B&W Report No. 5144

DEVELOPMENT OF A HIGH STRENGTH, HIGH MODULUS CERAMIC FIBER

June 29, 1967 - September 29, 1968

by

R. N. Fetterolf

FINAL SUMMARY REPORT

on

CONTRACT NO. NAS8-21186

CONTROL NO. DCN 1-7-54-20014 (IF), SI (IF)

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GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

THE BABCOCK & WILCOX COMPANY
Refractories Division, Augusta, Georgia
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FOREWORD

This report was prepared by The Babcock & Wilcox Company Research Center, Alliance, Ohio under Contract No. NAS8-21186, "Development of a High Strength, High Modulus Ceramic Fiber", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of Mr. Harry M. King, Project Engineer, Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center.

The author wishes to acknowledge the contributions of a number of his associates to the work reported herein, J.A. Kaurich, J.A. Maurer, R.A. Mordew, and R.C. Young for the manufacturing and testing of the filaments and G.K. Dray for performing the X-ray diffraction analyses and aiding in their interpretation. The author wishes to thank J.E. Blaze not only for his research effort and helpful discussions in this area but also for introducing him to the area of salt decomposition technology.

ABSTRACT

The goal of this program is the development of a high-strength, high-modulus, continuous ceramic fiber by the B&W salt decomposition process. The desired properties of such a fiber are a length greater than 1,000 feet, diameter of less than 125 microns, tensile strength greater than 250,000 psi, modulus of elasticity greater than 30,000,000 psi and corrosion resistance equal to or better than that of E-glass fiber.

An overall process for the production of a ceramic oxide continuous filament from a B&W fiberizable salt solution has been defined. The process consists of five unit operations:

1. Solution preparation
2. Fiber formation by extrusion-attenuation
3. Fiber collection
4. Fiber drying
5. Fiber calcination to oxide form.

Fiber quality yardsticks have been defined as fired or unfired fiber diameter, uniformity of diameter with respect to length, and tensile strength and modulus of elasticity. Variables in all the above operations which affect fiber quality have been determined. In addition, fiber tensile strength has been found to increase as fiber diameter decreases. Study and eventual control of variables found to affect fiber quality have been almost completed for the first two unit operations.

On a batch basis, identical fiberizable solutions of the same composition can be routinely prepared on a day-to-day basis.

Through control of extrusion variables, unfired fiber of 8 to 20 microns diameter can be routinely produced. Implementation of control of extrusion temperature, and concurrently solution viscosity remains to be completed and should succeed in both lowering and narrowing the fiber diameter range being produced.

Fibers are converted to the oxide form through fast firing in a tunnel kiln or slow firing in a periodic kiln, depending on fiber diameter. Firing temperatures of 1850 F or 1950 F have resulted in average tensile strengths as high as 230,000 psi and modulus of elasticity as high as 30×10^6 psi.

The extruded fiber is uniform in diameter with respect to length and appears uneffected by atmospheric humidity. That is, the "as measured" fiber tensile strength and modulus of elasticity appear uneffected by atmospheric humidity.

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SECTION I
INTRODUCTION

The specific goal of this program has been the development of a low-cost method of forming a continuous, strong, high-modulus of elasticity ceramic oxide monofilament. This fiber must have a:

1. Length greater than 1,000 feet
2. Tensile strength of 250,000 psi minimum
3. Modulus of elasticity of 30 million psi minimum
4. Diameter of 125 microns maximum
5. Resistance to atmospheric corrosion equal to or better than that of type "E"-glass fiber.

The Babcock & Wilcox Company for the last five years has been actively pursuing the development of refractory oxide fibers based on a low-cost "salt decomposition" process. From this work a general method capable of transforming inexpensive inorganic salts into polycrystalline fibers[1] has been developed. This process was specifically designed to make low-cost short fiber in bulk form for high-temperature insulation. However, the process has potential for making low-cost fibers for reinforcement applications because of the versatility of the process, the relatively simple equipment used, and the known properties of the fibers formed.

Specifically, the B&W salt decomposition process of making fibers consists of transforming inexpensive inorganic metal salts into syrup-like liquids that can be fiberized at room temperatures into fibers using simple techniques. The resulting "salt" fibers are then converted to the oxide by calcining at relatively low temperatures.

Since fibers made by the salt decomposition process can be made of pure oxides and in a crystalline form, they can have a high modulus of elasticity. Because of this, an Air Force Materials Laboratory contract was awarded in July of July 1966 to determine the feasibility of developing short, pure Al_2O_3 (99+%) fibers with high modulus and high tensile strength[2]. The results showed that fibers with tensile strength and modulus of about 185,000 psi and 30×10^6 psi respectively could be obtained. That effort, as well as results obtained from earlier B&W in-plant work with insulation fibers, showed that additions of specific oxides to the pure Al_2O_3 fiber could result in increases

in the modulus of elasticity as well as the tensile strength over those of the pure fiber. With the additions of acid oxides, it was not uncommon to obtain individual fibers with tensile strength over 300,000 psi and modulus of elasticity approaching 40×10^6 psi.

The reason for the improvement in both strength and modulus through the use of oxides added to the Al_2O_3 fiber is not fully understood. However, several concepts can be offered to explain the resultant improvement in fiber properties. First, it is speculated that additives reduce the apparent porosity of the fiber, since they act as sintering aids. Reducing the porosity can result in improved strength and modulus of most ceramics[3][4]. The second possibility is that the additives used may help in minimizing grain growth within the filaments. Reducing grain growth in a ceramic is another well-known method of improving the strength of ceramics[5]. Using additive oxides can result in obtaining the same density or porosity in the fiber at lower calcining-sintering temperatures. The use of lower calcining-sintering temperatures can result in finer grain size in the fiber. The third reason the fiber may become stronger is that the added oxide can control the crystal phase change. Phase transformation occurring in a ceramic system can produce stresses which weaken the resulting structure[6][7]. Of all the factors considered, phase transformation may be of paramount importance. In the case of a pure alumina fiber as it is heated for the first time, a transformation from gamma to iota to alpha alumina takes place, resulting in a theoretical increase in density from 2.6-2.9 g/cc to 3.6-3.97 g/cc. The stresses produced by this density change can limit the strength of the alumina fiber. Adding SiO_2, B_2O_3, or P_2O_5 to Al_2O_3 produces a mullite structure with a density of about 3 g/cc. This final density is much closer to that of gamma alumina (2.6-2.9 g/cc), the crystal phase first formed in the calcining process of the salt decomposition Al_2O_3 fiber system.

Besides increasing the actual strength and stiffness of the filaments, these additions to Al_2O_3 fiber have another important advantage which should also be mentioned. The additive oxides reduce the theoretical density of the fiber from about 4 g/cc to about 3 g/cc. This reduction in density makes the fiber more attractive as a reinforcement filament just for the weight decrease. Reduction of density, although not a specific goal of the project, is an additional benefit realized by modifying pure alumina fibers in order to increase their strength.

The salt decomposition process by virtue of the inexpensive materials employed and the simple technique used is known to be capable of producing low-cost, short, fibers that satisfy all of the contract requirements except length. Therefore, the principal objective of this program has been to translate the present salt decomposition technology of producing discontinuous fiber into a method of manufacturing continuous length filaments with the strength and modulus characteristics stated above.

Our approach to this problem has been to first develop an apparatus capable of forming a continuous fiber from a fiberizable salt solution and to define an overall process leading to the ultimate ceramic oxide filaments, without regard to fiber quality or actual length.

Secondly, through process refinements, the fiber strength would be maximized. Finally, with sufficient knowledge of the process at hand, apparatus for producing continuous filaments could be designed and incorporated into the overall system.

The apparatus and process, once defined, were broken down into the following unit operations:

1. Solution preparation
2. Fiber formation
3. Fiber collection
4. Fiber drying
5. Calcination to oxide form.

The identification of variables affecting fiber quality within each unit operation and a measure of that fiber quality was the next phase of our program. Through identification of operation variables and determination of the effect of those variables on fiber quality, the degree of control necessary over each variable and corresponding unit operation gradually became known. The application of this concept to each successive unit operation defined above ultimately leads to a point where no fiber quality differences (diameter, tensile strength, modulus of elasticity, etc.) can be observed as due to that particular operation under study. At this point, the operation is considered under control and the study of the next succeeding operation is begun.

As more variables in each operation are brought under the degree of control dictated by observed fiber characteristics, not only does the ultimate

fiber approach the goals of the contract and become more reproducible, but additional process variables, heretofore unseen, begin to surface. The additional variables, while no less important than those preceding, have a less marked effect on fiber quality or reproducibility and thus are masked or hidden from view until the variables responsible for gross differences in fiber quality are brought under control. These additional relatively minor variables can be identified within the unit operation under study, or can be traced back to an operation which had been previously brought under all control necessary at the time.

Our research has thus been aimed at the control of all the process steps and variables therein which affect the ultimate ceramic oxide fiber product. The goal is to systematically and successively determine the operating conditions for each unit operation within the process, backtracking when necessary to a previous operation to further improve control with respect to production of a uniform, reproducible fiber with properties as outlined in the contract goals.

SECTION II

EXPERIMENTAL PROCEDURES AND TESTS

A. FIBERIZABLE SOLUTION PREPARATION

The success of the B&W method of making fibers from a salt solution is dependent on the physical and chemical properties built into that solution during preparation. The requirements for a successful fiberizable salt solution are:

1. Low surface tension
2. High viscosity
3. High equivalent oxide content
4. Chemical and physical stability
5. Solvent volatile at room temperatures
6. Salts decomposable by heat to a solid oxide form.

The fiberizable salt system used by B&W giving these desired properties consists of acid-deficient inorganic salts. These salts can be readily made from inexpensive raw materials using standard chemical techniques.

The method used to make the fiberizable salt solution for this work starts with either concentrated inorganic acids or an inorganic acid salt solution or both. Aluminum metal is added to either of these acidic solutions. Heating the mix initiates a rapid exothermic reaction in which aluminum is being dissolved with the concurrent liberation of hydrogen gas according to the equation:

$$2Al + 6H_3O^+ \rightarrow 2Al^{3+} + 3H_2 \uparrow + 6H_2O$$

The reaction is allowed to continue until the rate of aluminum dissolution is very slow. The undissolved aluminum is removed from the solution by screening. Additives such as colloidal silica, boric acid, and phosphoric acid can be mixed into the aluminum salt solution, as desired, to modify the properties of the finished fiber.

The solution is then further heated to evaporate excess water and to obtain the desired solution viscosity and equivalent solids content. A viscosity range of 300 to 3000 poise has been found desirable. At this point the complex salt solution is clear and colorless, and a final addition of acetic acid is made to stabilize the solution with respect to viscosity and time.

B. FIBERIZING THE SOLUTION

The fiberizable salt solution has been transformed into monofilaments by using a room temperature extrusion apparatus similar to that designed by B.T. Fellows[8] for the manufacture of zirconia base ceramic monofilaments. The apparatus is essentially a small pressure vessel. Experimental results and progress have dictated several modifications of the original extrusion vessel as work progressed. The pressure extrusion system currently in use can be seen in Figure 1. In operation, the pressure vessel (A) is filled with fiberizable solution and pressure applied to the system through the fitting (B). The pressure can be varied between 0 and 250 psig using compressed nitrogen gas as the pressure source. The fiberizable solution is pushed through an in-line high pressure filter holder (C). The high pressure filter holder is a product of Millipore Corp. and Millipore Mitex type (Teflon) filters of 5 and 10 micron pore size have been successfully used in this application. After the filtration operation, the solution proceeds to the spinnerette holder (D) where it is pressure extruded through a spinnerette (E). The spinnerettes are manufactured by Englehard Industries of Carteret, New Jersey. Through use of the in-line filter to remove foreign particles from the fiberizable solutions, orifice sizes of 0.002" to 0.004" diameter have been successfully used for the production of pressure extruded fibers. All components of this system have been constructed of stainless steel to resist the corrosive nature of the viscous salt solutions.

The "green" or raw fiber produced as described above, is allowed to fall by gravity to a collector below the nozzle. The fiber is allowed to fall from 3 to 15 feet before being picked up on the drum. A four or a six foot circumference drum rotated by a precision speed control motor is used to further attenuate and collect the extruded fiber. These relatively large drums and vibration-free winding motors have been incorporated into the system to allow faster fiber collection rates at reduced collection drum RPMs and concurrent reduced air turbulence which otherwise can lead to mechanical breakage of the fiber.

Once the fibers are formed and collected on the drum, they are ready for calcining.

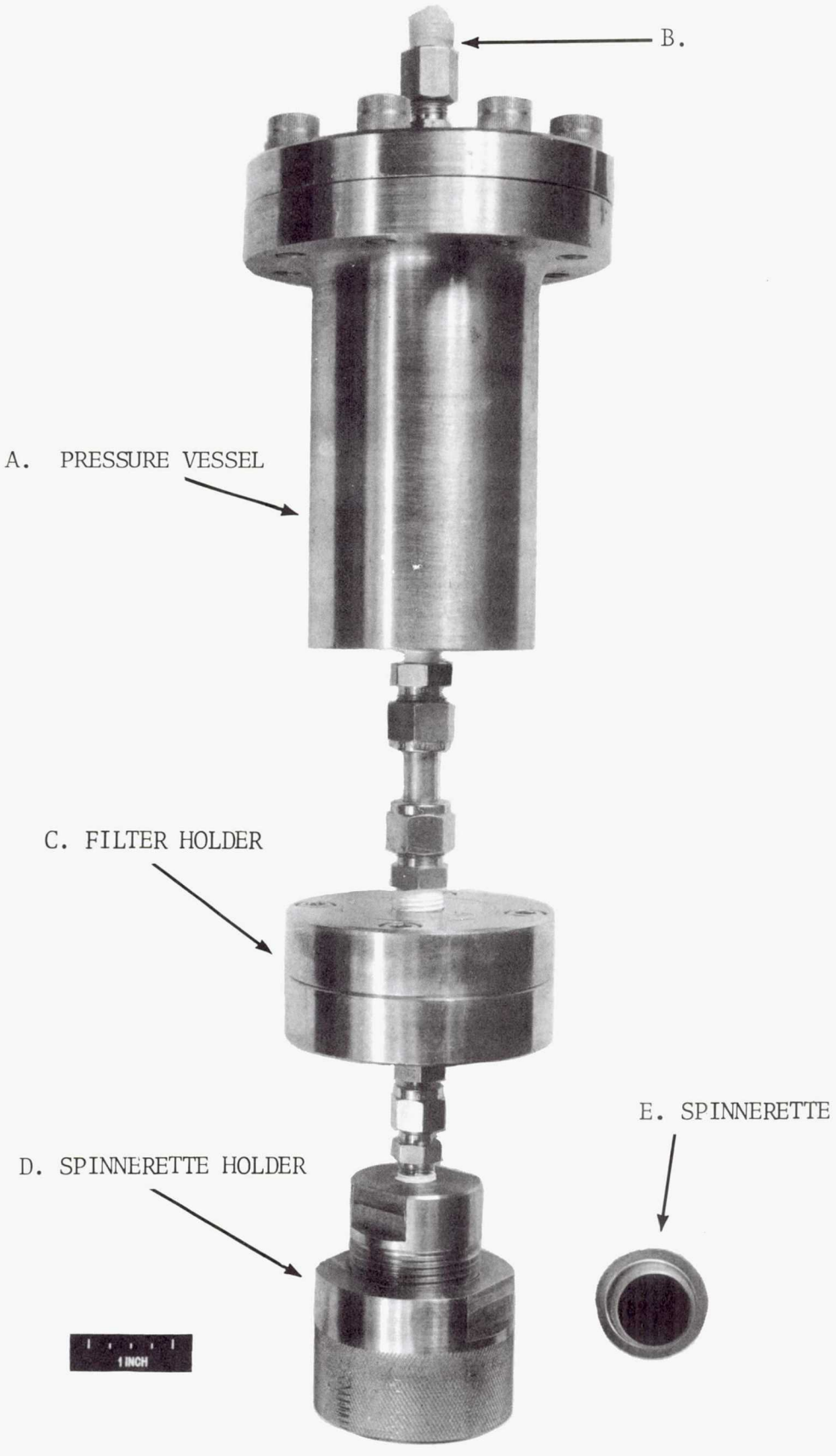

FIGURE 1 STAINLESS STEEL PRESSURE EXTRUSION SYSTEM USED FOR PRODUCING MONOFILAMENT FIBER

C. CALCINING FIBERS

The collected fibers must be calcined to be transformed into the desired oxide form. Two basic methods have been used; a slow fire in a periodic kiln and a fast fire in a tunnel kiln.

In the case of the slow firing method, the collected fibers are removed from the collector drum and either stored in a low humidity area or immediately placed in an electrical resistance furnace equipped with silicon carbide elements which is at room temperature. The furnace and fibers are then heated at a slow rate (20 F to 50 F/hr) to approximately 1200 F. The heating rate is then increased to about 400 F/hr until a maximum temperature of 1750 F to 1950 F is reached. The furnace is held at the desired maximum temperature for 15 to 20 minutes, then the calcined fiber is removed from the furnace and stored in plastic boxes to await testing and evaluation.

In the other method, the fibers are fast fired in a gas fired tunnel kiln. The tunnel kiln, designed by Fostoria Corp. and B&W, is 20 feet long and can calcine the fiber to 1850 F to 2100 F in a period of 30 to 140 minutes depending on furnace settings and belt speed. This tunnel kiln has been operated with a normal combustion atmosphere and also with an introduced steam atmosphere.

D. TESTING PROCEDURES

1. Viscosity Measurements

Two testers are used for the measurement of viscosity. The first apparatus is a hand-held Rion Viscotester, distributed by Fisher Chemical Company. This viscometer is a battery-powered, direct-reading instrument which uses various spindles to cover the range of viscosity desired. The Viscotester was used principally to check hot solutions and mixes whose corrosive vapors may damage the more delicate but more accurate Brookfield viscometer, the second apparatus used to determine viscosity.

The Brookfield, Model HAT, viscometer having 8 speeds and 7 spindles was used principally to check the viscosity of the fiberizable solutions before fiberizing and to calibrate the Rion Viscotester. Although portable, the Brookfield viscometer was used only on a bench stand to increase its precision and to avoid instrument damage.

2. Fiber Diameter

Two different means were used to determine the diameter of the fiber. The first apparatus, a Vickers A.E.I. split-image eyepiece mounted on a Leitz light microscope was used to observe the fiber at 675x magnification. This allowed us to measure with a precision of ±0.1 micron.

The second apparatus used to measure diameter was the screw micrometer eyepiece manufactured by Leitz. It is about as precise as the Vickers split-image, but is slightly more difficult to use since the orientation of the fiber is important in the measurement. Fiber diameters are measured whenever possible at the point of break of the fiber after tensile testing.

3. Tensile Strength

The room temperature tensile strength of fibers has been determined on either of two pieces of equipment. The first is a bench tester patterned after an apparatus originally used by W.H. Otto of Owens-Corning Fiberglas[9].

Several crosshead speeds are available with this tester ranging from 0.05 to 2"/min. Sample length can be varied from 1/4 to 3", but generally 1" was used in this work. Load force measurements are made from approximately 1/2 to 1,000 grams, but a 10-gram full load was used in this work. Load readout was displayed as an oscillographic trace recorded photographically on Polaroid film.

