

WET SPINNING OF POROUS POLYACRYLONITRILE FIBERS  
AND AFFECT ON FIBER OXIDATION,

by

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## I. INTRODUCTION

Graphite fibers of commercial importance are manufactured from organic precursor fibers by a series of heating steps which proceed at relatively low speeds resulting in high costs and selling prices. The high prices have restricted the use of graphite fibers and their most important present applications appear in the manufacture of "ablative" materials and structural materials, such as compressor blades and aircraft structural members. Recent process refinements have resulted in "tailor made" lower cost fibers for applications such as golf clubs and tennis rackets. The production processes are apparently limited by the relatively slow oxidation stage which involves diffusion of reactants, products, and heat. The use of a porous precursor to reduce the required residence times appeared worthy of investigation. The adverse effects of pores on the ultimate strength, due to concentration of stresses, etc., may be acceptable for lower strength applications if the use of porous precursors yield significant reductions in production costs.

Polyacrylonitrile was chosen as the precursor for this study, and this study involved:

- 1) The design, construction, and testing of suitable equipment

for production of porous PAN fibers.

2) Fiber properties were measured to ensure the apparatus reasonably duplicated commercial processes.

3) Porosity of the fibers was measured and the effect on oxidation of the fibers was examined using thermogravimetric analysis.



## II. LITERATURE REVIEW

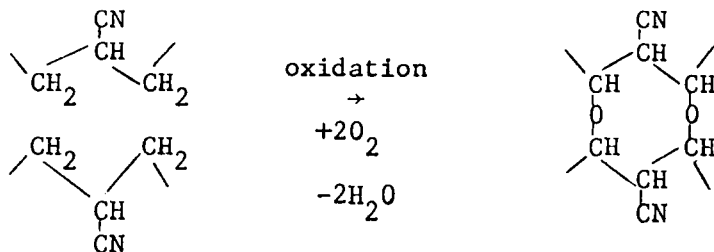
Information pertaining to this study is presented here.

### Introduction to Graphite Fibers

The production of graphite material involves several chemical and physical changes during successive exposure to higher temperatures. The stages of the process are generally referred to as oxidation, carbonization, and graphitization. Graphite material is a relatively recent development and manufactures are not prepared to disclose production techniques for obvious reasons; hence, the following brief process description is given as a general guide only.

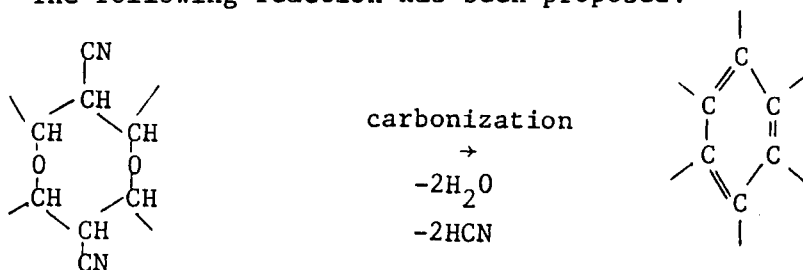
Precursors. Several raw materials have been used, including polyacrylonitrile (PAN), rayon, and pitch. The most notable progress has been made using PAN precursors. The following description applies directly to PAN, but processes for other precursors are similar, in general, except for the specific reactions and tensioning.

Oxidation. The fibers are exposed under tension to temperatures of 200°-250°C in air for several hours. Some toxic products are formed and a chemical reaction is thought to occur in which oxygen is incorporated into the material as follows:



The work of Watt<sup>(1)</sup> showed a significant improvement in the final modulus of graphite fibers if tension were applied during oxidation. It was postulated that the tension prevents shrinkage and preserves the molecular orientation along the fiber axis, allowing greater intermolecular bonding. A black shiny fiber results from oxidation.

Carbonization. The fiber is elevated to temperatures of 1000°-1500°C without stretching in an inert atmosphere. A change from an organic to carbon fiber occurs and a range of toxic, volatile gases are liberated, including hydrogen cyanide, ammonia, and others. Carbonization produces a carbon ring structure having a crystalline form. The following reaction has been proposed:



A large weight loss occurs, the fiber shrinks in diameter, and the length decreases with most of the shrinkage occurring below 800°C. Most of the volatiles are released below 1000°C, but traces of organic material remain until 1400°-1500°C. The crystals are very small, but show good alignment parallel to the fiber axis.

Graphitization. This treatment develops the crystals, and aligns the crystals within a few degrees of the longitudinal fiber axis. Since fiber stiffness increases with temperature

and maximum tensile strength occurs in fibers treated at about 1500°C, some material is not graphitized but sold as a very high strength product with moderately high modulus. The loss of elasticity at higher temperatures produces very high modulus materials, even though the tensile strength actually decreases for fibers treated at higher temperatures. The fiber is heat treated at temperatures ranging from 1600 to 3000°C in electrically heated graphite furnaces to graphitize it. A major requirement during graphitization is the complete exclusion of air, since minor amounts of air cause significant deterioration of product properties. Argon gas is usually used for the inert atmosphere. The heating rates could be much higher than those used in oxidation or carbonization, since no volatiles are removed and the graphite structure develops quickly.

The production rates appear to be limited by the ability of the reactants to diffuse through the fiber structure and the rates at which the products and heat are released. Watt<sup>(1)</sup> states that the oxidation stage appears to be diffusion controlled. Most commercial products and successful research work use precursors of fine filaments (1-3 denier) while larger diameter precursor fibers require longer heat treatment exposure. Ezekiel<sup>(2)</sup> reported great difficulty in oxidizing large quantities of fiber due to the dissipation of the heat of reaction.

The long processing time is a key factor in the relatively high cost of graphite fibers. Efforts to obtain faster conversion

rates have been carried out by doping PAN precursors with metal additives. The use of a precursor having a porous structure to increase the conversion rates would also appear worthy of investigation. The use of a porous structure is certainly debatable since work such as that by Johnson<sup>(3)</sup> concludes that the tensile strength of PAN based graphite fibers is largely controlled by the presence of discrete flaws. The failures were associated with voids and other included structures which, in most cases, were close to or on the surface. However, the presence of pores appears necessary for rapid diffusion of reactants and products in large fibers and there is probably a compromise between the physical properties and cost. It appears reasonable that the controlled introduction of small pores could produce significant savings in processing costs while yielding a product with useful and acceptable properties.

#### Polyacrylonitrile Fiber Production

Both the wet and dry spinning processes are used commercially today, while the use of melt spinning has received some minor attention in the research laboratories. A list of some well known PAN fibers is shown in Table I, along with the production method thought to be used.

Solvents used to dissolve the PAN include dimethylformamide, dimethyl sulfoxide, dimethyl acetamide, and ethylene carbonate. Sometimes oxalic or phosphoric acid is added in small quantities (1%)

Table I

WELL KNOWN MANUFACTURERS OF PAN FIBERS AND SPINNING PROCESS USED

| <u>Producer</u>          | <u>Trademark</u> | <u>Products</u>                      | <u>Process</u> |
|--------------------------|------------------|--------------------------------------|----------------|
| Chemstrand<br>(Monsanto) | Acrilan          | Staple                               | Wet Spinning   |
| American Cyanamid        | Creslan          | Staple and<br>Continuous<br>Filament | Wet Spinning   |
| du Pont                  | Orlon            | Staple and<br>Continuous<br>Filament | Dry Spinning   |
| Dow Badische             | Zefran           | Staple                               | Wet Spinning   |
| Courtaulds               | Courtelle        | Staple and<br>Tow                    | Wet Spinning   |

to the spinning dope as heat stabilizers to prevent discoloration during the preparation of the dope.

Dry spinning, in which the solvent is DMF, is done with cabinet temperatures of 220-250°C and take up speeds of 100-300 meters per minute. Stretching and relaxation are usually done in batch operations at elevated temperatures. The wet spinning operations are usually done at lower production rates. The process involves spinning, stretching, washing, and drying as a continuous operation. Coagulants used, when DMF is the solvent, include water, glycerol, and aqueous salt solutions such as calcium chloride.

Fiber consisting of 100% PAN, referred to as homopolymer yarn, has only a small amount of thermoplasticity which adversely affects the stretching and crimping operations. A certain amount of another monomer such as vinyl acetate, acrylates, methacrylates, etc. is usually copolymerized to break up the highly oriented structure and give some degree of thermoplasticity. The copolymers also aid in dyeing and affect the heat and solvent resistance of the fibers. Yarn containing at least 85% by weight of the acrylonitrile units ( $-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-$ ) is termed acrylic, while modacrylics is the term applied to yarn containing between 35% but not more than 85% by weight of the acrylonitrile units.

### Production of Porous PAN Fibers

The wet spinning of PAN fibers involves the extrusion of dope into a coagulation bath where the polymer is precipitated due to diffusion of the nonsolvent and solvent. Literature indicates that a gelled polymer structure is formed, characterized by a network of pores or voids of varying size, depending on the particular bath composition, residence time, and temperature. Drying of the gelled structure, usually with heated rollers, causes the collapse of the pores. The production of porous fibers using general wet spinning techniques while avoiding compressive pressures after coagulation appeared worthy of investigation. Various other methods which were comparatively difficult were reviewed. Briefly, these are as follows:

1) Dry spinning a polymer mixture of PAN and cellulose acetate followed by acetone extraction of the CA. Calculations using the technique of Crowley<sup>(4)</sup> indicated that DMF would dissolve CA. Experiments confirmed the solubility of CA in DMF and the insolubility of PAN in acetone.

2) Phase separation spinning of a PAN and caprolactam mixture followed by a water wash to extract the caprolactam or PAN, urea, and dimethyl sulfoxide followed by a butanol wash. Several recent theses<sup>(5,6,7)</sup> have explored the use of phase separation spinning and all have concluded that a porous structure is produced.

3) Wet spinning using ligroin in the coagulation bath. A patent<sup>(8)</sup> discloses the use of a mixture of ligroin fractions and methanol used as the coagulation bath for a PAN and DMF spinning dope. The ligroin diffuses into the porous structure and is later removed by exposure to temperatures above its boiling point. It was postulated that the ligroin aided in preserving the porous network.

Various articles indicated that the amount and size of the pores was significantly affected by the conditions and composition of the coagulation bath. Fibers having a harsh hand or very opaque were reportedly<sup>(9)</sup> produced when the bath conditions were varied.

#### Porosity Measurement

The pore volume was measured using a porosimeter and the results were compared to calculated values. Nelson<sup>(7)</sup> has reviewed the use of the mercury intrusion porosimeter to measure pore size and pore size distribution. Although the equipment appeared to have some limited capabilities, it was thought to be useful in gaining some insight as to size and size distribution of the pores. His recommendations for improving the accuracy were followed, including the use of the smallest penetrometer covering the range of volume changes and elimination of readings below atmospheric pressure.

The porosimetry technique is based on the fact that a liquid that does not wet a solid's surface (liquids with contact angles of



greater than 90°) will not penetrate into the solid's pores unless pressure is applied. Assuming the pores possess a cylindrical geometry, the following equations are presented by Nelson<sup>(7)</sup>.

Force pulling the nonwetting liquid out of pore =  $-\pi d \delta \cos \theta$

Minimum applied force to keep liquid in pore =  $\frac{\pi d^2}{4} P$

Equating these two forces results in

$$P = - \frac{4 \delta \cos \theta}{d}$$

where  $\delta$  = surface tension of liquid (mercury = 474 dynes/cm at 25°C)

P = Applied Pressure (psia)

$\theta$  = contact angle of liquid on solid surface

d = pore diameter (microns).

The contact angle of mercury on polyacrylonitrile could not be found but a value of 140°C was felt to be a good approximation. Known contact angles for polymers range from 138 to 150°. Substituting these values allows the following to be derived:

$$d = \frac{210.7}{P}$$

The slope of the pressure-volume curve indicates the amount of pores of various sizes using the following:

$$D(d) = \frac{P^2}{105.35} \frac{dv}{dP}$$

where  $D(d)$  = pore size distribution function

$dv/dp$  = slope of pressure-volume curve.

