	14.47
435	3.4605	0.1247	19.17	15.35
436	3.4461	0.1240	19.38	15.65
437	3.5067	0.1265	18.55(18.43)	14.65
438	3.2348	0.1165	17.35	14.87
439	3.3510	0.1207	18.97	15.75
440	3.3426	0.1203	19.03	15.85
441			18.76	
442			19.10	

Table VIII

Values of Young's Modulus on Mechanically Drawn Fibers of UARL Experimental Glasses As Determined by Measurements Either on Tensile Test Equipment or Thin-Line Ultrasonics

	Young's Modulus 10^6psi			Young's Modulus 10^6psi			Young's Modulus 10^6psi		
Glass Number	Tensile	Standard Deviation 10^6psi	Glass Number	Tensile	Standard Deviation 10^6psi	Glass Number	Tensile	Standard Deviation 10^6 Tensile	Sonic
25	12.3	1.9	83**	15.35	2.4,1.95	161	14.3	1.8	
40	16.2	4.6	97	10.4	1.7	162			
56	10.7		98	10.8	2.5	166	13.6	5.4	
62	14.0		102	13.3		175	13.1	2.9	
63	13.0		108	12.5	2.7	176	16.7	9.9	
64	14.7		110	13.8	2.2	193	13.1	4.0	
65	13.8		114	15.1		200	14.6	3.3	
66	14.6	2.0	126	16.15	1.82,1.65	201	13.2	4.3	
67	12.7		127	15.2		210	15.0	2.0	
68	13.7		129	16.7	2.7,2.6	214	12.9	1.6	
69	13.6		131	12.5		215	13.3	3.0	
70	13.4		135	13.3		233	14.6	2.3	14.9
71	13.7		136	13.5		235	15.3	1.9	
72	12.5		137	13.9		237	18.8	7.9	
73	15.1		138	12.2		238	15.2	3.2	
74	13.8		140	15.0		260	10.4	1.5	
75	9.8		155	14.7	1.9	261	11.5	1.8	
76	10.4		157	13.1	2.8	275-10	15.93	2.2	15.94
77	11.0		159	15.7	5.0,2.2	276	17.0	6.2	
82*	13.3		160	14.6	3.0	278	11.3	1.8	

Table VIII (Cont'd)

Glass Number	Young's Modulus 10^6psi Tensile	Standard Deviation 10^6 Tensile	Sonic
279	6.2	3.3	
280	4.6	0.4	
281	5.7	0.5	
284	11.9	2.4	
285	12.9	4.7	
288-3	11.9	2.8	
289	13.1	1.5	
290-5	14.3	5.8	
290-6	13.0	3.7	
291	13.6	3.2	
299	12.8	3.6	
300	13.4	3.4	
309	14.8	1.9	
320B3	18.6	3.3	16.2
331	18.3	2.5	19.85
344	18.3	3.2	18.6
348	17.5	3.0	17.6,17.5
349	16.9	2.1	16.9,16.7
367	17.5	3.7	18.4,18.3
368	18.8	2.6	18.5

Glass Number	Young's Modulus 10^6psi Tensile	Standard Deviation 10^6 Tensile	Sonic
370	17.7	3.7	17.8
371	18.4	2.3	18.1
372	15.7	4.4	17.1
388	16.8	2.3	16.4,16.1
396	15.1	1.7	15.1,14.9
402	16.5	3.1	15.75,15.95
403	18.0	2.7	15.95,16.1
405	18.7	2.2	18.3,18.45
321A	17.4	3.6	18.2
E	11.8	3.9	
347	17.4	1.5	15.5,15.5
408	19.8	5.0	16.65,16.4
410	17.8	1.8	16.7,16.6
411	15.6	1.4	16.5,16.35
412			17.0,16.65
416	19.8	2.7	18.47,18.64
417	18.8	3.0	17.5,17.5
418	18.5	1.9	17.95,17.95
419	19.0	2.9	18.4,18.1
420	19.6	4.1	17.8,17.7

82*-Houze Glass U.S. 3,044,888
83**-Owens Corning Glass, U.S. 3,122,277(#4)

All tabulated observations are the average of 20 observations except for 40, 83, 126, 129, 233, 275-10, 320B3, 331-60

Compositional Direction Guide for Research on New Beryllia Containing Glasses

In Table IX all of our test data to date have been examined and those data which seemed to point the way to move in our search for an improved beryllia containing glass have been collected. The validity of the correlations shown here will be best tested in the next few months as new glasses based on these criteria are developed.