The second apparatus, a 10,000 pound capacity Instron Universal Testing Machine Model TT-C equipped with the tension load cell "A" (0-50 grams), can also be used to measure tensile strength. Fibers 1/2 to 10" long are mounted in specially made metal grips (cotter pin shape) using a thermoplastic glue. The crosshead speed used was 0.050"/min with a chart speed of 20"/min. The full-scale deflection across the strip chart recorder was set to be equal to either 2 or 10 grams. The breaking load was then read directly from the chart. The diameter of the fiber was then determined as previously described, and the tensile strength of the fiber was calculated as follows:

$$TS = \frac{1.811 \times 10^6 \cdot g}{d^2}$$

where

TS = tensile strength in psi

g = load in grams

d = fiber diameter in microns

4. Modulus of Elasticity

The tensile modulus of elasticity (E) was determined on the Instron Model TT-C tester using the stress-strain curve generated in the tensile strength tests. The modulus was then calculated as follows:

$$E = \frac{\text{stress}}{\text{strain}}$$

$$\text{stress} = \frac{1.811 \times 10^6 \cdot g}{d^2}$$

where

g = load in grams

d = diameter of the fiber, in microns at point of break

1.811×10^6 = conversion factor

$$\text{strain} = \frac{a \cdot S}{s \cdot \ell} = \frac{\frac{a \cdot S}{s} - CE}{\ell}$$

where

a = measured extension on the chart, in inches

S = crosshead speed in in./min

s = chart speed in in./min

ℓ = sample gage length in inches

CE = cell extension correction in inches

5. X-ray Analysis

X-ray diffraction patterns were obtained using a General Electric XRD-5 motor driven diffractometer synchronized with a Leeds and Northrup Speedomax, type "G" recorder. The calcined fibers were firmly ground in an agate mortar and then packed into a flat aluminum holder. Either cobalt or iron radiation was used and the sample scanned at a rate of 2 degrees per minute.

The X-ray was also used to determine crystallite size. Each of the main diffraction lines was scanned at a rate of 0.2 degree/min in order to measure the breadth of the diffraction line at 1/2 peak height. This broadening was compared with the broadening of a standard quartz sample in order to correct for the broadening due to the instrument.

The average crystallite size was then calculated in accordance with Klug & Alexander using the following formula[10].

$$DhKl = \frac{51.57\lambda}{B_1 \cos\theta}$$

where

DhKl = Diameter of the crystal

B_1 = broadening due to experimental method employed in observing it

51.57 = conversion factor

λ = X-ray wave length

θ = the Bragg angle

6. Fiber Composition

The composition of the calcined fibers was calculated using the starting materials as the basis for the calculations. The amount of aluminum metal digested is measured accurately to the nearest gram, and the purity of the metal used is 99.7+% Al, therefore, for each gram of Al dissolved, 1.88 g of Al_2O_3 will be produced. The colloidal silica used is a 40% sol thus, for each gram of sol used, 0.4 g of SiO_2 is added to the batch. The boric acid is used as the source of B_2O_3 and each gram of acid will equal 0.563 grams of B_2O_3. Thus, knowing the total equivalent oxide content of the solution, the percent of each oxide in the fiber can then be calculated on a weight basis.

SECTION III
RESULTS AND DISCUSSION

The process of manufacturing a ceramic oxide filamentary salt decomposition fiber by the extrusion-attenuation method can conveniently be divided into five unit operations:

A. Solution preparation
B. Fiber formation
C. Fiber collection
D. Fiber drying
E. Calcination to the oxide form.

For the sake of clarity, our discussion has been broken down into the five processing steps described above, in addition to a section on the chemical and physical characteristics of the ultimate fiber. While we can, for observation purposes, divide the process into the above five steps, the inter-dependency of all the processing steps with respect to the ultimate fired fiber is indivisible in practice. Variations in the fiber formation, for instance, can produce differences in the fiber which could lead to variations in the effect of the calcination on the fiber. Thus, cross referencing of the process steps and discussion thereof is mandatory for the understanding and explanation of much of the experimental data.

A. SOLUTION PREPARATION

From past B&W work it was felt that two solution variables which are controlled during preparation should have significant effects on the manufacture of a salt decomposition filament. These variables are:

1. Solution composition
2. Solution viscosity

1. Solution Composition

Solution composition, since it is directly related to the fired fiber composition, should influence the strength and modulus of elasticity of that fiber. Additive oxides, such as boric oxide, are known to influence the crystal structure of the fiber and varying amounts of these additives should also exert some influence on the fiber properties. Early in this work it was found that varying compositions resulted in little, if any, differences in the fired fiber properties. This is not to say there is no effect.

However, the effect is small compared to the much grosser changes in fiber characteristics due to other phases of fiber manufacture. Thus, for the most part, a solution has been used which would result in a fiber which contained about 75% Al_2O_3, 20% SiO_2, and 5% B_2O_3. This composition was known to be capable of producing fibers with good strength. Further investigations with varying compositions must wait until a degree of manufacturing reproducibility is reached which will allow us to observe fiber property differences due to composition changes.

2. Solution Viscosity

Viscosity is the one solution property important to fiberizability which can be measured directly and conveniently. In addition, solutions can be routinely prepared varying in viscosity from only several poise all the way to several hundred thousand poise. The viscosity is extremely temperature sensitive and varies with solution age. This property, therefore, has been our major quality control tool.

Viscosity of the fiberizable solutions has been found to increase from two to five times over a period of about a week. Thereafter the viscosity very slowly would increase until a glassy rock resulted some months later. This glassy rock could be remelted to the original liquid form. Addition of acetic acid to the solution directly before bottling has been found helpful in minimizing the secondary slow viscosity increase. However, no way has been found to control or negate the initial week-long rapid increase in viscosity. Thus our solutions are prepared to a viscosity of about one-half that desired for fiberizing. After setting for several days, the solution will be in the viscosity range desired or higher. Storing of the solution for several days following preparation serves two purposes. First, the viscosity is fairly well stabilized, and secondly, air bubbles are allowed to rise out of the solution. In addition, the aging seems to result in a more fiberizable solution. No concrete data can be supplied to support this as yet, and we can detect no influence on fiber properties. Yet there does seem to be an effect on fiberizability which might be due mainly to the deaeration mentioned above.

If the solution is at a higher than desired viscosity for extrusion, either a dilution with water can be made or the extrusion carried out at a

temperature which will result in the desired solution viscosity. The second method is preferred, since the effect of dilution on the molecular structure of the solutions and possible coinciding effect on the filament properties is unknown. The same thing could be said for heating of the solution, but it does appear to be the safer of the two alternatives. The viscosity-temperature relationship for these solutions has been determined on two instruments, as shown in Figure 2.

The viscosity of the solutions changes fairly rapidly with temperature; consequently the importance of controlling the temperature of the solutions during extrusion is emphasized. Also this figure shows that there is little difference in the temperature-viscosity effect because of solution composition, at least in the range tested. This viscosity study also showed that the solution behavior is that of a true Newtonian liquid since, for a changing shear rate, the apparent viscosity remains constant. This information should be helpful in predicting flow characteristics of the solutions as we advance our technology to include multi-hole orifices.

Also note on Figure 2 that the slope of the temperature-viscosity lines changes very little regardless of the viscosity. This point could allow the development of a working curve for determining the temperature necessary to obtain a desired solution viscosity.

B. FIBER FORMATION

The pressure vessel, solution filter media, and orifice holder developed during this investigation have been pictured in Figure 1, and described in Section II B. The arrangement of this apparatus and related equipment during operation is schematically shown in Figure 3. As in this overall program, two distinct work phases have been responsible for the development of the equipment described above. The first objective was to develop an apparatus capable of producing a collectable filament, regardless of quality or length. The second objective was to determine fiber quality yardsticks, identify the extrusion variables and their effect on fiber quality, and to modify the extrusion apparatus according to these findings.

1. Extrusion Apparatus

Solution viscosity, orifice size, extrusion pressure, winder speed, and relative humidity were felt to be important variables to consider for the

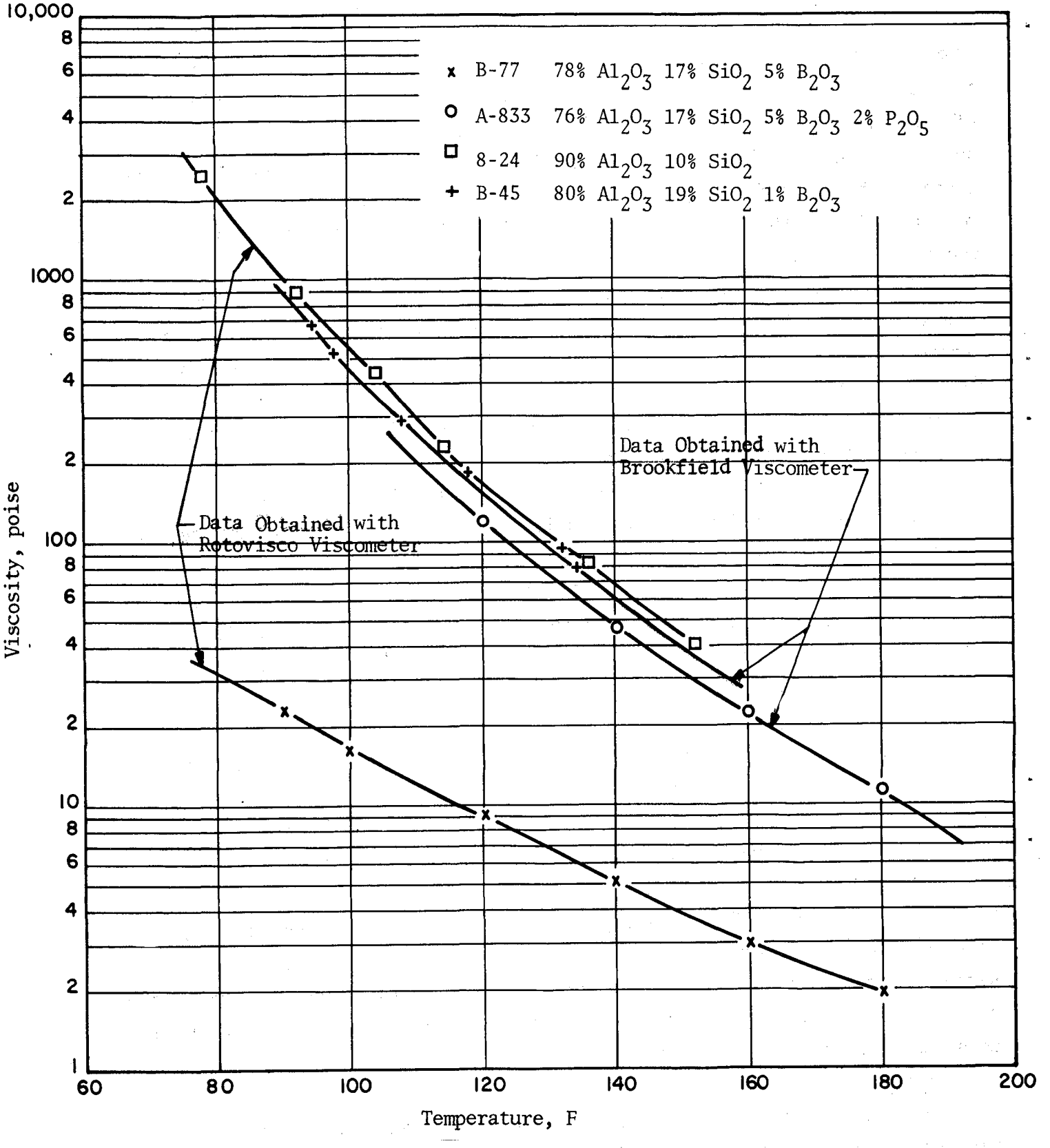

FIGURE 2. EFFECT OF TEMPERATURE ON VISCOSITY OF VARIOUS FIBER SOLUTIONS

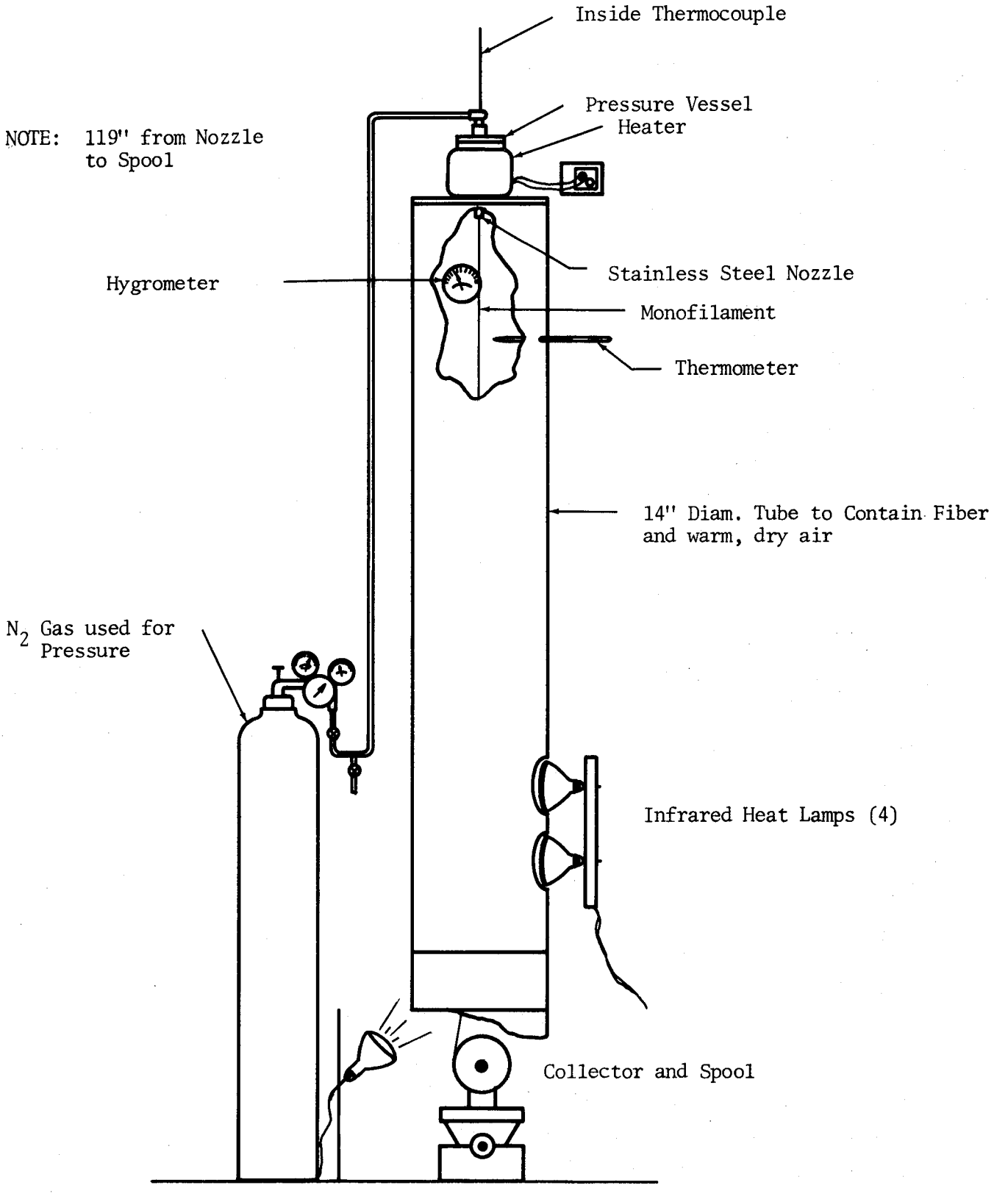

FIGURE 3. SCHEMATIC OF MONOFILAMENT APPARATUS

manufacture of a successful monofilament. Also, the approximate values for each of these variables were known, and the apparatus was constructed with these values in mind.

The apparatus was constructed for the following range of variables:

Solution viscosity	100 to 10,000 poise
Orifice size	0.0055 to 0.0135 inch
Extrusion pressure	0 to 400 psi
Winder speed	100 to 4,000 fpm
Relative humidity	10 to 80%

The first runs were made with one of our "standard" salt solutions used to make bulk insulation fiber. The solution was concentrated to 200,000 centipoise by evaporation of water. The best combination of operating variables was a 0.0085-inch orifice, 100 psig extrusion pressure, 100 fpm winding speed, and less than 60% relative humidity. However, the fiber always broke about 4 to 6 inches from the orifice. It was also difficult to prevent sticking of the fiberizable solution to the outside of the orifice, which caused continuous orifice plugging. In analyzing the problems, it was concluded that the breakage was due to fine air bubbles in the very viscous solution. These bubbles, when extruded through the orifice with the fiberizable solution, caused weak points and breakage in the fiber. This problem was eliminated by "fining" the fiberizable solution to remove the air bubbles. "Fining" was accomplished by warming the salt solution to about 170 F and maintaining it at that temperature for 1 to 2 hours. Warming the solution reduced its viscosity to about 10 to 40 poise (estimated) and allowed the air bubbles to rise to the surface.

The problem of plugging or sticking of the solution to the orifice was felt to be mainly due to the orifice construction or design. Several orifices were made to test different metals such as platinum, silver, and 304 stainless steel to see if the wettability of the metals was different enough to eliminate the problem. A high mirror-like polish was placed on the outside surface of the orifice to further reduce the wetting and plugging possibility. All three metals provided equally good results. Apparently the polishing of the area immediately adjacent to the orifice to a mirror-like finish to reduce wettability was the main requirement for a successful orifice design. However, the silver orifice proved to be too soft and was easily scratched in use. Because of cost,

stainless steel was chosen over platinum for these preliminary runs.

The appropriate orifice changes (using a polished stainless steel orifice of 0.0085-inch diameter) and the use of "fined" fiberizable solutions made the monofilament apparatus capable of producing uninterrupted fiber for 6 to 8 minutes at 300 to 1200 fpm collection rates before fiber breakage occurred. The longest fiber was about 8,000 feet in length uncalcined. The filaments formed were large and variable in diameter (40 to 90 microns) and were still damp when collected on the spool. Damp filaments shrink on further drying, causing breakage on the collecting spool or, if they are very damp, can stick to each other on the collecting spool. It was obvious that the fibers must be somewhat dried before being collected.

It was felt that sufficient drying of the fiber could be accomplished if:

1. The fiber had more time to dry between extrusion and collection
2. The temperature and relative humidity around the fiber could be controlled for fast-drying conditions
3. The diameter of the fiber could be reduced to increase its ratio of surface area to volume
4. The chemistry of the solution could be tailored so that the solution would require less water loss to obtain the desired end product.

Increasing the time for drying can be done by reducing collection speed and/or increasing the distance from the orifice to the collection spool. The latter change, although requiring extensive modifications to our fiberizing apparatus, was preferred, since reducing the collection speed would result in undesirable slower production rates. The distance from the orifice to collector was increased from 3 to 15 feet in our new fiber forming facility. However, increasing this distance required that the fiber be protected from air currents, which could make collection of the fiber nearly impossible. Thus, a 14-inch diameter tube was added to protect the fiber from room air currents. This tube is shown in Figure 3, a schematic drawing of our apparatus. The tube not only served to protect the fiber, but also acted as a container in which the air could be heated to reduce its relative humidity and increase its drying power. Infrared lamps were used as the heat source because they can supply heat without making violent air currents that can disrupt fiber winding.

In addition, it was found that relative humidity around the fiber must be controlled. Normal variations in atmospheric conditions were disastrous to routine production of extruded fibers. A complete fiber forming area with

control of such environmental factors as dust, temperature and relative humidity was built with B&W funds. With this equipment and work area, we feel that optimum fiberizing conditions can be more readily obtained.

Tests with this new apparatus at relative humidities of less than 40%, drying temperatures of more than 100 F, and winding speeds of 400 ft/min or less, resulted in fibers which could be collected with minimum breakage on the collection spool. The diameter of the "green" fibers was still in the range of 40 to 60 microns.