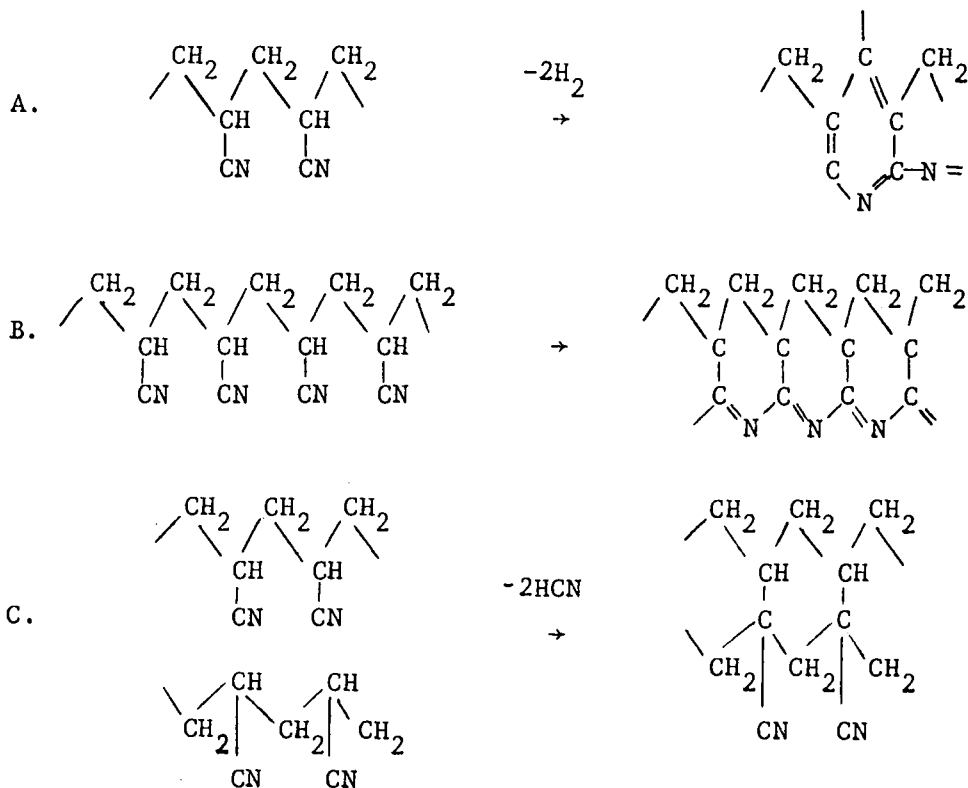
The compressibility of the fibers along with noncylindrical pore shapes are two possible sources of error. If these errors occur, the values should be at least of the correct order of magnitude and the shape of the size distribution should still be valid.

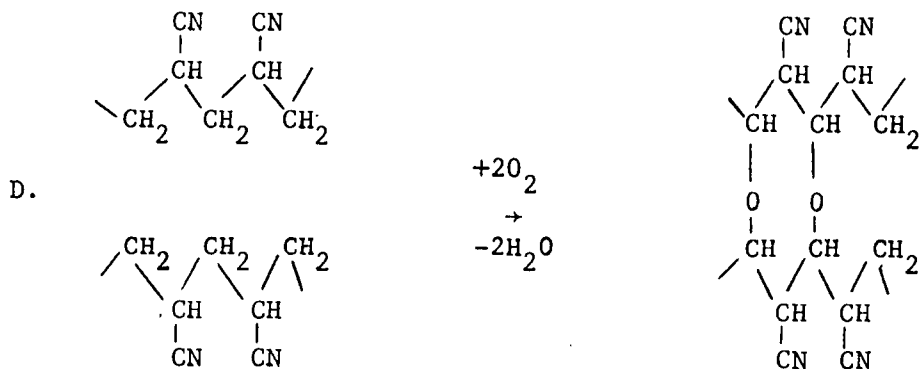
The void fraction was also calculated based on the measurements of fiber denier and fiber diameter as done by both Andrade<sup>(6)</sup> and Nelson<sup>(7)</sup>. The accuracy of this calculation is dependent on using correct values for density of void free PAN and the "true" diameter. Cross-sections of the fibers revealed a slightly crenulated and non-round shape. The problem of determining an average fiber diameter was encountered by Jones and Duncan<sup>(18)</sup> when the measurement was attempted for highly crenulated graphite fibers having the characteristic cross-section of the rayon precursor. They demonstrated fairly good agreement and a linear relationship between the average measured "apparent" diameter, obtained by optical measurement of the fiber width, and the true "equivalent" diameter, measured by calculations based on weights of cross-sectional photographs taken at a magnification of 1500X. For the purpose of this study, it was considered adequate to measure the width of the fibers at several points along the fiber length to obtain an average diameter. No values could be found for the density of void free PAN. Dry spun PAN fibers are thought to have only small pore volumes and density

figures of  $1.18 \text{ gr/cm}^3$  are given <sup>(20)</sup>. Therefore, a density of  $1.20 \text{ gr/cm}^3$  was used in the calculations and, due to the uncertainty of this value, the numbers for void fraction are intended to illustrate trends and should, otherwise, be used cautiously.

Oxidation of PAN

Oxidation is the term now applied to the first stage of graphitization since the most important change is thought to be incorporation of oxygen linkages between PAN molecules. Watt <sup>(1)</sup> has reviewed the literature and presents several possible reactions of PAN occurring at temperatures of  $200\text{--}250^\circ\text{C}$  in an air atmosphere. Some are presented as follows:





The polyacrylonitrile molecule has an atactic stereo arrangement which results in a noncrystalline fiber. The relatively large shrinkage upon heating can be explained to a large degree by the non-crystallinity. Watt concluded that many possible reactions can occur on heating PAN with or without the participation of oxygen and the different reactions proceed simultaneously but are dependent on the spatial arrangement of the reacting groups. Therefore, a key factor is that the extent to which any reaction will occur is governed by the approach distance of reacting groups, i.e., because of the atacticity of the molecular chains, a number of reactions are possible.

Watt did not review all of the possible reactions but mentions that measurements have shown HCN, NH<sub>3</sub>, and water are evolved when PAN is heated in air at temperatures of 200°-220°C. The carbon content of the fibers was found to increase after oxidation which indicates that the production of gaseous byproducts must be significant to offset the reduction in carbon content (by weight) resulting from the incorporation of oxygen according to equation D.

Weights were hung on the fibers to produce various length changes. The modulus of the graphite fibers appeared to increase with the increase in length of the fibers during oxidation. Watt concluded that the increased modulus values were due to the fact that the tension results in better orientation of the molecules resulting in a product with greater cross-linked orientation and higher strength along the fiber axis. The degree of cross linking and product properties will therefore be dependent on the ability of oxygen to diffuse throughout the fiber's structure.

The rate at which the reactants and byproducts are transferred into and out of the fiber structure will be subject to the diffusivity coefficient, pore size, and any boundary layer effects that exist.

#### Interpretation of Stress-Strain Behavior

Figure 1 is a reproduction of a typical stress-strain curve of relaxed yarn produced during this study. Examination of the curve shows an initial linear section (OA) where the yarn obeys Hooke's Law. This is characterized by recovery of the original length, or nearly so, upon removal of the stress. Beyond point A, the addition of incremental loads produce proportionately larger increases in elongation in region DC due to the propensity of the fiber to "creep" or slowly elongate under load. This "creep" allows rearrangement of the molecules and the improved orientation allows the material to withstand higher stresses. As the orientation improves, rate of

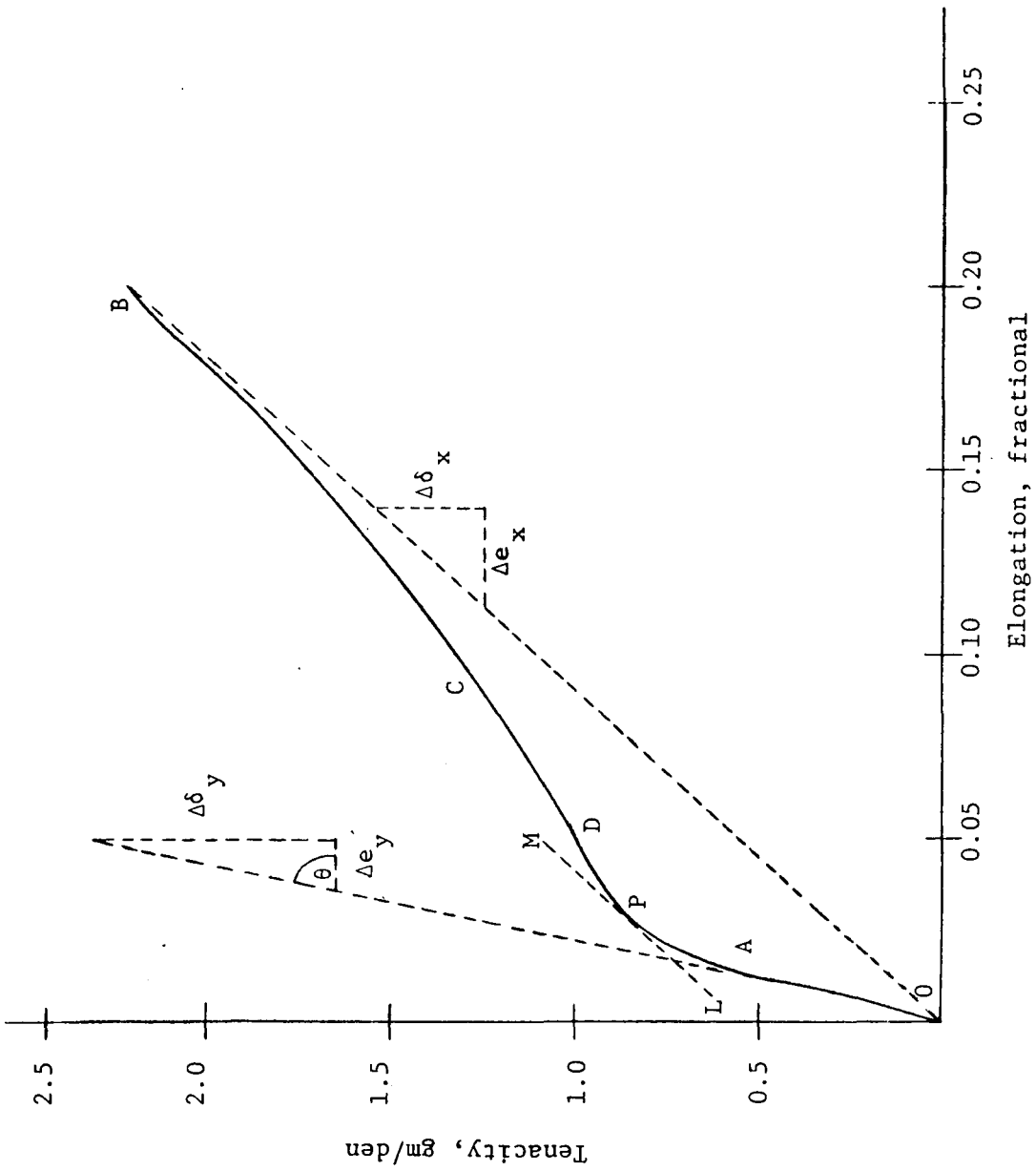


Figure 1. Typical Stress-Strain Curve for Relaxed PAN Fiber

elongation decreases. This "creep" region is, therefore, followed by a stiffening region CB where additional loads cause smaller changes in elongation until break occurs. Quantitative analysis of the curves was done using the following definitions:

Tenacity. Tenacity at break, point B

Elongation. Elongation at break, point B

Initial Young's Modulus or Elastic Modulus. Ratio of change in stress to change in strain within the elastic limit of the material. The modulus is, therefore, equal to  $\tan \theta$  or  $\Delta\delta_y/\Delta e_y$  where  $e_y$  is expressed as a fraction of the original length. Elastic fibers are characterized by low modulus values while high modulus values indicate a stiff nonflexible material.

Secant Modulus. Ratio of change in stress to change in strain between two points, particularly the points of zero stress and breaking stress<sup>(14)</sup>. The secant modulus is therefore equal to  $\Delta\delta_x/\Delta e_x$  where  $e_x$  is expressed as a fraction of the original specimen length. When the breaking values are used, the secant modulus is often referred to as the average stiffness, which is easily calculated by dividing the breaking tenacity by the breaking elongation.

Yield Point or Proportional Limit. Point which locates the region between Hookean behavior and "creep" behavior. It is the point at which the tangent to the curve is parallel to the line joining the origin and break point<sup>(15)</sup>. This is shown in Figure 1 as point P and the tangent is line LM.

Yield Stress. Tenacity at point P.

Yield Strain. Elongation at point P.



### III. EXPERIMENTAL

This section contains a plan of experimentation, a description of the procedures used, and the results obtained for this investigation.

#### Plan of Experimentation

This study was undertaken using the following plan of experimentation.