Compositional Direction Guide for Research on Non-Toxic Glass Compositions

In Table X the results of the scrutiny of all of our test data on non-toxic glass compositions is shown. Of the several hundred non-toxic glass compositions prepared to date, it is evident that only a relatively few point a direction in which to move to achieve high-modulus, high-strength non-toxic glass fibers. Far fewer dependable leads are available for the non-toxic glass compositions than is the case for the beryllia containing compositions. But the fact that this research is quite hopeful is evidenced both by the very high bulk moduli already attained and the ready fiberizability of some of the slightly lower moduli compositions. Again, however, the validity of these guide posts will be most evident after a few months more research.

CONCLUSIONS AND FUTURE PLANS

1. UARL 344 glass composition is highly suitable for the production of high-modulus, high-strength glass fibers as evidenced by the production of more than forty million feet of monofilament from this glass with strengths averaging 772,000 psi, a modulus of 18.6 million psi, a specific modulus of 157 million psi, and a potential price comparable to that of "S" glass.

2. Future research on UARL 344 glass is necessary, however, both to eliminate the present high degree of variability in strength and to prove that the composition can be successfully processed into glass fibers using multi-hole bushings.

3. No single non-toxic glass composition is as yet outstanding in all characteristics as is the beryllia-containing UARL 344 glass. However, some of these glasses have even higher moduli than does UARL 344 and other of these glasses with lower moduli have an even greater ease of fabrication into fibers and increased working range. Future extensive research in this area will be the largest part of our effort in the remaining contractual period.

Table IX

New Compositional Guide for Beryllia Containing Glasses

Glass	SiO_2	Al_2O_3	MgO	Li_2O	CaO	ZnO	La_2O_3	Ce_2O_3	B_2O_3	ZrO_2	BeO	Y_2O_3	${}^aCuO$ ${}^bRe_2O_3$ ${}^cTiO_2$	Young's Mod. 10^6psi	Spec. Mod. 10^6in.	Fiber Mod. 10^6psi
273[1,2]	30	12	12	12	12						22			18.4	186	---
275[1,2,3]	50	8.33				8.33	8.33				25			16.8	127	15.94
276[1,2,3]	50	8.33		8.33			8.33				25			15.8	129	17.0
323[2]	35	15	30	10							10			18.4	184	---
324[2]	30	12	24	12		12					10			17.78	166	---
325[3]	30	10	20	10		10					10	10		20.2	158	---
329	20	10	20	10		10				10	10	10		20.2	189	---
331[1,2]	39	12				12					25	12		20.9	158	19.8
336	35	15				10					30	10		21.0	166	---
340	25	10	20	10		10					15	10		20.9	163	---
344[1,2,3]	45	15	15								15	10		20.3	170	18.6
345[2]	45	15									30	10		21.1	175	---
347[1,2]	50	8.33				8.33	8.33				25			21.6	164	17.4
348[1,2]	50	8.33					8.33			8.33	25			17.7	134	17.5
350[2,3]	24	13	13	13	13						24			19.75	197	---
352	25	10				10				10	10	10		20.0	146	---
367[1]	39	12	12					2			25	10		19.03	149	17.5
368[1]	39	12	6			6		2			25	10		19.08	144	18.8
370[1]	39	12			6	6		2			25	10		18.5	142	17.7
371[1]	39	12	4		4	4		2			25	10		18.5	144	18.4
373	39	12		6	6			2			25	10		19.0	150	---
388[1]	24		12	12	12				10		14		b12 c 4	17.3	134	16.8
405[1,2]	49.3	14		0.7							14	22		19.7	146	18.7
408[1,2,3]	45	10				10	10				25			18.3	131	19.8
410[1,2,3]	45	15	15	3							15		b10	18.23	139	17.8

Table IX (Cont'd)