2. Extrusion Procedures

From past technology obtained by B&W, a fine fiber diameter was found to be extremely important in obtaining tensile strength in excess of 200,000 psi and a modulus of elasticity greater than 30 million psi. The construction and operation of the above described extrusion apparatus enabled us to identify operation variables which should influence fiber diameter. The most obvious variables to be investigated were:

a. Collection rate
b. Orifice size
c. Extrusion pressure
d. Solution viscosity
e. Solution temperature
f. Room temperature
g. Relative humidity

a. Collection Rate

Fiber collection will be thoroughly discussed in a later section. However, the operation is also pertinent to fiber formation, since the collection also influences fiber diameter. The slowest collection rate for extruded fiber would simply be that rate at which the fibrous material is extruded and pulled downward by the force of gravity. By increasing the collection rate through an increase in the collection drum speed, a stretching or attenuation of the extruded fiber is accomplished. The attenuation results in a decrease in fiber diameter over that of unstretched filament. The amount of diameter decrease is certainly dependent on the amount of pulling which is dependent on the collection rate, all other things being equal. Regardless of the absolute fiber diameters involved, attenuation is capable of reducing fiber diameter two to

three times over that of the unattenuated extruded fiber. This will be discussed in more detail later. For the moment, suffice it to say that collection rate is maintained at the maximum rate possible before undue fiber breakage occurs.

b, c. Orifice and Extrusion Pressure

Orifice size and extrusion pressure were both initially found to have a pronounced effect on the diameter of the fiber. Reducing the orifice size from 0.0085-inch to 0.007 or 0.0052-inch requires other operational changes so that orifice size and diameter cannot be directly correlated for the same spinning conditions. However, fibers made with various sizes of orifices produced various sizes of fibers as follows:

Orifice Size (in.)	"Green" Fiber Diameter (microns)
0.0085	62
0.0070	27
0.0052	18

This tabulation shows the size of fiber that could be made with each orifice size with the appropriate other operational changes and led us to believe that still smaller orifices, in the range of 0.003 to 0.004 inch, should be capable of making still finer fibers.

All other things being equal, one would expect fiber diameter to be proportional to extrusion pressure. As more pressure is applied to the extrusion vessel proportionately more solution is extruded resulting in a larger fiber and this was indeed found to be the case in preliminary experiments as tabulated below:

Extrusion Pressure (psig)	Orifice Size (in.)	Solution Viscosity (poise)	Green Fiber Avg. Diameter (microns)	Solution Temperature (F)
30	0.0055	1700 @ 75 F	44	100
40	0.0055	1700 @ 75 F	46	100
80	0.0055	1700 @ 75 F	59	100
120	0.0055	1700 @ 75 F	65	100

Spinnerettes of 0.002", 0.003", 0.004" and 0.005" orifice size were obtained from Englehard Industries. The 0.004" diameter orifice was immediately placed in operation and, as expected, the finer orifice resulted

in the production of much finer diameter fibers. Samples of green monofilament were prodcued with average diameters of 9 to 15 microns. When these samples were fired, fibers with 5 to 9 microns average diameters resulted*. During use of this smaller diameter orifice, a plugging problem arose intermittently.

On placing the 0.004" diameter orifice into operation as described above, the affect of extrusion pressure on fiber diameter was rechecked.

Figure 4 shows an observed relationship between extrusion pressure and "green" fiber diameter for both pulled or attenuated fibers and fibers formed only by gravity (free fall) from the pressure vessel over a ten-foot drop. It is readily apparent from Figure 4 that for a given fiberizable solution, there is an optimum extrusion pressure above and below which larger diameter fibers will be produced. This phenomenon is felt to be due to several factors. At low pressures the extruded fiber is falling or being pulled from the orifice so slowly that an excessive drying of the fiber takes place before the maximum amount of diameter reducing attenuation can take place. It should be pointed out that in all cases the filament collector drum is rotating at a rate such that excessive fiber breakage does not occur. At higher pressures, larger diameter fibers are obtained because the collector drum could not be run fast enough to attenuate the large volume of salt solution being extruded into fibrous form. This is not to say the drum and motor assembly is incapable of faster speeds. However, the two foot circumference drum when in use could only be run at a maximum of 250 to 300 rpm before the onset of excessive air turbulence and mechanical breakage of the fiber. The logical extension of this is the construction of a larger drum capable of high fiber pulling rates at relatively low rpm's.

Figure 4 also shows that at a given pressure and under the conditions of these experiments, attenuation is capable of reducing the free fall diameter of the fiber being formed by a factor of two.

It is also to be noted that in both tests shown in Figure 4, the minimum "green" fiber diameter produced was about 20 micron regardless of the salt solution used. It is probable that other factors limited further diameter reduction by means of attenuation. The two sets of data concerning extrusion pressure described above are not thought to be contradictory. They instead

* Complete fiber properties will be more fully discussed in Section III E.

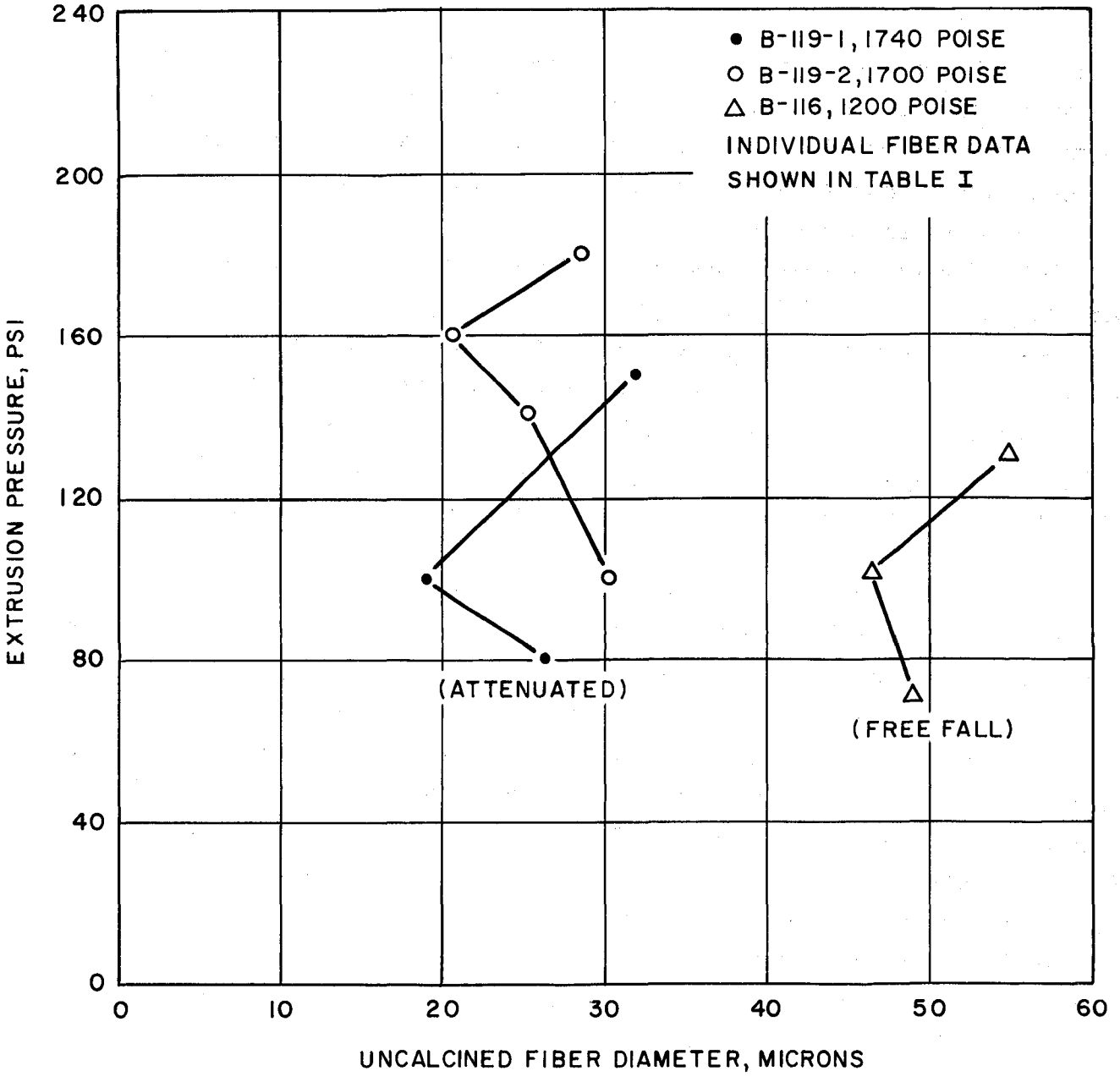

FIGURE 4. INFLUENCE OF EXTRUSION PRESSURE UPON UNFIRED DIAMETER OF FIBERS

point out the complexity of the system. While we must hold known operating parameters constant during the study of the effect of variation in one variable, we must realize that changes in these operating parameters may modify the effect of that variable on fiber quality. This has been found to be especially true of changes in orifice size.

Following the successful use of the 0.004" diameter orifice, attempts were made to put the 0.003" diameter orifice into operation. Orifice plugging now became a severe problem and an efficient solution screening step became a distinct necessity. A 325 mesh Tyler screen was successfully integrated into the pressure vessel directly ahead of the orifice. Once this innovation was made, orifice plugging was minimized and continuous operation with the 0.003" diameter orifice was realized. A 200 mesh Tyler screen was also tried and found equally successful.

Several fiber samples were produced using the 0.003" diameter orifice, and it was found that both the green and fired diameters were in the same range as those mentioned above for the 0.004" orifice.

Attempts to extrude monofilament using the 0.002" diameter orifice met with further difficulty. Salt solutions of 200 to 300 poise viscosity had been used with the 0.003" diameter orifice. Pressures up to 250 psig appeared incapable of extruding a sufficient flow of this viscosity solution through the 0.002" diameter orifice to form a monofilament. Solutions of 50 to 150 poise viscosity were tried. However, it appeared that the lower viscosity material did not have other properties (surface tension, e.g.) necessary for fiber forming. The solutions could be extruded, but a wetting of the orifice face and droplet formation occurred rather than fiber formation. Following this, a further attempt to extrude 200 to 300 poise solution through the 0.002" orifice was made. This time the pressure vessel containing the solution under pressure was held in a heat lamp until the solution was warm enough and the viscosity low enough to cause a flow which did result in fiber formation. The heat lamp was then removed and fiber could be drawn from the 0.002" orifice even as the solution cooled. However, once more, orifice pluggage was a large problem even with a 325 mesh screen in place. This led to the incorporation into the system of the in-line high pressure filter holder as shown in Figure 1, and the use of 5 to 10 micron pore size filters. With this more sophisticated

extrusion system, 200 to 300 poise solutions could be drawn from the 0.002" orifice with a minimum of difficulty. An early sample drawn using the 0.002" diameter orifice showed an average green diameter of 7.3 microns with a diameter range of 4.4 to 11.6 microns. This sample when fired should have an average diameter of less than 5 microns. Thus, the promise of attaining low diameter, high strength fibers using the 0.002" orifice appeared excellent. However, in producing the finer diameter fibers through use of smaller diameter orifices, three problems appeared as follows:

1. A pulsation of the solution during pressure extrusion
2. Fired fibers with milky appearing sections
3. Fired fibers which are very curly and kinky.

Problem two was found to be directly related to problem one. There is some evidence that problem three is also related to problem one, but other factors may be involved also.

The pulsation problem was actually an old problem which was erratic in its frequency of occurrences. That is, the problem would come and go and thus appeared to be at least partially controllable. This problem is a pulsing of the salt solution as it is pressure extruded from the orifice. The pulse can be best described as a larger volume of solution being extruded than immediately prior to the pulse. In the extreme, these pulses would be drops of solution connected by a somewhat normal extruded fiber.

In the past work during usage of the 0.005" and larger diameter orifices, these pulses were large and very evident to the naked eye when they occurred. Thus, fiber samples which had been collected while a pulsation was occurring were easily spotted and discarded. Also note that no problem with milky fiber sections was evident during this earlier work. The milky appearing sections can be found within a discrete fiber length terminated by clear, glassy appearing sections. This phenomenon is shown in Figure 5. The fracture patterns evident in the glassy fiber portion of Figure 5 are coincidental and not thought to be related to the problem. These milky sections are weak and powdery and appear to be porous. These sections of the fiber are always larger in diameter than the adjacent clear glassy fiber.

Figure 6 shows three examples of large pulses. These photos show an elongated air bubble and some foreign material trapped within the body of a pulsed section. While many pulses have been seen without air or foreign

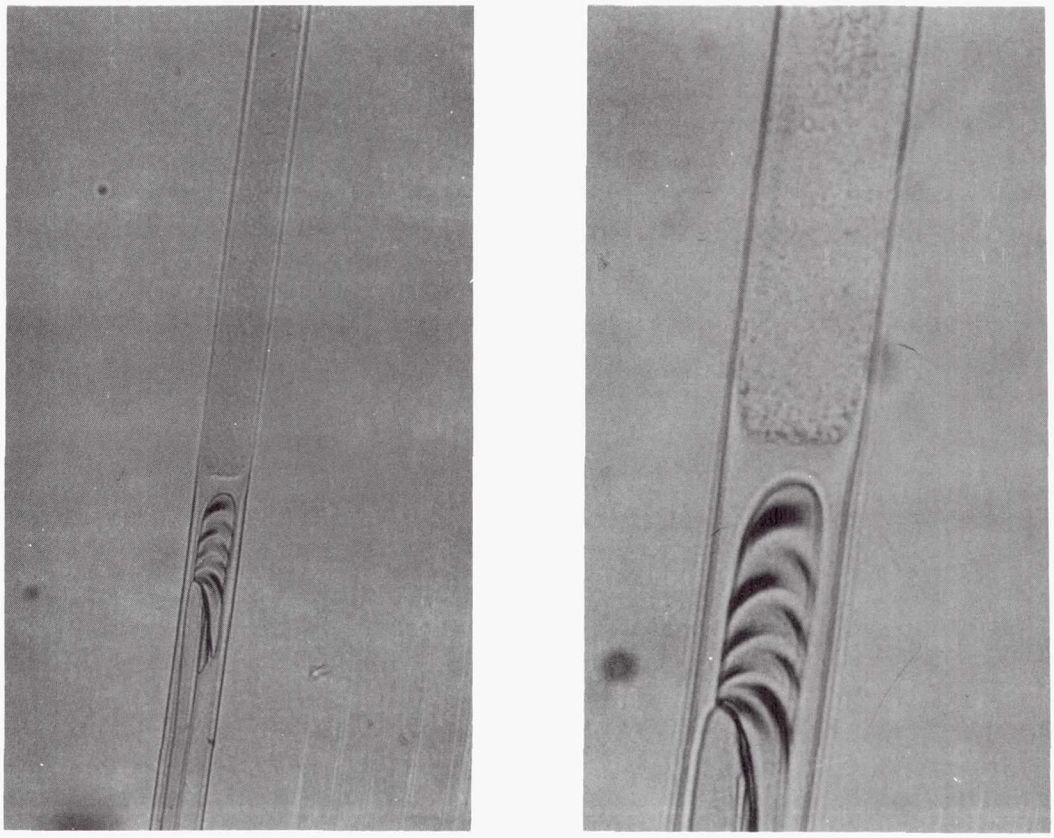

FIGURE 5. SECTION OF EXTRUSION-ATTENUATION FORMED FIRED FIBER SHOWING ADJACENT "MILKY" AND "GLASSY" APPEARING PORTIONS

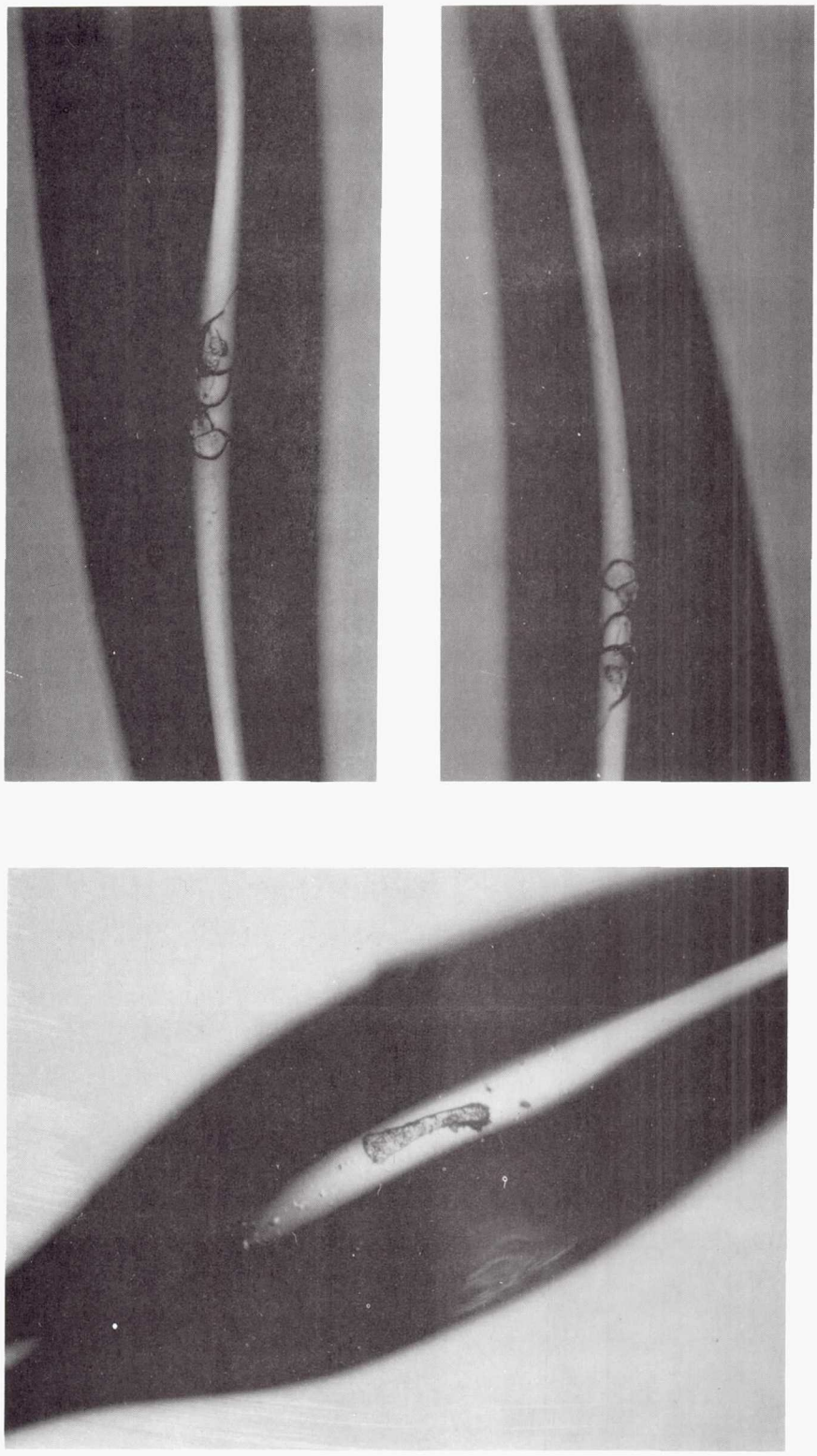

FIGURE 6. PULSES IN EXTRUSION-ATTENUATION FORMED GREEN FIBER SHOWN AT 120x WITH BOTTOM LIGHTING (0.005" DIAMETER ORIFICE)

particles entrapped within, these observations added impetus to the placing of an efficient filter apparatus within the pressure extrusion system. In addition, in Figure 7, one can see fibers with foreign particles entrapped where no pulse was formed. Objects such as these are probably weak spots within a fiber and their removal cannot help but improve fiber strengths.

When the smaller diameter orifices were placed in operation, this pulsing of the extruded solution became more prevalent. There was not a larger quantity of pulses. They occurred at about the same frequency but the problem was now present almost 100% of the time. With these smaller orifices, the pulses are now more subtle than with the larger orifices. Remembering that an attenuation is taking place which tends to elongate and smooth out the pulse, one can see that the more subtle the pulse becomes, the greater the chances of not seeing it.

With this point in mind, recall that the milky fiber sections noted above were produced when smaller orifices came into use and the milky sections all were of larger diameter than adjacent glassy sections. The 0.002" diameter orifice produces the most subtle pulsations. Figure 8 shows a 0.5 inch section of a fired fiber produced using the 0.002" orifice. The fiber was checked for diameter along the length and then photographed in sections and the photographs combined to give the overall picture. One can see that fiber diameter goes from 9 microns on one end to 34 microns in the middle then to 7 microns at the other end. The fiber diameter actually decreased further yet on each end, but this was not shown in Figure 8. One can also see that the larger diameter section is distinctly milky in appearance and fades out to a glassy appearance at either end. While the diameters noted on Figure 8 are real and are an accurate description of the diameter variation along the length of fiber, their actual position on the photographs is questionable since diameter measurement and photography are done at two different magnifications on two different microscopes. However, the point to be illustrated is readily apparent.