Equipment Design, Construction, and Testing. Initial efforts were expended on utilizing the spinning equipment used by Williams<sup>(5)</sup> in his thesis work and built in the Chemical Engineering shop at Virginia Polytechnic Institute and State University. After modifications were made to the equipment for a wet spinning operation, it became evident that the piston assembly and drive mechanism could not produce sufficient or consistent dope pressures to ensure uniform fiber properties. The variable speed at which the piston moved through the bored cylinder was further aggravated by the small quantities of dope used since the piston was especially unstable near the end of the stroke.

Spinning equipment more suitable for extrusion of small quantities of PAN was designed and fabricated at the Celco Plant of the Celanese Fibers Company where the author is an employee. The spinning unit consisted of a stainless steel cylindrical dope reservoir to which variable pressures could be applied using a cylinder of

nitrogen with a pressure regulator. The dope consisting of PAN dissolved in DMF was forced to a Zenith metering pump which provides accurate dope flow rates using an interlocking gear displacement mechanism. The metering pump supplied dope to a four-hole spinneret which was partially immersed in a coagulation bath of dimethylformamide and water. The yarn was taken up on a powered feed roll.

The stretching unit was positioned next to the spinning unit to allow continuous extrusion and stretching operations. After wrapping four times around the feed roll, the yarn was passed through a boiling water bath and collected on a take-up roll. The yarn was manually guided onto the take-up roll to build a fairly uniform package.

Electrical heating tapes and hotplates were used to maintain the desired temperatures of the coagulation bath, stretching bath, and the dope prior to extrusion. Temperatures of the dope and baths were monitored with thermocouples or thermometers and readings were made periodically.

Fiber Spinning, Stretching, and Sample Collection. The properties of fibers are known to be highly dependent on the extent to which the dope is filtered prior to extrusion. The dope was, therefore, filtered extensively prior to its use in the spinning apparatus.

The literature<sup>(9,10,11,12)</sup> revealed the use of many different dope compositions and the conditions chosen to remain constant throughout the spinning trials were an extrusion dope temperature

of 50°C and a dope composition of 17% PAN and 83% DMF by weight. The coagulation bath temperature and composition were varied to determine the effect on fiber properties, porosity, and stability. Two levels of stretching ratio were examined to determine the effect on fiber properties and porosity.

The fiber samples were collected on cardboard rolls slipped over the take-up roll. A chrome plated pigtail was used to guide the yarn onto the roll. After sufficient yarn was collected, the cardboard roll was removed and another one inserted for collection at different operating conditions.

Fiber Physical Testing. Denier of the four filament yarn was obtained by weighing known lengths. Measurement of fiber breaking tenacity and elongation were made using an Instron Tensile Tester. The rate of elongation was adjusted to 60% of the initial specimen length per minute as recommended<sup>(13)</sup>. Adjustments were also made to obtain the break point at 50-85% of the full scale reading. The specimen gage length was 16.7 cm. Samples were conditioned at 65% RH and 70°F prior to physical testing, which is the recommended ASTM standard.

Fiber Structure. The pore volume was measured using a mercury intrusion porosimeter and the results were compared with calculated values based on fiber diameter, denier, and the pore-free density of PAN. Some fibers were cut with a sharp razor blade to allow examination of the cross-section configuration.

Oxidation of PAN. The effect of pore volume on the oxidation of PAN was examined using thermogravimetric analysis. Approximately 10 mg of selected samples were cut into short pieces and placed in a du Pont Model 950 thermogravimetric analyzer for 200 minutes at a constant temperature of 225°C. The weight change was monitored in an atmosphere of air or argon. The rate of weight loss was used to indicate the effect of pore volume on the rate at which reactants and products could diffuse through the fiber structure.

#### Procedures

Dope Preparation. An appropriate amount of refrigerated (15°C) N,N-Dimethylformamide was added to a tared glass jar. Knowing the amount of DMF, sufficient polyacrylonitrile powder was added to the glass jar to yield a solution of 17% PAN by weight. Sample size varied from 50 grams to 400 grams. The PAN powder was preheated to 100°C in a capped jar. These temperatures were found to reduce the formation of lumps and reduce mixing time. The jar was then placed in a high speed laboratory shaker for 15 minutes, heated to 60°C for two hours, and placed on a slowly rotating tumbler overnight. The contents, after mixing, became viscous and had a brown color. Undissolved matter could be seen in the viscous dope indicating the obvious need for filtration.

Dope Filtration. The dope was placed in a 1-1/2" diameter cylinder and pressurized using a nitrogen cylinder with a pressure regulator. The dope was forced through various filter media by

increasing the pressure to a maximum of 160 psi and collected in a clean glass jar. The dope was recycled four times using progressively more retentive filter media. The four stages included a 25 x 100 mesh wire cloth with a rating of 100 microns, 40 x 150 mesh wire cloth with a rating of 60 microns, one layer of fiber filter paper with a layer of cotton sheeting on each side, and three layers of cotton batting with a layer of cotton sheeting on each side. The filtration was done at room temperature and the filtered dope was crystal clear but a slight yellow-greenish tint remained. The equipment was cleaned with 100% DMF between batches. An analysis of the particulate matter removed from the dope indicated that 60% by weight was organic while the remainder was inorganic material. The ashing of the filtered material was done at 575°C for three hours in a muffle furnace and indicated that most of the material was probably undissolved PAN. Measurements of the concentration of PAN in the dope were, therefore, made on each sample prior to spinning, even though these measurements revealed only very minor amounts of PAN remained undissolved.

Equipment Start-up. Prior to spinning, a small sample of dope was analyzed gravimetrically to determine the concentration of PAN. This procedure is detailed in the Appendix.

The hotplate used to boil the water in the stretching bath was turned up to maximum output, once the tray was filled with distilled water. An aluminum cover was used to reduce the heatup time. The

heating tape surrounding the glass tray, which served as the coagulation bath, was then activated and an on/off controller was used to maintain the desired temperature. The coagulation solution was either freshly made or reused from earlier trials. The concentration was measured using a Bausch and Lomb refractometer. The use of refractive index to measure concentration was found to be very accurate and the procedure and calibration curve is detailed in the Appendix.

The filtered dope was poured into the reservoir and pressurized to approximately 50 psi. The Zenith metering pump was turned on and the speed adjusted to give the desired rpm and associated dope flow rate. The dope pressure in the transfer line between the pump and spinneret was visually monitored and the pressure on the dope reservoir was varied to maintain the same pump inlet and outlet pressures.

The dope was allowed to flow from the spinneret until bubble free dope formed on the surface. The spinneret was then lowered into the coagulation bath and the feed and takeup rolls were started at the desired speed. Fibers began to form as soon as the spinneret contacted the bath. Using gloves, the fibers were collected and pulled through the bath while rollers were placed on top of the yarn bundle. The yarn end was then manipulated over the feed roll and feed roll guides which allowed the yarn to wrap the feed roll four times without overlapping. The yarn was then passed to the takeup roll and the stretching bath cover removed. The yarn was then

placed under two rollers attached to a ring stand which were then lowered into the boiling water. The takeup roll speed was slightly greater than the feed roll speed and the yarn had enough flexibility so that no difficulty was encountered during the entire threading operation.

A check of all temperatures and speeds was made to ensure proper operating conditions.

Sample and Data Collection. The Zenith metering pump speed was checked using a low speed hand tachometer. The feed roll and takeup roll speeds (rpm) were indicated on the control units, which were previously calibrated with a moderate speed hand tachometer. All speeds and temperatures were easily maintained but were periodically recorded between sample collections.

Once the apparatus was threaded and all operating conditions recorded, a cardboard roll was placed over the end of the takeup roll. The yarn, while being wound on the uncovered portion of the takeup roll, was then manually guided onto the cardboard roll using a pigtail. After several layers were collected on the cardboard roll, the yarn was guided back onto the uncovered portion. The fibers leading on and off the cardboard roll were cut with a wooden knife. The cardboard roll was then removed while running by applying pressure to the inside of the cardboard roll which extended past the end of the solid aluminum takeup roll. After the sample was collected, all operating conditions were re-recorded.

Table II shows the eight operating conditions for which samples were tested. Part of the sample was removed from the cardboard roll and wound into a hank. The hank was loosely hung on a bar and placed in a forced convection oven for eight minutes at 130°C. The hank of relaxed and a hank of unrelaxed yarn was placed in a conditioned atmosphere overnight for testing the next day.

Shut-down Procedures. After all samples were collected, the metering pump was turned off and the reservoir pressure released by closing off the nitrogen cylinder and opening a relief valve slowly. The feed roll, heaters, and takeup roll were turned off. The spinneret was raised out of the bath and the coagulating mixture was syphoned out of the tray through a standard funnel with filter paper and collected in a large jar for reuse.

The reservoir, pump, spinneret assembly, and all tubing were disassembled and cleaned in DMF, if the equipment was not to be reused shortly.

Concentrations and Temperatures. The extrusion dope temperature was maintained at 50°C. After initial trial and error, the variac setting of 90 was found to properly control the voltage to the heating tape which surrounded the tubing supplying the spinneret. The dope temperature did not vary more than  $\pm 1^\circ\text{C}$  as measured with the thermocouple. A cover was placed over the stretching bath to maintain temperatures closer to 100°C. The cover was left in place as long as possible and replaced whenever the



Table II

SPINNING CONDITIONS EXPLORED DURING STUDY

| Sample No. | Coagulation Bath Temp. (°C) | Coagulation Bath Composition wgt % DMF/wgt% water | Target Stretching Ratio, Takeup Speed/ Feed roll Speed |
|------------|-----------------------------|---|--|
| 1 and 10   | 50                          | 50/50   | 4/1  |
| 2 and 11   | 50                          | 50/50   | 5/1  |
| 3 and 12   | 25                          | 50/50   | 4/1  |
| 4 and 13   | 25                          | 50/50   | 5/1  |
| 5 and 14   | 50                          | 25/75   | 4/1  |
| 6 and 15   | 50                          | 25/75   | 5/1  |
| 7 and 16   | 25                          | 25/75   | 4/1  |
| 8 and 17   | 25                          | 25/75   | 5/1  |

Note: Samples 10 through 17 are portions of samples 1 through 8, respectively, which have been relaxed by heat treatment in air for eight minutes at 130°C.

temperature began dropping significantly. The arrangement, although cumbersome, allowed temperatures of 94°-97°C to be maintained.

A constant temperature controller was used to maintain the coagulation bath temperature. The first samples were collected at 50°C and the temperature was then lowered to 27°C without stopping the extrusion by turning off the controller and simultaneously draining the bath and adding additional cooled coagulant. To ensure a constant temperature, approximately five minutes were allowed before sampling was continued. Measurements showed no significant increase in the level of DMF in the bath since relatively small quantities of dope were extruded.

Fiber-Physical Testing. Total denier of the four filament yarn was obtained by measuring the weight of 90 cm lengths and the average denier per filament was calculated. Measurement of fiber tenacity and percent elongation at break was obtained using an Instron Tensile Tester with an attached recorder. The area compensation accessory was utilized to allow the direct readout of grams/denier instead of load in grams. The Instron unit was used with a gage length of 16.7 cm., crosshead speed of 10 cm per minute, and a chart speed of 50 cm per minute. The chart speed of 50 cm/min. was found to yield acceptable slopes of the stress-strain curves. As pointed out by Andrade<sup>(6)</sup>, it is recommended that the chart speed be such that the initial slope correspond to a 45° angle for the most accurate moduli measurements. The crosshead speed was used to

give a rate of extension equal to 60% of the initial specimen length per minute as recommended<sup>(13)</sup>. The load selector switch was varied for full scale reading of 2.0 to 4.0 grams per denier for the yarn produced at stretching ratios of about 4:1 and 5:1 respectively. This was done to maintain the reading at 50-85% of the full scale.

The samples were maintained overnight in a conditioned room at 70°F and 65% RH prior to testing. These are standard ASTM conditions for textile testing.

The fibers were composed of four filaments and, to obtain an indication of the variability between individual filaments, the denier per filament was measured using a vibroscope. The vibroscope is described by Kaswell<sup>(14)</sup> and is based upon the principle that the weight per unit length of a completely flexible string can be calculated from its lateral frequency vibration characteristics, its length, and the applied tension. The relationship is as follows:

$$\text{denier} = \frac{2.21 \times 10^8 T}{\ell^2 f^2} .$$

The denier is in grams per 9000 meters, T is tension in grams force,  $\ell$  is the effective fiber length in centimeters, and f is the resonant frequency in cycles per second. The fiber is vibrated transversely and a variable oscillator is used to adjust the frequency so that the harmonic modes are established.

