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DETERMINING AND ANALYZING THE STRENGTH AND IMPACT RESISTANCE OF HIGH MODULUS GLASS

by

James F. Bacon

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Final Report
Contract NASW-2209

United Aircraft Research Laboratories
UNITED AIRCRAFT CORPORATION
EAST HARTFORD, CONNECTICUT 06108

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FINAL REPORT

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REPORTED BY ____________
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FOREWORD

This document is the final report on the work carried out under contract NASW-2209. The NASA contractor monitor for this program was James J. Gangler of NASA/OART Washington Headquarters.

James F. Bacon was program manager. Other UARL personnel participated as follows; Drs. Daniel Scola and Roscoe Pike and Mr. Richard Novak have prepared and evaluated the composites of UARL glass fiber with the resins described in this report.

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SUMMARY

A number of new glass compositions have been prepared in the last twelve months with increased emphasis on compositions without beryllia. In direct contrast to our recent research under Contract NASW-2209 that preceded this contract and which concentrated on cordierite-rare earth glass systems and the invert analog systems of glass preparations, the work under this contract has been much more broadly based and has included as well the eutectic glass fields and the mullite-rare earth glass systems. Of these new glasses, the best non-toxic composition is UARL 472 with a bulk modulus of only 18.20 million psi but with a specific modulus of 157 million inches. UARL 499, also a non-toxic composition, has a somewhat higher modulus of 19.50 million psi but with a lower specific modulus of 150 million inches. The best beryllia containing glass originated during this period, however, UARL 422, is still better than either of the non-toxic compositions mentioned and has a bulk modulus of 20.6 million psi with a specific modulus of 171 million inches. It is evident, therefore, that the gap between the best non-toxic glasses and those containing beryllia continues to narrow but has not yet disappeared.

Early in the contractual year, a second experimental glass, UARL 417, was chosen for research in making large quantities of fiber in monofilament form. The twelve million and more feet of this monofilament have been largely used to form glass fiber-epoxy resin composites. Tests of these UARL 417 epoxy resin samples in comparison to similar composites made with the DuPont experimental organic fiber, PRD-49-1, show that the UARL composites have a compressive strength 4 1/2 times higher and a specific compressive strength at least 2 1/2 times greater. The UARL 417 glass fiber-epoxy resin composites are also better than similar composites prepared with the DuPont organic fiber, PRD-49-1, in flexural strength, short-beam shear strength, tensile strength, impact strength and have superior bending stress-strain and tensile stress-strain curves. The UARL 417 glass has a bulk modulus of 19.4 million psi, a specific modulus of 173 million inches, a fiber modulus of 18.8 million psi, and a density of 3.09 gms/cm^3. In preparing the UARL 417 it was necessary to develop a sizing applicator for the experimental sizing employed as well as to improve the type of compression strength test commonly made in order to accommodate the very high compressive strengths of this and similar fiber composites.

Much of the research effort during the year attempted to answer the question of why a given glass should have an impact strength superior to other glasses. No definitive answer to this question was found. However, tests carried out using unnotched Charpy impact samples of bulk glass gave an extremely preliminary indication that glasses containing both appreciable amounts of zinc oxide and aluminum oxide tend to have higher impact resistances than other glasses. Glasses to which only aluminum oxide is added do not have any increased impact resistance and the same is true for glasses which have only zinc oxide.

A critical reexamination of the UARL extensions to the C. J. Phillips method (Ref. 1) of predicting Young's modulus for a glass from the molar contributions of its constituents showed the need for a recalculation in the UARL computer program used to calculate Young's modulus from laboratory data. The data when corrected and examined as input material for the calculation resulted in new values for the contribution per mol of several of the oxides. The new value found for the zinc oxide molal factor is especially significant because it is slightly greater than the factor for beryllia for the types of glasses UARL prepared experimentally. This discovery provides a new tool of great value in the search for non-toxic, i.e. without beryllia, high modulus glasses and is doubly significant in view of the contribution of zinc oxide to impact strength already noted.

INTRODUCTION

This report is the final report for the UARL-NASA Headquarters contract NASW-2209, Determining and Analyzing the Strength and Impact Resistance of High Modulus Glass. This contract is the successor to the prior UARL contracts NASW-1301, Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems and NASW-2013, Investigation of the Kinetics of Crystallization of Several High Temperature Glass Systems. The time period covered by the present report is February 1, 1971 through January 31, 1972.

For the earlier NASA contracts, UARL studied the rate of crystallization of several unusual molten oxide systems not normally used for glass production. The two most directly applicable of these systems were the cordierite-rare earth oxide and the invert analog-rare earth oxide fields with both of these systems including at times beryllia additions. In each of these systems a number of high modulus, high strength glass compositions were found and some of these compositions could be fiberized by the usual technique of pulling the fiber through a platinum-rhodium bushing. The fibers thus produced were used to form glass fiber-epoxy resin composites and these were characterized as fully as possible. The strength and impact characteristics of these high modulus glasses in bulk form were not investigated, however.

The present contract did not exclude the continuation of these types of research but did emphasize a more systematic investigation of the properties of those high modulus glasses previously developed and added the preparation of glasses from the mullite-rare earth oxide glass systems and eutectic glass fibers as well. Attempts were made to correlate the bulk glass properties with composition and microstructure, to find out why a given glass is superior to other glasses in impact resistance or in tensile strength, and to develop glasses with superior impact resistance or tensile properties. This type of research investigation should, in a small way, fulfill the need for more information about glass in massive form that the National Materials Advisory Board of the National Research Council has indicated (Refs. 2,3) to be a prerequisite for the successful use of glass as an engineering material.

NEW GLASS COMPOSITIONS

The new glass compositions prepared in the year contractual period together with some of the more recent compositions prepared under the prior contract, NASW-2013, but not fully characterized at that time are shown in Table I (compositions in weight %) and Table II (compositions in mol %). Many of the glass systems studied can be readily recognized by examining Table II. For example, compositions UARL 416 through UARL 423 are slightly altered or variant compositions of UARL 344 to see what improvement in properties of this glass can readily be obtained. As is shown in Table III in a later section all of these glasses have a higher specific modulus and UARL 421, 422, 423 have a higher absolute modulus as well. The glass of this series with the best working characteristics is UARL 417 and for this reason this glass was selected when large quantities of a second experimental glass were to be produced. All the glasses of this series are based on the cordierite-rare earth oxide-beryllia glass field.

Other groups of glasses that can be readily recognized in Table II are glasses 460 through 472 which are additional extensions of the UARL invert analog series of glasses and glasses 442 through 446 which are also UARL invert analog glasses but with the addition of beryllia. Glasses 473, 474, and 475 are base glasses from which McMillan (Ref. 4) was able to prepare glass-ceramics of high moduli. These glasses were studied to see if the action of pulling fibers would furnish a sufficient heat treatment to develop crystals in such phosphate catalyzed glass-ceramics. Unfortunately at the maximum furnace temperature, 1700°C, which was felt to be safe for the aged heating elements in our platform furnace, these glasses were much too stiff to allow either fiber formation or the aspiration of rods for modulus evaluation. At this temperature, these glasses had the consistency of an extremely heavy grease. We were unable, therefore, to use these glasses to answer our question concerning the contribution made by a relatively small number of crystals to the resultant modulus and strength of a glass fiber.

Composition UARL 476 is derived from Bastian, U. S. Patent 2,978,341 by taking maximum amounts of the more important ingredients mentioned and is intended to supply a comparison of one of the most readily fiberizable high beryllia content glasses previously developed with the current UARL experimental glasses. While this glass does not yield as high a value for Young's modulus as do our glasses, its specific modulus is truly outstanding because of the very low value of density claimed. UARL 425 and 425B are the same as the most high modulus glass developed by the National Bureau of Standards in an earlier investigation (Ref. 5) and contain approximately three parts of beryllia and three parts of magnesia for every five parts of silica and 1 part of alumina. It is a very high temperature extremely fluid glass and our study like that of the Bureau of Standards shows it to be very hard to fiberize.

Table I

New Glass Compositions
(In Weight %)

Actual Ingredient	400	401	402	403	404	405	406
SiO_2	18.98	18.27	18.04	17.45	17.62	30.65	24.85
Al_2O_3	---	9.9	9.8	9.47	9.56	14.65	11.97
Li_2O	3.78	1.81	1.79	1.74	1.74	0.22	0.18
CaO	10.63	8.16	6.06	3.9	1.97	---	---
MgO	8.13	9.77	9.67	9.33	9.43	---	---
B_2O_3	12.33	11.82	11.7	11.32	11.42	---	---
La_2O_3	---	---	---	---	---	---	60.14
CuO	---	1.93	1.91	1.34	1.86	---	---
TiO_2	---	---	2.87	2.78	2.82	---	---
BeO	---	---	---	---	0.88	3.6	2.94
Fe_2O_3	---	---	---	5.55	5.61	---	---
Y_2O_3	39.96	38.26	37.93	36.7	37.03	51.1	---
ZnO	6.16	---	---	---	---	---	---

	407	408	409	410	411	412
SiO_2	38.16	30.95	25.85	31.87	31.95	24.55
Al_2O_3	10.79	11.97	13.48	18.03	18.06	15.62
ZnO	8.61	9.55	10.73	---	---	---
MgO	---	---	---	7.13	7.14	6.18
La_2O_3	---	38.2	43.11	---	38.45	49.9
BeO	7.93	7.33	6.88	4.42	4.43	3.83
Re_2O_3	34.6	---	---	38.72	---	---

	413	414	415	416	417	418
SiO_2	42.78	29.24	31.63	37.2	39.24	38.9
Al_2O_3	12.09	12.38	---	16.84	22.22	21.95
Li_2O	---	---	5.09	1.24	1.31	1.29
CaO	---	---	9.55	---	---	---
ZnO	9.64	9.89	---	---	---	---
MgO	---	---	6.85	8.32	8.78	8.69
La_2O_3	---	39.65	---	---	---	---
BeO	8.89	9.11	8.5	5.16	5.45	6.47
Y_2O_3	26.78	---	38.47	31.06	23.05	22.75

Table I (Cont'd)

Actual Ingredient	419	420	421	422	423	424
SiO_2	34.2	34.55	35.68	34.78	34.07	31.6
Al_2O_3	20.73	16.73	14.4	13.28	13.0	21
Li_2O	1.2	1.23	1.27	2.16	0.85	---
CaO	---	---	---	---	---	15.9
ZnO	---	3.34	---	---	3.46	---
MgO	8.19	8.28	11.38	10.5	10.29	10.5
ZrO_2	---	---	---	---	---	10.5
BeO	5.08	5.13	5.31	6.51	6.38	10.5
Y_2O_3	30.62	30.87	31.94	32.66	32.0	---

	425	426	427	428	429	430
SiO_2	52.4	13.58	17.20	12.42	12.71	24.64
Al_2O_3	14.3	23.00	13.12	13.55	13.85	8.37
Li_2O	---	4.12	4.71	5.74	4.52	---
CaO	---	12.68	11.34	13.27	12.71	---
ZnO	---	---	---	---	---	6.67
MgO	20.9	9.11	5.76	9.52	6.09	---
B_2O_3	---	---	9.95	6.19	6.31	---
La_2O_3	---	---	---	---	---	26.73
BeO	12.4	5.65	5.72	5.92	9.82	6.16
Y_2O_3	---	31.92	32.30	33.40	34.07	---
Nd_2O_3	---	---	---	---	---	27.62

	431	432	433	434	435	436
SiO_2	25.44	31.87	33.33	33.75	31.85	32.00
Al_2O_3	8.64	10.82	10.92	11.22	13.82	13.89
Li_2O	---	---	---	---	2.43	2.44
CaO	---	---	---	---	1.52	1.53
ZnO	---	---	---	---	6.64	6.67
MgO	3.42	7.72	7.82	8.00	5.48	5.49
La_2O_3	27.61	34.55	36.05	36.65	---	---
CuO	---	---	---	---	2.16	---
TiO_2	---	---	---	---	---	2.10
BeO	6.36	7.96	8.13	8.20	5.09	5.12
Y_2O_3	---	---	---	---	30.62	30.79
Nd_2O_3	28.50	7.14	3.56	1.78	---	---

Table I (Cont'd)

Actual Ingredient	437	438	439	440	441	442
SiO_2	32.30	23.50	33.13	32.66	31.48	34.00
Al_2O_3	14.01	13.74	14.38	14.18	21.86	---
Li_2O	2.46	2.41	2.53	2.49	2.40	2.60
CaO	1.54	1.51	1.58	6.25	1.50	1.63
ZnO	6.73	6.57	---	---	---	11.82
MgO	5.56	5.43	9.10	5.62	5.41	9.37
B_2O_3	---	9.38	---	---	---	---
CuO	---	2.14	2.24	2.22	2.14	2.31
BeO	5.12	5.06	5.29	5.22	5.03	5.45
Fe_2O_3	4.39	---	---	---	---	---
Y_2O_3	31.08	30.43	31.86	31.44	30.26	32.82

	443	444	445	446	447	448
SiO_2	33.55	31.06	31.27	33.05	19.60	19.42
Al_2O_3	---	13.52	13.62	8.64	---	---
Li_2O	2.46	2.38	2.39	2.53	3.92	2.70
CaO	6.42	7.45	1.50	1.58	10.97	10.88
ZnO	11.65	8.64	6.52	6.89	10.62	8.41
MgO	5.77	---	10.77	7.96	7.99	7.82
B_2O_3	---	---	---	---	11.82	11.70
CuO	2.28	2.11	2.12	2.24	---	2.06
TiO_2	---	---	---	---	---	2.07
BeO	5.37	4.98	1.67	5.29	---	---
Y_2O_3	32.36	29.95	30.20	31.88	35.38	35.02

	449	450	451	452	453	454
SiO_2	19.50	18.87	31.15	23.83	30.72	29.68
Al_2O_3	---	7.67	---	---	---	7.62
Li_2O	2.72	2.62	3.91	2.99	2.54	2.45
CaO	10.92	6.33	10.89	8.41	10.82	6.28
ZnO	4.24	4.09	10.64	6.51	4.20	4.06
MgO	10.47	10.12	7.89	6.05	10.74	10.15
B_2O_3	11.77	11.37	---	---	---	---
CuO	2.06	2.00	---	1.59	2.60	2.52
TiO_2	3.12	3.05	---	2.40	3.91	3.78
Y_2O_3	35.24	34.03	35.42	27.10	34.90	33.76

Table I (Cont'd)

Actual Ingredient	455	456	457	458	459	460
SiO_2	23.36	22.85	23.05	22.70	20.68	20.38
Li_2O	6.96	6.82	6.88	4.51	5.75	5.26
CaO	13.07	12.80	8.61	12.70	10.79	9.87
ZnO	18.98	18.57	18.70	18.42	15.68	14.33
MgO	9.40	6.13	9.28	9.12	8.32	7.10
B_2O_3	10.82	15.90	15.98	15.76	7.66	12.25
Y_2O_3	17.57	17.18	17.28	17.02	31.06	30.59

	461	462	463	464	465	466
SiO_2	23.74	20.18	20.27	23.45	19.49	24.78
Li_2O	6.13	4.68	5.23	7.01	5.42	7.42
CaO	11.50	9.78	9183	13.13	10.19	13.92
ZnO	16.71	13.09	14.31	13.07	14.77	20.20
MgO	8.28	6.49	6.53	9.44	7.31	10.00
B_2O_3	14.29	11.22	11.26	16.30	13.53	14.38
TiO_2	---	4.30	2.16	---	---	---
Y_2O_3	19.43	30.32	30.50	17.62	29.28	9.33

	467	468	469	470	471	472
SiO_2	20.84	20.54	20.25	21.22	34.05	35.95
Al_2O_3	11.32	11.13	11.00	11.53	20.78	9.80
MgO	8.38	8.25	8.15	8.54	16.42	17.31
Li_2O	4.15	2.85	2.16	6.33	3.35	3.54
CaO	11.65	11.47	11.33	7.92	---	6.65
ZnO	16.93	16.68	16.45	17.25	---	---
B_2O_3	4.83	7.60	9.37	4.92	---	---
Y_2O_3	21.90	21.57	21.32	22.35	25.18	26.72