It appeared then that we had a pressure extrusion system capable of producing green monofilament less than 7 microns in diameter which on firing would be less than 5 microns in diameter. The problem remained to eliminate the pulsing which was producing variable diameter fibers, since this variable diameter introduced other fiber property variations (strength e.g.)

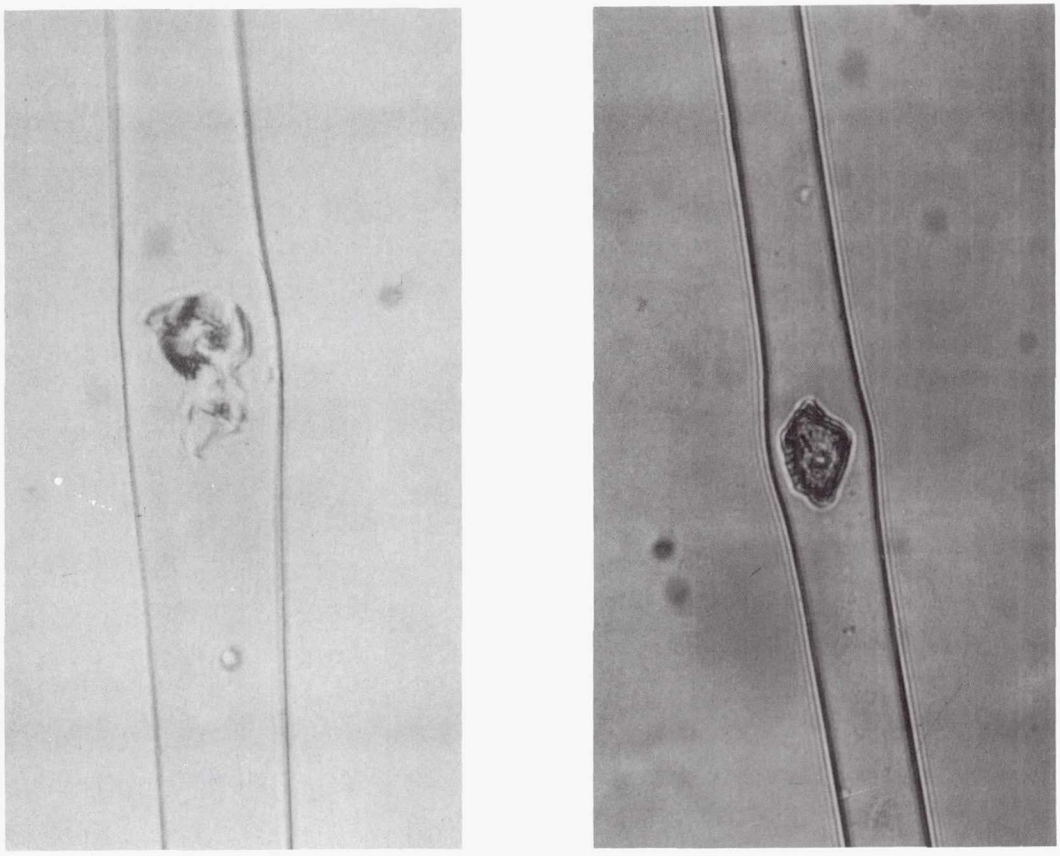

FIGURE 7. 500x PHOTOGRAPHS OF EXTRUSION-ATTENUATION FORMED FIRED FIBER WITH ENTRAPPED FOREIGN PARTICLES

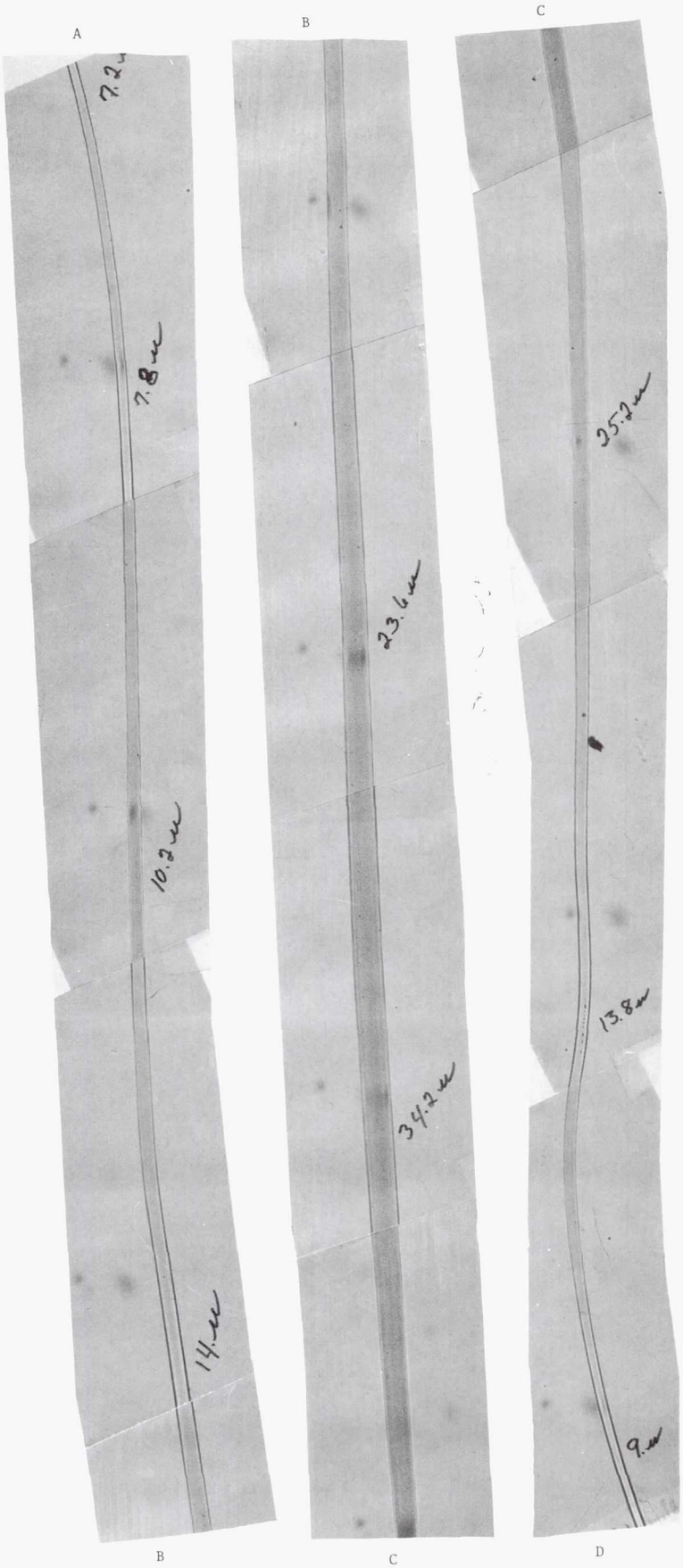

FIGURE 8. 0.5" SECTION (AB+BC+CD = 0.5" SECTION AD) OF EXTRUSION-ATTENUATION FORMED FIRED FIBER (0.002" DIAMETER ORIFICE) AT 200x SHOWING DIAMETER VARIATION AND "MILKY" LARGER DIAMETER

Operating conditions for the smaller orifices were then varied of necessity to overcome the solution pulsation which results in nonuniform diameter fibers. Increasing the extrusion pressure appeared capable of eliminating the solution pulsation. Further experiments were then carried out to compare the diameters of fibers extruded using different orifice sizes. The results of these experiments are tabulated below.

Batch No.	Pressure System	Extrusion Pressure	Orifice Size (in.)	Collection Rate	Unfired Diameter* (microns)
A-900-1	Zenith Pump	450 psig	0.002	340 ft/min	15.9
A-900-2	Zenith Pump	450 psig	0.002	480 ft/min	16.3
A-900-3	Gas Pressure	275 psig	0.003	600 ft/min	16.5

* Complete data shown in Table II.

The point of interest here is the similarity of diameters regardless of experimental conditions. As was pointed out above, fiber diameters were in the same range whether produced with the 0.003" or 0.004" diameter orifice. The additional data concerning use of the 0.002" orifice confirm that orifice size, within limits, does not affect ultimate fiber diameter. However, the process conditions (extrusion pressure, viscosity, etc.) necessary to produce a uniform diameter fiber would vary depending on orifice size. We could further assume that the extrusion-attenuation apparatus has been sophisticated to the point that fiber diameter is no longer limited by equipment, but by the fiberizable solution and operational parameters now in use.

With the above thoughts in mind, routine extrusion experiments have been carried out using 250 psig extrusion pressure and the 0.003" diameter orifice simply because it is most convenient and easiest to use. It is important to note here that a new dimension had been found by which to judge extruded fiber quality. Not only are we attempting to make fibers with diameters less than ten microns, but the fibers must also be uniform in diameter with respect to length.

d, e Solution Viscosity and Solution Temperature

These two dependent variables had been first studied in our early work when the extrusion operation was ill-understood and little control had been developed. Both solution temperature and solution viscosity were shown to affect fiber diameter. The inability to evaluate the size and mode of these effects were due to lack of real control over other extrusion variables

responsible for grosser effects on fiber diameter. Once orifice size, extrusion pressure, relative humidity and room temperature were brought under a degree of control, the evaluation of solution viscosity and temperature could be made with some confidence.

Extrusion temperature and the dependent extrusion viscosity of the solution appear to be of paramount importance to fiber diameter. The following tabulation shows data from some of these experiments.

Sample	Room Temp (F)	Relative Humidity	Viscosity (poise @ F)		Extrusion Temp (F)	Diameter* (average microns)	Collection Rate (ft/min)
B-252-1	80	30	800	75	95	10.1	700
B-252-2	80	30	800	75	95	9.4	800
B-252-4	90	29	1000	72	94	26.3	800
B-252-5	90	29	1000	72	94	28.7	800
B-252-6	90	29	1000	72	105	15.0	1100
B-252-7	82	28	700	77	88	16.1	800
B-252-8	82	28	700	77	95	13.5	900
B-252-9	82	28	700	77	96	13.6	900
B-252-10	82	28	700	77	100	14.6	1100

* Diameter average of 25 individual unfired fibers.

B-252 is one solution (B-168 type) which was fiberized on several different days to make up the number of individual fiber samples above. The viscosity differences are due to the viscosity increase with solution age as discussed in Section III A. The fiber collection rate was adjusted to the maximum allowable before excessive fiber breakage occurred. The point to be made is that almost any high-viscosity solution can be extruded and attenuated to fine diameter fibers as long as the extrusion temperature is such that the extrusion viscosity is at an optimum for drawing. Preliminary estimates indicate a viscosity of 300 poise is optimum, producing our finest diameter runs. The solution obviously can be either too thick or too thin for optimum drawing of fiber on a continuous basis.

The importance of the above indicates that precise temperature control of our extrusion vessel is important.

f, g Room Temperature and Relative Humidity

Studies have shown that relative humidity and room temperature appeared to be more important to fiber collection and less important to routine production of identical unfired (green) fibers. We thus have set our relative humidity at 30% and are building air cooling capabilities for a constant 80 F room temperature. This is not to say these variables are unimportant to the unfired fiber being produced. However, at present, the other known variables appear more important and responsible for larger variations in green fiber production as discussed above. As we implement the controls specified in the previous sections, the importance of these two variables is expected to increase with respect to production of a uniform diameter, low diameter fiber continuously. These variables are expected to be especially important in the vicinity of the orifice where the fiber is born and given its life long characteristics.

C. FIBER COLLECTION

Our first green fiber collector was a drum two feet in circumference and run by a variable speed motor. With this fiber attenuation-collection system, two limiting factors were quickly encountered. Both factors are involved with the rotational speed of the collection drum. The faster the drum is rotated during collection, the more the green fiber is attenuated to a finer diameter. A point is eventually reached where the green fiber is not strong enough to withstand further attenuation and breakage occurs. The second factor is that the higher the circumferential speed of the drum, the more turbulence is introduced which leads to mechanical fiber breakage. The problem of devising a collection system for continuous monofilament production has been set aside until fiber with high strengths can be made via the extrusion process. Of immediate concern was the reduction of mechanical degradation to our existing green fiber in order to take maximum advantage of the strength we already have.

To circumvent this difficulty, vibration-free winding motors with precision speed control were purchased by B&W and four and six foot circumference fiber collecting drums were constructed. With this improved collection system, 600 to 1000 feet per minute collection rates have been realized with increased attenuation of the green fiber also evident. With the two foot circumference drum, green fibers of 40 to 60 micron diameter could be attenuated (250 to 300 RPM maximum) to about 20 to 30 microns in diameter. Use of a six foot

circumference drum at 100 to 170 RPM has allowed us to attenuate an extruded green fiber of about 35 microns diameter down to a collected green fiber diameter of about 13 microns. Thus by reducing turbulence and mechanical breakage of the green fiber, faster collection rates and a greater degree of fiber attenuation have been realized.

The finer diameter fibers as mentioned above have also been the result of other improvements in our monofilament apparatus as discussed previously.

Relative humidity and temperature in the collector area have been found important to the fiber collection. These are both related to fiber drying. The transformation of a green extruded fiber to a calcined oxide fiber involves a fiber shrinkage of about one third its length. Too low a humidity causes excessive fiber drying with concurrent shrinkage and results in extreme fiber breakage on the collection wheel. Too high a humidity results in too little fiber drying and a sticky mass results.

Essentially, the same appears true of the temperature of the room. Collection of fiber under today's conditions appears to be carried out best in room temperatures of 80 F and relative humidities of about 30%.

D. FIBER DRYING

This phase of the overall process has received little attention as such. The major consideration has been given to what we may call a preliminary fiber drying. That is, sufficient drying must take place between initial formation by extrusion and collection such that the fiber will maintain its integrity for collection on our existing apparatus. This point has been more thoroughly discussed above. Our fiberizable salt solutions contain about 35% solids on the oxide basis. For the fiber to maintain its integrity during collection, this solids content must be increased to at least 45% on the oxide basis after extrusion and before collection.

Fiber drying and fiber shrinkage go hand-in-hand and both will take place over a period of time before equilibrium is reached at any given temperature from room temperature up to about 500 F.

While we have not really studied this aspect as yet, knowledge of fiber drying characteristics will be essential to the construction of continuous fiber collection equipment. Information with regard to fiber shrinkage versus amount of drying and drying temperature and fiber strength versus amount of drying, drying temperature and rate of drying will be necessary.

Information with regard to fiber drying versus ultimate fired fiber strength is also lacking. Drying of the fiber could have a large influence on densification or minimization of porosity and is felt to be one means of increasing fiber strength.

One experiment with regard to fiber drying was carried out before experimental priorities forced it aside for the time. A large number of B-119 series fiber samples will be described later in this report. The best of these B-119 samples had tensile strengths on the order of 140,000 psi and a modulus of about 22×10^6 psi with diameters about 12 microns. When these B-119 samples were produced, a fiber bundle (B-119-9) was placed in a desiccator over magnesium perchlorate desiccant. The sample was undisturbed for about 60 days at which time it was removed and fired at 25 F/hr to 1750 F. This sample tested at 9.5 micron average diameter*, 168,000 psi tensile strength* and 25.6×10^6 psi modulus*. This desiccator dried sample was thus superior to all other B-119 samples. Further work with this sample to determine why it was stronger was not carried out and duplicate experiments were unsuccessful. However, this one sample does confirm the need for extensive fiber drying investigations at a later date.

E. FIBER CALCINATION AND OXIDE STRUCTURE

The effect of calcining rate on fiber strength was the first investigation made. The following tabulation shows the effect of various heating rates and ultimate temperature on the strength and modulus of elasticity of the same composition fiber.

Batch No.	Calcining Conditions		Tens. Str. (avg. psi**)	Modulus(E) $_6$ (psi x 10^6)	Diameter (microns**)
	Rate (F/hr)	Temp. (F)			
B-67-7	1800	1860	49,000	16.3	13.4
B-67-5	800	1750	46,000	18.6	16.6
B-67-10	25	1850	78,000	19.0	13.5
B-116-1	30	1750	49,000	19.3	13.8
B-116-2	30	1750	70,000	21.7	20.2
B-116-3	35	1850	127,000	20.1	11.1
B-116-4	25	1850	141,000	21.2	11.2
B-116-40	35	1950	140,000***	21.5***	14.0***
B-119-50	30	1920	108,000***	19.8***	17.7***

* Individual fiber data shown in Table III.

** Data for individual fiber tests shown in Tables IV through VI.

*** Average of six replicate runs (60 fibers).

The data above imply that as long as slow calcining rates are used, five to ten degrees per hour difference in rate does not appreciably affect fiber properties. The superior fibers resulting from a slow calcination is not unexpected when one considers the relatively larger diameter fibers then being produced by the extrusion-attenuation method; i.e., larger fibers when compared to the fine discontinuous fibers produced by B&W using the salt decomposition process. The slower calcining rate is thus necessary to allow the salts to decompose slowly and allow sintering to take place in the fiber without trapping of the decomposition products within the larger diameter fiber.

As the above tabulation also shows, tests have been run to determine the influence of ultimate calcining temperature on the strength and modulus of the fiber. There appears to be a significant increase of tensile strength in fibers fired to 1850 F and 1950 F over those fired to 1750 F. This effect is even more apparent when the individual fiber data shown in Tables IV through VI are perused.

There appears to be no real affect on modulus here except between the fast and slow fired samples.

X-ray studies of fibers calcined under the above described conditions were made. Under all conditions mullite was the major crystalline phase present in the calcined fiber. The crystallite size in all these fibers also appeared to be approximately the same, 200 $\mathring{A}$. One possible difference between the fibers was the presence of gamma alumina in apparently varying degrees of crystallinity from fiber sample to fiber sample. These results were preliminary and pointed toward the definitive studies in this area to be described below.

When the extrusion technology had reached the point where finer diameter fibers were being produced, the effect of calcination rate and temperature on fiber properties was reinvestigated. This was felt necessary since earlier experiments had shown that changes in one fiber producing variable sometimes brought about changing effects of other variables on the fiber.

Green fibers were now produced with average diameters of 9 to 15 microns. Since past B&W experience has shown that small diameter fibers could be successfully fast-fired in a tunnel kiln, samples of these lower diameter fibers were both slow-fired as usual and fast-fired. The gas fired tunnel kiln processing was carried out with both a normal combustion atmosphere and also with the introduction of steam into that atmosphere.

The first smaller diameter fibers produced using the 0.004" orifice and slow-fired in a periodic kiln were blemished with the milky sections described in Section III B (page 31) and were very weak. Comparable fibers fast-fired in the tunnel kiln came out strong. These calcining experiments were repeated and the results can be seen in Table VII along with data obtained by X-ray diffraction analysis. It should be pointed out that weak, milky appearing sections were still evident in all the slow-fired samples described below. However, these samples were not nearly so blemished as the first batches mentioned above.

It appears that four conclusions can be drawn from the data presented in Table VII.

1. For the most part, the average diameters of the fiber samples are all in a close range.
2. In all cases within either the B-153 or B-168 series fast-fired fiber samples show higher strengths than comparable slow-fired samples.
3. The B-153 fiber series fired at 1950 F shows higher modulus of elasticity than the B-168 fiber series fired at 1850 F.
4. Tunnel kiln firing in a normal combustion atmosphere appears to result in stronger fibers than those produced when steam is introduced into the combustion atmosphere, which may or may not be statistically significant.

In drawing the above conclusions, several points must be kept in mind. All slow-fired samples within each series were fired in the same periodic kiln at the same time. In making comparisons between the B-168 series and the B-153 series, note that the B-168 composition was about four percent higher in silica than the B-153 composition. Composition difference could account for some of the modulus and strength differences noted.