Porosity Measurement. A mercury intrusion porosimeter was used to gain some insight into the size and distribution of pores. The equipment has been adequately described by Nelson<sup>(7)</sup>. A penetrometer was used having a maximum scale range of 0.02 cm<sup>3</sup> due to the small sample size. As recommended by Nelson, the filling procedure was modified so that the mercury level reads zero at atmospheric pressure to eliminate volume changes due to filling voids between the fibers. The procedure used to operate the Aminco porosimeter is found in the Aminco-Winslow-Porosimeter Instruction Manual No. 597<sup>(19)</sup>. Porosity measurements were made of unrelaxed samples only (Numbers 1 to 8), since the relaxed fibers were expected to have lower void fractions and less porosity. Twenty two readings were taken on each sample tested.

The pore volume was also calculated using the measured fiber diameter and a theoretical density for void free PAN. The fiber diameter was measured at three points along each of the four filaments in the fiber for a total of 12 measurements. The width of the filaments was measured using a Leitz microscope at a magnification of 500 X, obtained with a 50X objective and a 10X Filar micrometer eyepiece. The focus was adjusted until both sides were distinctly outlined. The hairline in the eyepiece was moved across the fiber outline and the change in dial readings was used as the fiber diameter. The eyepiece was calibrated using a standard calibration grid with spacings of 100 microns. The calibration revealed that 5.64

divisions on the eyepiece was equivalent to 600 microns. Therefore, one division was equivalent to 17.7 microns. The dial markings refined one division to 100 subdivisions, which were read directly. It was therefore possible to obtain readings to within approximately 0.2 microns. The filament denier was calculated by dividing the total denier by four, thereby resulting in an average denier per filament. A value for the void free density of PAN could not be found. Polyacronitrile fibers have a density of 1.17 to 1.18 gr/cm<sup>3</sup>. Therefore a value of 1.20 gr/cm<sup>3</sup> was used in the calculation. The absolute values for the void fractions must be used cautiously.

A sample of dry spun yarn was obtained for comparative purposes. The yarn end contained 383 filaments averaging 1.76 dpf. The yarn was thought to be dry spun, since many filaments had a trilobal cross-section and only round cross-sections are thought to be produced by wet spinning processes. The filament diameter was measured to be 16.8 microns, which is much smaller than all other samples evaluated.

Thermogravimetric Analysis. A du Pont Model 950 Thermogravimetric Analyzer was used to observe the weight loss of fiber samples on exposure to temperatures of 220°-230°C for several hours. If the oxidation process is diffusion controlled, it was thought that the rate of weight loss would correlate with the amount of pores, pore size, or pore size distribution. The basic procedures are shown in the TGA instruction manual; however, some special procedures had to be developed due to the nature of the fiber samples.

A platinum-rhodium sample pan was used which is roughly cylindrical with a diameter of 3/16" and a length of 3/8" hung from its side and having open ends. Sample weights could range from one to 60 mg. A small weight loss was expected (1-5% by weight), so a sample size of about 10 mg was chosen to allow more accurate weight readings from the chart paper. It was also found that larger amounts of samples resulted in tight packing of the sample pan which may affect the gas flows and the subsequent weight loss readings. Therefore the variation in sample size was minimized also.

The fibers were cut into 1/4" lengths using a sharp razor blade to minimize the introduction of significant amounts of surface area at the ends of the fibers. This also facilitated the loading of the sample pan.

The fiber was heated isothermally and the sample temperature was checked periodically by switching from the time to temperature mode. All temperatures were within 220-230°C indicating adequate isothermal operation. The thermocouple used to measure the temperature near the sample pan was carefully adjusted to within 1 mm to ensure accurate measurement. The target temperature was set and equilibration allowed to occur, which required 5-10 minutes, before the weight recording was started.

Exposure time was 200 minutes for all but one of the five selected samples. The sample weight was continuously recorded with time and the weight loss calculated. The equipment has the capability

of being adjusted for greater sensitivity of weight loss, but the calibration procedures indicated some electronic instability and this option was not used.

The sample can be heated in a vacuum or a purged gas atmosphere. The samples were first run in air at carefully measured flow rates. The flow rates were measured using two rotameters in series to ensure accurate readings. Different air flow rates had a major influence on the sample temperature and readjustment was necessary at various air flow rates. As discussed later, the weight loss was significantly affected by the air flow rate. Samples were run under an atmosphere of argon gas to eliminate any data variability which may be due to competing reactions. Without the oxidation reaction, the weight loss should result from the evolution of pyrolysis byproducts such as HCN,  $\text{NH}_3$ , and water. It was felt that significant increases in weight loss rates, due to evolution of these byproducts, should indicate that the mass transfer rate was greater and increased transfer rates of oxygen into the fiber could be projected.

### Results

The tensile testing indicated the yarn had physical properties similar to that of commercially available products. Table III shows the denier and diameter of the fibers and filaments along with calculated values of stretching ratio, shrinkage during relaxation, and void fraction. Table IV lists the physical properties of tenacity,

elongation, average stiffness, yield tenacity, yield elongation, and initial modulus.

Figure 2 shows the tenacity as a function of calculated stretch ratio for the unrelaxed fibers while Figure 3 shows the same for the relaxed fibers. The effect of calculated stretch ratio on elongation of relaxed yarn is seen in Figure 4.

The results of porosimeter measurements are shown in Figure 5 which indicates the relationship between pressure and penetrated volume. Figure 6 shows the correlation between maximum penetrated volume and the calculated void fraction.

Percent weight loss as a function of time is illustrated in Figure 7 for samples exposed to temperatures of 220°-230°C in an argon atmosphere.



Table III

RESULTS DERIVED FROM WEIGHT, LENGTH, AND DIAMETER MEASUREMENTS

| Sample No. | Avg. Yarn Denier | Avg. Denier per Filament | Avg. Filament Diameter (10 <sup>4</sup> ) | Feed Roll Denier | Calc. Stretching Ratio | Calc. Relaxation Shrinkage | Calc. Void Fraction |
|------------|------------------|--------------------------|---|------------------|------------------------|----------------------------|---------------------|
| 1          | 47.0             | 11.75                    | 61.1                                      | 199.0            | 4.25:1                 |                            | 0.63                |
| 2          | 35.0             | 8.75                     | 40.0                                      | 199.0            | 5.70:1                 |                            | 0.36                |
| 3          | 50.8             | 12.50                    | 53.3                                      | 200.0            | 4.00:1                 |                            | 0.48                |
| 4          | 37.0             | 9.25                     | 38.4                                      | 200.0            | 5.40:1                 |                            | 0.26                |
| 5          | 41.0             | 10.25                    | 52.3                                      | 193.0            | 4.71:1                 |                            | 0.69                |
| 6          | 31.0             | 7.75                     | 43.3                                      | 193.0            | 6.23:1                 |                            | 0.51                |
| 7          | 46.0             | 11.50                    | 51.6                                      | 200.0            | 4.35:1                 |                            | 0.49                |
| 8          | 36.0             | 9.0                      | 38.4                                      | 200.0            | 5.55:1                 |                            | 0.28                |
| 10         | 56.0             | 14.0                     | *   |                  |                        | 16.1                       |                     |
| 11         | 40.0             | 10.00                    | 39.6                                      |                  |                        | 12.5                       | 0.25                |
| 12         | 62.5             | 15.625                   | 53.3                                      |                  |                        | 20.0                       | 0.36                |
| 13         | 41.0             | 10.25                    | 40.8                                      |                  |                        | 9.8                        | 0.27                |
| 14         | 48.0             | 12.00                    | *   |                  |                        | 14.6                       |                     |
| 15         | 36.5             | 9.125                    | 41.3                                      |                  |                        | 15.1                       | 0.34                |
| 16         | 55.5             | 13.875                   | 49.7                                      |                  |                        | 17.1                       | 0.34                |
| 17         | 39.5             | 9.875                    | 39.5                                      |                  |                        | 8.9                        | 0.25                |

- Notes: 1. Avg. Yarn Denier (grams per 9000 meters) - average of two measurements
2. Avg. Yarn Denier divided by 4 since 4 filaments per end
3. Yarn Diameter (cm) - average of twelve measurements
4. Feed Roll Denier (grams per 9000 meters) - one measurement taken to allow calculation of stretching ratio
5. Calculated Stretching Ratio (dimensionless) - equal to Feed roll denier divided by final yarn denier
6. Calculated Shrinkage (percent) - samples 10 through 17 are portions of samples 1 through 8, respectively, which have been relaxed. For example:

$$\text{Shrinkage \#10} = \frac{\text{Avg. yarn denier \#10} - \text{avg. yarn denier \#1}}{\text{Avg. yarn denier \#10}} \times 100$$

7. Calculated Void Fraction (dimensionless)

\*Not measured.

Table IV  
PHYSICAL PROPERTIES OF WET SPUN SAMPLES

| Sample No. | Average Breaking Tenacity | Average Breaking Elongation | Calc. Average Stiffness | Average Yield Stress | Average Yield Strain | Average Initial Modulus |
|------------|---------------------------|-----------------------------|-------------------------|----------------------|----------------------|-------------------------|
| 1          | 1.75                      | 8.7                         | 20.1                    | 0.67                 | 1.8                  | 44.5                    |
| 2          | 2.30                      | 6.6                         | 34.8                    | 0.78                 | 1.6                  | 54.8                    |
| 3          | 2.02                      | 11.7                        | 17.3                    | 0.67                 | 2.0                  | 44.3                    |
| 4          | 2.53                      | 10.6                        | 23.9                    | 0.73                 | 1.8                  | 53.4                    |
| 5          | 1.80                      | 8.5                         | 21.2                    | 0.67                 | 1.8                  | 46.3                    |
| 6          | 2.70                      | 6.1                         | 44.3                    | 0.87                 | 1.4                  | 72.9                    |
| 7          | 2.37                      | 7.8                         | 30.4                    | 1.56                 | 3.4                  | 53.5                    |
| 8          | 2.86                      | 6.7                         | 42.7                    | 0.78                 | 1.3                  | 72.5                    |
| 10         | 1.31                      | 23.4                        | 5.6                     | 0.62                 | 4.0                  | 23.2                    |
| 11         | 2.19                      | 19.4                        | 11.3                    | 0.85                 | 2.7                  | 45.7                    |
| 12         | 1.60                      | 23.4                        | 6.8                     | 0.81                 | 3.2                  | 38.6                    |
| 13         | 2.48                      | 23.0                        | 10.8                    | 0.78                 | 3.4                  | 28.8                    |
| 14         | 1.47                      | 22.9                        | 6.4                     | 0.75                 | 3.2                  | 37.7                    |
| 15         | 2.08                      | 18.4                        | 11.3                    | 0.92                 | 2.7                  | 46.1                    |
| 16         | 1.91                      | 23.6                        | 8.1                     | 0.85                 | 3.3                  | 40.6                    |
| 17         | 2.53                      | 22.6                        | 11.2                    | 0.72                 | 3.1                  | 35.5                    |

- Notes:
1. All values are averages of 3, 4, or 5 tests
  2. Average Breaking Tenacity - grams/denier
  3. Average Breaking Elongation - percent
  4. Average Stiffness - grams/denier. Calculated by dividing breaking tenacity by fractional elongation at break
  5. Average Yield Stress - grams/denier - Stress at yield point
  6. Average Yield Strain - percent - Strain at yield point
  7. Average Initial modulus - grams/denier - slope of initial stress-strain curve