Table I (Cont'd)

Actual Ingredient	473	474	475	476	477	478
SiO_2	80.00	76.07	68.7	43.0	45.5	47.5
Al_2O_3	---	6.47	---	---	16.23	13.43
MgO	---	---	---	10.0	2.14	2.12
Li_2O	6.08	5.87	4.88	7.0	---	---
CaO	---	---	---	14.0	---	---
ZnO	10.32	---	26.8	---	---	---
Y_2O_3	---	---	---	---	29.97	29.80
P_2O_5	2.40	6.92	---	---	---	---
K_2O	1.13	4.60	---	---	---	---
BeO	---	---	---	9.0	5.31	4.29
CoO	---	---	---	---	0.99	2.97
Co_2O_3	---	---	---	7.0	---	---
ZrO_2	---	---	---	2.0	---	---
TiO_2	---	---	---	8.0	---	---

	479	480	481	482	483	484
SiO_2	58.01	48.15	41.05	49.26	47.32	51.20
Al_2O_3	6.06	---	21.53	15.43	20.96	9.36
MgO	2.39	2.34	8.51	6.11	3.41	9.02
CaO	---	9.79	---	---	---	---
BeO	5.94	5.83	---	---	---	---
Y_2O_3	26.78	32.87	28.05	28.50	27.35	29.60
CoO	1.11	1.09	0.93	0.95	0.91	0.98

	485	486	487	488	489	490
SiO_2	47.48	44.45	45.15	39.13	37.06	39.47
Al_2O_3	15.25	15.30	12.97	13.53	29.42	22.26
MgO	6.15	5.06	5.13	5.72	8.99	8.79
Li_2O	1.12	---	---	---	1.18	11.55
CaO	---	7.03	7.13	7.45	---	---
BeO	---	---	---	3.32	---	---
Y_2O_3	28.75	28.30	28.72	30.0	8.88	17.40
CoO	0.95	---	0.95	1.00	---	---
ZrO_2	---	---	---	---	3.23	---
Cu_2O	---	---	---	---	11.27	11.03

Table I (Cont'd)

Actual Ingredient	491	492	493	494	495	496
SiO_2	33.46	33.90	32.57	52.85	43.25	32.38
Al_2O_3	20.53	20.78	20.14	---	---	---
MgO	8.09	8.22	7.96	6.55	6.10	7.23
Li_2O	1.07	1.08	1.05	---	---	4.02
CaO	---	---	---	9.10	8.49	10.06
ZnO	---	9.00	8.74	---	12.65	---
Y_2O_3	26.74	27.08	26.25	30.54	28.50	33.83
CoO	---	---	---	1.02	0.95	2.24
Cu_2O	10.17	---	3.33	---	---	---
BeO	---	---	---	---	---	5.61
TiO_2	---	---	---	---	---	4.78

	497	498	499	500	501	502
SiO_2	34.06	42.85	31.30	22.83	22.35	30.07
Al_2O_3	---	10.03	3.54	---	---	---
MgO	7.99	---	9.45	10.20	9.49	5.38
Li_2O	5.08	0.76	0.78	1.14	0.74	0.67
CaO	14.28	15.85	11.68	10.63	8.34	7.48
Y_2O_3	31.95	28.70	29.40	34.30	33.58	25.10
CoO	2.12	1.90	0.33	0.32	0.46	0.83
ZrO_2	---	---	6.42	5.60	6.86	2.74
TiO_2	4.53	---	7.28	8.11	10.87	8.89
B_2O_3	---	---	---	7.05	6.90	---
Ce_2O_3	---	---	---	---	---	7.29
ThO_2	---	---	---	---	---	11.75

	503
SiO_2	29.75
MgO	7.86
Li_2O	0.76
CaO	10.67
Y_2O_3	28.56
CoO	0.95
ZrO_2	9.38
TiO_2	12.17

Table II

New Glass Compositions
(In Mol %)

Actual Ingredient	400	401	402	403	404	405
SiO_2	25	25	25	25	25	49.3
Al_2O_3	---	8	8	8	8	14.0
Li_2O	10	5	5	5	5	0.70
CaO	15	12	9	6	3	---
ZnO	6	---	---	---	---	---
MgO	16	20	20	20	20	---
B_2O_3	14	14	14	14	14	---
CuO	---	2	2	2	2	---
TiO_2	---	---	3	3	3	---
BeO	---	---	---	---	3	14.0
Fe_2O_3	---	---	---	3	3	---
Y_2O_3	14	14	14	14	14	22.0

	406	407	408	409	410	411
SiO_2	49.3	50	45	39	45	45
Al_2O_3	14.0	8.33	10	12	15	15
Li_2O	0.70	---	---	---	---	---
La_2O_3	22.0	---	10	12	---	10
BeO	14.0	25	25	25	15	15
ZnO	---	8.33	10	12	---	---
MgO	---	---	---	---	15	15
Re_2O_3	---	8.33	---	---	10	---

	412	413	414	415	416	417
SiO_2	40	50	40	34	45	45
Al_2O_3	15	8.33	10	---	12	15
Li_2O	---	---	---	11	3	3
CaO	---	---	---	11	---	---
ZnO	---	8.33	10	---	---	---
MgO	15	---	---	11	15	15
La_2O_3	15	---	10	---	---	---
BeO	15	25	30	22	15	15
Y_2O_3	---	8.33	---	11	10	7

Table II (Cont'd)

Actual Ingredient	418	419	420	421	422	423
SiO_2	45	42	42	42	40	40
Al_2O_3	15	15	12	10	9	9
Li_2O	3	3	3	3	5	2
ZnO	---	---	3	---	---	3
MgO	12	15	15	20	18	18
BeO	18	15	15	15	18	18
Y_2O_3	7	10	10	10	10	10

	424	425	426	427	428	429
SiO_2	28.8	42.9	16	20	14	14
Al_2O_3	11.6	7.0	16	9	9	9
Li_2O	---	---	10	11	13	10
CaO	15.9	---	16	14	16	15
MgO	14.7	25.6	16	10	16	10
B_2O_3	---	---	---	10	6	6
ZrO_2	4.8	---	---	---	---	---
BeO	23.5	24.6	16	16	16	26
Y_2O_3	---	---	10	10	10	10

	430	431	432	433	434	435
SiO_2	41.66	41.66	41.66	41.66	41.66	39
Al_2O_3	8.33	8.33	8.33	8.33	8.33	10
ZnO	8.33	---	---	---	---	6
MgO	---	8.33	15	15	15	10
La_2O_3	8.33	8.33	8.33	8.33	8.33	---
BeO	25	25	25	25	25	15
Nd_2O_3	8.33	8.33	1.66	.83	.42	---
Li_2O	---	---	---	---	---	6
CaO	---	---	---	---	---	2
CuO	---	---	---	---	---	2
Y_2O_3	---	---	---	---	---	10

Table II (Cont'd)

Actual Ingredient	436	437	438	439	440	441
SiO_2	39	39	29	39	39	39
Al_2O_3	10	10	10	10	10	16
Li_2O	6	6	6	6	6	6
CaO	2	2	2	2	8	2
ZnO	6	6	6	---	---	---
MgO	10	10	10	16	10	10
B_2O_3	---	---	10	---	---	---
CuO	---	---	2	2	2	2
TiO_2	2	---	---	---	---	---
BeO	15	15	15	15	15	15
Fe_2O_3	---	2	---	---	---	---
Y_2O_3	10	10	10	10	10	10

	442	443	444	445	446	447
SiO_2	39	39	39	39	39	25
Al_2O_3	---	---	10	10	6	---
Li_2O	6	6	6	6	6	10
CaO	2	8	10	2	2	15
ZnO	10	10	8	6	6	10
MgO	16	10	---	20	14	15
B_2O_3	---	---	---	---	---	13
CuO	2	2	2	2	2	---
BeO	15	15	15	5	15	---
Y_2O_3	10	10	10	10	10	12

	448	449	450	451	452	453
SiO_2	25	25	25	38	38	38
Al_2O_3	---	---	6	---	---	---
Li_2O	7	6	6	10	7	6
CaO	15	15	9	15	15	15
ZnO	8	4	4	10	8	4
MgO	15	20	20	15	15	20
B_2O_3	13	13	13	---	---	---
CuO	2	2	2	---	2	2
TiO_2	3	3	3	---	3	3
Y_2O_3	12	12	12	12	12	12

Table II (Cont'd)

Actual Ingredient	454	455	456	457	458	459
SiO_2	38	25	25	25	25	25
Al_2O_3	6	---	---	---	---	---
Li_2O	6	15	15	15	10	14
CaO	9	15	15	10	15	14
ZnO	4	15	15	15	15	14
MgO	20	15	10	15	15	115
CuO	2	---	---	---	---	---
TiO_2	3	---	---	---	---	---
Y_2O_3	12	5	5	5	5	10
B_2O_3	---	10	15	15	15	8

	460	461	462	463	464	465
SiO_2	25	25	25	25	25	25
MgO	13	13	12	12	15	14
Li_2O	13	13	12	13	15	14
CaO	13	13	13	13	15	14
ZnO	13	13	12	13	10	8
B_2O_3	13	13	12	12	15	15
ZrO_2	---	10	---	---	---	---
Y_2O_3	10	---	10	10	5	10
TiO_2	---	---	4	2	---	---

	466	467	468	469	470	471
SiO_2	25	25	25	25	25	40.5
Al_2O_3	---	8	8	8	8	14.5
MgO	15	15	15	15	15	29.0
Li_2O	15	10	7	5	15	8.0
CaO	15	15	15	15	10	---
ZnO	15	15	15	15	15	---
B_2O_3	12.5	5	8	10	5	---
Y_2O_3	2.5	7	7	7	7	8.0

Table II (Cont'd)

Actual Ingredient	472	473	474	475	476	477
SiO_2	40.5	78.78	78.0	70.1	36.5	57
Al_2O_3	6.5	--	3.9	--	--	12
MgO	29.0	--	--	--	12.7	4
Li_2O	8.0	12.0	12.1	10	12.0	--
CaO	8.0	--	--	--	12.8	--
ZnO	--	7.5	--	20	--	--
Y_2O_3	8.0	--	--	--	--	10
P_2O_5	--	1.00	3.00	--	--	--
K_2O	--	0.72	3.00	--	--	--
ZrO_2	--	--	--	--	0.8	--
TiO	--	--	--	--	5.1	--
$CoO(Co_2O_3)$	--	--	--	--	1.7	1.0
BeO	--	--	--	--	18.4	16

	478	479	480	481	482	483
SiO_2	60	65	55	55	65	65
Al_2O_3	10	4	--	17	12	17
MgO	4	4	4	17	12	7
CaO	--	--	12	--	--	--
Y_2O_3	10	8	10	10	10	10
$CoO(Co_2O_3)$	3	1	1	1.0	1.0	1.0
BeO	13	16	16	--	--	--

	484	485	486	487	488	489
SiO_2	65	62	58	59	49	47
Al_2O_3	7	12	12	10	10	22
MgO	17	12	10	10	10	17
Li_2O	--	3	--	--	--	3
CaO	--	--	10	10	10	--
Y_2O_3	10	10	10	10	10	3
$CoO(Co_2O_3)$	1.0	1.0	--	1.0	1.0	--
BeO	--	--	--	--	10	--
Cu_2O	--	--	--	--	--	6

Table II (Cont'd)

Actual Ingredient	490	491	492	493	494	495
SiO_2	51	47	47	45	65	57
Al_2O_3	17	17	17	17	--	--
MgO	17	17	17	17	12	12
Li_2O	3	3	3	3	--	--
CaO	--	--	--	--	12	12
ZnO	--	--	6	6	--	8
Y_2O_3	6	10	10	10	10	10
CoO(Co_2O_3)	--	--	--	--	1.0	1.0
BeO	--	--	--	--	--	--
Cu_2O	6	6	--	2	--	--

	496	497	498	499	500	501
SiO_2	36	40	56	40	30	30
Al_2O_3	--	--	7.75	2.66	--	--
MgO	12	14	--	18	20	20
Li_2O	9	12	2	2	3	2
CaO	12	18	22.25	16	15	12
ZnO	--	--	--	--	--	--
Y_2O_3	10	10	10	10	12	12
TiO_2	4	4	--	7	8	11
CoO (Co_2O_3)	2	2	2	0.33	0.33	0.5
BeO	15	--	--	--	--	--
Cu_2O	--	--	--	--	--	--
B_2O_3	--	--	--	--	8	8
ZrO_2	--	--	--	4	3.66	4.5

	502	503
SiO_2	45	39
MgO	12	15
Li_2O	2	2
CaO	12	15
Ce_2O_3	2	--
ZrO_2	2	6
Y_2O_3	10	10
TiO_2	10	12
CoO(Co_2O_3)	1	1
ThO_2	4	--

The glass series UARL 455 through 470 are invert analogs with an extensive replacement of part of the silica by boric oxide to lower the density of such glasses and to increase their specific moduli. None of these glasses showed a sufficient decrease in density to offset the loss in absolute value of Young's modulus when boric oxide is substituted for silica. Finally, Young's modulus was calculated in advance of preparation using the Phillips method (Ref. 1) for glasses UARL 495, 499, 500, and 503. Agreement of predicted value with experimental value was excellent for two of these glasses (UARL 495 and 500) but only fair for UARL 499 and 503 which are multi-oxide systems with nine and eight components, respectively.

REVISED PROGRAM FOR CALCULATION OF YOUNG'S MODULUS OF BULK GLASS SAMPLES

In our summary report (Ref. 6) a computer program was written for the determination of the elastic modulus of a material in the form of a cylinder using the formulae developed by Pickett (Ref. 7).

The determination of the elastic modulus simply requires the evaluation of the following expression:

$$E = (C)\ (\text{weight})\ (\text{resonant frequency})^2.$$

The constant C is evaluated according to the expression

$$C = 0.0041632\ (L/D)^3\ T$$

with the parameter T evaluated for the diameter and length of the specimen according to

$$\text{(A)} \qquad T = 1.0 + 81.79(D/2L)^2 - (1314(D/2L)^4)/(1 + 81.09(D/2L)^2) - 125(D/2L)^4.$$

For this calculation, Poisson's ratio has been taken as 1/6, and the factors T and C are those which yield an approximate solution to the differential equations for transverse vibrations as determined by Goens.

In addition to the straightforward calculation, a feature of the program used is a subroutine which can be used to sort the output data in terms of any desired parameter, such as sample diameter. With this feature, checks for systematic variations in calculated modulus values with a chosen parameter can easily be made. The program itself is written in FORTRAN IV for use with a time-shared computing system. The Research Laboratories provides this capability by either an in-house PDP-6 (Digital Equipment Corp.) computer, or by subscription to the General Electric time-shared computing system.

Unfortunately, when this program was stored in the computer, the first exponent in Eq. (A) was changed from 2 to 3. This fact gave us a series of wrong moduli values reported in our last two reports (Refs. 8,9). The program in the computer has now been corrected as shown below and the corrected results for Young's moduli of recent experimental glasses are given in the next section.