One can see from the tabulation that samples B-153-1 and B-153-9, although slow-fired, showed rather good strength properties (consider the higher diameter of B-153-1). One can also see that sample B-168-8, fired in the tunnel kiln with steam showed strength properties comparable to those of fibers fired in the normal combustion atmosphere. Thus, there are apparent contradictions to the conclusions drawn above.

In an effort to determine the reasons behind fiber quality differences and the apparent contradictions to observed trends, as shown in Table VII, the

chemical structure of the fibers shown in Table VII was investigated and studied with respect to calcination of the fiber.

Since not only chemical form of a fiber but also crystallite size is thought to be of importance to the ultimate strength of a fiber, a series of X-ray diffraction analyses were carried out. The results of these analyses can be seen in Table VII. From this data, one can see that:

1. Samples slow-fired to 1950 F all contain mullite as the major crystalline constituent.
2. Samples slow-fired or fast-fired to 1850 F contain no major crystalline constituents.

While there is not a clear cut relationship, the stronger samples do have generally smaller mullite crystallite sizes. Since the fast-fired samples all show good strength and modulus values, one could theorize that the fibers actually contain a major amount of crystalline mullite, but this mullite is of a smaller crystallite size than the X-ray diffraction technique can determine. This is strictly conjecture. However, it would be of importance to the future production of high-strength fibers via the salt decomposition technique to show that there is a clear cut relationship between fiber strength and crystallite size within that fiber. If this be the case, one could say that the highest strength fibers would be those with a crystallite size below that which X-ray diffraction can determine. However, slow-fired samples B-168-2 and B-168-3 would seem to belie this statement. For while the X-ray saw not even a minor mullite phase, a minor mullite was apparent in the comparable fast-fired samples. Thus, one might also expect mullite in the slow-fired samples and in this case it would be logical to assume mullite of a crystallite size so small that the X-ray could not detect it. However, these samples are also low in strength.

One other aspect of fiber calcination was brought to light by accident. Through a furnace malfunction, several batches of monofilament were inadvertently soaked for 102 hours at 1950 F. Routine testing showed that fibers within these batches had diameters as high as 35 microns and surprisingly, high strengths. Therefore, several batches of green fibers known to be relatively coarse were fired to 1950 F (25 F/hr) and purposely soaked at that temperature for 60 hours. The following tabulation shows the results of this test:

Batch No.	Orifice Size (in.)	Tensile Strength (avg psi*)	Modulus (E) ($psix10^6$*)	Diameter (microns*)
B-152-A1	0.006	102,000	17.3	30.5
B-152-A2	0.006	90,000	17.6	36.2
B-153-A1	0.006	89,000	19.0	25.7
B-153-A2	0.006	62,000	17.9	30.4

* Individual fiber data shown in Table IX.

While these strengths are not outstanding per se, they are rather surprising considering the large fiber diameters and the heat treatment used to attain these strengths. One would expect a long soak time to lead to excessive crystallite growth and consequent loss of strength.

Since delivery of our finer diameter orifices followed the experiment. described above, emphasis on improving such large diameter fibers was put aside. However, these experiments further point out the need for a very thorough understanding of the drying-calcining operation with respect to producing strong fibers of any diameter.

The large diameter samples noted above also serve to bring out another point. It has been noted that as fiber diameter has gone down, the fibers have a tendency to become curly and kinky during either a fast firing or a slow firing operation. This fact not only detracts from fiber appearance, but would seem to affect measured fiber strength also. During fiber testing, the additional stresses placed on that fiber due to the straightening of a curl or kink would weaken the fiber causing breakage from factors other than the normal tensile load. Thus, a curly fiber would appear to be less strong than a comparable straight fiber. How much of this curling effect is due to the pulsation and resultant diameter variations noted in Section III B is a moot question at present. However, it has been noticed that the most uniform diameter fiber samples have exhibited a minimum of curling effect. It has also been noticed that our most uniform diameter samples and straightest fiber samples have been those of high diameter as shown in Table IX.

It appears then that there are trends in fiber properties with respect to chemical form and structure and that this chemical form and structure depends highly on the calcination of the fibers. Moreover, it appears that the calcination procedures necessary to optimize chemical form, structure and strength of the fiber are highly dependent on the diameter of the fiber. We must, therefore,

conclude that while the calcination operation is extremely important to fiber quality, its exact role cannot be determined until the quality of the green fiber can be assured from batch to batch. With this information, we have, therefore, returned to the extrusion-attenuation operation for further optimization toward reproducible and predictable diameter fibers so that we may study calcination with respect to fiber diameter. The goal would be production of predictably strong fibers of predictable diameter through process variations.

F. PHYSICAL CHARACTERISTICS OF FIBER

1. Fiber Strength Versus Fiber Diameter

The report has stressed the importance of obtaining fine diameter fibers since past technology, obtained by B&W, has shown that strong filaments can be obtained from the salt decomposition technique only when fiber diameter is less than ten microns. Figures 9 and 10 show graphically the effect of fiber diameter on tensile strength and modulus of elasticity for salt decomposition fibers made by the centrifugal spinning process and the extrusion process. The data show that as the fiber diameter decreases, the tensile strength of the fiber increases, while the modulus is essentially constant. The tensile strength increase is especially noticeable in fibers with diameters less than 10 microns. It is also interesting to note that the fibers made by the present extrusion-attenuation process can be potentially stronger than comparable diameter fibers made by centrifugal spinning. Thus the reasoning behind concentrating our efforts toward obtaining finer filaments.

Conclusive data concerning why the finer filaments are stronger cannot be offered at present, but at least two factors may be contributing to the results noted. First, the finer fibers may have a greater density and secondly, the finer fiber should have considerably fewer flaws. Attempts to show that fibers have a variation in density and flaw frequency with respect to diameter have not been successful. In the meantime, continued attempts are being made toward implementing improvement in fiber properties by decreasing fiber diameter.

2. Uniformity of Fiber Diameter

Extrusion pulsation as described in Section III B with the resultant fiber diameter variation with respect to fiber length as shown in Figure 8 caused some concern as to the validity of our testing and reported fiber strengths. Previously, fiber diameter was checked only at the point of break during routine

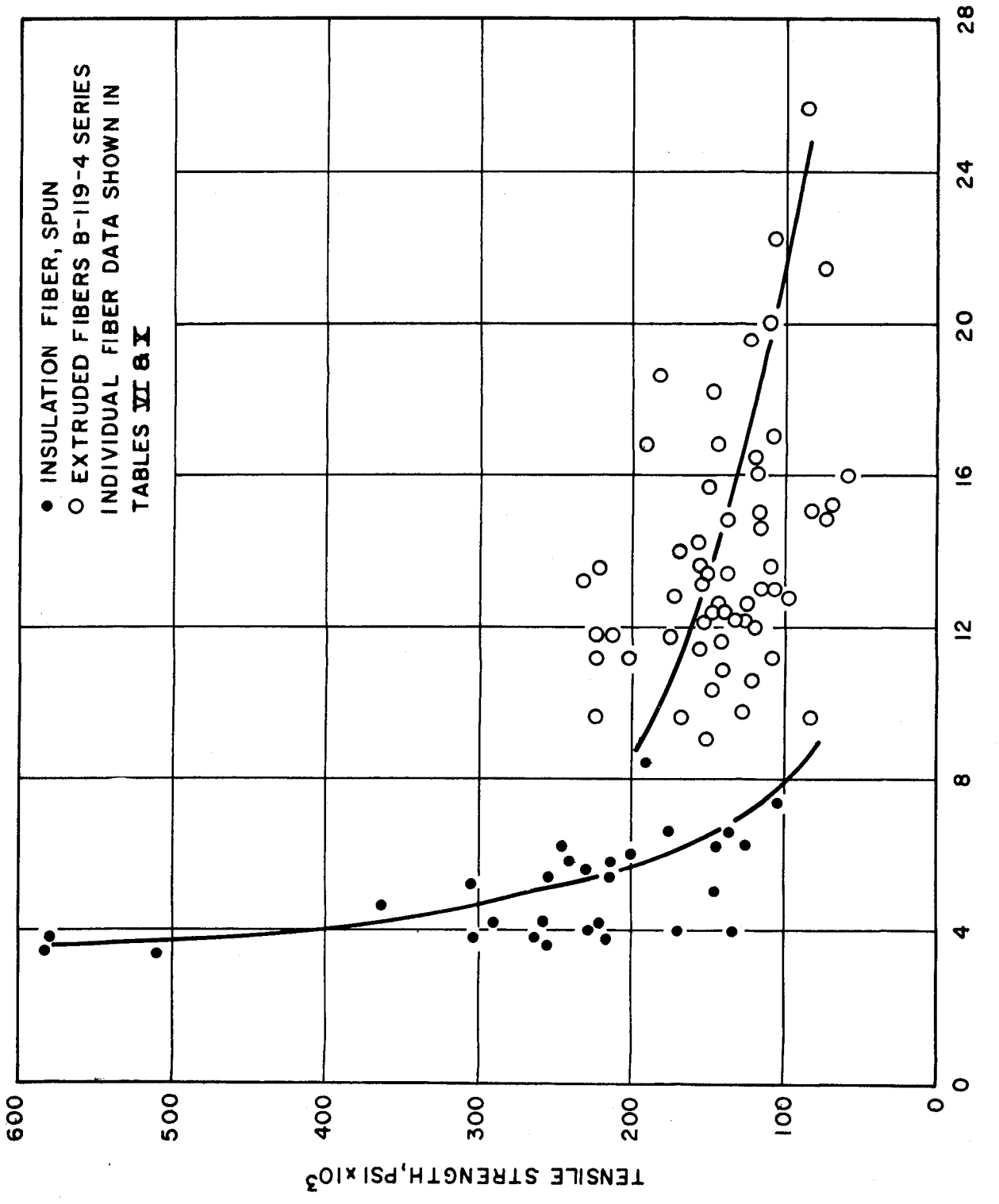

FIGURE 9. INFLUENCE OF FIBER DIAMETER ON TENSILE STRENGTH OF CERAMIC FIBERS MADE BY DIFFERENT METHODS

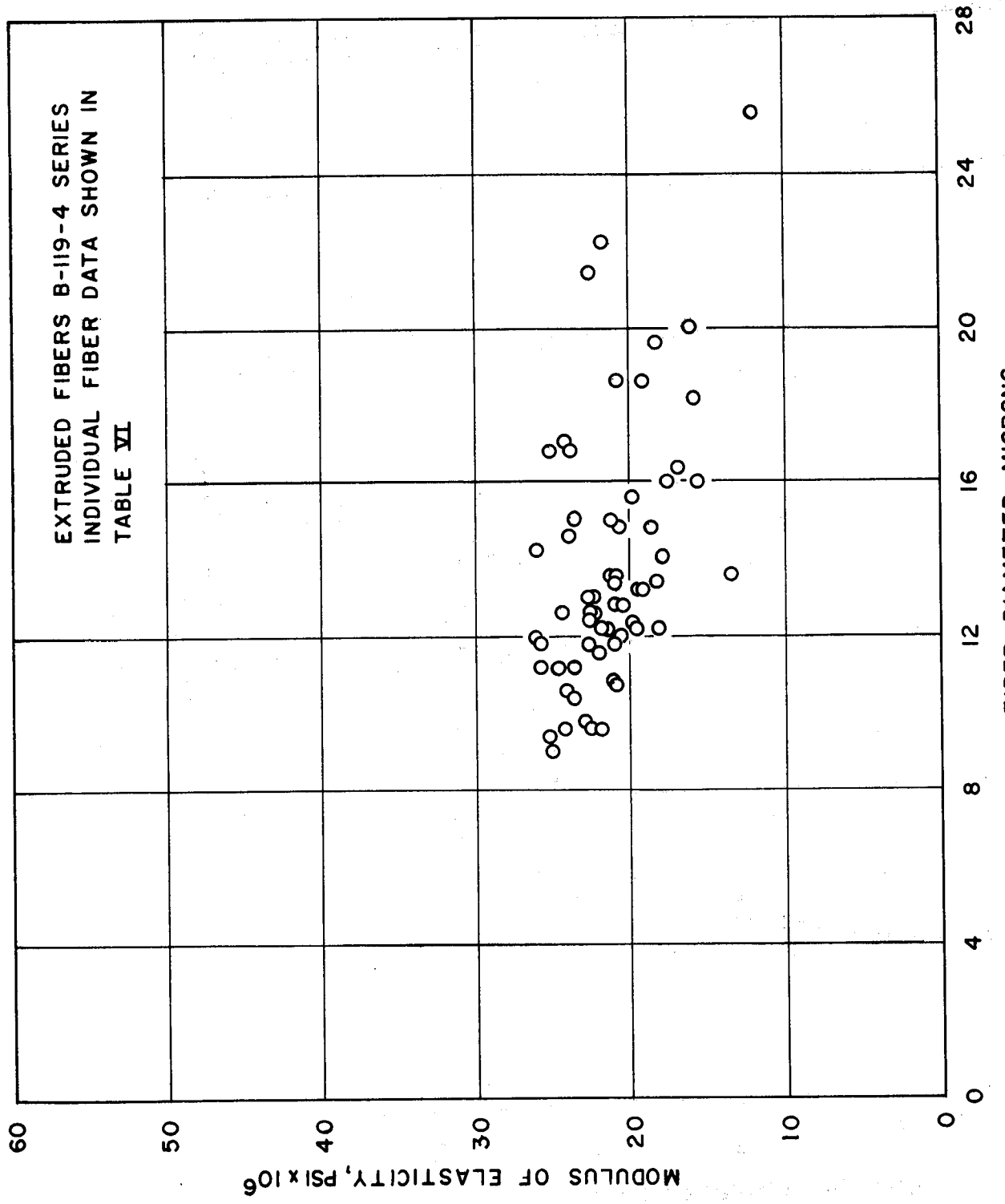

FIGURE 10. INFLUENCE OF FIBER DIAMETER ON MODULUS OF ELASTICITY OF CERAMIC FIBERS MADE BY EXTRUSION METHOD

tensile and modulus testing. This diameter was then used in calculating the strength of that fiber. If this diameter at break is not found over the whole 1" gage length, the calculated strength would only be valid for the portion of the fiber having that diameter, rather than for the 1" standard test length. A program of fiber scanning to check diameter uniformity with respect to length was thus begun. Four extruded fiber samples were slow-fired (25 F/hr) to 1950 F and soaked 0.5 hour at 1950 F. These fibers were routinely tested for tensile strength and modulus of elasticity. These results are tabulated below.

Batch No.	Tens. Str. (avg.psi*)	Modulus $(E)_6$ (avg.psix10^6*)	Diam. at Break (avg.microns*)
A-900-1	109,000	25.1	11.9
A-900-2	101,000	22.4	13.7
A-900-3	131,000	22.9	15.7
A-900-4	64,000	21.6	13.9

* Individual fiber data shown in Table XI.

Each of the fibers tested in the four samples described above were also scanned along the 1" gage length used for testing and the fiber diameter measured at five equidistant positions immediately prior to testing. These diameters were averaged and tensile strength and modulus of elasticity recalculated using these average diameters. The results of these recalculations can be seen below.

Batch No.	Tens. Str. (avg.psi*)	Modulus $(E)_6$ (avg.psix10^6*)	Diameter (avg.microns*)
A-900-1	104,000	24.0	12.1
A-900-2	96,000	21.2	14.1
A-900-3	123,000	21.7	15.7
A-900-4	59,000	20.1	14.2

* Individual fiber data shown in Table XII.

From the above tabulations and the individual fiber data as shown in Tables XI and XII, it is readily apparent that fiber diameter has been made very uniform, at least within the 1" gage length used for testing. The strengths calculated on the basis of average diameter are for all intents and purposes equivalent to those calculated from a diameter measured at the fiber breaking point. These calculations have added confidence to the assumption that eliminating solution pulsations will produce extruded fibers

of uniform diameter with respect to length. This fact, in turn, adds confidence to our strength testing procedures. A question which remains to be answered is that of uniformity of fiber diameter within a sample, for, although the data show excellent uniformity of diameter with respect to a 1" gage length, the variation from fiber to fiber within a batch is still rather broad.

An additional point is that no difficulty with weak, milky fiber sections was experienced with any of the batches described above. Unfortunately, the four samples did not emerge from the firing operation uniformly straight and free from curls and kinks. However, it is informative to note that sample A-900-4, the weakest sample, was curly and extremely kinky. Samples A-900-1, A-900-2, and A-900-3 were slightly curly but almost completely free of any kinkiness.

3. Atmospheric Corrosion of Fibers

The effect of atmospheric moisture and normal storage and handling on fiber strength and modulus of elasticity are rather important to the commercial usage of the product. This characteristic of our fiber has thus been checked. A constant humidity test vessel was devised. A layer of water was placed in the vessel and fiber samples B-119-4-3 and B-119-4-5 were also placed in the vessel above the water level. The vessel was sealed, placed in a constant 80 F room, and left undisturbed for 30 days. After 30 days the vessel was opened, the samples removed, air dried, and retested for tensile strength and modulus of elasticity.

Samples B-119-4-3 and B-119-4-5 were originally made and tested in December 1967. Table XIII describes the individual fiber data from these tests. The samples, after testing, were stored in unsealed plastic bags. No effort was made to store them in any particular controlled environment or to place them in an area where they would be free of any handling. In June 1968, these samples were taken out of storage and retested to determine the effect of storage and handling on the fiber properties. This data can be seen in Table XIV. The samples were then tested for atmospheric corrosion as described above. The results of an average of ten tests are summarized below:

	B-119-4-3			B-119-4-5		
	Dia. (μ)	Tens. Str. (psi)	Mod.(E)$_6$ (psix10^6)	Dia. (μ)	Tens. Str. (psi)	Mod.(E)$_6$ (psix10^6)
Tested 12/67	13.4	148,000	21.6	12.1	147,000	22.7
Retested 6/14/68	13.9	124,000	19.7	11.2	104,000	19.3
30 Days in Humidity Chamber. Retested*	12.9	134,000	20.0	11.4	149,000	21.1

* Individual fiber data shown in Table XV.

The analysis of this data shows a loss in strength as a result of storage and handling which may or may not be statistically significant. Certainly the data shows the absence of any deleterious effect due to atmospheric humidity which is known to seriously degrade glass fibers.

We must point out that throughout our process no effort is made to protect our fibers from normal environmental humidities except during the extrusion and collection of unfired fiber. That is to say that perhaps atmospheric humidity has already acted upon the fiber to produce the 150,000 psi tensile strengths noted. We can say then that drastic humidity conditions do not further affect our fiber. However, proof of this would necessitate the formation and testing of a "virgin" fiber; i.e., one that has not been subjected to abrasion by other fibers or atmospheric humidity of any sort during and after drying and calcining. We have chosen to pursue the properties of fibers that would approximate a final produce of commerce.

Tables XIV and XV show both fiber diameter at break and a diameter average of five readings along the one-inch gage length. The average diameters demonstrate once more the uniformity of our fibers with respect to length. This data is not available for Table XIII since it was not being taken at the time of the initial testing of these fibers.

SECTION IV
SUMMARY OF RESULTS

An overall process for the production of a ceramic oxide continuous filament from a B&W fiberizable salt solution has been defined. The process consists of five unit operations:

1. Solution preparation
2. Fiber formation by extrusion-attenuation
3. Fiber collection
4. Fiber drying
5. Calcination to the oxide form.

Through procedural control, identical fiberizable solutions of the same composition can be routinely prepared on a day-to-day basis.

Through control of the following extrusion variables, 8 to 20 micron diameter unfired fibers which are uniform in diameter with respect to length can routinely be produced.

Extrusion pressure - 250 psig
Orifice size - 0.003"
Extrusion viscosity - 200 poise to 800 poise
Extrusion temperature - 80 F to 105 F
Collection rate - 600 to 1000 ft/min.

Implementation of more precise extrusion temperature and extrusion viscosity control so that extrusion can be carried out at the temperature required to obtain optimum solution viscosity (∿300 poise) should allow routine production of uniform 8 micron diameter or less fibers.