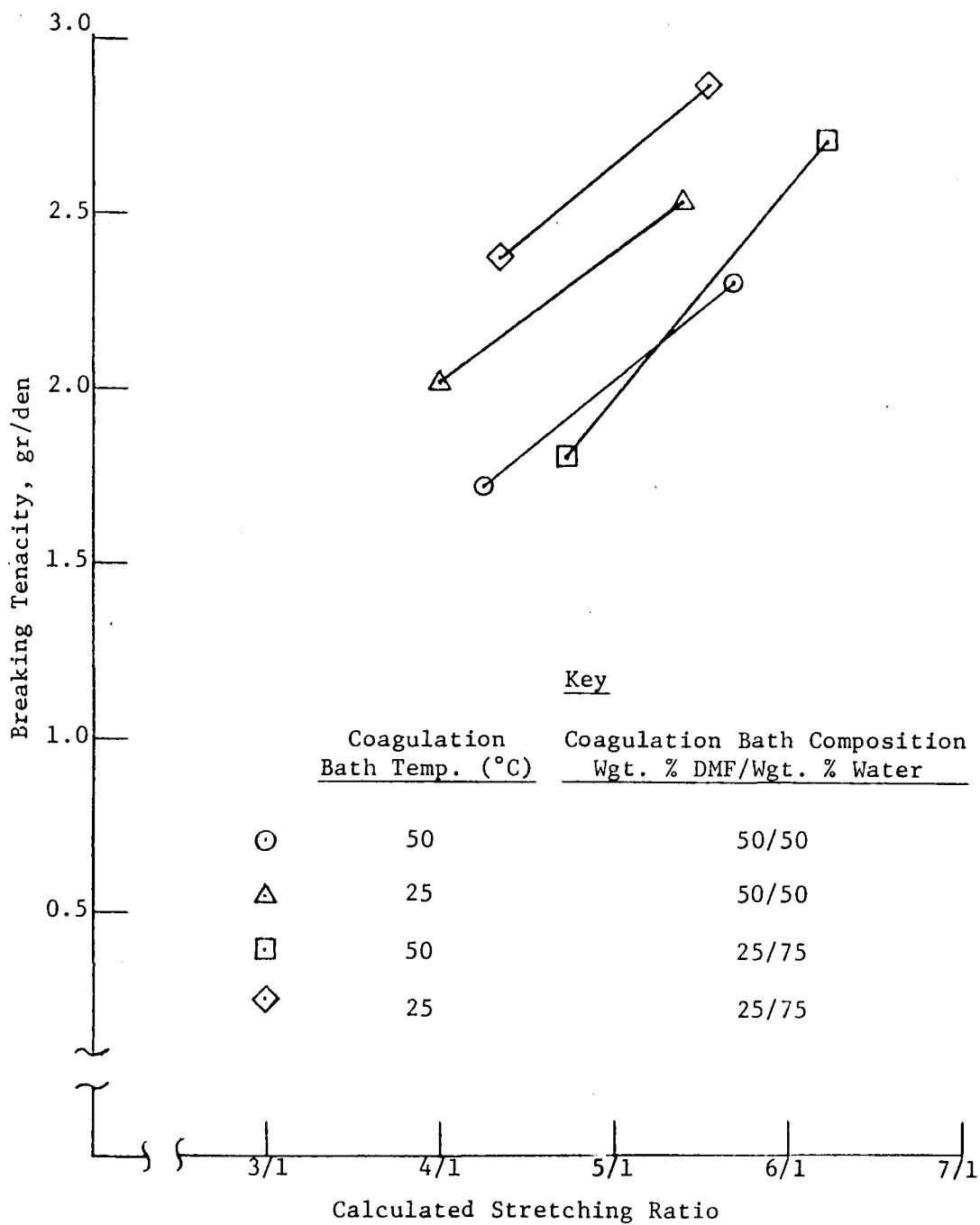


Figure 2. Effect of Stretching Ratio on Unrelaxed Yarn Tenacity

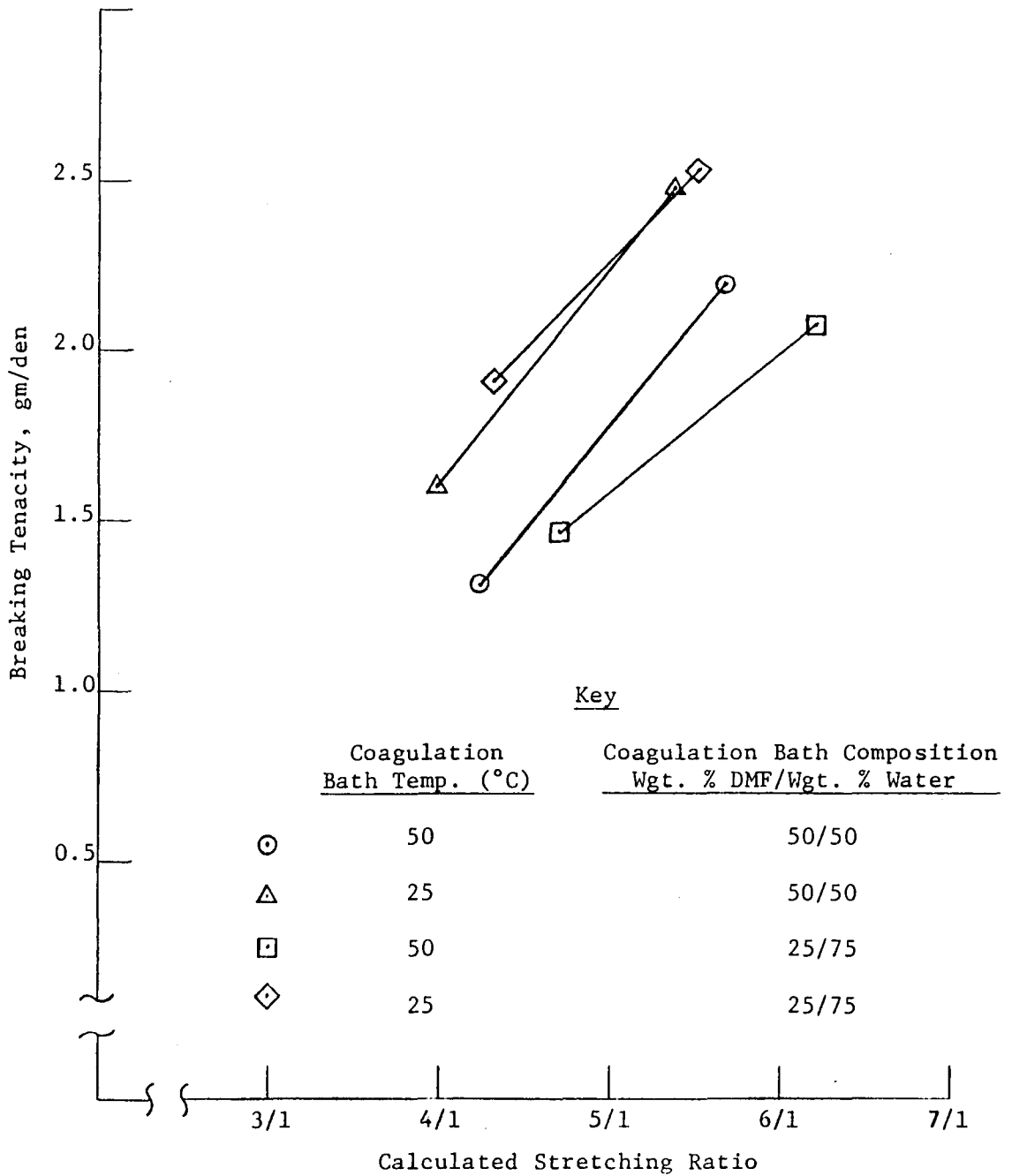


Figure 3. Effect of Stretching Ratio on Relaxed Yarn Tenacity

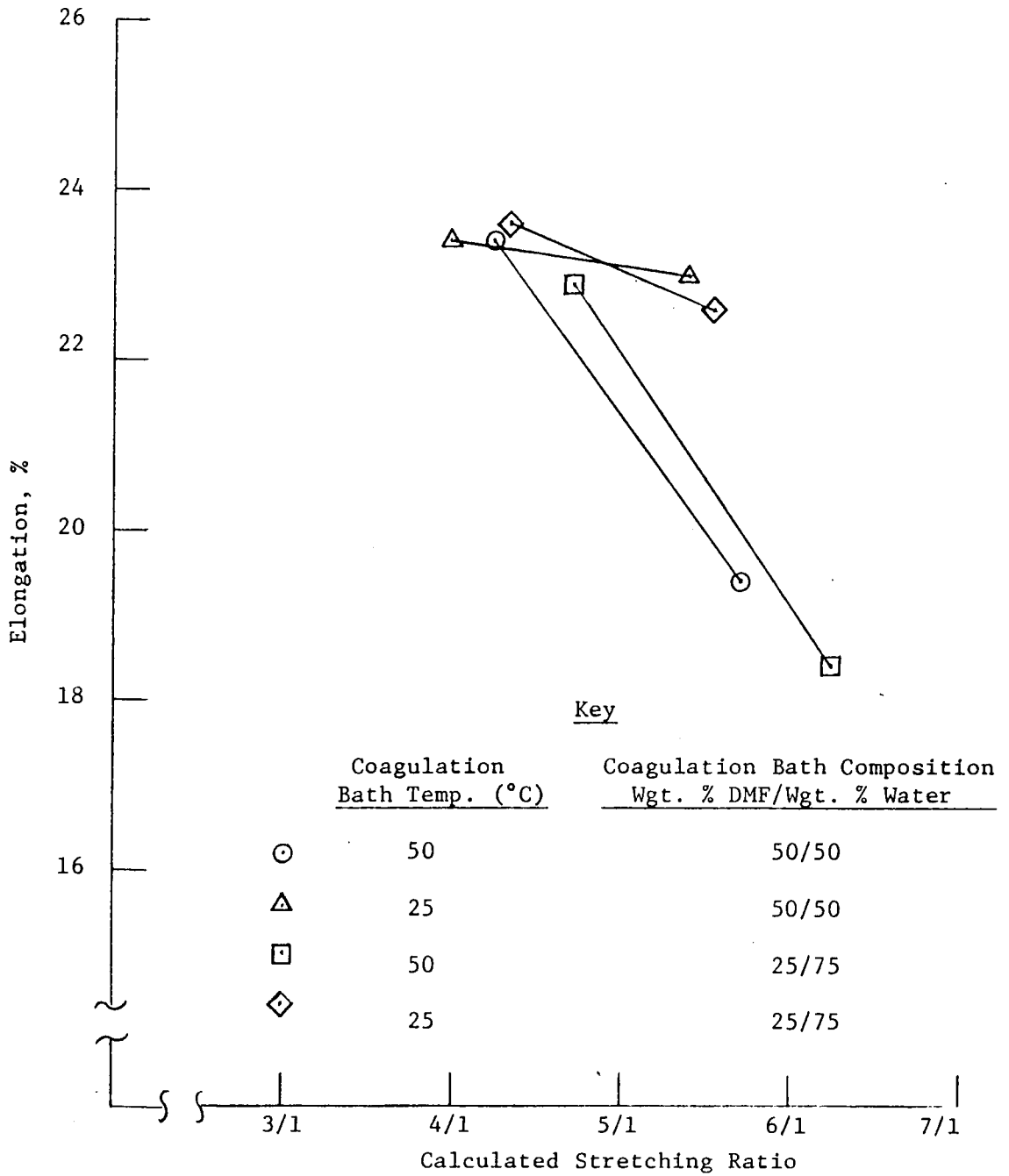


Figure 4. Stretching Ratio versus Relaxed Yarn Elongation

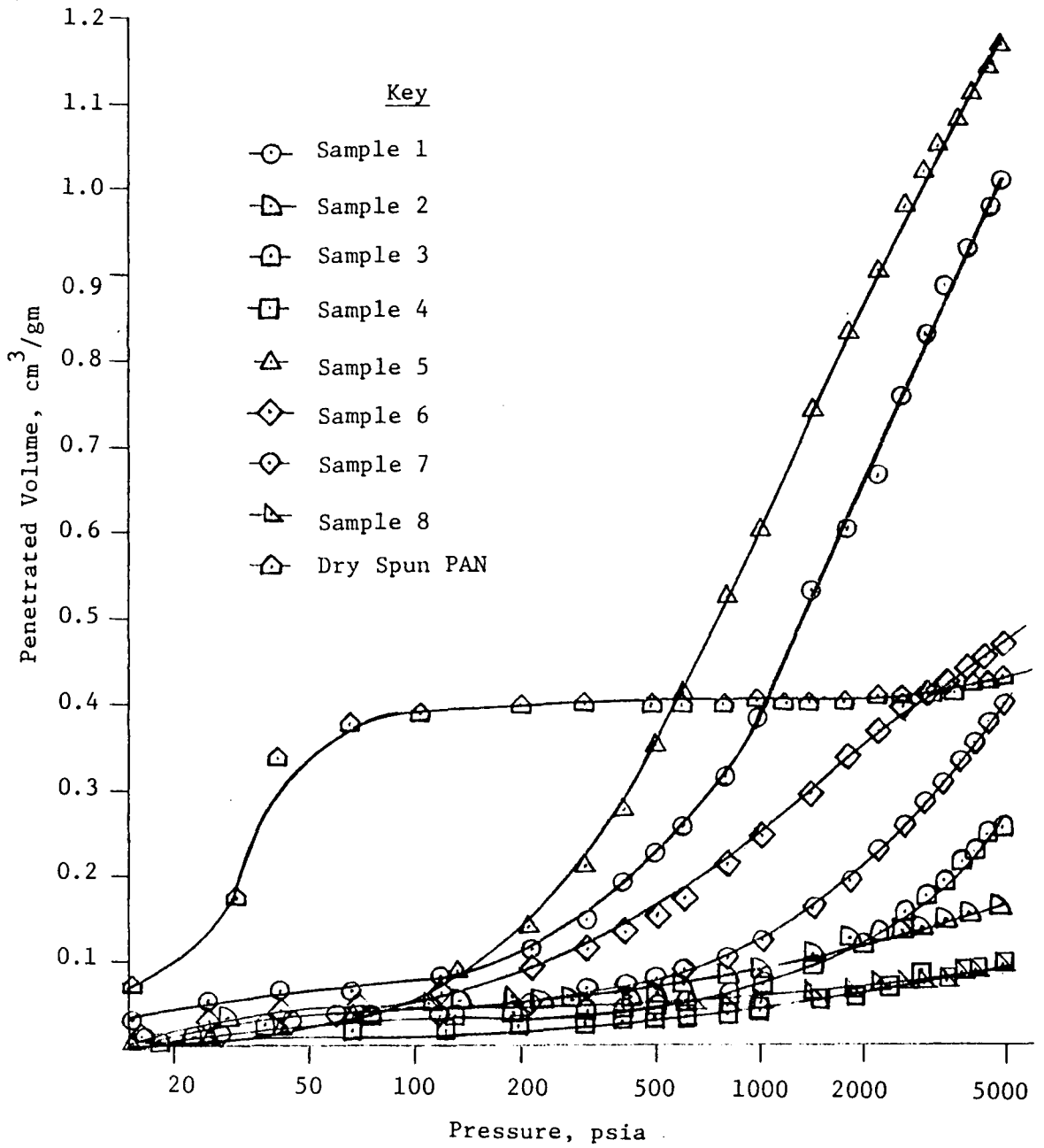


Figure 5. Mercury Intrusion Pressure-Volume Curve

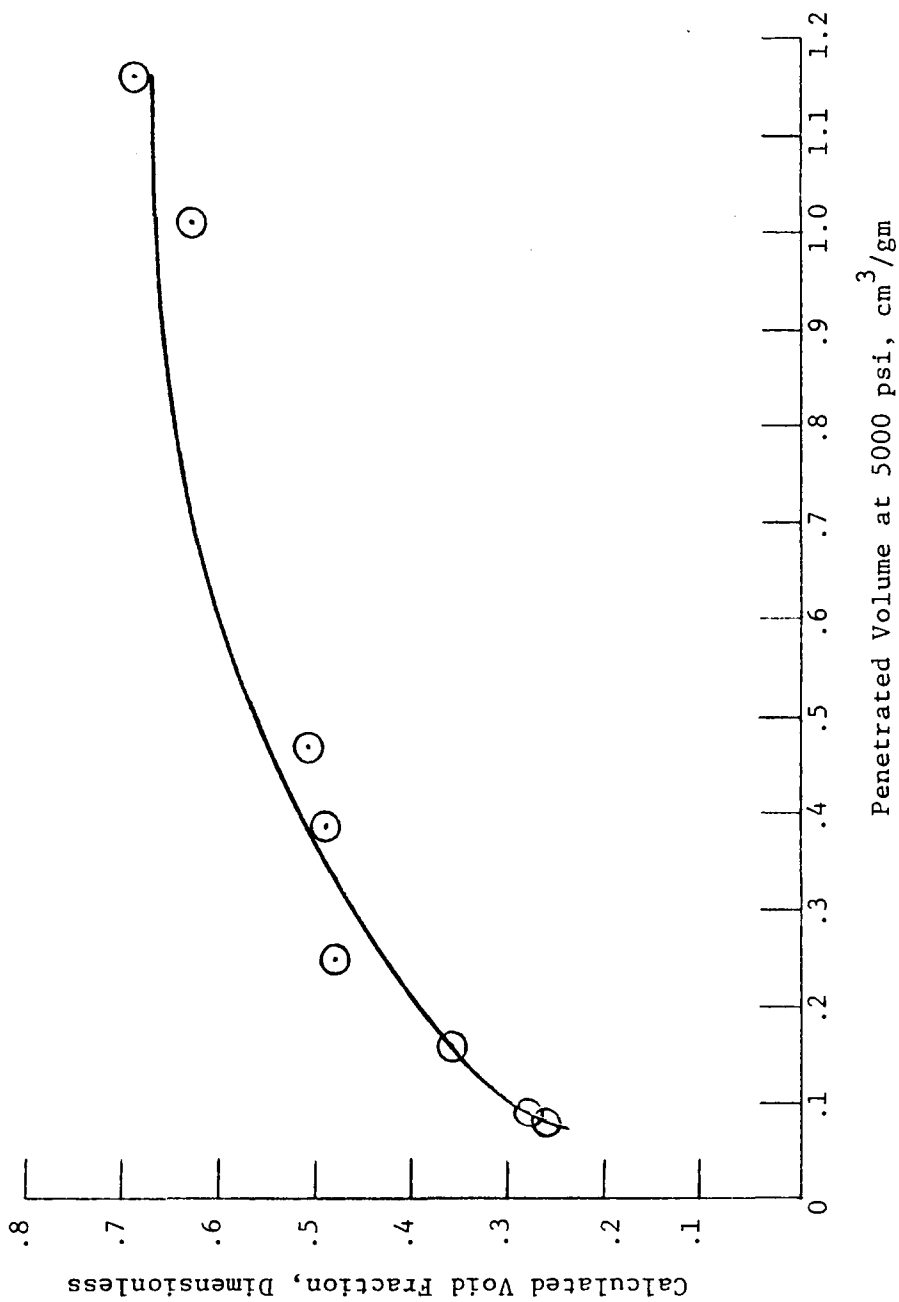


Figure 6. Penetrated Volume at 5000 psi versus Calculated Void Fraction for Samples 1-8

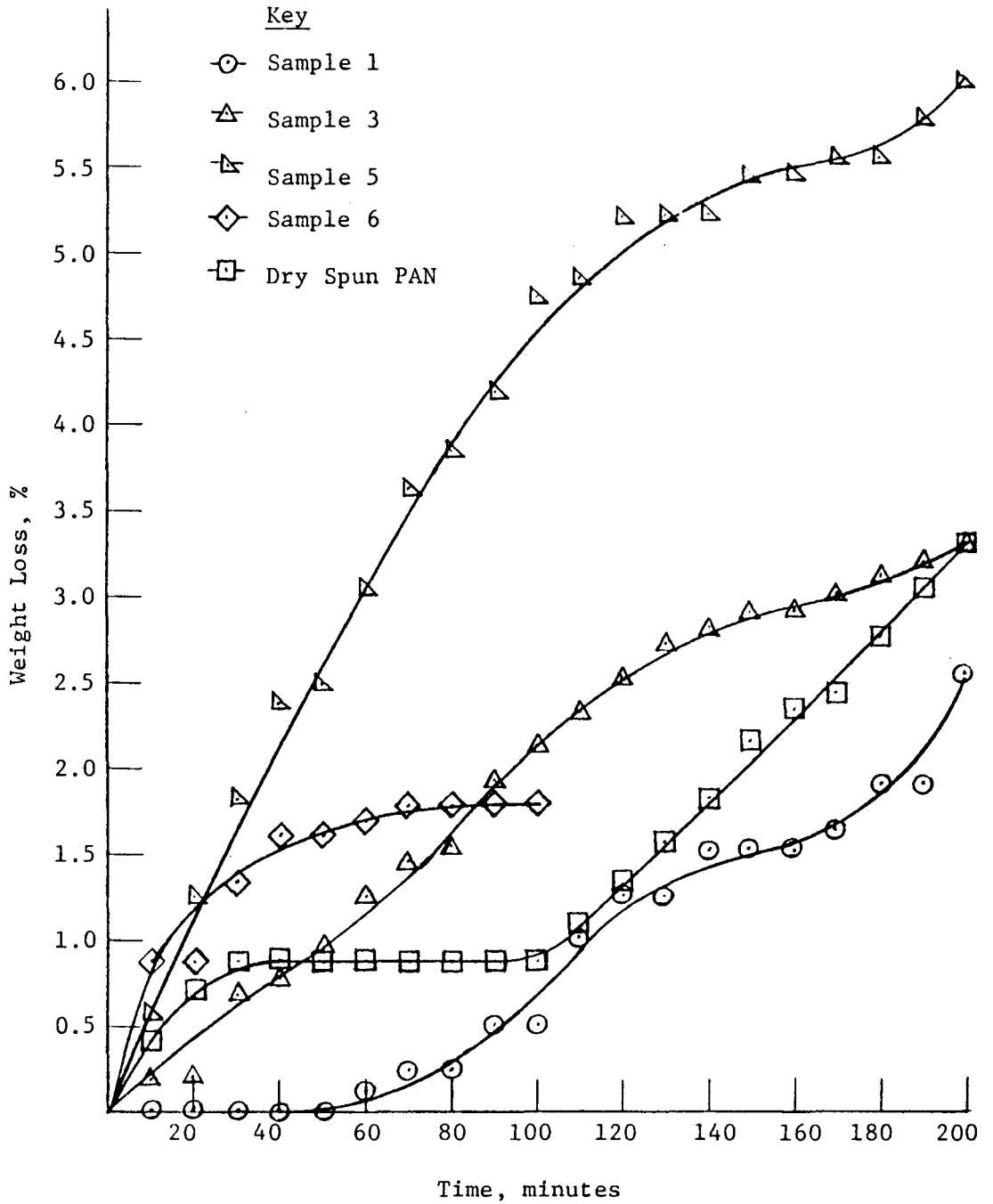


Figure 7. Percentage Weight Loss as a Function of Exposure Time



#### IV. DISCUSSION

The following are comments concerning the logic, procedures, and equipment used in this investigation. The results are discussed along with recommendations for further study.

##### Objective and Approach

A significant part of the high cost for graphite material is the long processing time. It is felt that the carbonization and oxidation stages restrict the production rate and are limited by diffusion of oxygen and volatile reaction products along with adequate heat dissipation. The controlled introduction of small pores appeared a worthwhile technique for increasing the mass transfer rates and dissipation of heat.

The literature indicated that the wet spinning operation produces a porous fiber during the coagulation step and the pores are eliminated to a great extent during the following steps of stretching, relaxation, and drying. The objective of this study was then to determine if mild operating conditions could preserve this network of pores. The yarn was then analyzed to determine if significant changes could be detected in the oxidation rate using thermogravimetric analysis.

##### Safety

The solvent, N-N dimethylformamide, was used cautiously and gloves were used whenever contact was necessary. When samples

containing the solvent were dried, vacuum ovens were used to prevent explosive buildup of the vapors or leakage of toxic byproducts. No smoking was permitted in areas where vapors could exist. The nitrogen cylinder was securely fastened to the wall and normal caution was used when handling hot solutions. Safety glasses were worn whenever the spinning equipment or analyzing apparatus was used.