Corrected Computer Program

```
CCCC PRØGRAM TØ CALCULATE GLASS BULK MØDULUS BY THE FØRMULATIØN OF PICKETT
CCC INPUT DATA GLASS IDENTIFICATIØN, WEIGHT IN GRAMS, DIAMETER
CCC IN INCHES, LENGTH IN INCHES, RESØNANT FREQUENCY IN KILØCYCLES
CCC
CCC
  DIMENSIØN DIA(50),WT(50),RF(50), E(50)
  DIMENSIØN INDEX(50)
  REAL LE
  ALPHA TITLE
  DIMENSIØN TITLE(10), LE(50)
  READ("PICKVAL",81)NTØT,TITLE
  81 FØRMAT(5X,13,10A4)
  READ("PICKVAL",85)(WT(N),DIA(N),LE(N),RF(N), N=2,NTØT)
  85 FØRMAT(5X,4F10.4)
  NN = NTØT -1
  DØ 50 N=2,NTØT
  M = N-1
  INDEX(M) = M; WT(M)=WT(N); DIA(M)=DIA(N);LE(M)=LE(N);RF(M)
 & = RF(N)
  50 CØNTINUE
  DØ 55 N = 1,NN
  A = DIA(N)/(2.*LE(N))
  T=1. + 81.79*A**2 - 131.4*A**4/(1. + 81.09*A**2) -
 & 125.*A**4
  C = 0.004163/DIA(N) * (LE(N)/DIA(N))**3 * T
  E(N) = C * (WT(N)/453.59) * RF(N)**2
55 CØNTINUE
CALL SØRT( DIA, NN, INDEX )
PRINT 123, TITLE
123 FØRMAT(1H , 10X,10A4)
PRINT," "
PRINT," J  L    DIA     LENGTH     WEIGHT      FREQ
&      MØDULUS"
DØ 501 J=1,NN
L = INDEX(J)
PRINT 135,J,L,DIA(J),LE(L),WT(L),RF(L),E(L)
501 CØNTINUE
135 FØRMAT(1H ,2I3,3F10..4,2F14.4)
STØP; END
SUBRØUTINE SØRT( A, NPØINTS,INDEX)
```

```
CCC INDEX IS FILLED WITH INDEXING INTEGERS FRØM 1 TØ NPØINTS
CCC ARRAY IS BRØUGHT IN AS A SINGLY SUBSCRIPTED ARRAY
  DIMENSIØN A(50),INDEX(50)
  M = NPØINTS
  1 M = M/2
    1F ( M .EQ. 0 ) RETURN
    K = NPØINTS - M
    J = 1
    2I = J
    3IM = I + M
    IF[A(I)-A(IM)]5,5,4
CCC SWITCH VALUES AND ARRANGE INDEX ARRAY
  4 SAV = A(I); NSAV = INDEX(I)
    A(I) = A(IM); INDEX(I) = INDEX(IM)
    A(IM) = SAV; INDEX(IM) = NSAV
    I = I-M
    IF (I. GE. 1) GØ TØ 3
    5J = J + I
    IF (J-K)2,2,1
    END
```

RECENT DETERMINATIONS OF YOUNG'S MODULUS OF BULK GLASS SAMPLES

Using the corrected program, new values for Young's modulus were determined for all glasses previously calculated with the erroneous program and these values are listed in Table III. The magnitude of the change may be seen from the fact that the old value for UARL 468 glass was 15.48 x 10^6 psi while the corrected value is 17.01 x 10^6 psi. Since the erroneous equation has been erased from the computer's memory bank, no further trouble is anticipated in the programmed calculation of Young's from the raw laboratory data.

It will be noted that glasses UARL 415, 419, 421, 422, 423, 426, 435, 439, 442, 443, and 446 have values for Young's modulus of twenty million psi or slightly higher. These glasses without exception contain beryllia so it is obvious that the search for a fiberizable high modulus high strength non-beryllia containing glass is not finished. The best non-beryllia glass discovered to date that can be readily fiberized is UARL 237 with a value for Young's modulus of 18.3 million psi and a specific modulus of 152 million inches, while the next best is UARL 449 with the corresponding values of 18.08 million psi and 148 million inches. High moduli non-beryllia glasses such as UARL 383 with a value for Young's modulus of 22.75 million psi and a specific modulus of 200 million inches and UARL 329 with values of 20.7 million psi and 189 million inches respectively have been made but not successfully fiberized.

Table III

Corrected Values for Young's Modulus Measured on Circular Rods Formed Directly from Melt

Glass No.	Density gms/cm^3	Density lbs/in^3	Young's Modulus millions psi	Specific Modulus 10^7 inches
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	13.80
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
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

Table III (Cont'd)

Glass No.	Density gms/cm^3	Density lbs/in^3	Young's Modulus millions psi	Specific Modulus 10^7 inches	Glass No.	Density gms/cm^3	Density lbs/in^3	Young's Modulus millions psi	Specific Modulus 10^7 inches
433	3.6325	0.1308	19.12	14.65	458	3.2094	0.1158	15.23	13.15
434	3.5304	0.1273	19.43	15.35	459	3.4538	0.1242	17.34	13.95
435	3.4605	0.1247	20.36	16.33	460	3.3785	0.1215	16.83	13.84
436	3.4461	0.1246	19.90	16.05	461	3.0354	0.1092	14.80	13.54
437	3.5067	0.1265	19.41	15.35	461[1]	3.3823	0.1218	26.0	21.3
438	3.2348	0.1165	18.28	15.68	462	3.3294	0.1198	16.53	13.82
439	3.3510	0.1207	20.03	16.63	463	3.4296	0.1235	17.85	14.45
440	3.3426	0.1203	19.72	16.37	464	3.0700	0.1105	16.12	14.60
441	3.2739	0.1181	19.52	16.52	465	3.3184	0.1193	16.66	13.95
442	3.5959	0.1297	20.02	15.45	466	3.0731	0.1108	15.95	14.42
443	3.6695	0.1326	20.10	15.17	467	3.4302	0.1238	16.82	13.55
444	3.5011	0.1263	19.33	15.35	468	3.4426	0.1242	17.01	13.70
445	3.4488	0.1245	17.63	14.16	469	3.3773	0.1219	16.33	13.39
446	3.5049	0.1263	20.01	15.85	470	3.3020	0.1193	16.75	14.05
447	3.2975	0.1188	18.23	15.35	471	3.1743	0.1145	17.90	15.63
448	3.5173	0.1268	17.08	13.45	472	3.2183	0.1162	18.20	15.67
449	3.3944	0.1223	18.08	14.80	473	too high a forming temperature			
450	3.3598	0.1212	17.78	14.65	474	too high a forming temperature			
451	3.5527	0.1280			475	too high a forming temperature			
452	3.6114	0.1302			476[2]	2.9125	0.1048	18.44	17.57
453	3.6837	0.1327			477	3.2277	0.1166	18.62	15.95
454	3.6142	0.1303	18.93	14.53	478	3.2992	0.1189	18.46	15.52
455	3.2860	0.1186	15.96	13.46	479	3.0768	0.1108	16.69	16.55
456	3.2099	0.1158	15.02	13.00	480	3.3397	0.1204	18.12	15.54
457	3.1765	0.1144	15.93	13.89	481	3.2284	0.1167	18.30	15.70

[1] crystallized

[2] UARL 476 is Bastian, U.S. Patent 2,978,431 - max. ingredients

Table III (Cont'd)

Glass No.	Density gms/cm^3	Density lbs/in^3	Young's Modulus millions psi	Specific Modulus 10^7 inches
482	3.1492	0.1137	16.83	14.81
483	3.1451	0.1135	16.69	14.69
484	3.1560	0.1138	15.98	14.05
485	3.2110	0.1157	16.83	14.55
486	3.1853	0.1145	16.10	14.07
487	3.2004	0.1155	16.08	13.93
488	3.3235	0.1200	17.87	14.90
489	3.0710	0.1108	16.72	15.12
490	3.2900	0.1187	17.78	14.98
491	3.4625	0.1248	18.68	14.95
492	3.3920	0.1223	18.55	15.15
493	3.4562	0.1247	18.64	15.28
494	3.2678	0.1180	16.30	13.82
495	3.5578	0.1287	17.24	13.42
496	3.3972	0.1226	19.18	15.65
497	3.3829	0.1222	18.63	15.27
498	3.2500	0.1175	16.22	13.80
499	3.6049	0.1303	19.50	14.95
500	3.5944	0.1297	18.97	14.63
501	3.6174	0.1307	19.02	14.58
502	3.8924	0.1403	19.02	13.57
503	3.6528	0.1318	19.55	14.85
134A	3.0983	0.1116	16.86	15.12
152	4.3834	0.1580	15.27	
160	3.2452	0.1170	17.09	14.53
345B	3.3594	0.1216	20.66	17.00
425B[3]	2.7561	0.0995	18.81	18.90

[3] UARL 425 is National Bur. of Standards Glass 389 (Ref. 5)

RECENT GUIDE LINES FOR THE DEVELOPMENT OF NEW NON-TOXIC GLASS FIBERS

The directions in which UARL is moving toward the goal of a high modulus high strength non-toxic glass fiber can be seen by examination of Table IV. Because of the newness of our recent discovery (discussed in the next section) that zinc oxide can make a major contribution to Young's modulus, this table fails to reflect adequately the extent of our progress. The table likewise does not show that we have found recently that zirconia additions cause a marked alteration in the viscosity-temperature curves of highly fluid glasses. Finally, the fiberization characteristics of some of the glasses contained in Table IV are still under investigation. With all these reservations in mind, it would appear, however, that compositions similar to UARL 237, 402, and 449 are most likely to provide the final answers.

NEW FACTORS AND CALCULATIONS FOR THE PREDICTION OF YOUNG'S MODULUS

The corrected values for Young's modulus from Table III together with the earlier values for UARL glasses 1 through 424 which required no correction since they were calculated by hand and not by computer were used to form the input data for an extension of the C. J. Phillips (Ref. 1) method of predicting Young's modulus from the composition. This method is based on the procedure of expressing each oxide in mol percent and multiplying it by a modulus factor peculiar to that oxide. Originally, Phillips derived coefficients only for 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. This series of calculations extends the list of coefficients available to include those for Y_2O_3, ZrO_2, La_2O_3, Ta_2O_5, TiO_2, CoO, Ce_2O_3 and makes a small correction in the value for MgO as well as a very large correction for ZnO. Of course, the glasses prepared at UARL have been primarily either cordierite base-rare earth oxide glasses or invert analogs with major rare-earth additions so that the calculations are not necessarily universally applicable to the more common commercial glasses but would be expected to hold for all glasses used to produce glass fibers since these normally contain very little alkali.

As stated above, the numerical value for the predicted Young's modulus of a given glass is the sum of the terms

$$C_1 P_1 + C_2 P_2 + \dots + C_n P_n$$

where C_1, C_2, ... C_n are molal coefficients and P_1, P_2, ... P_n are the molar percentages of the corresponding oxides. The agreement obtained as well as the details of the calculations are shown for 58 of the UARL experimental glasses. The calculations start with simple ternary oxide systems such as silica-alumina-magnesia and build through quarternary systems to systems involving nine or ten oxides. The results of the new determinations of all the molal

Table IV

A Further Guide to the Development of a Nontoxic Fiberizable Composition Having an Absolute Modulus Greater than 15.6 x 10^6 psi, Specific Modulus 14.6 x 10^7 in or Better and Readily Fiberizable. Includes N.B.S. 389 (UARL 425) for Comparison Although this Glass Cannot Be Readily Fiberized and Does Contain Beryllia

Glass No.	Mol Sum	Density gms/cm^3	Modulus 10^6 psi	Spec. Mod. 10^7 in.	SiO_2	Al_2O_3	MgO	Li_2O	CaO	ZnO	ZrO_2	Y_2O_3	BeO	CoO	B_2O_3	TiO_2	Cu_2O	Fe_2O_3	Re_2O_3	Ce_2O_3	Can be Fiberized
231		3.43	18.05	14.6	40	14	36					10									
235		3.33	17.4	14.4	50	10	30					10									X
236			17.8	14.3	43	15	30					10									
237		3.33	18.3	15.2	45	15	30					10									X
266	61.5	3.187	16.7	14.5	25	15	15	15	15	15											
270	70.13	3.53	20.3	15.9	25	8	15	15	15	15		7									
304		3.62	19.65	15.2	35	15	30			10		10									
306		3.67	18.9	14.3	35	15	30			5		10		5							
321		3.63	18.7	14.2	40	15	30					15									X
329		3.03	20.7	18.9	22.2	11.11	22.22	11.11		11.11	11.11	11.11									
333		3.71	18.9	14.1	39	12	25			12		12									
337		3.94	20.9	14.9	30	15	30			12.5		12.5									
357	91.6	3.40	17.6	14.4	39	12	24	6		6		3							10		
360	76.9	3.52	18.5	14.6	39	12	24	6		6		10		3							
361	79.2	3.50	18.5	14.8	39	12	24	6		6		10						3			
362	77.0	3.50	18.0	14.3	39	12	24	6		6		10					3				
363	76.3	3.57	19.26	14.9	39	12	24	6				10			6		3				
383	64.9	3.14	22.75	20.02	24	3	16	12	12	8	12				10		3				
391A	78.5	3.31	17.38	14.6	17	6	16	12	12	8		12			17						
402	83.1	3.31	17.77	14.85	25	8	20	5	9			14			14	3	2				X
403	86.2	3.37	17.17	14.05	25	8	20	5	6			14			14	3	2	3			X
449	77.0	3.39	18.08	14.8	25		20	6	15	4		12			13	3	2				X 15.82
450	79.7	3.36	17.78	14.65	38		15	10	15	10		12									
454	80.5	3.61	18.93	14.53	38	6	20	6	9	4		12				3	2				
464	64.1	3.07	16.12	14.6	25		15	15	15	10		5			15						X 14.83
466	60.5	3.07	15.95	14.4	25		15	15	15	15		2.5			12.5						
471	70.8	3.17	17.9	15.63	25	8	15	15	10	15		7			5						
480	68.7	3.34	18.12	15.54	55		4		12			10	16	1							readily?
481	80.6	3.23	18.30	15.70	55	17	17					10		1							
491	84.8	3.46	18.68	14.95	47	17	17	3				10					6				
492	83.4	3.39	18.55	15.15	47	17	17	3		6		10									
494	73.96	3.27	16.30	13.8	65		12		12			10		1							readily?
502	90.12	3.89	19.02	13.6	45		12	2	12		2	10		1		10			$4ThO_2$	2	readily?
425B	49.3	2.74	18.81	18.99	42.9	7	25.6						24.6								
425A	49.5	2.74	19.51	19.7	42.9	7	25.6						24.6								
461 cryst.	63.4	3.38	26.0	21.3	25		13	13	13	13	10				13						

coefficients are given in Table V. It will be noted that beryllia makes a contribution of nineteen kilobars/mol to Young's modulus and that ceria, lanthana, zinc oxide, zirconia, and yttria all make a contribution at least as large. The result for zinc oxide for the UARL glasses is especially surprising since the original work of Phillips showed a contribution of only 1.75 kilobars/mol rising with R_2O increase while this work shows a value of 20.0 kilobars/mol. Phillips (Ref. 1) original calculations for zinc were based primarily on barium silicate glasses while the present investigation is concerned largely with silica-magnesia-alumina-yttria-zinc oxide systems and it may be possible that in such systems tightens the divalent oxygen ions in exactly the same manner as beryllia (Ref. 10). The contribution of 20 kilobars/mol of zinc oxide therefore appears much more likely than the value of 1.75 kilobars/mol. The details of these calculations are shown in Appendix I.

RECENT EXPERIMENTAL GLASS FIBERS

The results for those glass fibers produced recently by drawing through a single-hole platinum-rhodium bushing are listed in Table VI. The measured values for Young's modulus shown in this table are determined by thin-line ultrasonic techniques as described in our earlier report (Ref. 6). Glasses 402, 403, 448, 449, and 464 are non-beryllia containing glasses while the other glasses contain major amounts of beryllia. Several of the glasses, i.e. UARL 417, 418, and 464, have densities approximately equal to 3.09 gms/cm^3 and the other glasses have higher densities. UARL 417 fiber not only has one of the highest absolute values for Young's modulus, 17.5 million psi measured on the fiber, but also the highest fiber specific modulus, 157 million inches. It was normal, therefore, to select UARL 417 as the second glass from which large quantities of fiber in monofilament form would be produced and used to form fiber glass-epoxy resin composites for evaluation. The first experimental glass produced in quantity was, of course, UARL 344 and the results for composites of this glass were described in detail in an earlier report (Ref. 6).