No effort has been directed toward collection of continuous lengths of fiber. A maximum of four feet long fiber swatches are currently produced.

Fiber is currently dried only sufficient to allow convenient collection. Fiberizable solutions are about 35% solids on the oxide basis. This must be increased to at least 45% solids content for the fiber to maintain its integrity after initial fiber formation.

The calcination operation determines the chemical and physical structure of the ultimate fiber and thus has a large effect on the tensile strength and modulus of elasticity of the fiber. The affect of the calcination on the fiber

depends on the diameter of the fiber and different calcination procedures are required for large diameter fibers as opposed to small diameter fibers. Relatively large fired fibers have been produced with diameters as low as 12 microns and as high as 40 microns. Through optimization of the fiber firing process, that is, by firing these large diameter fibers at slow rates (25 to 50 F/hr) to 1850 F or 1950 F, fiber strengths were increased to greater than 100,000 psi tensile strength.

Through use of an improved fiber extrusion-attenuation system and 0.002" to 0.004" diameter spinnerettes, green fibers from 6 to 15 microns in diameter could be produced. These green fibers could be fast-fired in a tunnel kiln at 1850 F or 1950 F to 5 to 10 microns diameter and resulted in fibers with 175,000 to 230,000 psi average tensile strength and 22 to 30×10^6 psi average modulus of elasticity.

The tensile strength of the fibers has been found to increase with a decrease in fiber diameter. The modulus of elasticity is independent of fiber diameter.

The fibers lose strength during storage and handling but appear to be unaffected by atmospheric humidity.

SECTION V
RECOMMENDATIONS

The process for creating a continuous ceramic oxide filament from a B&W fiberizable salt solution has been defined. Fiber quality yardsticks have been devised and process variables which affect fiber quality have been determined. Some of these variables have been brought under control, notably most of those in the extrusion operation.

We recommend for future work in this area the development of further process controls according to the studied affects of known and presently unknown process variables on fiber quality. We recommend this be done in a systematic manner by successively bringing each process unit operation under control, backtracking when necessary to a previous operation. Implementation of temperature-viscosity control over the extrusion vessel should permit the production of reproducible and predictable diameter fibers of uniform diameter and the diameter desired.

The production of a constant quality (constant diameter, uniform diameter) green fiber would be followed by an investigation into fiber drying effects and optimization of fiber calcination for that diameter fiber.

1. Fiber Drying
    a. Amount of drying vs strength
    b. Amount of drying vs shrinkage
    c. Drying temperature vs amount of drying
    d. Rate of drying vs strength

Information such as that above should facilitate the design and construction of equipment necessary to the production of continuous lengths of fired fiber.

2. Calcination
    a. Atmosphere
    b. Rate
    c. Temperature

Much data is already available concerning calcining. What remains is to optimize for a constant quality product.

In addition, some additional fiber quality yardsticks should be determined. Fired fiber density and porosity versus calcination variables versus fiber tensile strength and modulus of elasticity should be investigated.

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TABLE I

INDIVIDUAL FIBER DATA SHOWING THE INFLUENCE OF EXTRUSION PRESSURE UPON UNCALCINED FIBER DIAMETER

Batch	Extrusion Pressure (psi)	Fiber Diameter Unfired (microns)	Solution Viscosity (poise)
B-119-1	150	40.0 37.4 27.6 21.6 32.6 31.8 Avg	1740
B-119-1	100	15.6 15.0 27.6 15.4 16.2 22.4 20.6 25.2 11.8 22.2 19.1 Avg	1740
B-119-1	60	28.0 14.4 32.6 26.8 29.4 26.2 Avg	1740
B-119-2	180	40.0 24.6 34.6 22.0 22.6 28.8 Avg	1700
B=119-2	160	15.4 19.0 24.2 27.2 18.4 20.8 Avg	1700

TABLE I (Cont'd.)

Batch No.	Extrusion Pressure (psi)	Fiber Diameter Unfired (microns)	Solution Viscosity (poise)
B-119-2	140	32.4 21.2 25.2 33.6 14.4 25.4 Avg	1700
B-119-2	100	35.2 43.0 16.4 35.6 20.2 30.1 Avg	1700
B-116-1	130	55.8 54.0 54.8 55.4 54.6 54.9 Avg	1200
B-116-1	100	51.0 50.0 41.2 40.4 49.4 46.4 Avg	1200
B-116-1	70	49.6 46.4 48.4 50.8 48.8 Avg	1200

TABLE II

DIAMETER OF UNFIRED FIBERS
PRODUCED IN SEVERAL EXTRUSION EXPERIMENTS

A-900 Composition: 76.8% Al_2O_3, 17.0% SiO_2, 4.7% B_2O_3, 1.6% P_2O_5

	A-900-1 (microns)	A-900-2 (microns)	A-900-3 (microns)
Diameters of Ten Individual Unfired Fibers	16.4	16.4	15.4
	22.0	13.4	15.0
	13.0	18.0	18.4
	14.2	13.6	22.2
	18.8	14.2	14.8
	12.4	15.0	18.8
	13.2	13.6	15.0
	21.6	24.2	14.6
	12.0	16.6	14.0
	15.4	17.4	16.8
	15.9 Avg	16.3 Avg	16.5 Avg

A-900-1 Zenith pump at 450 psig, 0.002" orifice, 340 ft/min

A-900-2 Zenith pump at 450 psig, 0.002" orifice, 480 ft/min

A-900-3 Gas pressure at 275 psig, 0.003" orifice, 600 ft/min

TABLE III

TENSILE STRENGTH AND MODULUS OF ELASTICITY DATA
FOR INDIVIDUAL FIBERS DRIED 60 DAYS IN DESICCATOR
AND CALCINED TO 1750 F (25 F/hr)

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus of (E) (psix10^6)	Diameter (microns)
B-119-9	78.4 Al_2O_3	229,000	22.8	10.4
	16.6 SiO_2	177,000	28.9	8.2
	5.0 B_2O_3	108,000	23.2	8.0
		209,000	27.2	10.4
		46,000	26.7	11.4
		60,000	22.9	9.0
		217,000	27.1	9.0
		204,000	25.0	10.4
		231,000	26.5	9.4
		199,000	25.7	9.2
		168,000 Avg	25.6 Avg	9.5 Avg

TABLE IV

TENSILE STRENGTH AND MODULUS OF ELASTICITY DATA
FOR INDIVIDUAL FIBERS CALCINED AT VARIED RATES

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell.

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus of (E) (psix10^6)	Diameter (microns)	Calcining Rate	Cond. Temp.
B-67-7	77.3 Al_2O_3	14,000	9.9	17.0	1800 F/hr	1860 F
	17.7 SiO_2	85,000	18.9	12.8		
	5.0 B_2O_3	64,000	19.8	10.2		
		69,000	23.1	16.2		
		18,000	6.2	14.4		
		33,000	6.8	12.6		
		63,000	14.7	11.9		
		70,000	41.5	11.4		
		48,000	14.0	14.7		
		23,000	7.9	12.4		
		49,000 Avg	16.3 Avg	13.4 Avg		
B-67-5	77.3 Al_2O_3	24,000	13.6	20.9	800 F/hr	1750 F
	17.7 SiO_2	43,000	22.1	16.8		
	5.0 B_2O_3	50,000	23.3	16.8		
		59,000	19.2	16.5		
		25,000	13.6	15.9		
		32,000	17.9	16.3		
		70,000	20.3	14.8		
		74,000	20.7	14.3		
		55,000	19.7	15.8		
		32,000	15.4	17.9		
		46,000 Avg	18.6 Avg	16.6 Avg		
B-67-10	77.3 Al_2O_3	23,000	17.8	13.6	25 F/hr	1850 F
	17.7 SiO_2	85,000*	18.7	14.6		
	5.0 B_2O_3	26,000	13.1	14.2		
		93,000*	20.4	12.8		
		134,000	26.5	11.4		
		44,000	17.1	14.6		
		104,000	18.2	13.2		
		83,000	19.1	12.8		
		92,000*	19.7	14.0		
		92,000*	19.0	14.0		
		78,000 Avg	19.0 Avg	13.5 Avg		

* Fiber did not break, strength based on full load of 10 grams.

TABLE V

TENSILE STRENGTH AND MODULUS OF ELASTICITY DATA FOR INDIVIDUAL FIBERS CALCINED AT VARIOUS RATES AND TEMPERATURES

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell.

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus of (E) ($psix10^6$)	Diameter (microns)	Calcining Rate	Cond. Temp.
B-116-1	77.1 Al_2O_3	55,000	19.2	18.2	30 F/hr	1750 F
	17.6 SiO_2	36,000	16.0	13.0		
	5.3 B_2O_3	73,000	27.5	15.8		
		75,000	20.9	9.0		
		38,000	20.8	9.6		
		17,000	11.1	12.8		
		38,000	19.2	13.8		
		39,000	27.1	21.6		
		95,000	23.6	12.0		
		23,000	11.9	12.4		
		49,000 Avg	19.3 Avg	13.8 Avg		
B-116-2	77.1 Al_2O_3	56,000	20.8	33.6	30 F/hr	1750 F.
	17.6 SiO_2	86,000	37.2	24.4		
	5.3 B_2O_3	59,000	25.7	16.4		
		74,000	27.8	33.6		
		71,000	22.5	16.6		
		37,000	9.3	33.2		
		54,000	21.7	15.2		
		73,000	19.5	8.4		
		133,000	16.7	7.7		
		53,000	15.9	12.6		
		70,000 Avg	21.7 Avg	20.2 Avg		
B-116-3	77.1 Al_2O_3	27,000	11.3	12.6	35 F/hr	1850 F.
	17.6 SiO_2	76,000	21.7	15.4		
	5.3 B_2O_3	153,000	21.3	9.8		
		124,000	19.4	12.8		
		172,000	24.5	8.8		
		193,000	23.3	9.0		
		205,000	21.8	8.6		
		105,000	20.3	12.6		
		106,000	20.4	11.6		
		104,000	16.7	9.6		
		127,000 Avg	20.1 Avg	11.1 Avg		

TABLE V (Cont'd.)

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus of (E) ($psi \times 10^6$)	Diameter (microns)	Calcining Rate	Cond. Temp.
B-116-4	77.1 Al_2O_3	89,000	19.9	12.0	25 F/hr	1850 F.
	17.6 SiO_2	115,000	21.7	9.9		
	5.3 B_2O_3	92,000	19.0	15.6		
		142,000	23.5	9.8		
		75,000	24.3	12.0		
		111,000	19.6	10.6		
		367,000	----*	6.8		
		104,000	20.5	12.0		
		180,000	21.1	13.0		
		141,000 Avg	21.2 Avg	11.2 Avg		

* Results not included because data exceeds theoretical maximum.

TABLE VI

INDIVIDUAL STRENGTH DATA FOR
FIBERS MADE BY THE EXTRUSION-ATTENUATION METHOD

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, Fibers Calcined 35 F/hr to 1950 F.

Batch No.	Composition (wt %)	Fiber Diameter (microns)	Tensile Strength (psi)	Modulus of (E) ($psix10^6$)
B-119-4-1	78.4% Al_2O_3	16.8	142,000	25.1
	16.6% SiO_2	25.6	85,000	12.0
	5.0% B_2O_3	13.2	234,000	19.8
		13.6	222,000	21.5
		15.0	82,000	21.3
		21.4	73,000	22.7
		9.4	146,000	25.3
		11.6	140,000	22.0
		22.2	106,000	21.8
		20.0	110,000	16.0
		16.9 Avg	134,000 Avg	20.8 Avg
B-119-4-2	78.4% Al_2O_3	12.6	124,000	22.6
	16.6% SiO_2	12.4	147,000	22.7
	5.0% B_2O_3	12.4	140,000	20.0
		13.6	108,000	13.6
		18.6	182,000	19.3
		10.6	121,000	24.3
		15.6	149,000	20.1
		11.2	109,000	23.9
		15.2	69,000	31.8
		18.6	145,000	20.9
		14.1 Avg	129,000 Avg	21.9 Avg
B-119-4-3	78.4% Al_2O_3	17.0	108,000	24.3
	16.6% SiO_2	11.8	175,000	21.1
	5.0% B_2O_3	10.8	140,000	21.3
		11.2	202,000	24.9
		13.0	107,000	22.4
		11.2	222,000	25.8
		19.6	123,000	18.4
		12.8	99,000	20.5
		14.0	169,000	18.0
		12.2	132,000	19.7
		13.4 Avg	148,000 Avg	21.6 Avg

TABLE VI (Cont'd.)

Batch No.	Composition (wt %)	Fiber Diameter (microns)	Tensile Strength (psi)	Modulus of (E) ($psi \times 10^6$)
B-119-4-4	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	13.4	150,000	21.2
		13.4	138,000	18.4
		11.8	213,000	22.8
		16.0	57,000	15.6
		13.6	153,000	21.0
		11.8	222,000	25.9
		18.2	145,000	16.8
		13.0	113,000	22.9
		12.6	145,000	24.2
		12.2	127,000	21.6
		13.5 Avg	146,000 Avg	21.1 Avg
B-119-4-5	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	10.4	156,000	23.7
		9.0	150,000	25.1
		9.8	127,000	23.0
		16.0	118,000	17.6
		9.6	223,000	24.3
		9.6	84,000	22.0
		9.6	167,000	22.7
		16.8	191,000	23.9
		15.0	116,000	23.6
		14.8	137,000	20.7
		12.1 Avg	147,000 Avg	22.7 Avg
B-119-4-6	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	13.2	151,000	19.7
		12.2	132,000	21.9
		14.8	72,000	18.7
		12.0	120,000	20.7
		14.6	116,000	24.1
		12.2	151,000	18.1
		12.8	172,000	20.8
		14.2	156,000	26.3
		16.4	118,000	17.0
		10.8	137,000	21.3
		13.3 Avg	133,000 Avg	20.8 Avg

TABLE VI (Cont'd.)

Batch No.	Composition (wt %)	Fiber Diameter (microns)	Tensile Strength (psi)	Modulus of (E) ($psix10^6$)
B-119-5-1	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	19.2	67,000	21.3
		25.4	77,000	15.4
		16.8	81,000	21.0
		21.6	59,000	21.1
		18.2	127,000	19.3
		20.6	73,000	17.2
		28.2	47,000	23.0
		23.6	101,000	19.5
		25.0	130,000	22.6
		19.6	69,000	19.9
		21.8 Avg	83,000 Avg	20.0 Avg
B-119-5-2	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	14.6	116,000	20.8
		18.2	122,000	18.8
		12.6	88,000	19.9
		15.4	58,000	16.1
		14.4	132,000	14.3
		15.0	151,000	18.2
		23.2	71,000	16.5
		24.6	109,000	17.7
		16.2	107,000	17.9
		16.6	128,000	21.0
		17.1 Avg	108,000 Avg	18.1 Avg
B-119-5-3	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	15.2	114,000	18.7
		20.0	121,000	20.0
		16.6	166,000	23.5
		16.8	165,000	24.1
		18.0	92,000	13.5
		14.0	143,000	21.4
		23.6	93,000	14.4
		16.8	83,000	20.8
		13.6	124,000	20.2
		15.6	54,000	20.9
		17.0 Avg	116,000 Avg	19.8 Avg

TABLE VI (Cont'd.)

Batch No.	Composition (wt %)	Fiber Diameter (microns)	Tensile Strength (psi)	Modulus of (E) ($psix10^6$)
B-119-5-4	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	16.0	70,000	20.6
		15.4	139,000	19.4
		16.6	145,000	20.9
		16.6	126,000	19.1
		14.2	75,000	20.9
		11.6	134,000	20.6
		11.8	166,000	22.0
		13.2	104,000	20.5
		14.8	150,000	20.3
		15.2	78,000	19.0
		14.5 Avg	119,000 Avg	20.3 Avg
B-119-5-5	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	20.6	85,000	19.4
		19.2	120,000	21.7
		11.6	107,000	23.1
		18.2	102,000	20.9
		16.2	143,000	24.8
		18.4	111,000	15.9
		13.6	117,000	20.8
		23.0	68,000	20.2
		17.2	102,000	19.2
		15.0	113,000	26.8
		17.3 Avg	107,000 Avg	21.3 Avg
B-119-5-6	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	18.4	131,000	19.5
		19.7	123,000	18.2
		17.8	95,000	19.7
		16.0	84,000	18.1
		17.0	122,000	20.6
		21.6	131,000	19.6
		23.2	110,000	18.3
		16.2	109,000	21.0
		13.0	65,000	19.1
		19.6	150,000	19.0
		18.3 Avg	112,000 Avg	19.3 Avg

TABLE VII

AVERAGE TENSILE STRENGTH, MODULUS OF ELASTICITY AND X-RAY DIFFRACTION DATA FOR EXTRUDED AND FIRED FIBERS CALCINED IN VARIOUS WAYS

(0.004" diameter orifice)

Batch No.	Calcination Rate	Calcination Temp.	Diameter (microns*)	Tens. Str. (avg psi*)	Modulus$_6$(E) (psix10^6*)	Crystalline Const. X-ray Major	Crystalline Const. X-ray Minor	Crystalline Size of Mullite (angstrom)
B-153-3	25 F/hr	1950 F	8.0	68,000	26.8	Mullite	γ-Al_2O_3	380
B-153-2	25 F/hr	1950 F	9.1	78,000	22.8	"	"	324
B-153-4	25 F/hr	1950 F	7.8	85,000	19.5	"	"	232
B-153-1	25 F/hr	1950 F	17.3	95,000	20.8	"	"	332
B-153-5	25 F/hr	1950 F	6.0	115,000	27.0	"	"	328
B-153-6	25 F/hr	1950 F	8.7	137,000	26.1	"	"	276
B-153-9	25 F/hr	1950 F	11.3	175,000	30.8	"	"	255
B-153-8	1800 F/hr	1950 F*	8.4	183,000	29.4	Non-Cryst.	Mullite γ-Al_2O_3	178
B-168-1	25 F/hr	1850 F	10.4	54,000	22.3	----	----	---
B-168-2	25 F/hr	1850 F	8.7	56,000	18.0	Non-Cryst.	γ-Al_2O_3	Mullite pattern too weak to determine crystalline size.
B-168-3	25 F/hr	1850 F	6.0	111,000	25.6	" "	" "	
B-168-7	1600 F/hr	1850 F (steam)**	6.6	157,000	22.9	" "	Mullite γ-Al_2O_3	
B-168-6	1600 F/hr	1850 F (steam)	5.3	159,000	21.0	" "	" "	
B-168-8	1600 F/hr	1850 F (steam)	9.6	199,000	23.6	----	----	
B-168-11***	1600 F/hr	1850 F**	7.8	195,000	20.8	Non-Cryst.	Mullite γ-Al_2O_3	
B-168-5	1600 F/hr	1850 F**	5.9	227,000	23.1	" "	" "	

* Individual fiber data shown in Table VIII.
** Twelve minute soak time at temperature.
*** This sample produced using 0.003" diameter orifice.

TABLE VIII

TENSILE STRENGTH AND MODULUS OF ELASTICITY DATA FOR INDIVIDUAL FIBERS CALCINED UNDER VARIOUS CONDITIONS

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell.

Batch No. & Orifice Size	Composition (wt %)	Tens. Str. (psi)	Modulus (E) (psix10^6)	Diameter (microns)	Calcination Rate	Calcination Temp.
B-153-3	78.4 Al_2O_3	68,000	21.8	8.0	25 F/hr	1950 F
0.004"	16.6 SiO_2	46,000	20.8	8.2		
	5.0 B_2O_3	66,000	23.6	6.6		
		52,000	26.5	6.0		
		49,000	22.3	7.8		
		49,000	33.2	13.6		
		66,000	20.4	12.4		
		19,000	24.8	10.8		
		44,000	33.3	12.8		
		74,000	41.2	12.8		
		53,000 Avg	26.8 Avg	9.9 Avg		
B-153-2	78.4 Al_2O_3	93,000	23.2	10.0	25 F/hr	1950 F
0.004"	16.6 SiO_2	52,000	----	11.2		
	5.0 B_2O_3	92,000	24.6	8.4		
		105,000	22.2	8.4		
		18,000	----	10.4		
		60,000	22.5	8.4		
		119,000	26.5	7.4		
		90,000	22.9	8.8		
		93,000	18.8	9.4		
		59,000	21.3	8.8		
		78,000 Avg	22.8 Avg	9.1 Avg		
B-153-4*	78.4 Al_2O_3	130,000	26.5	7.2	25 F/hr	1950 F
0.004"	16.6 SiO_2	49,000	22.3	6.0		
	5.0 B_2O_3	101,000	18.5	6.8		
		58,000	12.2	11.4		
		88,000	17.9	7.4		
		85,000 Avg	19.5 Avg	7.8 Avg		

* Only five individual tests made on these batches.