#### Spinning Procedures and Equipment

The use of heated PAN powder and cooled DMF was found to reduce the tendency of lump formation upon mixing and decreased the time required for dissolution. No information was supplied with the PAN powder, except that the intrinsic viscosity was 2.18. Many various constants for the Mark-Howwink equation could be found in the literature. Using  $K = 197.0 \times 10^{-5}$  and  $a = 0.625$ <sup>(9)</sup> a number average molecular weight of 74,000 was calculated. No constants for the weight average molecular weight could be found which yielded a value within the recommended molecular weight range for those constants. For estimating purposes, one set of constants with a maximum recommended average molecular weight of 90,000 yielded a value of  $\bar{M}_W = 196,000$ . This information indicates the molecular weight may have been on the high side but the spinnability of PAN has been reported<sup>(17)</sup> to be good at  $\bar{M}_W = 150,000-200,000$  for narrowly dispersed PAN fractions.

The dope solutions were not colorless liquids as reported<sup>(9)</sup> but rather discolored and contained many multi-colored particles. The discoloration was thought to be degradation, perhaps, and the

mixing temperatures were therefore held low at 60°C. Small amounts of oxalic or phosphoric acid are added to PAN dopes as heat stabilizers to prevent discoloration<sup>(12)</sup>. One sample was prepared with 1.4% by weight of oxalic acid and less discoloration resulted. However, this did not appear to be of major importance for this study and the use of heat stabilizers was not pursued. The particles which were removed during filtration were ashed and data indicated 40% by weight was inorganic material thought to be salts and metals.

The filtering equipment worked well, but required a lot of time when larger samples of approximately 500 grams were filtered. The spinning and stretching apparatus worked smoothly and the small amount of fibers produced, did not significantly change the coagulation bath composition. No coalescence of filaments in the yarn was found.