SELECTED GLASS FIBERS PREPARED IN LARGE QUANTITY AS MONOFILAMENTS

Of the more than 500 glass compositions investigated, about one hundred could be drawn into glass fibers using the UARL single hole platinum-rhodium bushing or its predecessor the platinum crucible with reinforced bottom and hole drilled in the bottom. One of the more outstanding high modulus beryllia containing glasses developed at UARL under the earlier contracts is the glass composition UARL 344. Intensive investigation of this composition showed that it could be readily fiberized, and fibers continuously drawn at high rates of speed and restarted at will. Over a quarter billion feet of this fiber has been drawn through an orifice of 0.038 in. diameter (platinum-20% rhodium bushing) at orifice

Table V

Summary of All Experimentally Determined Molar Modulus Coefficients

Oxide	Contribution Per Mol (kilobars)	Oxide	Contribution Per Mol (kilobars)
SiO_2	7.3	ZnO	20.0
Al_2O_3	12.1	ZrO_2	23.8
CaO	11.45	MgO	13.64
Li_2O	7.0	Ce_2O_3	19.6
B_2O_3	7.2	Y_2O_3	28.6
TiO_2	15.0	La_2O_3	18.6
BeO	19.0	Ta_2O_5	19.4
		CoO	11.0

Table VI

Young's Modulus for Mechanically Drawn Fibers of UARL Glasses

(All measurements by thin-line ultrasonics)

Glass Number	Young's Modulus 10^6 psi	Glass Number	Young's Modulus 10^6 psi
402	15.75, 15.95	418	17.95, 17.95
403	15.95, 16.1	419	18.4, 18.1
405	18.3, 18.45	420	17.8, 17.7, 17.6
408	16.65, 16.4	433	17.39
410	16.7, 16.6	434	16.83
411	16.5, 16.35	438	16.48
412	17.0, 16.65	448	15.88
416	18.47, 18.64	449	15.82
417	17.5, 17.5	464	14.83

temperatures of 1260°C to 1310°C with heads of molten glass from 3/8 to 1 1/2 in., and at winding speeds of 4000 to 8000 ft/min (the top speed of our winder). The glass fibers processed under these conditions show excellent properties. Diameters vary from 0.2 to 0.4 mils with a Young's modulus of 18.6 million psi, a specific modulus of 157 million inches, and strengths which, in 22 consecutive measurements, overaged 772,000 psi and ranged from 600,000 to 1,000,000 psi with a few extreme values discarded.

In this contract, a second experimental glass, UARL 417, has now been prepared in quantity as a monofilament (about forty million feet). In contrast to the UARL 344 which has a fiber density of 3.29 gms/cm^3, the UARL 417 fiber has a bulk density of 3.09 gms/cm^3 with a probable fiber density of about 3.00 gms/cm^3 and a Young's modulus of 17.5 million psi.

The large quantities of monofilament of UARL 344 and 417 have been used as reinforcements to form fiber glass-epoxy resin composites and have given exceptional properties to these composites as we show in a later section. In order to evaluate the composite samples it was necessary to develop an improved compressive strength test and we shall examine this procedure first before considering the results for the composites.

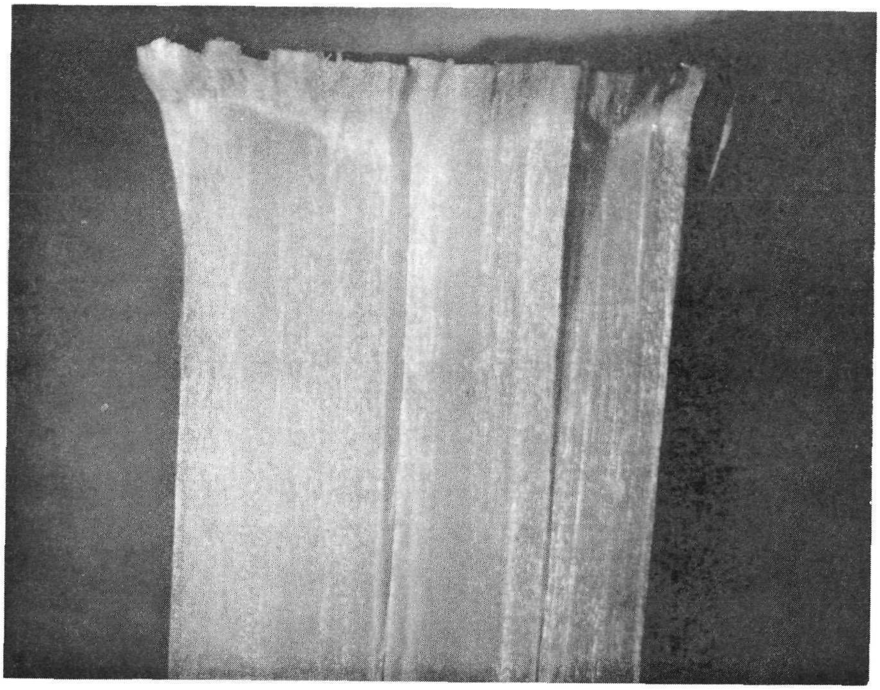
IMPROVED COMPRESSIVE STRENGTH MEASUREMENTS

Initially, UARL tried to evaluate the compressive strength of UARL 417 glass fiber-epoxy resin composites by using the currently accepted ASTM procedure (Ref. 11) for short cylinders whose length was equal to three times the diameter and loading these cylinders with spherically-seated bearing blocks in the usual Tinius-Olsen Universal Testing Machine. This approach resulted in too low a value for compressive strength as shown in Table II, and resulted in the mushroomed samples pictured in Fig. 1.

Fortunately, the Celanese Corporation had already fully faced the problem of testing filament reinforced composites (Ref. 12). To at least partially eliminate the problem they designed a compression jig which allows the compressive forces to be induced by shear stresses on bonded tabs in a collet-type grip, which does not come in contact with the test specimen. The special design used is shown in Fig. 2 and the Celanese Corporation design compression jig is shown in Fig. 3. Using this equipment, we were able to completely eliminate any mushrooming effect and instead obtained gage-length failures which appear reasonable. As shown in Table VII, the average compressive strength found for the UARL 417 glass fiber-epoxy resin composite with the improved procedure is 220,000 psi. In our opinion, this still represents a lower limit for this type of test and further testing may raise this value appreciably as we learn more about the preparation of composites.

FIG. 1

MUSHROOMING OF FIBER GLASS-EPOXY COMPOSITE IN NORMAL UARL COMPRESSION TESTING



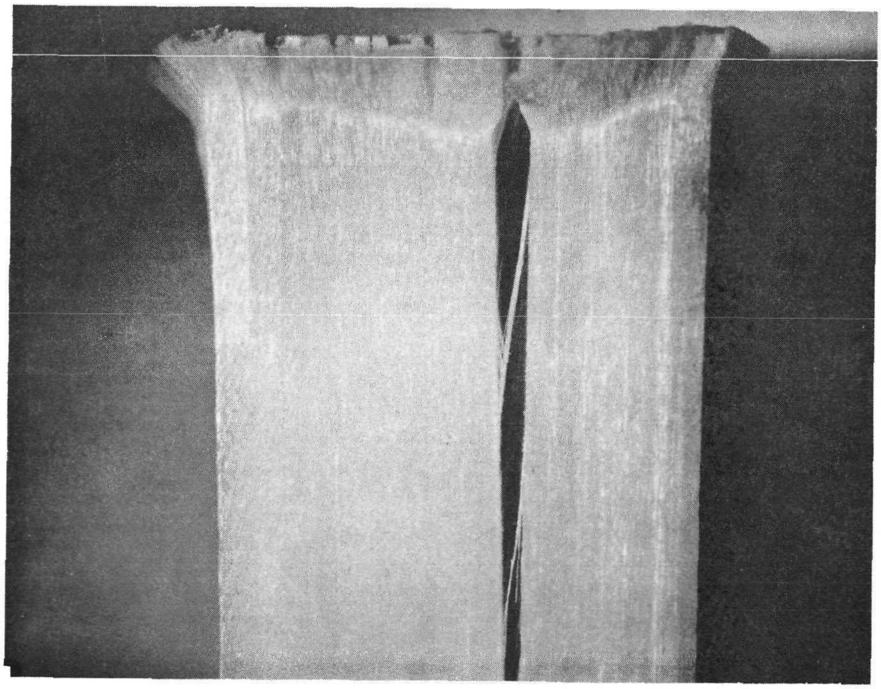


FIG. 2

TEST SAMPLE FOR SPECIAL CELANESE CORPORATION COMPRESSION JIG

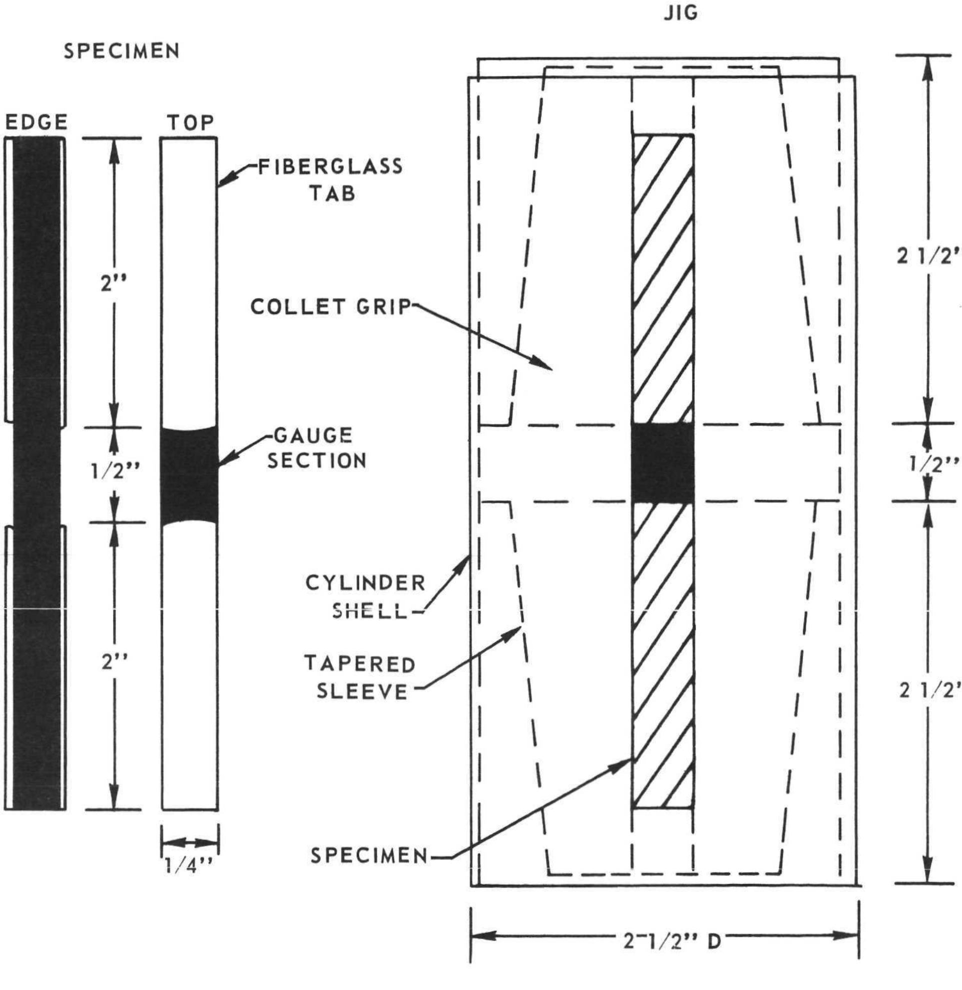
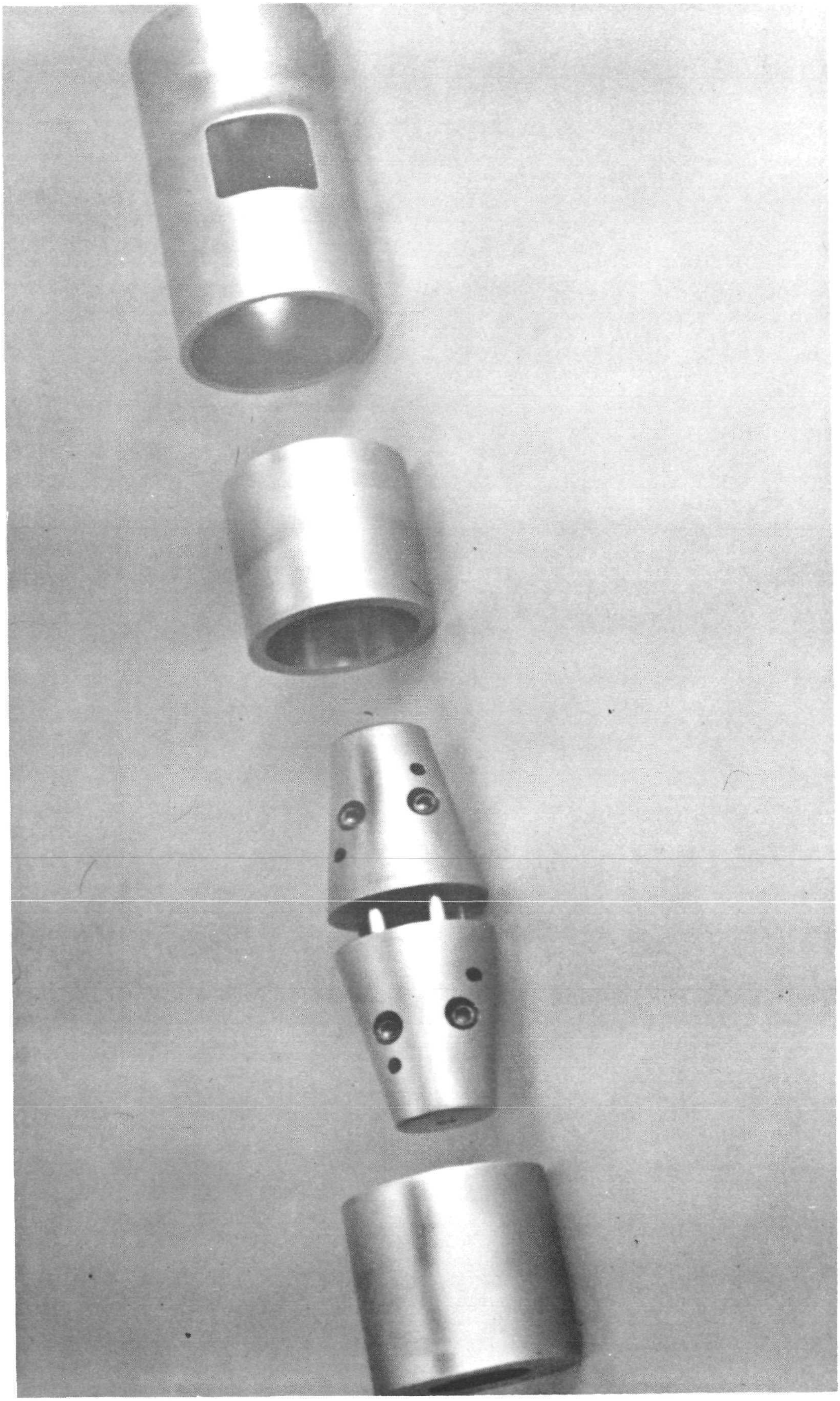


FIG. 3



CELANESE CORPORATION DESIGN COMPOSITE COMPRESSION RIG

Table VII

Compressive Strengths of Fiber-Epoxy Resin Composites

Specimen Identity	Voids %	Fiber Volume %	Fiber Modulus millions psi	Compressive Strength thousands psi
UARL 417 fiber-epoxy (unsupported specimen)	1.0	71.5	17.5	117-122
UARL 417 fiber-epoxy (tabbed bar)	1.0	71.5	17.5	218-227
DuPont PRD-49-1		65	20.0	40-50

PROPERTIES OF GLASS FIBER-EPOXY RESIN COMPOSITES MADE WITH UARL GLASS FIBERS

To produce the UARL experimental glass fibers in form suitable for reinforcement of epoxy resins, it was necessary to learn to apply the surface finish and size as the fiber is pulled. After several false starts the sizing applicator shown in Fig. 4 was developed. It worked satisfactorily but the sizing solvent proved to have too low a flash point and the initial startup of the glass fiber inevitably caused a flash fire. However, about three million feet of UARL 344 glass fiber was successfully coated after the fire was extinguished. To improve the flash point of the size solvent solution, higher molecular weight solvents were tried but using the method of mixing we had at that time, these solvents caused precipitation of the size. Since then this problem has been solved.