TABLE VIII (Cont'd.)

Batch No. & Orifice Size	Composition (wt %)	Tens. Str. (psi)	Modulus (E) ($psi \times 10^6$)	Diameter (microns)	Calcination Rate	Calcination Temp.
B-153-1	78.4 Al_2O_3	104,000	20.9	18.0	25 F/hr	1950 F
0.004"	16.6 SiO_2	95,000	20.7	17.6		
	5.0 B_2O_3	26,000	25.4	17.2		
		121,000	19.6	15.8		
		120,000	16.3	17.4		
		90,000	17.1	17.2		
		90,000	22.2	17.8		
		120,000	23.1	17.2		
		90,000	22.2	17.2		
		94,000	20.4	17.2		
		95,000 Avg	20.8 Avg	17.3 Avg		
B-153-5*	78.4 Al_2O_3	86,000	22.0	6.4	25 F/hr	1950 F
0.004"	16.6 SiO_2	112,000	35.7	5.2		
	5.0 B_2O_3	170,000	34.1	5.0		
		125,000	27.2	6.8		
		83,000	15.8	6.8		
		115,000 Avg	27.0 Avg	6.0 Avg		
B-153-6	78.4 Al_2O_3	132,000	27.6	6.0	25 F/hr	1950 F
0.004"	16.6 SiO_2	185,000	29.7	8.0		
	5.0 B_2O_3	179,000	30.4	8.0		
		163,000	27.5	8.6		
		75,000	25.0	8.2		
		141,000	20.5	8.8		
		105,000	29.8	7.6		
		140,000	35.9	12.6		
		146,000	19.0	9.0		
		105,000	15.9	10.2		
		137,000 Avg	26.1 Avg	8.7 Avg		
B-153-9	78.4 Al_2O_3	41,000	16.3	12.2	25 F/hr	1950 F
0.004"	16.6 SiO_2	177,000	20.5	12.4		
	5.0 B_2O_3	263,000	44.8	11.2		
		140,000	23.1	24.0		
		97,000	25.4	9.4		
		216,000	30.0	8.0		
		113,000	27.8	7.8		
		258,000	54.4	6.8		
		275,000	43.7	8.2		
		169,000	22.2	12.6		
		175,000 Avg	30.8 Avg	11.3 Avg		

* Only five individual tests made on these batches.

TABLE VIII (Cont'd.)

Batch No. & Orifice Size	Composition (wt %)	Tens. Str. (psi)	Modulus$_6$(E) (psix10^6)	Diameter (microns)	Calcination Rate	Calcination Temp.
B-153-8	78.4 Al_2O_3	168,000	23.7	12.6	1800 F/hr	1950 F**
		143,000	28.9	13.0		
0.004"	16.6 SiO_2	210,000	33.2	6.0		
	5.0 B_2O_3	225,000	31.7	7.6		
		181,000	25.0	7.4		
		198,000	34.9	8.4		
		155,000	30.0	5.2		
		193,000	24.4	8.2		
		140,000	39.0	6.8		
		219,000	23.4	8.6		
		183,000 Avg	29.4 Avg	8.4 Avg		
B-168-1*	74.7 Al_2O_3	28,000	14.5	10.2	25 F/hr	1850 F
		36,000	24.1	22.4		
0.004"	20.4 SiO_2	38,000	23.5	7.0		
	4.9 B_2O_3	10,000	23.5	5.8		
		160,000	27.0	8.8		
		54,000 Avg	22.3 Avg	10.8 Avg		
B-168-2*	74.7 Al_2O_3	42,000	26.1	6.4	25 F/hr	1850 F
		34,000	----	6.8		
0.004"	20.4 SiO_2	107,000	15.3	9.6		
	4.9 B_2O_3	67,000	12.6	14.2		
		28,000	----	6.6		
		56,000 Avg	18.0 Avg	8.7 Avg		
B-168-3	74.7 Al_2O_3	168,000	27.9	5.4	25 F/hr	1850 F
		34,000	----	5.8		
0.004"	20.4 SiO_2	130,000	27.0	5.8		
	4.9 B_2O_3	173,000	32.4	6.2		
		170,000	27.2	5.4		
		92,000	27.1	6.4		
		107,000	17.1	5.6		
		54,000	21.0	7.0		
		33,000	27.6	6.2		
		145,000	23.1	6.6		
		111,000 Avg	25.6 Avg	6.0 Avg		

* Only five individual tests made on these batches.
** Twelve minute soak time at temperature.

TABLE VIII (Cont'd.)

Batch No. & Orifice Size	Composition (wt %)	Tens. Str. (psi)	Modulus (E) ($psix10^6$)	Diameter (microns)	Calcination Rate	Calcination Temp.
B-168-7	74.7 Al_2O_3	211,000	25.5	5.6	1600 F/hr	1850 F
0.004"	20.4 SiO_2	257,000	24.2	6.4		(steam)**
	4.9 B_2O_3	321,000	31.6	5.2		
		131,000	22.4	7.2		
		138,000	21.7	6.6		
		119,000	22.2	7.6		
		121,000	19.1	8.0		
		128,000	22.4	6.2		
		92,000	20.7	6.0		
		51,000	19.1	6.8		
		157,000 Avg	22.9 Avg	6.6 Avg		
B-168-6	74.7 Al_2O_3	109,000	15.4	5.6	1600 F/hr	1850 F
0.004"	20.4 SiO_2	203,000	29.2	4.2		(steam)
	4.9 B_2O_3	145,000	21.1	5.2		
		151,000	19.0	5.0		
		206,000	22.2	5.2		
		186,000	17.6	5.8		
		233,000	21.2	4.5		
		139,000	23.8	6.8		
		56,000	20.5	4.6		
		160,000	20.1	6.0		
		159,000 Avg	21.0 Avg	5.3 Avg		
B-168-8	74.7 Al_2O_3	181,000	26.1	7.2	1600 F/hr	1850 F
0.004"	20.4 SiO_2	128,000	19.4	26.6		(steam)
	4.9 B_2O_3	243,000	23.8	6.2		
		145,000	18.8	8.4		
		119,000	16.9	11.2		
		258,000	25.0	6.8		
		199,000	22.8	6.0		
		272,000	30.0	6.0		
		242,000	29.3	8.2		
		199,000 Avg	23.6 Avg	9.6 Avg		

** Twelve minute soak time at temperature.

TABLE VIII (Cont'd.)

Batch No. & Orifice Size	Composition (wt %)	Tens. Str. (psi)	Modulus$_6$(E) (psix10^6)	Diameter (microns)	Calcination Rate	Calcination Temp.
B-168-11	74.7 Al_2O_3	235,000	25.6	6.8	1600 F/hr	1850 F**
0.003"	20.4 SiO_2	234,000	32.3	8.2		
	4.9 B_2O_3	179,000	17.7	8.0		
		226,000	23.7	6.8		
		189,000	22.9	7.2		
		234,000	19.6	5.6		
		250,000	23.3	5.8		
		50,000	7.6	16.0		
		191,000	16.8	7.2		
		157,000	18.5	6.8		
		195,000 Avg	20.8 Avg	7.8 Avg		
B-168-5	74.7 Al_2O_3	195,000	19.3	5.8	1600 F/hr	1850 F**
0.004"	20.4 SiO_2	215,000	23.1	5.8		
	4.9 B_2O_3	221,000	23.9	6.4		
		272,000	26.0	5.2		
		225,000	22.7	5.8		
		189,000	28.8	5.8		
		189,000	27.2	5.8		
		239,000	22.3	6.4		
		272,000	25.7	6.2		
		259,000	12.4	5.8		
		227,000 Avg	23.1 Avg	5.9 Avg		

** Twelve minute soak time at temperature.

TABLE IX

TENSILE STRENGTH AND MODULUS OF ELASTICITY DATA
FOR INDIVIDUAL FIBERS CALCINED TO 1950 F AND SOAKED 60 HOURS

(0.006" diameter orifice)

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "B" cell.

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus (E) ($psi \times 10^6$)	Diameter (microns)
B-152-A1	78.2 Al_2O_3	81,000	18.6	29.6
	16.8 SiO_2	95,000	18.1	29.6
	5.0 B_2O_3	75,000	17.3	30.8
		106,000	15.7	32.6
		99,000	17.7	30.2
		147,000	17.8	30.2
		102,000	17.6	30.8
		112,000	18.1	30.8
		97,000	16.0	29.2
		101,000	17.7	31.2
		102,000 Avg	17.5 Avg	30.5 Avg
B-152A2	78.2 Al_2O_3	97,000	18.3	35.8
	16.8 SiO_2	101,000	17.2	36.0
	5.0 B_2O_3	72,000	18.9	35.0
		124,000	17.5	36.0
		98,000	18.0	36.8
		83,000	17.8	36.2
		92,000	18.0	36.0
		60,000	18.3	36.8
		104,000	17.4	38.0
		65,000	17.0	35.8
		90,000 Avg	17.8 Avg	36.2 Avg
B-153-A1	78.4 Al_2O_3	100,000	17.5	26.8
	16.6 SiO_2	98,000	18.4	34.2
	5.0 B_2O_3	124,000	19.5	22.0
		70,000	20.9	24.6
		94,000	17.2	34.0
		56,000	18.7	25.6
		83,000	18.9	26.8
		91,000	20.9	18.0
		101,000	19.1	19.6
		68,000	19.9	25.0
		89,000 Avg	19.1 Avg	25.7 Avg

TABLE IX (Cont'd.)

Batch No.	Composition (wt %)	Tensile Strength (psi)	Modulus (E) ($psix10^6$)	Diameter (microns)
B-153-A2	78.4 Al_2O_3 16.6 SiO_2 5.0 B_2O_3	35,000	18.0	29.6
		49,000	18.8	28.6
		87,000	16.8	30.4
		50,000	17.8	36.8
		44,000	17.9	29.0
		70,000	20.6	28.8
		85,000	18.4	27.8
		74,000	19.3	28.6
		83,000	20.3	28.8
		47,000	12.9	36.0
		62,000 Avg	18.1 Avg	30.4 Avg

TABLE X

INDIVIDUAL TENSILE STRENGTH DATA FOR INSULATION FIBERS MADE BY SPINNING

Test Conditions: Daytronic Tester, 1/2-inch Gage Length, 0.05"/min Crosshead Speed.

Batch No.	Diameter (microns)	Tensile Strength (psi)
A-729	6.2	145,000
	7.4	105,000
	3.8	265,000
	5.2	310,000
	5.6	175,000
	3.4	510,000
	4.0	170,000
	4.0	135,000
	5.6	135,000
	4.2	220,000
	4.9 Avg	217,000 Avg
A-758	6.2	245,000
	8.4	190,000
	5.4	255,000
	6.2	125,000
	5.6	230,000
	4.4	365,000
	6.0	200,000
	3.6	253,000
	5.0	145,000
	5.8	240,000
	5.7 Avg	225,000 Avg
A-730	4.2	258,000
	3.4	583,000
	4.0	228,000
	5.8	214,000
	5.4	215,000
	4.2	290,000
	3.8	215,000
	3.8	302,000
	2.0	425,000
	3.8	580,000
	4.0 Avg	331,000 Avg

TABLE XI

INDIVIDUAL FIBER DATA FOR FIBERS EXTRUDED UNDER VARIOUS CONDITIONS AND SLOW FIRED TO 1950 F

(Calculations using fiber diameter measured at break)

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell

Batch No.	Composition (wt %)	Tens. Strength (psi)	Modulus (E) (psix10^6)	Diam. at Break (microns)
A-900-1	76.8 Al_2O_3	83,000	27.7	9.2
	17.0 SiO_2	179,000	26.3	11.2
	4.7 B_2O_3	83,000	25.2	14.0
	1.6 P_2O_5	123,000	24.0	14.8
		146,000	24.5	13.6
		33,000	----	9.6
		134,000	24.7	10.4
		83,000	22.5	14.4
		135,000	26.1	10.6
		87,000	24.4	10.8
		109,000 Avg	25.1 Avg	11.9 Avg
A-900-2	76.8 Al_2O_3	152,000	22.9	14.8
	17.0 SiO_2	173,000	24.5	15.0
	4.7 B_2O_3	94,000	23.6	10.3
	1.6 P_2O_5	79,000	21.9	9.8
		55,000	23.5	24.6
		106,000	23.8	10.2
		124,000	24.6	14.6
		59,000	18.1	12.6
		54,000	18.4	10.9
		118,000	22.9	14.2
		101,000 Avg	22.4 Avg	13.7 Avg
A-900-3	76.8 Al_2O_3	93,000	23.7	13.6
	17.9 SiO_2	156,000	22.3	11.0
	4.7 B_2O_3	161,000	21.2	9.6
	1.6 P_2O_5	178,000	23.7	14.4
		164,000	23.6	12.2
		157,000	25.1	12.0
		30,000	18.7	24.6
		98,000	24.0	21.6
		137,000	25.6	11.8
		131,000	21.0	22.4
		131,000 Avg	22.9 Avg	15.3 Avg

TABLE XI (Cont'd.)

Batch No.	Composition (wt %)	Tens. Strength (psi)	Modulus$_6$(E) (psix10^6)	Diam. at Break (microns)
A-900-4	76.8 Al_2O_3	67,000	21.4	14.8
	17.0 SiO_2	80,000	23.6	8.4
	4.7 B_2O_3	54,000	----	7.6
	1.6 P_2O_5	34,000	16.8	23.6
		79,000	25.1	8.0
		23,000	15.1	24.0
		55,000	22.0	10.4
		119,000	23.8	8.6
		90,000	24.7	23.6
		43,000	----	9.6
		64,000 Avg	21.6 Avg	13.9 Avg

TABLE XII

INDIVIDUAL FIBER DATA FROM TABLE XI RECALCULATED USING AVERAGE OF FIVE EQUIDISTANT FIBER DIAMETER MEASUREMENTS FOR EACH ONE-INCH TEST SECTION

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, "A" cell

Batch No.	Tensile Strength (psi)	Modulus (E) ($psix10^6$)	Diameter (microns) 1	2	3	4	5	Avg
A-900-1	68,000	22.5	10.4	10.2	10.2	10.0	10.2	10.2
	161,000	23.7	11.8	11.6	12.2	11.6	11.9	11.8
	86,000	26.0	13.9	13.8	13.8	13.8	13.8	13.8
	122,000	24.0	14.8	15.0	14.7	14.9	14.8	14.8
	146,000	24.5	13.6	13.8	13.4	13.4	13.9	13.6
	31,000	----	9.8	9.7	10.1	10.1	9.8	9.9
	124,000	22.9	10.9	11.0	11.0	10.6	10.3	10.8
	88,000	23.8	14.0	13.6	13.9	13.9	14.4	14.0
	135,000	26.0	10.9	10.6	10.4	10.6	10.7	10.6
	81,000	22.6	11.4	11.1	11.2	11.2	11.2	11.2
	104,000 Avg	24.0 Avg						12.1 Avg
A-900-2	150,000	22.6	14.8	14.8	14.6	15.1	15.0	14.9
	162,000	23.0	15.4	15.6	15.4	15.6	15.4	15.5
	83,000	20.7	11.0	10.9	11.0	10.6	11.3	11.0
	75,000	20.6	9.8	10.1	10.3	10.2	9.9	10.1
	63,000	22.4	25.2	25.3	25.2	25.4	25.0	25.2
	106,000	23.8	11.1	11.1	11.2	11.2	10.2	10.2
	109,000	21.5	15.6	15.6	15.6	15.7	15.5	15.6
	60,000	18.7	12.4	12.5	12.5	12.4	12.2	12.4
	48,000	16.5	11.4	11.5	11.6	11.6	11.3	11.5
	116,000	22.6	14.6	14.3	14.6	14.2	14.0	14.3
	96,000 Avg	21.2 Avg						14.1 Avg
A-900-3	88,000	22.4	14.0	13.9	14.0	13.9	14.0	14.0
	156,000	22.3	11.1	11.0	11.0	11.2	11.0	11.0
	155,000	20.3	9.6	9.8	9.8	9.9	9.8	9.8
	164,000	21.8	15.2	15.2	15.0	14.9	14.7	15.0
	159,000	22.8	11.5	12.9	12.5	12.3	12.8	12.4
	147,000	23.5	12.4	12.5	12.4	12.5	12.2	12.4
	31,000	19.7	24.0	24.1	24.0	24.2	23.8	23.2
	85,000	20.8	22.7	23.2	23.8	23.6	22.6	23.2
	118,000	22.1	12.4	12.5	12.8	12.8	13.1	12.7
	131,000	21.0	22.4	22.3	22.6	23.2	21.6	22.4
	123,000 Avg	21.7 Avg						15.7 Avg

TABLE XII (Cont'd.)

Batch No.	Tensile Strength (psi)	Modulus$_6$ (E) (spix10^6)	Diameter (microns) 1	2	3	4	5	Avg
A-900-4	67,000	21.7	14.9	14.8	14.8	14.6	14.5	14.7
	67,000	19.7	9.0	9.2	9.2	9.1	9.2	9.2
	45,000	----	8.2	8.1	8.3	8.4	8.5	8.3
	34,000	17.1	23.2	23.6	23.6	23.1	23.6	23.4
	65,000	20.8	8.6	8.8	9.0	9.0	8.8	8.8
	22,000	14.7	24.0	24.3	24.2	24.3	24.5	24.3
	50,000	20.0	11.0	11.1	10.7	10.9	11.0	10.9
	113,000	22.8	8.8	8.9	8.5	8.9	9.0	8.8
	89,000	24.5	24.4	23.7	23.9	23.4	22.9	23.7
	40,000	----	10.7	10.0	10.6	9.6	9.9	10.0
	59,000 Avg	20.1 Avg						14.2 Avg

TABLE XIII

INDIVIDUAL STRENGTH DATA FOR
FIBERS MADE BY THE EXTRUSION-ATTENUATION METHOD

Tested December 1967

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min, Fibers Calcined 35 F/hr to 1950 F

Batch No.	Calculated Composition	Diameter at Break (microns)	Tens. Str.* (psi)	Modulus$_6$(E)* (psix10^6)
B-119-4-3	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	17.0	108,000	24.3
		11.8	175,000	21.1
		10.8	140,000	21.3
		11.2	202,000	24.9
		13.0	107,000	22.4
		11.2	222,000	25.8
		19.6	123,000	18.4
		12.8	99,000	20.5
		14.0	169,000	18.0
		12.2	132,000	19.7
		13.4 Avg	148,000 Avg	21.6 Avg
B-119-4-5	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	10.4	156,000	23.7
		9.0	150,000	25.1
		9.8	127,000	23.0
		16.0	118,000	17.6
		9.6	223,000	24.3
		9.6	84,000	22.0
		9.6	167,000	22.7
		16.8	191,000	23.9
		15.0	116,000	23.6
		14.8	137,000	20.7
		12.1 Avg	147,000 Avg	22.7 Avg

* As calculated using fiber diameter at break.