When the cover was removed from the boiling water bath, the temperature began dropping slowly from about 98°C. About two samples could be collected before the temperature dropped to around 94°C, at which time the bath was recovered and the temperature brought back to 98°C. The maximum stretching ratio was found to be near six for these conditions. The yarn would usually break at one of the rollers used to guide the yarn through the bath. Higher stretching ratios are felt to be possible, if a higher stretching bath temperature is used. To test this, a piece of stretched yarn was dipped in a beaker of glycerol at 150°C and then quickly stretched by pulling. The yarn easily stretched another 200-300% and indeed the yarn only needed to

be held in the vapors to be stretched. Glycerol has been reportedly<sup>(9)</sup> used at 165°C for the stretching bath with stretching ratios of 15:1 resulting. Higher stretching temperatures should offer significant improvements in yarn tenacity and especially elongation. The use of glycerol would be suitable for laboratory work but would probably require recovery on a large scale. Higher extrusion speeds or larger deniers may require modifying the apparatus to provide longer coagulation and stretching baths for increased residence time.

The method used to collect samples was adequate; however, an automated takeup unit would make the operation much more convenient. The yarn did not stick to the cardboard rolls and was easily removed. The use of a refractometer to measure the coagulation bath composition was reliable, accurate, and very convenient.

#### Denier Measurement

The four filament yarn deniers obtained in this study, i.e., 31.0-62.5, are in the commercially useful range. Of course, various deniers could be made by adjusting the drawdown ratio, dope concentration, dope temperature, or the spinneret hole size. The denier accuracy was probably  $\pm 1.0$  gram since a milligram Mettler Balance was used to weigh 90 cm lengths which weighed no more than 0.007 grams.

The deniers of the four individual filaments in the yarn were checked on two samples with a vibrascope to determine the variability of the denier per filament (dpf). A comparison between the calculated

average dpf and the values obtained with the vibroscope is shown in Table V. The maximum variability of dpf was found to be 1.3 gr/denier, which indicates a moderate amount of variability for sample 8. The other sample showed a range of 0.6 dpf. The sharp break point during tensile testing which occurred for all samples, indicates that no filaments were extremely abnormal in size and all had similar physical properties.

#### Tensile Properties

Table VI compares some of the physical fiber properties with a few of the commercially available fibers. The values shown in the table indicate that the properties of yarn made in this study were similar to commercially available wet spun yarn except for slightly greater stiffness, resulting in lower break elongations and higher initial moduli. It is felt that the use of higher stretching bath temperatures could result in matching and even surpassing those of commercially available wet spun yarns.

Breaking Tenacity. The relaxation operation reduced the tenacity of every sample. The higher tenacity yarns were generally less affected by the same high temperature exposure. This could be caused by the higher tenacity yarn having a more oriented molecular structure, requiring greater quantities of thermal energy to break down. The percent shrinkage due to the relaxation stage was based on denier changes and revealed that the high tenacity yarns shrank only 1/2-3/4 as much as the lower tenacity yarns. This, again, indicates the

Table V  
COMPARISON OF DENIERS OBTAINED BY WEIGHING  
VERSUS VIBRASCOPE MEASUREMENT

|                                  | <u>Sample No. 4</u> | <u>Sample No. 8</u> |
|----------------------------------|---------------------|---------------------|
| Total Denier by Weighing         | 37.0                | 36.0                |
| No. of Filaments                 | 4                   | 4                   |
| Average Denier per Filament      | 9.25                | 9.00                |
| Denier per Filament - Vibroscope | 8.9                 | 8.5                 |
|                                  | 9.1                 | 9.4                 |
|                                  | 8.5                 | 9.4                 |
|                                  | 8.9                 | 9.8                 |
|                                  | <hr/>               | <hr/>               |
| Total Denier by Vibroscope       | 35.4                | 37.1                |
| Difference                       | +1.6                | -1.1                |

Table VI

SOME COMPARATIVE MECHANICAL PROPERTIES OF EXPERIMENTAL  
AND COMMERCIAL WET SPUN PAN FIBERS

| Wet Spun<br>Acrylic Yarns     | Dry Breaking<br>Tenacity<br>(gpd) | Dry Breaking<br>Elongation<br>(%) | Average<br>Stiffness<br>(gpd) |
|-------------------------------|-----------------------------------|-----------------------------------|-------------------------------|
| (1) Acrilan<br>(Monsanto)     | 2.0-2.7                           | 36-40                             | 4-7                           |
| (1) Creslan<br>(Am. Cyanamid) | 2.5                               | 32                                | 10.3                          |
| (1) Zefran<br>(Dow Badische)  | 3.5                               | 33                                | 11.0                          |
| This study                    |                                   |                                   |                               |
| a) Before<br>relaxation       | 1.8-2.8                           | 6-12                              | 17-44                         |
| b) After<br>relaxation        | 1.3-2.5                           | 18-24                             | 6-11                          |

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Data Obtained from Reference 14

Note: The values shown are thought to be for fibers. Most published data refers to staple properties which may involve shorter gauge lengths and crimp complications.

greater retention of the oriented structure during relaxation for the higher tenacity yarns.

Figures 2 and 3 show the tenacity as a function of calculated stretching ratio. As expected, increasing the stretching ratio resulted in larger tenacity values in every case. The parallel slopes indicate that, for samples produced with the same coagulation bath composition, the changes in stretching ratio have a consistent and repeatable effect on tenacity. The tenacity of yarns produced with the same coagulation composition was higher at the lower temperature in every case.

Breaking Elongation. The elongation of unrelaxed yarn did not correlate with any of the operating conditions. It is felt that this may be due in part to the stretching bath temperatures used. Figure 3 shows the relationship between elongation and stretching ratio for relaxed yarns. In all cases, the breaking elongation decreased with higher stretching ratios. This is in agreement with the concept that higher stretching ratios result in greater orientation along the fiber axis. Therefore, the molecules are less coiled, resulting in less extension at various stress levels. The effect of the relaxation operation on elongation can be seen by the range of percent elongation before relaxation of 6-11% compared to an elongation range of 18-23% after relaxation. Shrinkage due to relaxation ranged from 8.9-20.0%, which shows that the operation allows disorientation of molecules to occur; thereby increasing the elongation at break and decreasing the tenacity at break.



Initial Modulus and Yield Point. The modulus was taken as the initial slope of the stress-strain curve which was linear. The data shows the initial modulus was lowered 13-50% by the relaxation operation. The yield stresses are about the same before and after relaxation, while the yield strains are much higher after relaxation. Again, relaxation produces greater flexibility of the molecules, thereby lowering the modulus values since modulus is stress divided by strain. This translates into lower stiffness and a softer, more pleasant hand for the relaxed yarn.

It should be noted that the break point was generally sharp, indicating good uniformity between the individual filaments. Figure 8 shows a comparison of the typical stress-strain curves for stretched yarn with and without relaxation. The much steeper curve for the unrelaxed yarn will, of course, make accurate measurements of initial modulus and the yield points more difficult.

#### Fiber Diameter and Porosity

The filament diameter was measured using a Filar micrometer eyepiece at 500X magnification. The width of each filament was measured at three points and the average filament diameter was based on a total of 12 measurements since each fiber had four filaments.

The calculation of void fraction was done using the filament diameter, as just mentioned, the average denier per filament, and the density for void free PAN. No values for pore free density

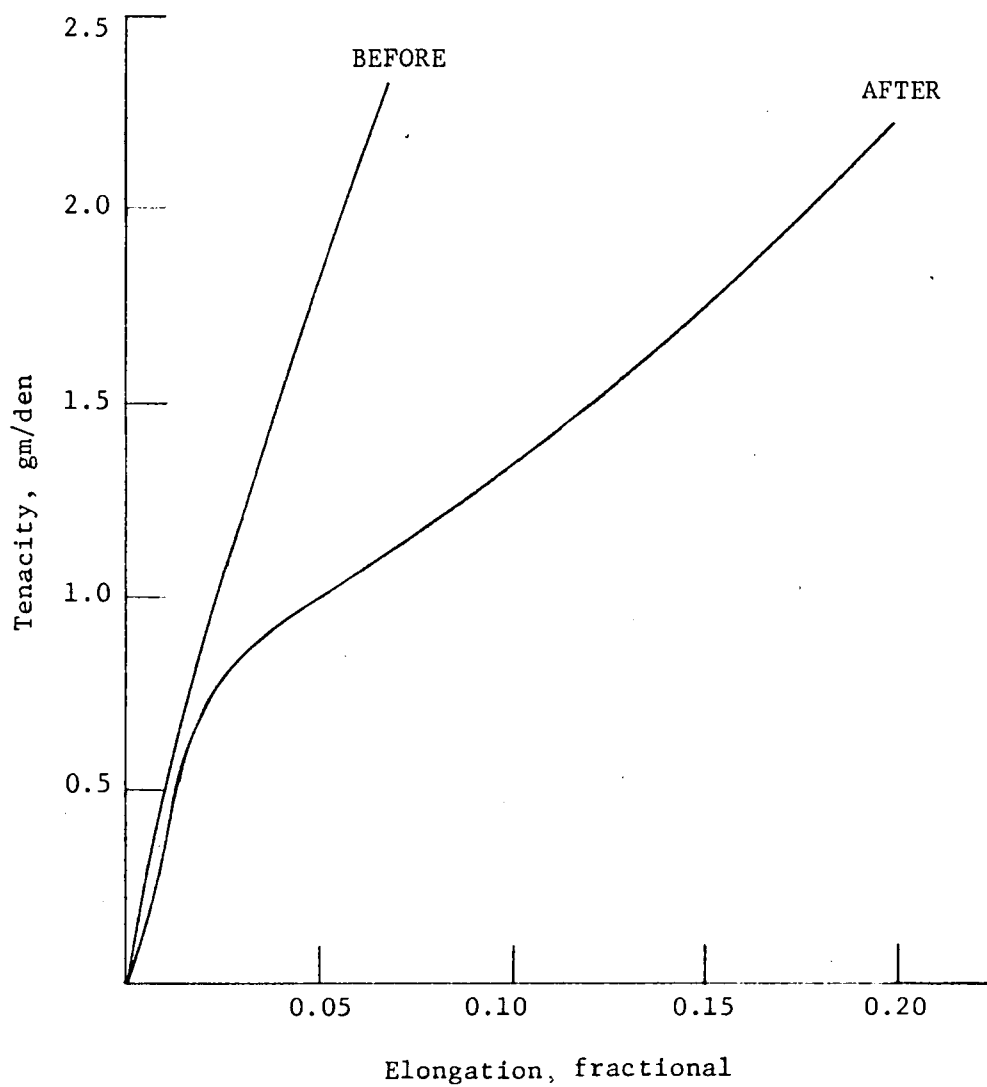


Figure 8. Stress-Strain Curves of Yarn Before and After Relaxation

could be found so an arbitrary value of  $1.20 \text{ gr/cm}^3$  was used. This is slightly higher than the value of  $1.18 \text{ gr/cm}^3$  which was found as the density of dry spun polyacrylonitrile. It is stressed, therefore, that the values presented for void fraction are intended to illustrate a trend and that the actual values are of little significance.

Values for void fraction shown in Table III clearly demonstrates that relaxation tends to reduce the pore volume. This is in agreement with earlier data which shows that relaxation causes shrinkage along the fiber length and increased denier. The shrinkage apparently coincides with total or partial collapse of the pores.

Another trend indicated by the data in Table III is that the most porous structures are formed at coagulation bath temperatures of  $50^\circ\text{C}$  compared with those at  $25^\circ\text{C}$ . In every case the yarn which was processed at higher stretching ratios had less pore volume. Overall, the fibers produced with a 25/75 DMF/water coagulation bath composition had greater pore volume than those using a 50/50 DMF/water composition. These trends would indicate that lower concentrations of solvent in the coagulation bath results in faster diffusion of the solvent from the fiber, creating more void structures. Higher temperatures would also appear to cause faster and less uniform diffusion of the solvent from the fiber and faster diffusion of nonsolvent into the fiber structure, resulting in a porous structure.

Figure 6 shows a surprisingly good correlation between the calculated void fraction and the penetrated volume obtained with the porosimeter. Therefore, the previous statements would also apply to the porosimetry data. The agreement between the two porosity measurements would indicate that the porous structure existed throughout the fiber and was not confined to the fiber surface. If pores existed only at the surface, it is doubtful that the relative calculated void fractions would correlate well with the porosimetry data.