Glass	SiO_2	Al_2O_3	MgO	Li_2O	CaO	ZnO	La_2O_3	Ce_2O_3	B_2O_3	ZrO_2	BeO	Y_2O_3	[a]CuO [b]Re_2O_3 [c]TiO_2	Young's Mod. 10^6psi	Spec. Mod. 10^6in.	Fiber Mod. 10^6psi
411[1,2,3]	45	15	15				10				15			18.0	135	15.6
416[1,2]	45	12	15	3							15	10		19.61	164	19.8
417[1,2]	45	15	15	3							15	7		19.4	173	18.8
418[1,2]	45	15	12	3							18	7		19.4	172	18.5
419[1,2]	42	15	15	3							15	10		20.2	170	19.0
420[1,2]	42	12	15	3		3					15	10		19.5	161	19.6
421[2]	42	10	20	3							15	10		20.4	169	---
422	40	9	18	5							18	10		20.6	171	---
423	40	9		2	18	3					18	10		20.7	165	---
425[2]	42.9	7.0	25.6								24.6			19.5	197	
426	16	16	16	10	16						16	10		20.6	165	
433[1,2]	41.66	8.33	15				8.33				25					
434[1,2]	41.66	8.33	15				8.33				25					
438[1,2]	29	10	10	6	2	6			10		15	10	a 2			

[1]Fiberizable

[2]Forms clear glass slug

[3]Has favorable liquidus

Table X

Compositional Guide-Posts for the Development of Non-Toxic (No BeO) Improved High Modulus Glasses

Glass	Composition in Mol Percent												Bulk Properties			
	SiO_2	Al_2O_3	MgO	Li_2O	CaO	ZnO	La_2O_3	Ce_2O_3	B_2O_3	ZrO_2	Y_2O_3	ᵃCuO ᵇRe_2O_3 ᶜTiO_2	Young's Mod. 10^6psi	Spec. Mod. 10^7in.	Fiber Mod. 10^6psi	Molar Sum
125	41.66	25	18.33							10			16.1	161		70.1
126[xy]													16.8	134	16.15	83.0
127[xy]	60	10	20								10		16.1	137	15.2	79.2
129[xy]	50	13.33	26.66								10		16.5	138	16.7	77.8
237[x]	45	15	30								10		18.3	152	18.8	77.0
270	25	8	15	15	15	15					7		20.25	159		70.13
290[xyz]	25	8	15	15		15			15		7		14.5	123	14.3	72.2
291[xyz]	25	12	12	12		12			15		12		15.67	131	13.6	83.0
299[x]	25	8	15	15			7		15	15			14.6	127	12.8	75.4
300[xyz]	25		15	15	15	15			15				14.45	139	13.4	56.6
304[y]	35	15	30			10					10		19.2	147		79.1
320B3[xy]	45	15	30							10			16.0	151	18.6	66.7
321A[xy]	40	15	30							15			18.7	142	17.4	85.3
337	30	15	30			12.5					12.5		20.9	147		83.8
363	39	12	24	6		6			6		10	a 3	19.3	149		76.3
383[y]	24	3	16	12	12	8			10	12		c 3	22.75	200		64.9
390[yz]	20	6	16	12	12	8			14		12		16.8	139		78.2
402[xy]	25	8	20	5	9				14		14	a 2 c 3	17.77	148.5	16.5	83.1
403[xy]	25	8	20	5	6				14		14	a 2 b 3 c 3	17.17	140.5	18.0	86.2

[x] Fiberizable

[y] Good quality glass

[z] Favorable liquidus

PERSONNEL ACTIVE ON PROGRAM

Personnel active on the program throughout the second quarter have been James F. Bacon, Principal Investigator and Francis Hale and John Schmitter, Experimental Technicians. In addition, Mr. Roy Fanti and Dr. Michael DeCrescente of United Aircraft have closely followed the program and continued to use their considerable influence in getting other people interested in the UARL 344 glass as well as in getting additional work done on the properties of this glass over and beyond that which could be carried out under the contractual funds. Dr. Daniel Scola has been actively engaged in preparing composites of UARL 344 glass fibers and epoxy resins as well as in sizing research for retention of the properties of this fiber. Mr. Richard C. Novak has been active on predictions of the advantages of the 344 fiber especially in modulus-limited applications.

Liaison throughout this program and the prior programs has been constantly and regularly furnished by Peter H. Stranges of the UARL Washington Office. Throughout this program and the earlier programs UARL personnel have reported progress to and received friendly, courteous, and helpful advice from James J. Gangler of NASA/OART Washington Headquarters.