TABLE XIV

INDIVIDUAL STRENGTH DATA FOR
FIBERS MADE BY THE EXTRUSION-ATTENUATION METHOD

Tested December 1967, Stored and Retested 7/15/68

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min

Batch No.	Calculated Composition	Diameter (microns) at break	Diameter (microns) Avg of 5	Tens. Str.* (psi)	Modulus$_6$(E)* (psix10^6)
B-119-4-3	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	10.0	9.9	165,000	18.4
		19.8	19.0	101,000	18.2
		11.2	11.4	86,000	17.6
		12.6	13.5	95,000	20.7
		13.0	14.3	241,000	22.8
		12.7	13.0	139,000	20.6
		21.2	21.6	119,000	18.7
		11.0	11.1	113,000	19.4
		13.6	14.1	70,000	19.1
		14.0	14.6	107,000	21.1
		13.9 Avg	14.2 Avg	124,000 Avg	19.7 Avg
B-119-4-5	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	9.4	9.7	149,000	19.8
		11.0	11.2	90,000	18.9
		10.0	10.0	112,000	19.2
		10.0	10.2	84,000	20.5
		14.4	14.8	145,000	20.6
		13.6	13.1	87,000	18.2
		13.3	13.3	79,000	13.0
		9.9	10.0	118,000	27.6
		10.2	10.2	73,000	17.1
		10.0	9.8	107,000	18.4
		11.2 Avg	11.2 Avg	104,000 Avg	19.3 Avg

* As calculated using fiber diameter at break.

TABLE XV

INDIVIDUAL STRENGTH DATA FOR
FIBERS MADE BY THE EXTRUSION-ATTENUATION METHOD

Tested December 1967, Stored Till 6/14/68, Sealed in Humidity Chamber 6/14/68, Retested 7/19/68

Test Conditions: Instron Tester, 1-inch Gage Length, 0.02"/min Crosshead Speed, Chart Speed 20"/min

Batch No.	Calculated Composition	Diameter (microns) at break	Diameter (microns) Avg of 5	Tens. Str.* (psi)	Modulus$_6$ (E)* (psix10^6)
B-119-4-3	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	12.8	12.9	172,000	19.9
		10.6	11.0	200,000	21.6
		12.6	12.6	122,000	18.7
		12.7	12.7	149,000	19.8
		11.0	11.4	42,000	13.8
		15.8	16.0	136,000	20.2
		13.6	13.6	169,000	20.2
		11.0	11.2	153,000	21.6
		16.6	17.5	131,000	21.5
		12.9	13.2	69,000	23.0
		12.9 Avg	13.2 Avg	134,000 Avg	20.0 Avg
B-119-4-5	78.4% Al_2O_3 16.6% SiO_2 5.0% B_2O_3	15.2	15.4	171,000	25.6
		11.0	11.0	132,000	20.3
		12.4	12.4	121,000	21.2
		8.2	8.8	164,000	22.0
		11.6	11.6	144,000	20.1
		12.7	12.7	157,000	20.7
		9.3	9.4	176,000	19.8
		12.6	13.2	97,000	20.3
		8.4	9.4	164,000	23.8
		12.4	12.4	164,000	16.8
		11.4 Avg	11.6 Avg	149,000 Avg	21.1 Avg

* As calculated using fiber diameter at break.

APPENDIX A

RELIABILITY OF THE MONOFILAMENT FIBER ESTIMATES

Since we were noticing measured variations in diameter, tensile strength and modulus of elasticity within given batches of calcined fibers, a study was made to determine the reliability of these measurements. That is, we wanted to determine the confidence level for average measurements as related to the properties of the entire batch of fibers. The previously tabulated data (see Table VI) for the B-119-40 and B-119-50 series were used for this study.

The reliability of an estimated parameter depends on the number of measurements that are obtained and the variability that is recognized between the measurements within a given sample. For this reason, there was concern as to the accuracy or reliability of the estimates of certain physical properties of the monofilament fibers based on a fixed number of measured samples. These physical properties are identified as the average fiber diameter, tensile strength and modulus of elasticity.

The ascertainment of the accuracy of the averages is based on the measurements acquired for experimental runs B-119-40 and B-119-50. In each of these runs, 60 fibers were used, their diameters were measured and the fibers were tested for tensile strength and modulus of elasticity. To assure a representative sample of the manufactured fibers, each batch was broken up into six distinct groups (a group corresponding with time of production) and ten fibers were selected at random from each group. The derivation of the estimates, averages and measures of variability, and the determination of the reliability of these measures follows.

Reliability Measures

The frequency distributions of the fiber diameter, tensile strength and modulus of elasticity for the B-119-40 and B-119-50 batches were also made. The averages and standard deviations (measures of dispersion) calculated for these distributions are:

Run No. B-119-40	Average	Standard Deviation
Diameter (microns)	13.96	3.43
Tensile Strength ($psix10^3$)	139.47	40.68
Modulus ($psix10^6$)	21.48	3.29

Run No. B-119-50	Average	Standard Deviation
Diameter (microns)	17.67	3.74
Tensile Strength ($psix10^3$)	107.38	30.32
Modulus ($psix10^6$)	19.80	2.45

The standard deviation(s) defines the dispersion of the measurements from the averages. A ± 1s will include approximately 68% of the measurements, a ± 2s will include approximately 95% of the measurements and a ± 3s will include approximately 99% of the measurements from the calculated average.

Taking into consideration the variabilities encountered in the two experimental runs, and as shown above, it was possible to estimate the reliability or the degree of accuracy with which the averages are estimated for various sample sizes. These results are displayed for the diameter, tensile strength and modulus of elasticity in the form of reliability curves in Figures A1 to A3 respectively. Accordingly, it is possible to determine the number of fibers that would have to be measured to obtain a desired accuracy in the calculated average at a specified level of confidence. Or, conversely, it is possible to establish the accuracy of the average at a specified confidence level for a given sample size. For example, with a sample size of 10 fibers and a confidence level of 90%, the accuracy of the calculated fiber diameter will be within a ± 1.8 microns, the average tensile strength within a ± 18,500 psi and the modulus of elasticity within a ± 1,400,000 psi.

Sample Size

In determining the size of the sample required for estimating an average, two factors were considered; 1) the allowable error that could be tolerated, and, 2) the amount of risk (α) we are willing to take in that the estimated mean will not exceed the true mean by the allowable error. Knowing the confidence limits for an estimated average is:[1]

(1) N.L. Johnson and F.C. Leone, Statistics and Experimental Design, John Wiley & Sons, New York 1964, Volume 1, pp 187-192.

$$\Pr\left(\bar{x} - u_\alpha \sigma/\sqrt{n} < \mu < \bar{x} + u_\alpha \sigma/\sqrt{n}\right) = 1-\alpha \quad (1)$$

where:

$\bar{x}$ = is the calculated or estimated average

u_α = the number of standard deviations from a given average for a predetermined probability

σ = the population standard deviation

n = the sample size

μ = the true population average

$1-\alpha$ = confidence level

it is possible to determine the sample size. Rearranging the terms in (1) we obtain

$$\Pr\left(- u_\alpha \sigma/\sqrt{n} < \mu-\bar{x} < + u_\alpha \sigma/\sqrt{n}\right) = 1-\alpha \quad (2)$$

The allowable error we are willing to tolerate is the difference between the true population mean and the estimated mean, or $\mu-\bar{x}$. Let this quantity equal L. Then

$$L = \pm u_\alpha \sigma/\sqrt{n}$$

or, the required sample size is

$$n = \left(\frac{u_\alpha \sigma}{L}\right)^2 \quad (3)$$

The values for u_α could be obtained from tables defining the percentage points of a normal distribution.

The population standard (σ) deviation was estimated with a sample standard deviation. Since we were dealing with two sets of data (B-119-40 and B-119-50), each set provided an estimate for this parameter, s_{40} and s_{50}. It is possible to pool these estimates and obtain an overall estimate of the standard deviation (s_p) for the two samples by using the following relationship:

$$s_p = \sqrt{\frac{(n_{40}-1)\, s^2_{40} + (n_{50}-1)\, s^2_{50}}{n_{40} + n_{50} - 2}} \quad (4)$$

where n_{40} and n_{50} represent the actual sample size for the B-119-40 and B-119-50 fibers. Substituting this value in (3), we obtain

$$n = \left[\frac{u_\alpha s_p}{L}\right]^2 \tag{5}$$

The reliability curves were generated by calculating s_p, obtaining u_α for a fixed confidence level and varying L, the difference that could be tolerated between the estimated average and the true population average.

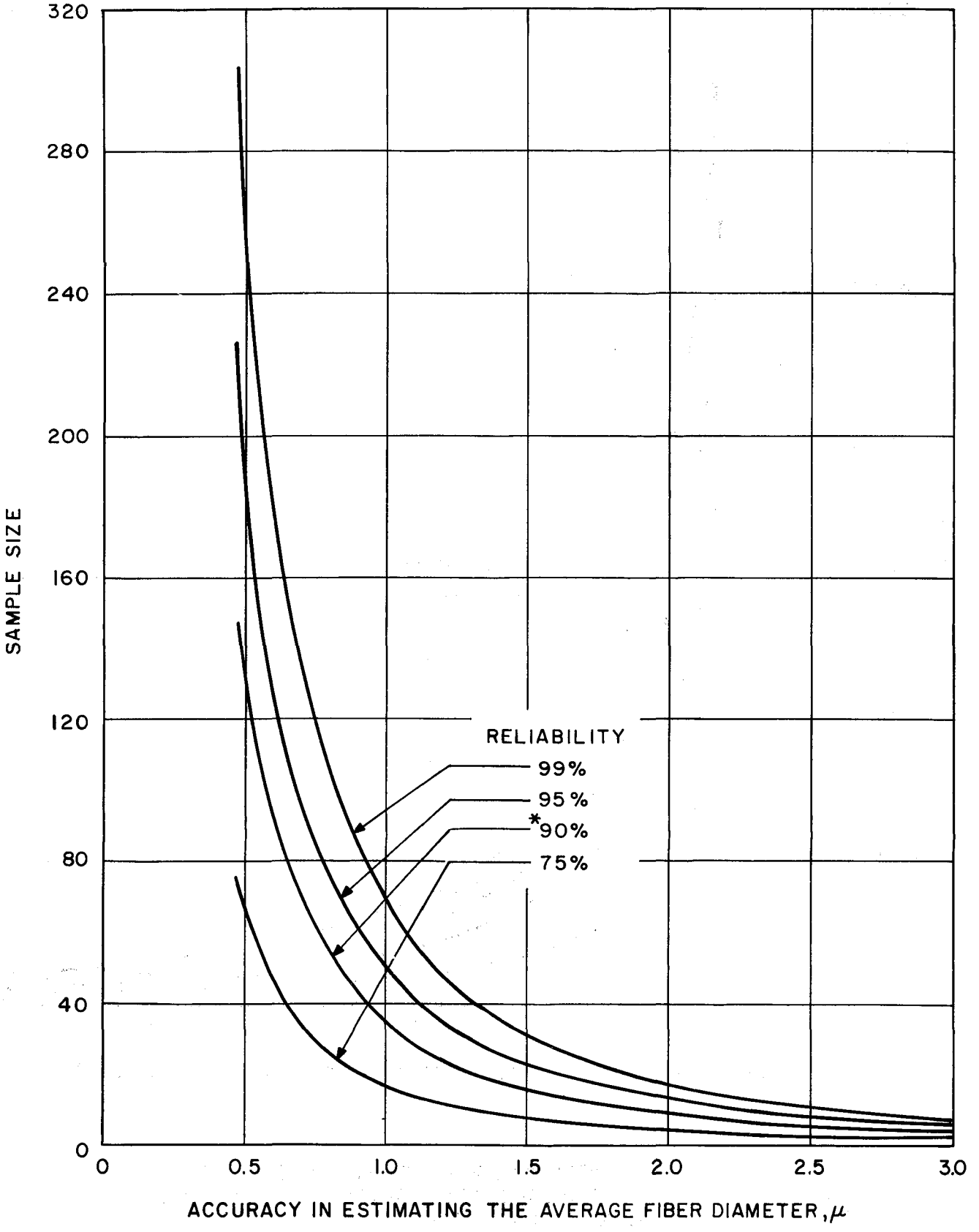

FIGURE A1. RELIABILITY CURVES FOR DETERMINING SAMPLE SIZE REQUIRED FOR ESTIMATING AVERAGE MONOFILAMENT FIBER DIAMETER

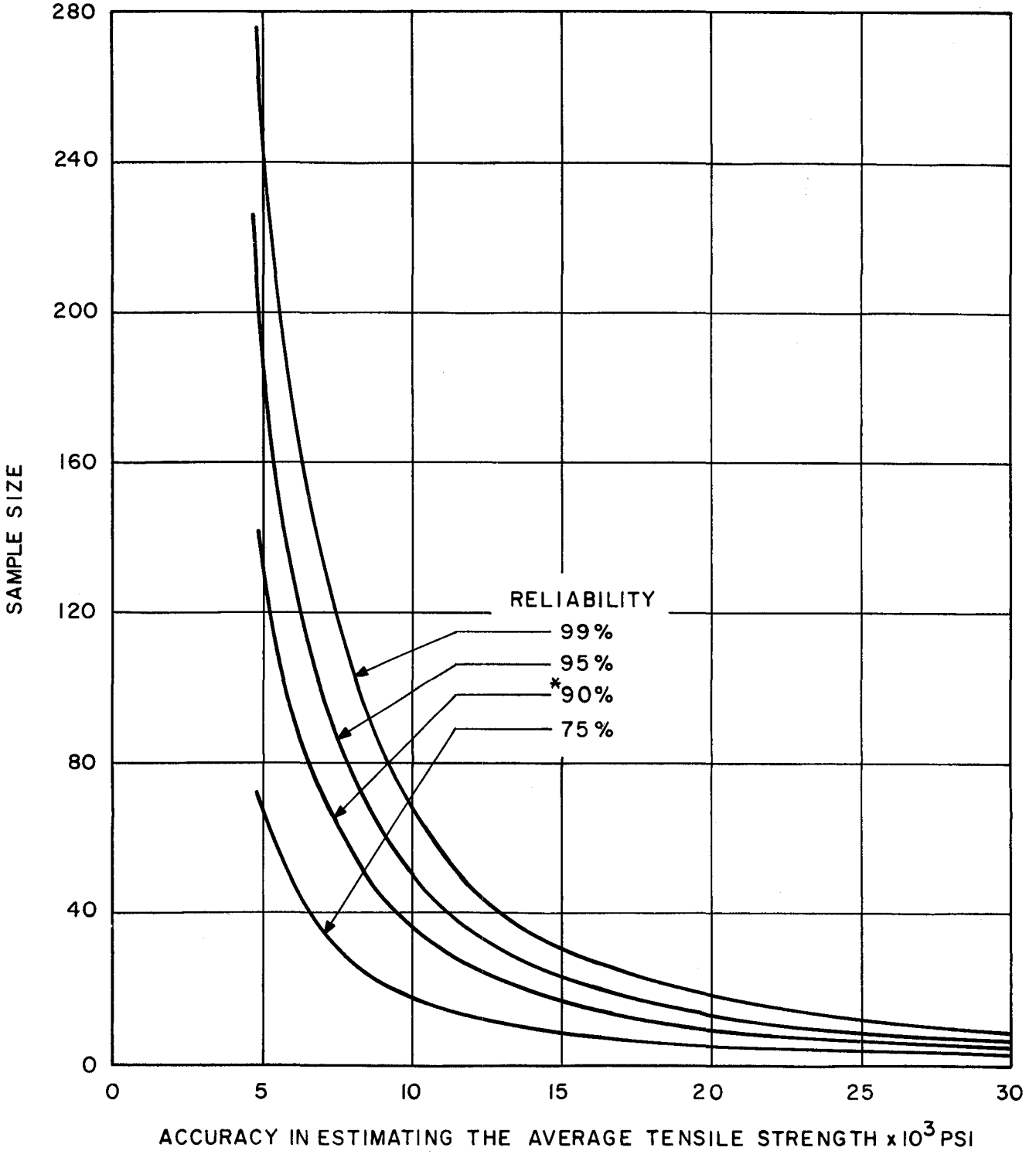

FIGURE A2. RELIABILITY CURVES FOR DETERMINING SAMPLE SIZE REQUIRED FOR ESTIMATING AVERAGE MONOFILAMENT FIBER TENSILE STRENGTH

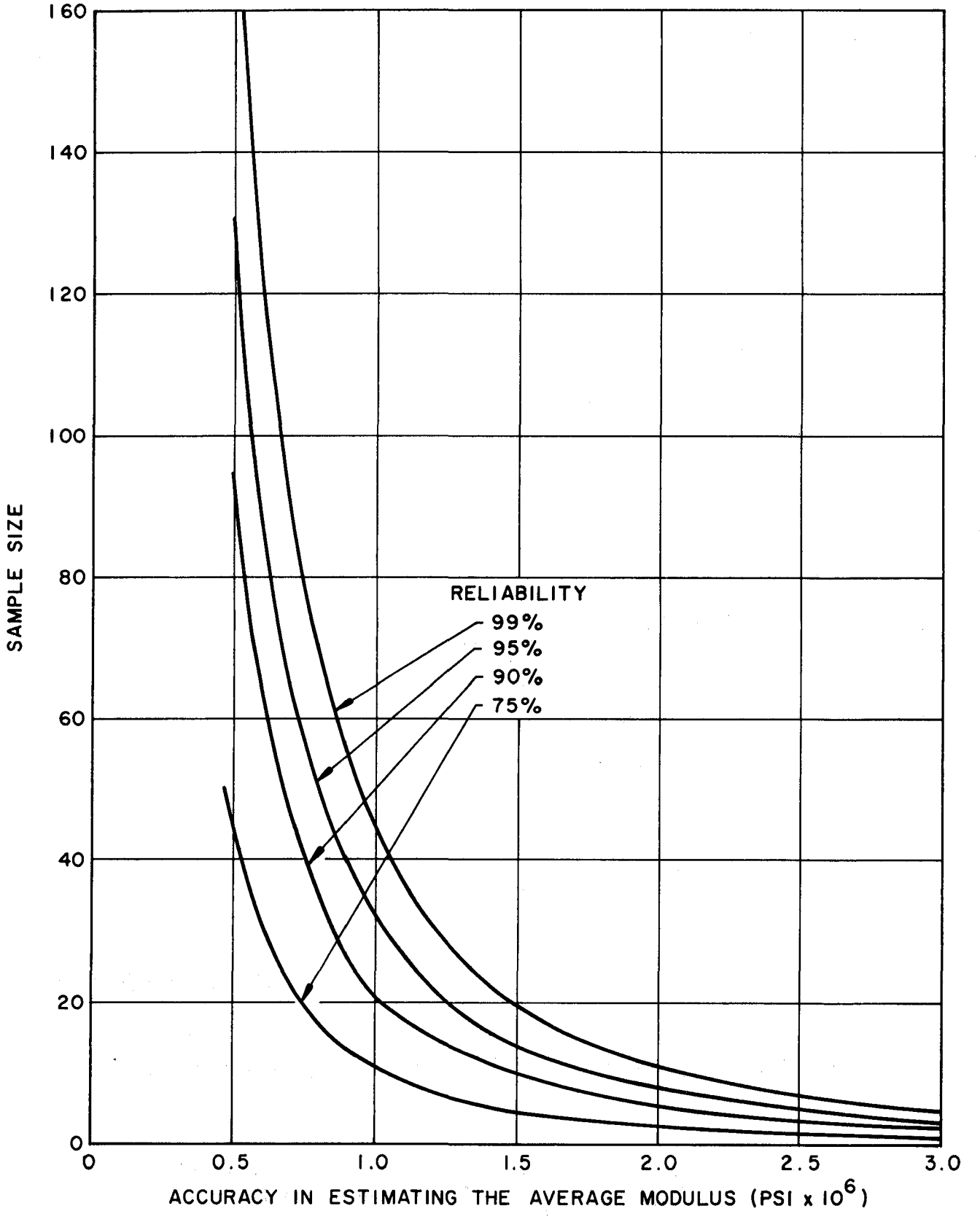

FIGURE A3 RELIABILITY CURVES FOR DETERMINING SAMPLE SIZE REQUIRED FOR ESTIMATING MONOFILAMENT FIBER MODULUS

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