The properties of the UARL experimental glass fibers in epoxy-resin matrices are very promising. UARL scientists calculated for a 70% volume content of glass fiber, a glass-fiber epoxy resin composite matrix with ±45° alignment would have resultant values of:

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

and these properties are fully realized making such matrices useful for spar and shell blades, torque tubes, and rotary machinery in general.

The properties of the UARL experimental glass fibers are more comprehensively examined in Table VIII where the properties of four epoxy resin-fiber composites are shown. The "S" glass, UARL 344, and UARL 417 glass fiber-epoxy resin composites were all made in this laboratory using identical procedures but the data for the DuPont PRD-49-1 fiber composite was taken from the DuPont brochures. The data of Table VIII show that the glass fiber-epoxy resin composites are superior in flexural strength (both absolute and specific), short-beam shear strength (both absolute and specific), compressive strength (both absolute and specific), impact strength, and in absolute tensile strength in comparison to the DuPont PRD-49-1 epoxy resin composite. This absolute strength of the UARL fiber epoxy resin composite indicates a very high strength retention for the UARL 417 fiber without sizing and after the considerable amount of handling necessary to form a glass fiber-epoxy resin composite.

The tensile stress-strain curves for the UARL 417 epoxy resin composite and the DuPont PRD-49-1 composite are shown in Fig. 5 and similar bending stress-strain curves for the composites are shown in Fig. 6. In both cases the comparison favors the UARL 417 glass fiber.

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FIG. 4

FIRST EXPERIMENTAL SIZING APPLICATOR

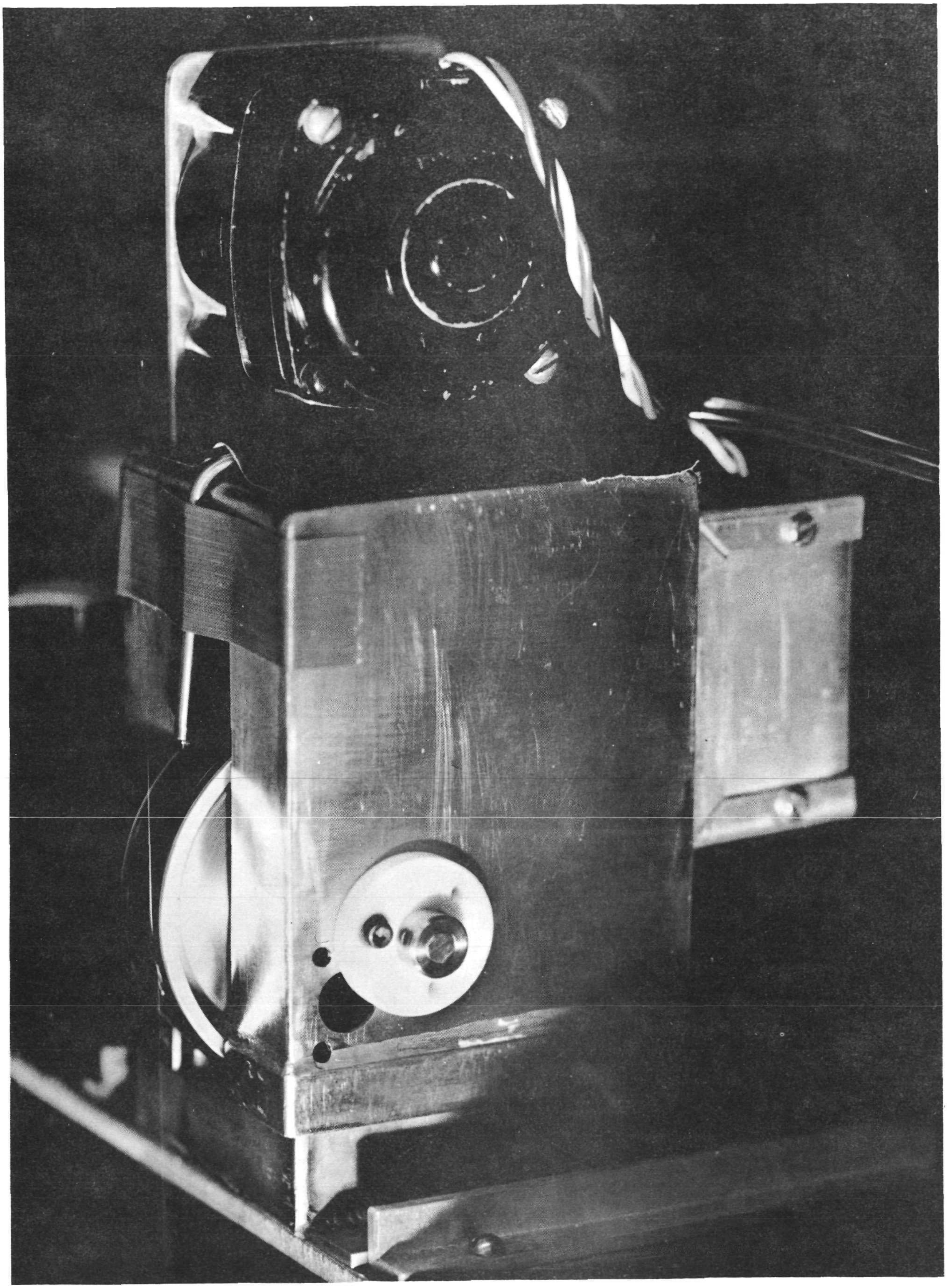


Table VIII

Comparison of Several Fiber-Resin Composites

Composite and Glass Identity	634 (S glass)	Average of 7 Composites UARL 344	695* UARL 344	UARL 417	DuPont PRD-49-I
Fiber Finish	Commercial	Proprietary	Proprietary	Proprietary	None
% Voids	0.6	3.1	2.5	1.0	--
% Fiber	67	62	60	71.5	65
Density of Composite gms/cm^3	2.07	2.47	2.49	2.55	1.38
Flexural Strength 10^3 psi	215	254	290	228	95
Flexural Modulus 10^6 psi	---	11.3	11.2	12.07	17
Short Beam Shear Strength 10^3 psi	13.9	14.4	16.7	15.5	7.5
Tensile Strength 10^3 psi	266	250	250	298	200
Tensile Modulus 10^6 psi	8.27*	10.9	10.9	11.9	14.0
Notched Charpy Impact Value ft. lbs/in^2	435	242	242	214	150
Compressive Strength 10^3 psi				218-227	40-50

S glass has a density of 2.49 gms/cm^3 and a Young's Modulus of 12.4×10^6 psi.
UARL 344 glass fiber has a density of 3.29 gms/cm^3 and a Young's Modulus of 18.6×10^6 psi.
UARL 417 glass fiber has a density of 3.09 gms/cm^3 and a Young's Modulus of 17.5×10^6 psi.
DuPont PRD-49-I organic fiber has a density of 1.38 gms/cm^3 and a Young's Modulus of 20×10^6 psi.

*Estimate based on fiber % and known modulus of glass.

**Results obtained after an initial series of learning experiments had been carried out in making and testing UARL 344 glass fiber-epoxy resin composites.

FIG. 5

COMPOSITE TENSILE STRESS/STRAIN CURVES

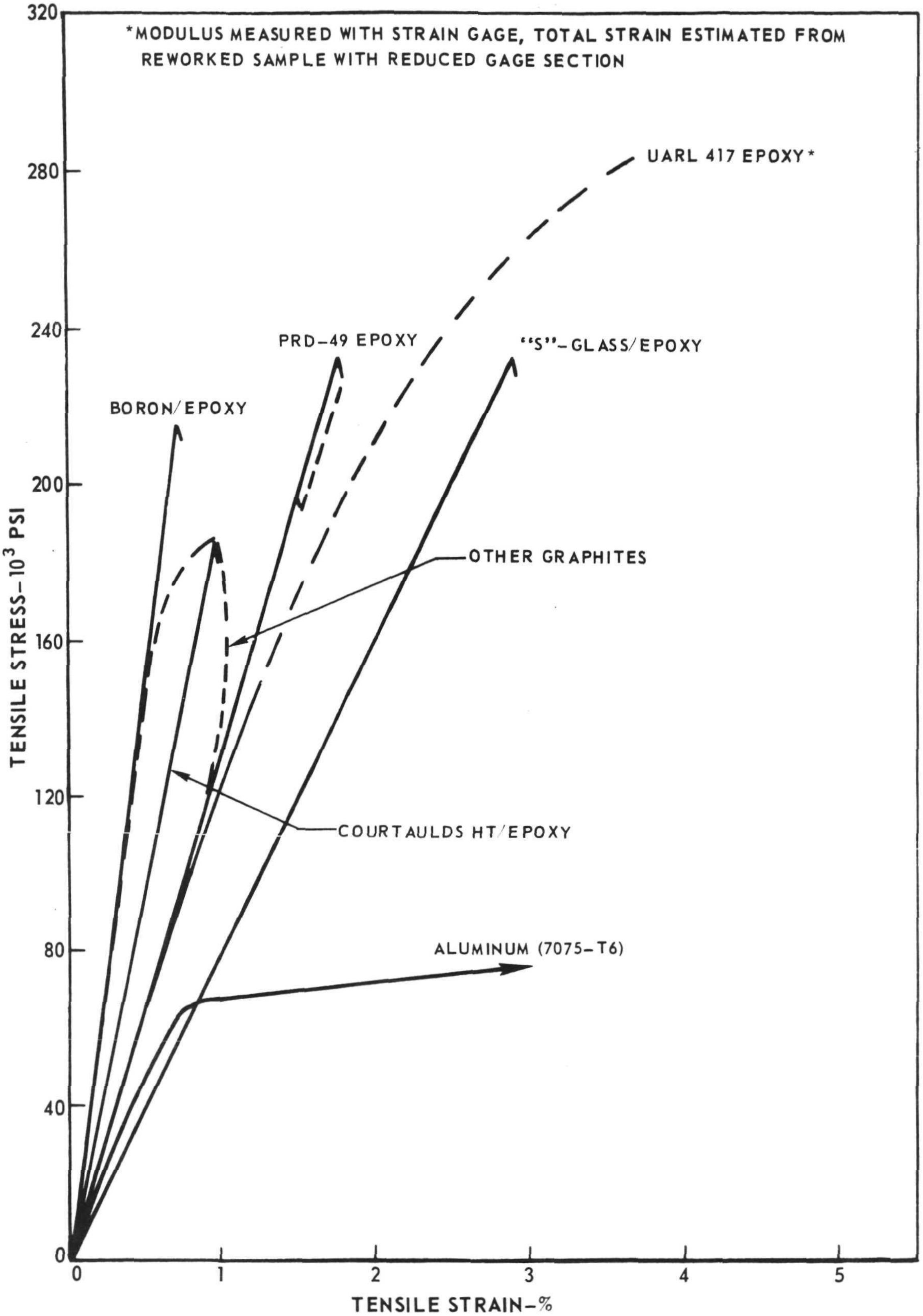
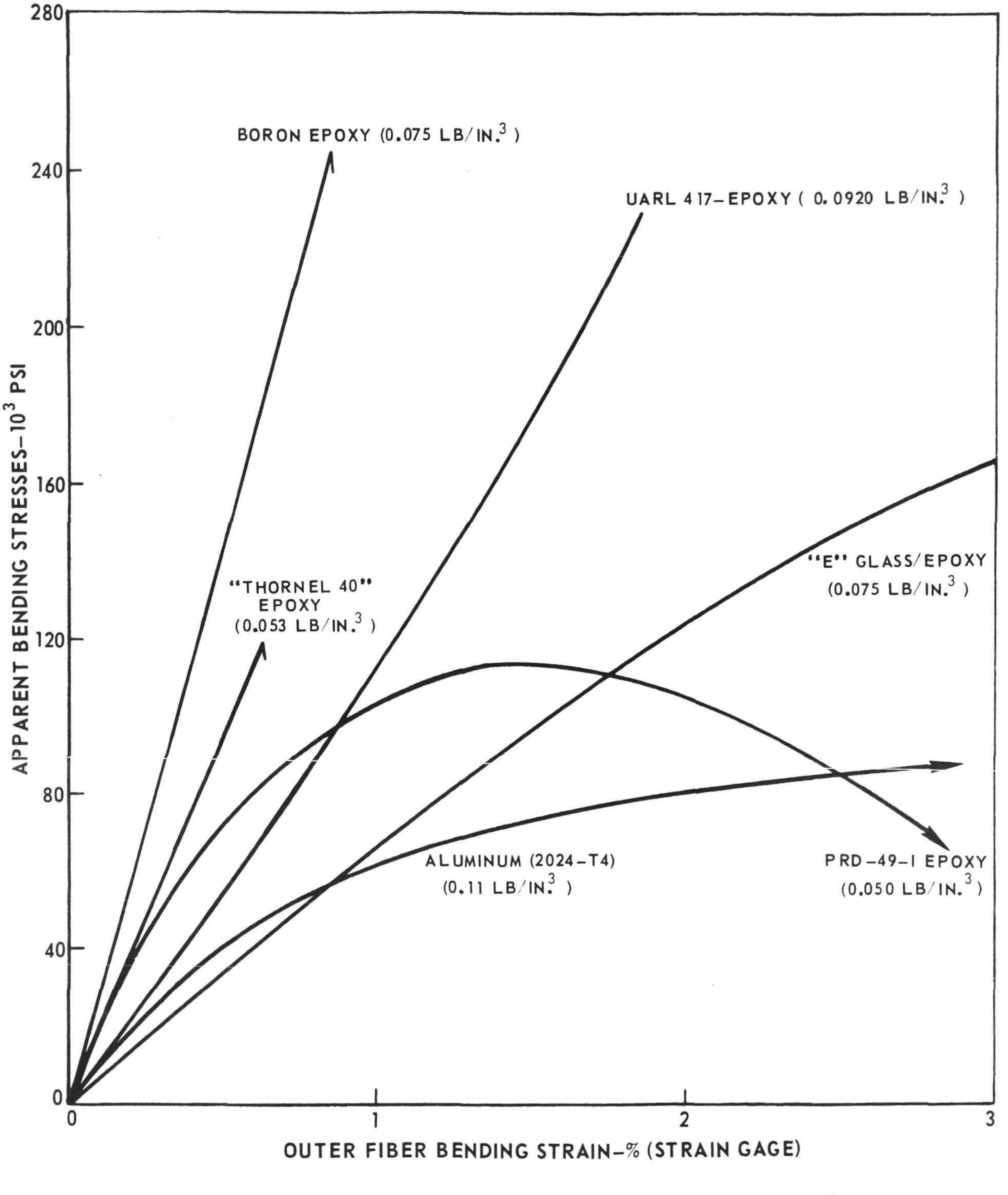


FIG. 6

COMPOSITE BENDING STRESS/STRAIN CURVES IN DIRECTION OF FIBER ALIGNMENT



COMPARATIVE IMPACT RESISTANCE OF SEVERAL UARL BULK GLASSES

As indicated in the introduction to this report, one of the more important objectives of this contract was to attempt to discover why a given glass has a superior impact resistance compared to other glasses. Eleven high modulus glasses were selected for the initial study and the results obtained with full-size notched Charpy specimens prepared by cutting from fully annealed glass discs are shown in Table IX together with a similar test for the usual commercial fiber glass "E" composition. For the "E" glass and UARL glasses 237, 304, 350, 383, 419, 425, and 447 four specimens were tested while for UARL glasses 323, 336, 344, and 454A two specimens were used to obtain the average values shown in Table IX.

It can be seen immediately that the notched full-size Charpy impact specimen does not give a clean-cut separation of these glasses on the basis of their impact strengths. All that can actually be said on the basis of this test data is that UARL 323 has the lowest impact strength, next "E" glass, UARL 350 and 425 (N.B.S. 389), then at a slightly higher level UARL glasses 237, 304, 344, 383, 419, 447, and 455A and finally UARL 336 with the highest impact strength. The separation on the basis of their impact strength for this type of test is much less than that found in preliminary experiments in which an unnotched Izod specimen was used (Ref. 13). It seemed, therefore, that the formation of the notch in the specimen damages it and that we were not measuring quantities directly dependent on the impact strength of the material because of the notch sensitivity of the material. It was decided, therefore, to carry out the subsequent tests discussed next using unnotched Charpy test specimens.

The appearance of a typical full-size Charpy impact specimen after failure is shown in Fig. 7 as observed by scanning electron microscopy. The propagation of the Charpy impact across the specimen can be clearly seen.

Table X shows the results of the impact tests after we shifted to hybrid sized unnotched Charpy specimens prepared directly from aspirated circular rods of bulk glass, 0.310 in. in diameter and standard full length. It was felt that samples prepared in this way have experienced the possible amount of surface damage. Each value tabulated is the average value of eight determinations. This method of determining impact resistance was found to give extremely consistent results. However, the absolute values tabulated were not well established because the capacity of the particular impact machine at hand was so large that all readings represent extrapolated values from a difference of less than one degree in swing.

As Table X shows, the impact resistance of the experimental glasses varies with composition, UARL 304 having the highest impact resistance and UARL 459 the lowest impact resistance.of those glasses investigated. UARL 304 contains both aluminum oxide and zinc oxide and this combination apparently contributes to its increased impact resistance since UARL 447, which contains zinc oxide but not alumina, is low in impact resistance as is UARL 419 which contains

Table IX

Impact Resistance of Bulk Glass As Determined by Full-Size Notched Charpy Test Samples

Glass No.	Impact Strength Result (in.-lbs)	Glass No.	Impact Strength Result (in.-lbs)
"E"	0.752	350	0.772
237	0.902	383	0.908
304	0.888	419	0.904
323	0.703	425	0.786
336	1.010	447	0.872
344	0.876	454A	0.900

FIG. 7

TYPICAL NOTCHED FULL-SIZE CHARPY TEST SPECIMEN AFTER FAILURE

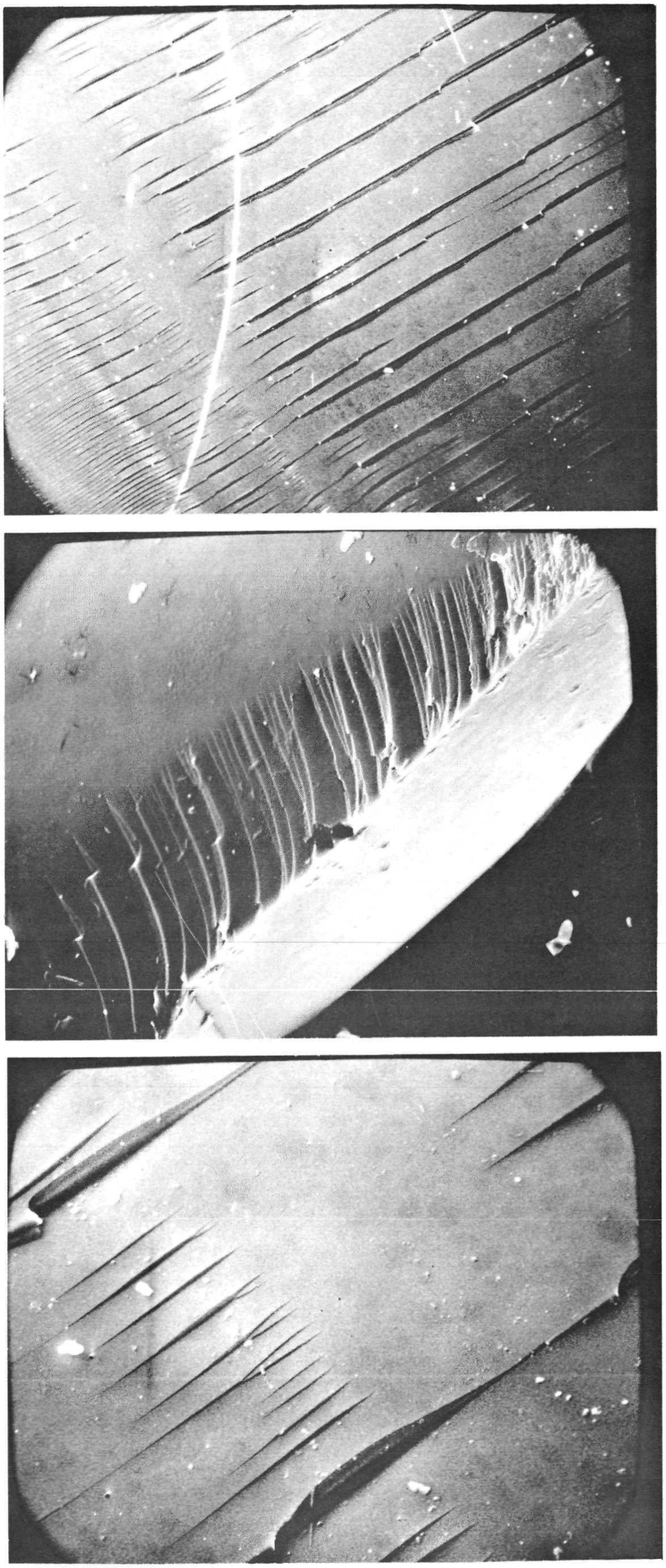


Table X

Composition Related to Impact Strength

Glass Number or Designation	Impact Resistance (in lbs)	Young's Modulus 10^6 psi	Compositions of Glasses Evaluated as Impact Specimens (Mol %)											
			SiO_2	Al_2O_3	MgO	Y_2O_3	BeO	ZnO	Li_2O	La_2O_3	CaO	B_2O_3	ZrO_2	TiO_2
237	0.75	18.3	45	15	30	10								
304	0.85	19.65	35	15	30	10		10						
323	0.59	18.4	35	15	30		10		10					
331	0.82	20.9	39	12		12	25	12						
336	0.80	21.0	35	15		10	30	10						
344	0.79	20.3	45	15	15	10	15							
347	0.82	21.6	50	8.33		25		8.33		8.33				
350	0.71	19.8	24	11	11		20		11		11			
383	0.71	22.75	24	3	16			8	12		12	10	12	3
417	0.71	19.35	45	15	15	7	15		3					
419	0.64	20.15	42	15	15	10			3					
425	0.54	19.51	42.9	7	25.6		24.6							
447	0.595	18.23	25		15	12		10	10		15	13		
459	0.48	17.34	25		15	10		14	14		14	8		
"E"	0.625	10.5	57	8.9	7.1						19.7	7.1		

alumina but not zinc oxide. Obviously, these are very preliminary clues as to the factors important in impact resistance and the dependence of impact resistance on composition needs to be much more carefully investigated.

The mechanism by which the impact resistance of UARL 304 is enhanced compared to UARL 459 is shown in Figs. 8 and 9 where optical macrographs showing typical fracture systems in these two glasses are compared. The much larger initiation zone, mist zone, and hackle zone for glass UARL 304 (Fig. 8) shows that it absorbed more energy before fracturing than did UARL 459 (Fig. 9). While these figures are from only one specimen of each glass, other specimens of the subject glasses showed exactly the same behavior, and it is felt that this behavior can be regarded as typical. With a different type of impact test it is felt that the ratio of the comparative impact resistance of these two glasses will be found to be much larger than the factor of two currently shown in Table X.

The third continuance of the study of the impact resistance of bulk glasses produced the results shown in Table XI. In this third study, eight specimens of each glass were prepared by aspirating the molten glass into a fused silica tube by means of a hypodermic syringe. The round glass rods were then cut to standard length for Charpy specimens and regarded as unnotched Charpy specimens. They were tested on a special tester belonging to P&WA, which is a Wiedeman-Baldwin Tester, an impact tester of Bell Laboratory design using a one foot pound hammer, a thirteen inch pendulum, and a two foot drop. As all who have used this type of test know, the results are somewhat variable so that the average test data listed in Table XI is designated as the "best logical average". A more precise idea of what we mean by this term can be obtained by examining the data of Table XII which shows just how much variation can occur in two typical sets of test data. For UARL 323 glass the best logical average is obtained by striking out the two extreme values found, while for UARL 417 glass the true average is employed although the data varies from 0.8159 to 1.057 ft-lbs/in.^{2}.

CONCLUSIONS

1. Glass fibers formed from the UARL experimental glasses 344 and 417 added to epoxy resins as reinforcements form composites superior in flexural strength, short-beam shear strength, compressive strength and absolute tensile strength compared to similar composites made with DuPont experimental organic fiber PRD-49-1. The curves describing the tensile stress-strain and bending stress-strain for the UARL 417 glass fiber-epoxy resin composites are superior to those for the DuPont fiber PRD-49-1 in similar composites. Finally, the impact strengths of the glass fiber-epoxy resin composites are much higher than the impact strength of the organic fiber-epoxy resin composite.

OPTICAL MACROGRAPH AND SKETCH OF REPRESENTATIVE SAMPLE OF UARL NO. 304

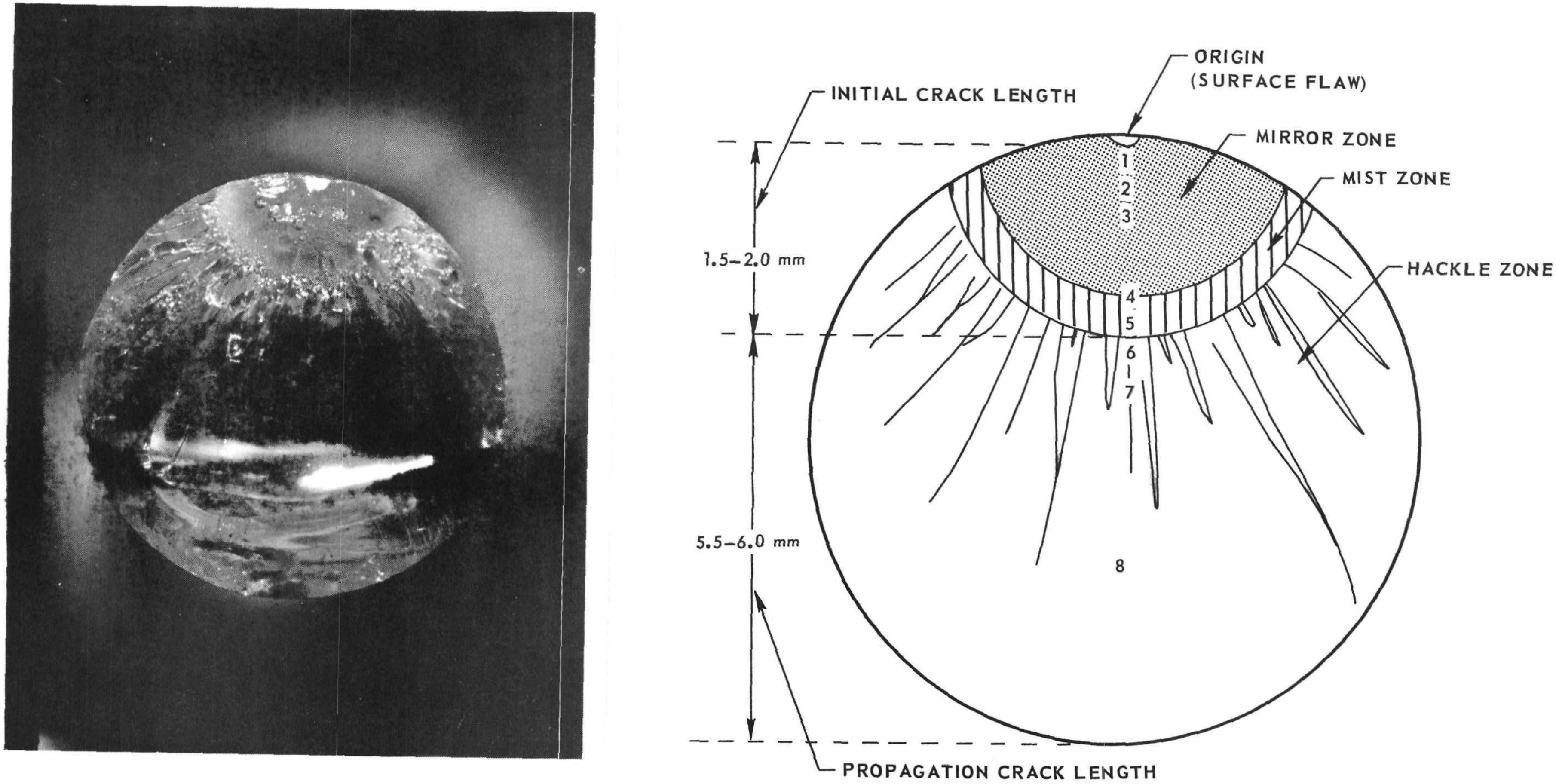


FIG. 8

OPTICAL MACROGRAPH AND SKETCH OF REPRESENTATIVE SAMPLE OF UARL NO. 459

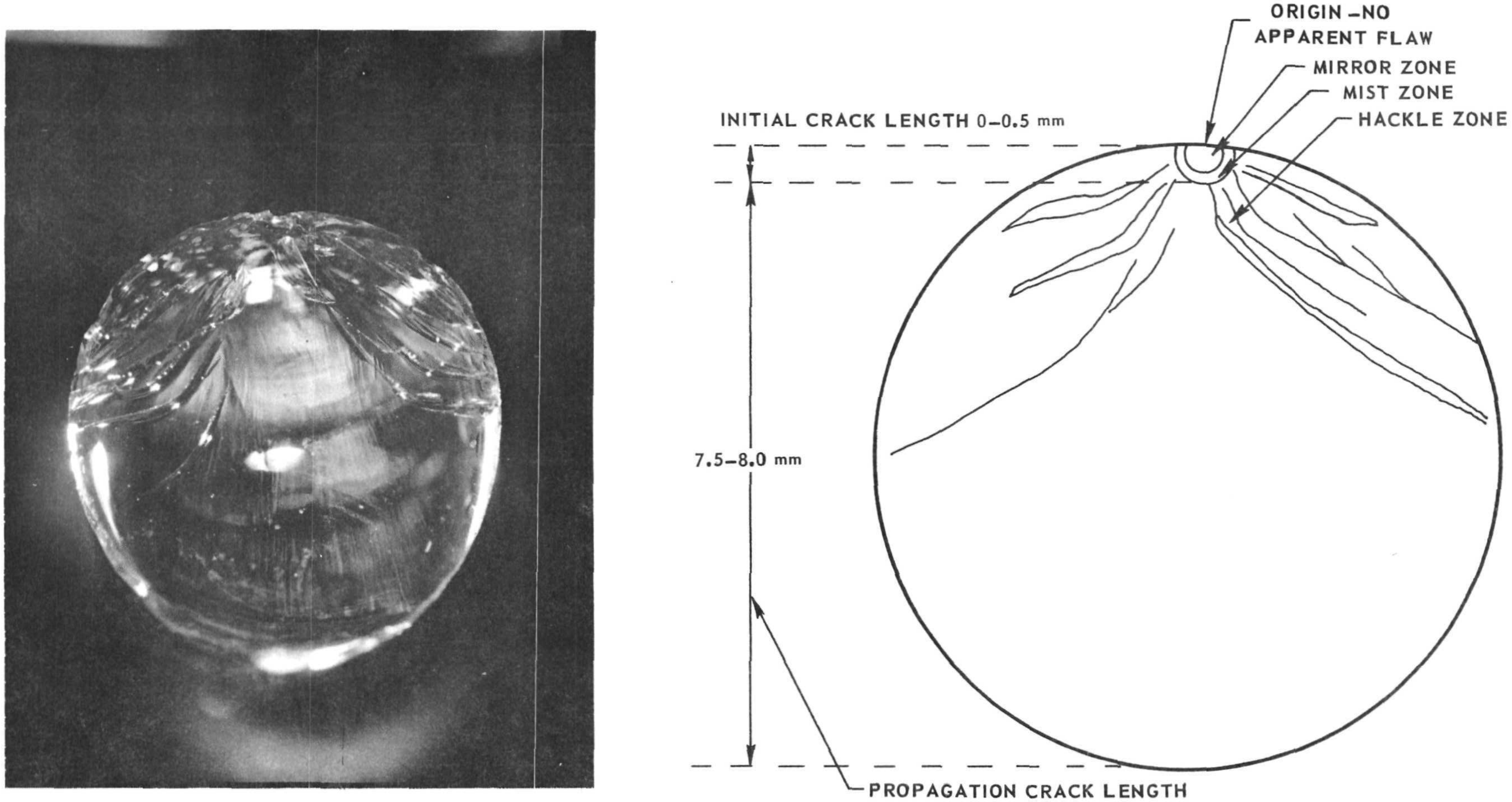


FIG. 9

Table XI

Latest Impact Resistance Test Results

Glass No. UARL	Impact Value ft-lbs/in.^{2} (best logical average)	Glass No. UARL	Impact Value ft-lbs/in.^{2} (best logical average)
454	1.103	459	1.017
347	1.188	304	1.098
419	1.008	383	0.887
336	1.0013	350	0.902
344	0.954	425	0.867
447	0.947	417	0.926
237	0.976	323	0.775
331	1.116	"E"	0.711

Tests were carried out using a one foot pound hammer on the Wiedemann-Baldwin tester, an impact tester of the Bell Laboratory design with a thirteen inch pendulum and a two foot drop. The specimens are all round rod asperated samples and are used as unnotched Charpy specimens

Table XII

Impact Resistance Test in Detail for Two Typical Bulk Glasses

Glass No.	Impact Value ft/lbs	Diameter inches	Area Square Inches	Corrected Impact Value ft-lbs/in^2
417	0.065	0.311	0.0760	0.8557
	0.060	0.301	0.0712	0.8432
	0.060	0.306	0.0735	0.8159
	0.085	0.320	0.0804	1.0570
	0.07175	0.316	0.0784	0.9149
	0.07575	0.312	0.0764	0.9909
	0.07175	0.308	0.0745	0.9631
	0.06970	0.306	0.0735	0.9478
			Logical Average	0.926
323	0.054	0.296	0.0688	0.7848
	0.055	0.307	0.0740	0.7431
	0.08945	0.307	0.0740	~~1.2085~~
	0.04175	0.312	0.0764	~~0.5461~~
	0.05125	0.303	0.0716	0.7155
	0.0640	0.304	0.0726	0.8818
	0.05935	0.318	0.0794	0.7473
	0.0575	0.307	0.0740	0.7768
			Logical Average	0.775

2. The data of this report indicate that it may be possible to prepare non-toxic (no beryllia) glasses equal in properties to the beryllia containing UARL 344 and 417 by the substitution of zinc oxide for the beryllia since zinc oxide mades a contribution of 20 kilobars/mol to Young's modulus compared to 19 kilobars/mol of beryllia.

3. The introduction of zinc oxide into a glass normally increases the fluidity of such glasses so that the addition of materials such as zirconia will probably be necessary to achieve glasses with satisfactory viscosity-temperature curves for the production of continuous fibers.

4. Bulk samples of selected experimental UARL glasses vary in impact strength by approximately a factor of two in the latest impact test procedures. Preliminary indications are that composition affects the impact strength and that both aluminum oxide and zinc oxide are necessary for increased impact strength. However, much more work remains to be done on the test procedures and other glasses need to be examined before any definite conclusions can be reached in this area.

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APPENDIX I

Latest Modulus Calculations Based on Method of C. J. Phillips (Ref. 1)

1. Using UARL glass #69 to determine MgO contribution

	Mol %	Kilobars/Mol	Contribution
SiO_2	57.3	7.3	418
Al_2O_3	14.6	12.1	177
MgO	28.0	X	28X
			595+28X

Actual exp. value for UARL 69 = 14.16 x 10^6 psi = 977 kilobars

$$\therefore x = \frac{977-595}{28} = 13.64 \text{ kilobars/mol for MgO}$$

2. Checking experimental data for glasses 1, 4, 14 using this value for MgO

SiO_2	52.3	7.3	382
Al_2O_3	18.7	12.1	226
MgO	29.2	13.64	398
			1006 kilobars calc.

Actual average exp. value for glasses 1, 4, 14 = 14.96 x 10^6 psi measured on ground rods cut from a fully annealed specimen. To reconcile the differences between the "as cast" (aspirated rods) usually used and the fully annealed rods used here, we find experimentally that we must subtract 0.3 x 10^6 psi.

$\therefore$ corrected exp. value for UARL glasses 1, 4, 14 =
14.66 x 10^6 psi = 1008 kilobars exp.

3. Checking experimental data for UARL glass #68 using this value for MgO

SiO_2	53.4	7.3	390
Al_2O_3	18.3	12.1	221
MgO	28.8	13.64	393
			1004 kilobars calc.

Using the values for the aspirated rods and those as well for the ground samples with the 0.3 x 10^6 million psi subtraction correction the average experimental value = 14.61 x 10^6 psi = 1008 kilobars exp.

APPENDIX I (Cont'd)

4. Using the experimental data for UARL glass 114 to derive an yttria factor

	Mol %	Kilobars/Mol	Contribution
SiO_2	51.7	7.3	377
Al_2O_3	22.5	12.1	272
MgO	15.8	13.64	216
Y_2O_3	10.0	X	10X
			865+10X

But experimentally UARL 114 has a value = 16.69 x 10^6 psi = 1151 kilobars exp.

$$\therefore Y_2O_3 \text{ factor} = \frac{1151-865}{10} = \frac{286}{10} = 28.6 \text{ kilobars/mol}$$

5. Using the experimental data for UARL glass 321 to check the yttria factor just found

SiO_2	40	7.3	292
Al_2O_3	15	12.1	182
MgO	30	13.64	409
Y_2O_3	15	28.6	429
			1312 kilobars calc.

Actual exp. glass for UARL glass 321A = 18.68 x 10^6 psi = 1288 kilobars exp.

6. Checking the yttria factor derived by use of data for glass 129

SiO_2	50	7.3	365
Al_2O_3	13.33	12.1	161
MgO	26.67	13.64	365
Y_2O_3	10	28.6	286
			1177 kilobars calc.

But experimentally UARL glass 129 = 16.57 x 10^6 psi - 1143 kilobars exp.

7. Checking the yttria factor derived against experimental data for UARL 127

SiO_2	60	7.3	438
Al_2O_3	10	12.1	121
MgO	20	13.64	273
Y_2O_3	10	28.6	286
			1118 kilobars cals.

But actual exp. value for UARL 127 = 16.13 x 10^6 psi = 1112 kilobars exp.

APPENDIX I (Cont'd)

8. Checking yttria factor derived against experimental data for UARL glass #70

	Mol %	Kilobars/Mol	Contribution
SiO_2	55.3	7.3	404
Al_2O_3	12.6	12.1	152
MgO	29.3	13.64	400
Y_2O_3	2.83	28.6	81
			1037 kilobars calc.

But experimentally the value for UARL glass 70 = 15.23 x 10^6 psi on fully annealed ground bars
= 14.93 x 10^6 corrected to correspond to aspirated bars
= 1030 kilobars exp.

9. Checking the yttria factor by use of data for UARL glass #64

	Mol %	Kilobars/Mol	Contribution
SiO_2	54.6	7.3	399
Al_2O_3	15.5	12.1	188
MgO	28.8	13.64	393
Y_2O_3	1.39	28.6	40
			1020 kilobars calc.

But experimentally UARL #64 on annealed, ground bars has a value = 15.18 x 10^6 psi correcting this to obtain a comparative aspirated rod value = 14.88 x 10^6 psi
= 1026 kilobars exp.

10. Checking the yttria fact by use of data for UARL glass #231

	Mol %	Kilobars/Mol	Contribution
SiO_2	40	7.3	292
Al_2O_3	14	12.1	169
MgO	36	13.64	491
Y_2O_3	10	28.6	286
			1238 kilobars calc.

But experimentally UARL glass #231 has a value = 18.65 x 10^6 psi = 1245 kilobars exp.

11. Checking yttria factor by use of data for UARL glass #235

	Mol %	Kilobars/Mol	Contribution
SiO_2	50	7.3	365
Al_2O_3	10	12.1	121
MgO	30	13.64	409
Y_2O_3	10	28.6	286
			1181 kilobars calc.

But experimentally #235 has an experimental value = 17.38 x 10^6 psi = 1200 kilobars exp.

APPENDIX I (Cont'd)

12. Checking yttria factor by use of data for glass 237A

	Mol %	Kilobars/Mol	Contribution
SiO_2	45	7.3	329
Al_2O_3	15	12.1	182
MgO	30	13.64	409
Y_2O_3	10	28.6	286
			1206 kilobars calc.

But experimentally UARL 237A has a value = 17.91 x 10^6 psi = 1235 kilobars exp.

13. Checking yttria factor by use of data for glass #151

SiO_2	49.4	7.3	351
Al_2O_3	6.1	12.1	74
MgO	36.5	13.64	498
Y_2O_3	8.0	28.6	229
			1152 kilobars calc.

But experimentally UARL glass 151 has a value = 16.9 x 10^6 psi = 1166 kilobars

14. Checking the yttria factor by use of data for glass #159

SiO_2	57.4	7.3	419
Al_2O_3	6.6	12.1	80
MgO	28.0	13.64	382
Y_2O_3	8.0	28.6	229
			1110 kilobars calc.

But experimentally UARL glass 159 has a value = 16.2 x 10^6 psi = 1118 kilobars

15. Computing the lanthana factor by use of data for UARL #263

SiO_2	67.3	7.3	491
Al_2O_3	12.1	12.1	146
MgO	3.9	13.64	53
La_2O_3	16.8	X	16.8X
			690+16.8X

But experimentally glass 263 = 14.49 x 10^6 psi = 1000 kilobars

$$\therefore La_2O_3 \text{ factor} = \frac{1000-690}{16.8} = \frac{310}{16.8} = 18.5 \text{ kilobars/mol}$$

APPENDIX I (Cont'd)

16. Checking lanthana factor by use of data for UARL #136

	Mol %	Kilobars/Mol	Contribution
SiO_2	53.31	7.3	389
Al_2O_3	15.56	12.1	188
MgO	28.89	13.64	394
La_2O_3	2.00	18.5	37
			1008 kilobars calc.

But experimental glass 136 has a laboratory modulus = 14.4 x 10^6 psi = 993 kilobars exp.

17. Checking lanthana factor by use of data for UARL #138

SiO_2	47.31	7.3	345
Al_2O_3	15.56	12.1	188
MgO	28.89	13.64	384
La_2O_3	8.00	18.5	148
			1065 kilobars calc.

But experimentally glass 138 = 15.3 x 10^6 psi = 1055 kilobars exp.

18. Checking the lanthana factor by use of the data for UARL #135

SiO_2	54.31	7.3	396
Al_2O_3	15.56	12.1	188
MgO	28.89	13.64	384
La_2O_3	1.00	18.5	19
			987 kilobars calc.

But experimentally UARL glass 135 = 14.3 x 10^6 psi = 986 kilobars exp.

19. Checking the lanthana factor by use of experimental data for UARL #152

SiO_2	49.4	7.3	361
Al_2O_3	6.1	12.1	74
MgO	36.5	13.64	488
La_2O_3	8.0	18.5	148
			1071 kilobars calc.

But experimentally UARL glass 152 has a value = 15.27 x 10^6 psi = 1053 kilobars exp.

APPENDIX I (Cont'd)

20. Checking the lanthana factor by use of experimental data for UARL #319

	Mol %	Kilobars/Mol	Contribution
SiO_2	45	7.3	328
Al_2O_3	15	12.1	182
MgO	30	13.64	409
La_2O_3	10	18.5	185
			1104 kilobars calc.

But experimentally glasses UARL 319 & 319A have a value = 16.21 x 10^6 psi = 1118 kilobars exp.

21. Checking the lanthana factor by use of experimental data for UARL #63

SiO_2	54.6	7.3	399
Al_2O_3	15.6	12.1	189
MgO	28.9	13.64	394
La_2O_3	0.95	18.5	18
			1000 kilobars calc.

But experimentally glass 63 has a value of 14.7 x 10^6 on fully annealed and ground bars and has a comparable value of 14.41 x 10^6 psi on aspirated rods = 994 kilobars exp.

22. Using the data for UARL experimental glass #117 we find factor for ceria

SiO_2	51.67	7.3	377
Al_2O_3	10	12.1	121
MgO	18.33	13.64	250
Ce_2O_3	20	X	20X
			748+20X kilobars calc.

But actually the exp. value for UARL glass 117 = 16.54 x 10^6 psi on fully annealed ground rods or = 16.24 x 10^6 psi after applying the correction necessary for comparison with aspirated rods, i.e. = 1120 kilobars

$$\therefore \text{ Ceria factor} = \frac{1120-748}{20} = \frac{372}{20} = 19.6 \text{ kilomars/mole}$$

APPENDIX I (Cont'd)

23. Using the data for UARL experimental glass #72 to check ceria factor found

	Mol %	Kilobars/Mol	Contribution
SiO_2	56.9	7.3	415
Al_2O_3	15.1	12.1	183
MgO	25.4	13.64	346
Ce_2O_3	2.60	19.6	51
			995 kilobars calc.

But experimentally UARL glass 72 has a value of 15.15 x 10^6 psi on fully annealed ground rods and arriving at corrected factor necessary for comparison with aspirated rods = 14.85 x 10^6. We have also measured aspirated rods of #72 with a result = 14.03 x 10^6 psi. Average of these values = 14.44 x 10^6 psi = 996 kilobars exp.

24. Using the data for UARL experimental glass #62 to check the ceria factor found

SiO_2	54.6	7.3	399
Al_2O_3	15.2	12.1	184
MgO	29.2	13.64	398
Ce_2O_3	1.0	19.6	20
			1001 kilobars calc.

But experimentally UARL glass 62 = 14.18 x 10^6 psi = 977 kilobars exp.

25. Using the experimental data for Owens-Corning OCX-2124 (Ref. 2) to obtain beryllia factor

SiO_2	70.0	7.3	511
Al_2O_3	12.5	12.1	151
BeO	17.4	X	17.4X
			662+17.4X

But Owens-Corning obtained experimentally 14.4 x 10^6 psi = 993 kilobars for this formulation

$$\therefore \text{ BeO factor} = \frac{993-662}{17.4} = 19.0 \text{ kilobars/mol}$$

26. Using the data for UARL glass 318 to verify beryllia factor just found

SiO_2	45	7.3	329
Al_2O_3	15	12.1	182
MgO	30	13.64	409
BeO	10	19.0	190
			1110 kilobars calc.

But experimentally UARL 318 has value = 15.97 x 10^6 psi = 1101 kilobars exp.

APPENDIX I (Cont'd)

27. Using the data for UARL #66 to calculate the zirconia factor

	Mol %	Kilobars/Mol	Contribution
SiO_2	53.7	7.3	392
Al_2O_3	15.3	12.1	185
MgO	28.3	13.64	386
ZrO_2	2.56	X	2.56X
			963+2.56X

But experimentally UARL 66 has a value = 15.14 x 10^6 psi on fully annealed ground rods and correcting this to obtain comparative value for an unannealed aspirated rod = 14.84 x 10^6 psi = 1024 kilobars

$$\therefore ZrO_2 \text{ factor} = \frac{1024-963}{2.56} = 23.8 \text{ kilobars/mol}$$

28. Using the experimental data for UARL 320 to verify the zirconia factor

SiO_2	45	7.3	329
Al_2O_3	15	12.1	182
MgO	30	13.64	409
ZrO_2	10	23.8	238
			1158 kilobars calc.

But experimentally UARL 320B3 = 16.58 x 10^6 psi = 1143 kilobars exp.

29. Using the data for UARL glass 155 to derive the value for the tantala factor

SiO_2	49.4	7.3	361
Al_2O_3	7.05	12.1	85
MgO	36.5	13.64	498
Ta_2O_5	7.05	X	7.05X
			944+7.05X

But experimentally UARL glass 155 = 15.675 x 10^6 psi = 1081 kilobars

$$\therefore Ta_2O_5 \text{ contribution} = \frac{1081-944}{7.05} = \frac{137}{7.05} = 19.4 \text{ kilobars/mol}$$

30. Using the data for UARL glass #67 to check the tantala factor just derived

SiO_2	54.7	7.3	399
Al_2O_3	15.3	12.1	185
MgO	29.3	13.64	400
Ta_2O_5	0.76	19.4	15
			999 kilobars calc.

But actual experimental value for UARL 67 = 14.43 x 10^6 psi = 995 kilobars exp.

APPENDIX I (Cont'd)

31. Using the experimental data for UARL 412 to check both lanthana and beryllia factors

	Mol %	Kilobars/Mol	Contributions
SiO_2	40	7.3	292
Al_2O_3	15	12.1	182
MgO	15	13.64	205
La_2O_3	15	18.5	278
BeO	15	19.0	285
			1242 kilobars calc.

But UARL glass 412 experimentally = 17.92 x 10^6 psi = 1236 kilobars exp.

32. Using the experimental data for UARL 276 to check both lanthana and beryllia factors

SiO_2	50	7.3	365
Al_2O_3	8.33	12.1	101
Li_2O	8.33	7.0	58
La_2O_3	8.33	18.5	154
BeO	25	19.0	475
			1153 kilobars calc.

But experimentally UARL 276 = 15.82 x 10^6 psi = 1091 kilobars exp.

33. Using the experimental data for UARL 232 to check yttria and ceria factors simultaneously

SiO_2	48	7.3	350
Al_2O_3	13.33	12.1	161
MgO	26.67	13.64	364
Y_2O_3	10	28.6	286
Ce_2O_3	2	19.6	39
			1200 kilobars calc.

But experimentally UARL glass 232 = 17.62 x 10^6 psi = 1215 kilobars exp.

34. Using the experimental data for UARL glass 236 to check simultaneously yttria and ceria factors

SiO_2	43	7.3	314
Al_2O_3	15	12.1	182
MgO	30	13.64	409
Y_2O_3	10	28.6	286
Ce_2O_3	2	19.6	39
			1230 kilobars calc.

Experimentally UARL 236 has a value = 17.83 x 10^6 psi = 1229 kilobars exp.

APPENDIX I (Cont'd)

35. Check of value found experimentally for UARL 494 glass against calculated value (CaO, Y_2O_3, CoO)

	Mol %	Kilobars/Mol	Contributions
SiO_2	65	7.3	475
MgO	12	13.64	164
CaO	12	11.45	137
Y_2O_3	10	28.6	286
CoO	1.0	11	11
			1073 kilobars calc.

But experimentally UARL glass 494 = 15.55 x 10^6 psi = 1069 kilobars exp.

36. Check of experimental value for UARL 480 glass against calculated value (CaO, Y_2O_3, BeO)

SiO_2	56.2	7.3	410
MgO	4.08	13.64	56
CaO	12.25	11.45	140
Y_2O_3	10.22	28.6	292
BeO	16.33	19.0	310
CoO	1.02	11	11
			1219 kilobars calc.

But experimentally UARL 480 = 18.12 x 10^6 psi = 1250 kilobars exp.

37. Determination of zinc oxide modulus factor from experimental data for UARL 266 glass

SiO_2	25	7.3	183
Al_2O_3	15	12.1	181
MgO	15	13.64	205
Li_2O	15	7.0	105
CaO	15	11.45	172
ZnO	15	X	15X
			846+15X

But experimentally UARL glass 266 = 16.73 x 10^6 psi = 1154 kilobars exp.

$$\therefore \text{ zinc oxide factor} = \frac{1154-846}{15} = \frac{308}{15} \cong 20 \text{ kilobars/mol}$$

Other calculations show 19.8 to 20.1

APPENDIX I (Cont'd)

38. Comparing experimental and calculated modulus for UARL 334 glass

	Mol %	Kilobars/Mol	Contributions
SiO_2	35	7.3	256
Al_2O_3	15	12.1	182
MgO	30	13.64	409
La_2O_3	10	18.6	186
ZnO	10	20.0	200
			1233 kilobars calc.

But experimentally UARL 334 glass has a modulus = 17.48 x 10^6 psi = 1206 kilobars exp.

39. Comparing experimental and calculated moduli for UARL glass 304

SiO_2	35	7.3	256
Al_2O_3	15	12.1	182
MgO	30	13.64	409
ZnO	10	20.0	200
Y_2O_3	10	28.6	286
			1333 kilobars calc.

But experimentally UARL 304 = 19.23 x 10^6 psi = 1326 kilobars exp.

40. Calculation of modulus expected from UARL glass 495 and comparison with experimental value

SiO_2	57	7.3	416
MgO	12	13.64	164
CaO	12	11.45	137
ZnO	8	20.0	160
Y_2O_3	10	28.6	286
CoO	1	11	11
			1174 kilobars calc.

But experimentally UARL 495 glass has a modulus = 17.24 x 10^6 psi = 1189 kilobars exp.

41. Comparison of calculated and experimental values for UARL 337 (appreciable number of crystals)

SiO_2	30	7.3	219
Al_2O_3	15	12.1	182
MgO	30	13.64	409
ZnO	12.5	20.0	250
Y_2O_3	12.5	28.6	358
			1418 kilobars calc.

But experimentally UARL glass 337 = 20.9 x 10^6 psi = 1441 kilobars exp.

APPENDIX I (Cont'd)

42. Check of experimental and calculated values for UARL 274

	Mol %	Kilobars/Mol	Contributions
SiO_2	25	7.3	183
Al_2O_3	15	12.1	181
Li_2O	15	7.0	105
MgO	15	13.64	205
BeO	15	19.0	285
ZnO	15	20.0	300
			1259 kilobars calc.

But experimentally UARL glass = 17.58×10^6 psi = 1212 kilobars exp.

43. Comparison of experimental and calculated values for UARL 257 glass

SiO_2	40	7.3	292
Al_2O_3	12	12.1	145
MgO	12	13.64	264
Li_2O	12	7.0	84
ZnO	12	20.0	240
La_2O_3	12	18.6	223
			1248 kilobars calc.

But experimentally UARL glass 257 = 18.06×10^6 psi = 1245 kilobars exp.

44. Comparison of experimental and calculated values for UARL glass 492

SiO_2	47	7.3	343
Al_2O_3	17	12.1	206
MgO	17	13.64	232
Li_2O	3	7.0	21
ZnO	6	20.0	120
Y_2O_3	10	28.6	286
			1208 kilobars calc.

But experimentally UARL glass 429 has a modulus = 18.55×10^6 = 1279 kilobars exp.

45. Check of experimental and calculated values for UARL 360

SiO_2	39	7.3	275
Al_2O_3	12	12.1	145
MgO	24	13.64	327
Li_2O	6	7.0	42
ZnO	6	20.0	120
Y_2O_3	10	28.6	286
CoO	3	11	33
			1228 kilobars calc.

But experimentally UARL 360 has a modulus = 18.19×10^6 psi = 1255 kilobars exp.

APPENDIX I (Cont'd)

46. Check of experimental and calculated values of UARL 329A glass (ZnO, ZrO_2, Y_2O_3)

	Mol %	Kilobars/Mol	Contributions
SiO_2	22.22	7.3	162
Al_2O_3	11.11	12.1	134
MgO	22.22	13.64	303
Li_2O	11.11	7.0	78
ZnO	11.11	20.0	222
ZrO_2	11.11	23.8	264
Y_2O_3	11.11	28.6	317
			1480 kilobars calc.

But experimentally UARL glass 329A has a modulus = 21.985 x 10^6 psi = 1516 kilobars exp.

47. Checking the experimental value for UARL 336 against its calculated value

SiO_2	35	7.3	256
Al_2O_3	15	12.1	182
Y_2O_3	10	28.6	286
BeO	30	19.0	570
ZnO	10	20.0	200
			1494 kilobars calc.

But UARL 336 glass has an experimentally determined modulus = 20.95 x 10^6 psi = 1445 kilobars

48. Comparison of calculated and experimental modulus for UARL 333

SiO_2	39	7.3	285
Al_2O_3	12	12.1	145
MgO	25	13.64	341
ZnO	12	20.0	240
Y_2O_3	12	28.6	343
			1354 kilobars calc.

But experimentally UARL 333 has a modulus = 18.9 x 10^6 psi = 1303 kilobars exp.

49. Comparison of calculated and experimental modulus for UARL glass 331

SiO_2	39	7.3	285
Al_2O_3	12	12.1	145
ZnO	12	20.0	240
Y_2O_3	12	28.6	343
BeO	25	19.0	475
			1488 kilobars calc.

But experimentally UARL 331 has a modulus = 20.85 x 10^6 psi = 1438 kilobars exp.

APPENDIX I (Cont'd)

50. Comparison of calculated and experimental moduli for UARL 471 glass

	Mol %	Kilobars/Mol	Contributions
SiO_2	25	7.3	183
Al_2O_3	8	12.1	97
MgO	15	13.64	205
Li_2O	15	7.0	105
CaO	10	11.45	115
ZnO	15	20.0	300
Y_2O_3	7	28.6	200
B_2O_3	5	7.2	36
			1241 kilobars calc.

But experimentally UARL 471 glass has a modulus = 17.90 x 10^6 psi = 1235 kilobars exp.

51. Comparison of calculated and experimental moduli for UARL 464

SiO_2	25	7.3	182.5
MgO	15	13.64	197.4
Li_2O	15	7.0	105
CaO	15	11.45	172
ZnO	10	20.0	200
Y_2O_3	5	28.6	143
B_2O_3	15	7.2	108
			1108 kilobars calc.

But experimentally UARL 464 glass has a modulus = 16.12 x 10^6 psi = 1112 kilobars exp.

52. Computation of the contribution made by titania to the modulus UARL 501

SiO_2	30	7.3	219
MgO	20	13.64	263
Li_2O	2	7.0	14
CaO	12	11.45	137
Y_2O_3	12	28.6	334
B_2O_3	8	7.2	58
TiO_2	11	X	11X
ZrO_2	4.5	23.8	117
CoO	.5	11	6
			1147+11X

But experimentally UARL 501 has a modulus = 19.02 x 10^6 psi = 1312 kilobars

$$\therefore \text{ titania factor} = \frac{1312-1147}{11} \cong 15 \text{ kilobars/mol}$$

APPENDIX I (Cont'd)

53. Calculation (in advance of preparation) of modulus to be expected from UARL 500

	Mol %	Kilobars/Mol	Contributions
SiO_2	30	7.3	219
MgO	20	13.64	273
Li_2O	3	7.0	21
CaO	15	11.45	172
Y_2O_3	12	28.6	343
B_2O_3	8	7.2	58
TiO_2	8	15	120
ZrO_2	3.66	23.8	87
CoO	.33	11	4
			1297 kilobars calc.

But UARL 500 glass when made actually had a modulus = 18.97×10^6 psi = 1309 kilobars exp.

54. Comparison of modulus to be expected from UARL 499 (in advance of preparation) with that actually found

SiO_2	40	7.3	292
Al_2O_3	2.66	12.1	32
MgO	18	13.64	246
Li_2O	2	7.0	14
CaO	16	11.45	183
ZrO_2	4	23.8	95
Y_2O_3	10	28.6	286
TiO_2	7	15	105
CoO	.33	11	4
			1257 kilobars calc.

But UARL 499 glass has a modulus = 19.50×10^6 psi = 1345 kilobars exp.

55. Comparison of calculated value for UARL 449 with value found experimentally

SiO_2	25	7.3	183
MgO	20	13.64	273
Li_2O	6	7.0	42
CaO	15	11.45	172
ZnO	4	20	80
Y_2O_3	12	28.6	343
B_2O_3	13	7.2	94
CuO	2	11	22
TiO_2	3	15	45
			1254 kilobars calc.

Experimentally UARL 449 glass = 18.08×10^6 psi = 1247 kilobars exp.

APPENDIX I (Cont'd)

56. Checking predicted and calculated values for Loewenstein (Ref. 9) Glass 73

	Mol %	Kilobars/Mol	Contributions
SiO_2	47.2	7.3	344
Al_2O_3	4.7	12.1	57
CaO	17.8	11.45	204
MgO	14.3	13.64	199
ZnO	4.7	20	94
TiO_2	11.2	15	168
			1066 kilobars calc.

Actually this glass Loewenstein #73 has a modulus = 1017 kilobars exp.

57. Calculation (in advanced preparation) of modulus to be expected from UARL 503 glass and comparison with that found experimentally

SiO_2	39	7.3	285
MgO	15	13.64	205
Li_2O	2	7.0	14
CaO	15	11.45	172
ZrO_2	6	23.8	143
Y_2O_3	10	28.6	286
CoO	1	11	11
TiO_2	12	15	180
			1296 kilobars calc.

But experimentally UARL 503 glass shows a modulus = 19.55 x 10^6 psi = 1348 kilobars exp.

58. Computation of the contribution of thoria to the modulus UARL 502

SiO_2	45	7.3	328.5
MgO	12	13.64	154
Li_2O	2	7.0	14
CaO	12	11.45	137
Ce_2O_3	2	19.6	39.2
ZrO_2	2	23.8	47.6
Y_2O_3	10	28.6	286
TiO_2	10	15	150
CoO	1	11	11
ThO_2	4	X	4X
			1168+4X kilobars

But experimentally UARL 502 glass has a modulus = 19.02 x 10^6 psi = 1312 kilobars

$$\therefore ThO_2 \text{ factor} = \frac{1312-1168}{4} = 36 \text{ kilobars/mol}$$

APPENDIX I (Cont'd)

All modulus calculations and computed moduli factors are for quenched samples and not for heat treated samples such as those used in Klaus Leopold Loewenstein, U.S. Patent 3,060,041 - Example 7. Such samples have moduli approximately 2 x 10^6 psi higher.

APPENDIX II

Publications, Papers Presented and Selected for Presentation, Patents Issued, and Patents Applied for In Connection with Contract

In 1971 two papers were published, one paper presented, and arrangements made to present two other papers.

1. Bacon, James F., "Studies of the Young's Modulus of Magnesia-Alumina-Silica-Rare Earth Glasses with Respect to their Composition and Crystallization Kinetics" was included in Frontiers in Glass Science and Technology, Editors S. Bateson and A. G. Sadler - The Proceedings of the 1969 Annual Meeting of the International Commission on Glass, Toronto, Canada.

2. Bacon, James F., "The Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems and Their Application to the Origination of High Modulus Glass Fibers", NASA CR-1856, National Aeronautics & Space Administration, Washington, D. C., November 1971.

3. Bacon, James F., "The Properties of Fiber Glass-Epoxy Resin Composites Prepared with High Modulus Glasses", a talk given at the Symposium on Ceramics in New England, held by the New England Section of the American Ceramic Society at Massachusetts Institute of Technology, Cambridge, Mass., Oct. 20, 1971.

4. Bacon, James F., "Characterization of High Modulus Glass Fibers and of Composites in Which They are Included", a paper to be given April 12, 1972 at the ASTM Symposium on Analysis of Test Methods for High Modulus Fibers and Composites at the Joint ASTM, AIAA Meeting at San Antonio, Texas. ASTM is to publish this paper also.

5. Bacon, James F., "High Modulus Glass Fibers and Composites Prepared with Them", a paper to be presented at the Symposium on High Temperature Fibers and Fiber Coatings to be held in New York City during the Fall American Chemical Society Meeting and to be published by the A.C.S. Division on Organic Coatings and Plastics Chemistry.

One patent issued during the contractual year:

1. Bacon, James F., U.S. 3,573,078, March 30, 1971. Glass Compositions with a High Modulus of Elasticity, and patent office action continued in connection with four other patent applications.