The penetrated volume in Figure 5 indicates the relative amounts of pores while the applied pressure indicates the pore size using the equation:

$$\text{diameter in microns} \approx \frac{210.7}{\text{applied pressure in psia}}$$

The pore size at the maximum pressure of 5000 psia is 0.042 microns. The shape of the pressure-volume curve indicates relative amounts of the various sized pores, since a steep slope indicates a large penetrated volume occurring for small changes in pressure, while flat slopes indicate the absence of any appreciable amounts of pores of that size. The curves would indicate that no significant amount of pores with diameters greater than 0.042 microns exist in samples 2, 4, or 8. Samples 3 and 7 show some volume of pores with diameters between approximately 0.04 and 0.2 microns. Sample 6 appears to have pores ranging in diameter from 0.04 to 0.4 microns.

Samples 1 and 5 have pores having diameters from 0.04 to 1.0 microns. The sample of dry spun polyacrylonitrile showed a large amount of large pores around 7 microns in diameter with very few, if any, smaller pores. Since these filaments were much smaller in diameter, it was reasoned that the initial slope of the curve was due to mercury filling between the fibers and not the pores. If the initial slope is neglected, the dry spun sample shows essentially no pore volume down to diameters of 0.042 microns. This was confirmed by a small calculated void fraction of 0.26.

No pore size distribution was calculated, since there were evidently smaller pores and the curves of V vs. P did not reach a slope of zero. It is essential to obtain a leveling off of the curve to allow the curve to be normalized and relative fractions calculated for a distribution. Indeed, there could be a considerable amount of smaller pores remaining in the sample but equipment capable of exerting more than 5000 psi would be needed to force the mercury into them for measurement.

#### Thermogravimetric Analysis

TGA analysis began with the examination of PAN weight loss under standard oxidation conditions reportedly used in the manufacture of graphite fibers, i.e., air at 220-230°C. Samples of dry spun yarn, supplied by Celanese, were exposed to these conditions using air flow rates of 2 CFH and 4 CFH which correspond to linear

velocities of 1.6 and 3.2 in/sec through the 7/8" diameter furnace tube. Figure 9 shows the percentage weight loss as a function of time for a sample exposed at 230°C in a flow rate of 2 CFH of air for 70 minutes, after which the air flow rate was increased to 4 CFH and the temperature readjusted quickly back to 230°C for 70 minutes of exposure. As can be seen, the sample did not lose any weight at the higher air flow rates after an appreciable loss at the lower flow rates. The following reasons may account for the lack of weight loss:

1. The difference between the thermocouple reading and actual sample temperature increases at higher flow rates. The sample temperature may have actually been below 200°C where no appreciable reactions and therefore, no weight loss are thought to occur.

2. The oxidation rate is increased significantly at the higher air flow rates, and increase in weight due to incorporation of oxygen is equal to the weight loss due to pyrolysis.

It is felt that the drop in sample temperature is the most probable cause, since the oxidation reaction rate is thought to be relatively slow and an air velocity of 1.6 in/sec should be more than enough to replenish the oxygen at the surface. The boundary layer thickness is not thought to be of major significance.

To eliminate the possibility that the oxidation may be extremely sensitive to air flow rates, it was decided to use an inert

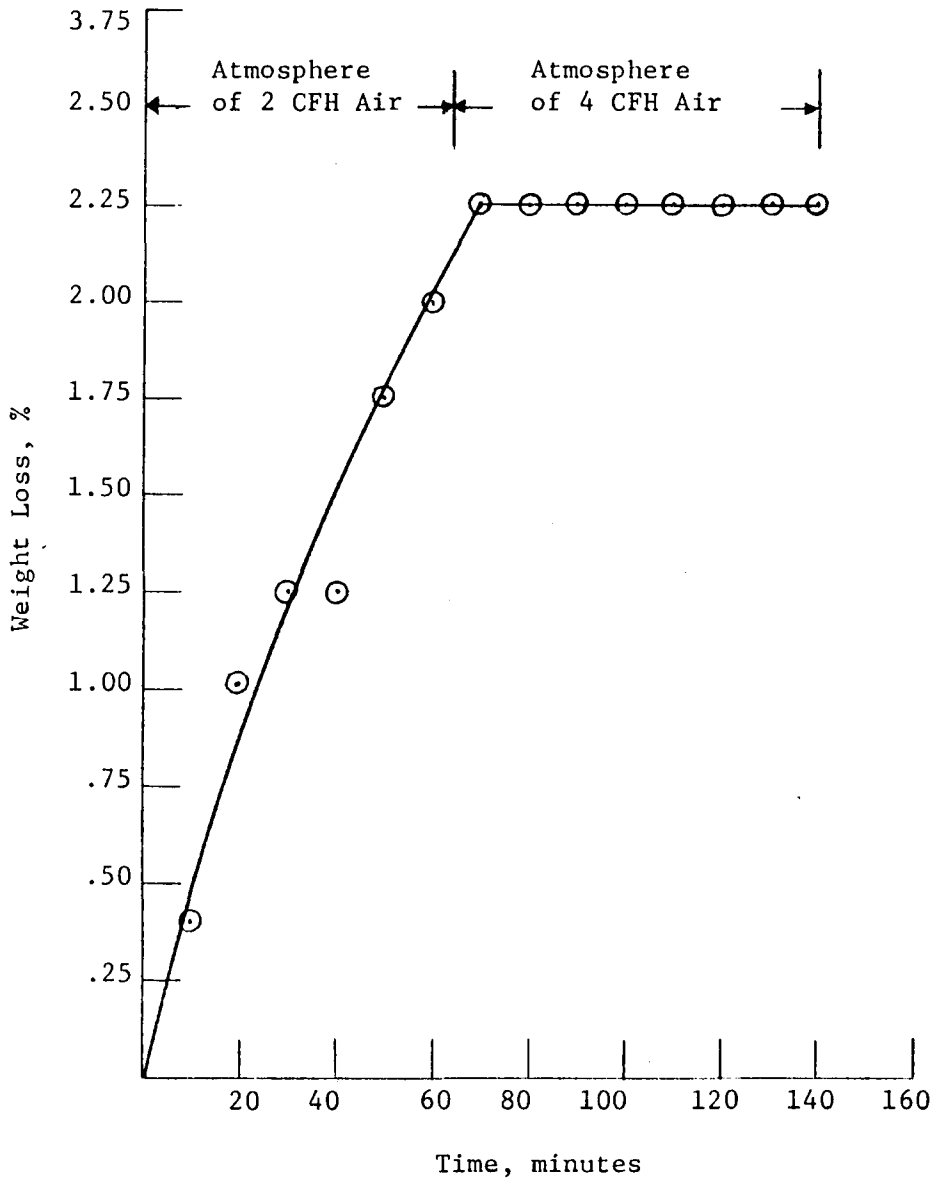


Figure 9. Effect of Air Flow Rate on Weight Loss during TGA Analysis at 230°C

atmosphere and examine the weight loss rate of the pyrolysis reactions which result in products such as HCN, NH<sub>3</sub>, water, etc. It was reasoned that, if pores cause higher weight losses or loss rates with pyrolysis reactions, it would be logical to assume that higher oxygen transfer rates into the fiber should also be obtained during oxidation.

High purity argon was used and Figure 7 shows the resulting percentage weight loss as a function of time. The porosimetry measurements and calculated void fractions do not correlate very well with the maximum weight loss after 200 minutes of exposure. The % weight loss rates (slope of curves) are variable and show no strong correlation with porosity. However, the most porous fiber (sample 5) did show both a much higher weight loss and a higher sustained loss rate. Sample 1, which was thought also to have a large pore volume, showed, unexpectedly, the lowest weight loss. Sample 3 had a relatively high weight loss. Some of the discrepancy in the data may be due to the existence and amount of very small pores which could not be measured with the porosimeter. It would have been much better to run duplicate samples, but the lack of additional sample made this impossible.

#### Recommendations

The following is a list of recommendations for equipment modifications and procedures for use in further studies.



Further Studies. The most immediate further study recommended is the more thorough analysis of the effect of pore size, distribution, and quantity on the oxidation of PAN. It is imperative that the reliability and repetitiveness of the TGA analysis be established. Once precision of TGA analysis has been determined, additional samples should be produced for porosity and oxidation analysis. If consistent results indicate improvements of the magnitude shown by sample 5, it would then be extremely worthwhile to further evaluate samples through the carbonization and graphitization stages. Further evaluation will require much more additional equipment to handle large enough fiber samples for physical testing, etc. It may be more expedient to have industrial firms, who are in the graphite business, evaluate any yarn produced in large enough quantities.

It is also recommended that the use of a density gradient column be investigated for obtaining accurate "apparent" densities of the produced fibers. This has been used to measure the density of graphite fibers<sup>(21)</sup> with both high accuracy and precision. The measurement of fiber density along with fiber diameter will allow pore volume to be determined quickly and accurately.

If porous fibers are to offer improvements in processing rates, it is important to obtain indications of the effect of pore size and quantity on the physical properties of the graphite product. This should be done as soon as repetitive thermogravimetric results show it is warranted.

Equipment and Procedure Modifications. The only significant problem associated with existing equipment is the maintenance of a consistent stretching bath temperature. It is recommended that an oil bath be used around the stretching bath to ensure high enough heat transfer to maintain a constant bath temperature.

The use of glycerol in the stretching bath should be investigated. It is felt that major improvement in the fiber strength and flexibility will result if stretching temperatures up to 150°C are examined. This will, of course, necessitate an additional washing or extraction step to remove the glycerol, if the yarn is to be examined on the TGA.

The design and construction of a winder to build uniform packages on the takeup roll would make the sample collection much easier.

## V. CONCLUSIONS

PAN fibers were produced using the wet spinning process and analyzed for physical properties and porosity. The affect of porosity on the oxidation rate of PAN was examined. The results of this study led to the following conclusions:

1. The equipment, constructed for this study, produces fibers having physical properties comparable with commercial PAN fibers.

2. Deniers as well as diameters of the fibers made varied inversely with stretching ratio.

3. Relaxation of the yarn (exposure to temperatures of 130°C) resulted in:

- a) increase of fiber elongation
- b) decrease of fiber tenacity
- c) shrinkage of fiber length, the amount of shrinkage varying indirectly with unrelaxed tenacity
- d) reduction of pore volume
- e) little change in yield point tenacity
- f) increases in yield point elongation
- g) reduction of the average initial modulus
- h) reduction of the average stiffness value

4. The four filaments comprising the fiber were of uniform size and have similar physical properties.

5. The breaking tenacity varies directly with stretching ratio.

6. Elongation varies inversely with stretching ratio.
7. The amount of pore volume in the fibers increased with higher coagulation bath temperatures and lower solvent concentrations in the bath.
8. Porosimetry measurements show good correlation with calculated values of the pore volume. The amount of pores and the pore size vary greatly between samples produced under different extrusion and stretching conditions.
9. The smallest measurable pore size was 0.044 microns, but significant quantities of smaller pores may exist in the fibers.
10. Pore size and size distribution may have a significant impact on the rate of PAN fiber oxidation.

## VI. SUMMARY

The first objective of this study was to design, build, and test an apparatus for making porous polyacrylonitrile fibers. An effort was then made to determine the effect of a porous structure on the oxidation rate of PAN fibers. Increases in oxidation rates may significantly increase the production rates of the graphite process resulting in lower cost to the purchaser and wider uses of graphite fibers.

The wet spinning process was evaluated for porous PAN fiber production. A large range of fiber properties could be obtained by varying the stretching ratio and exposure to elevated temperatures. Analysis indicates that fibers containing significant quantities of pores, can be produced under suitable coagulation bath conditions. The quantity of pores increased when a low amount of stretching was applied and the yarn was not allowed to relax at elevated temperatures. Even under these conditions it is thought that sufficient orientation of the PAN molecules may exist in the fibers to yield graphite yarn properties which are acceptable for some lower strength applications.

The effect of pore volume on oxidation rate was examined assuming that increased weight loss rate during pyrolysis in the absence of air would indicate proportional increases in oxidation rate. The weight loss rates appeared highly variable and did not correlate directly with pore volume. The limit of precision of the

TGA analyzer is thought to contribute to the inconsistency of the results, while the existence of pores, too small to be measured, may also be a factor.

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## VIII. APPENDIX

The appendix contains information which would be required to reproduce the results of this investigation. A few procedures are detailed along with a complete listing of materials and equipment used in this study.

### Data Tables

This section contains the data obtained during the investigation. Table VII contains the fiber diameters from optical measurements while Table VIII includes the penetrated volumes obtained using the porosimeter. Tables IX and X contains the weight measurements resulting from the thermogravimetric analysis.

### Sample Calculations

These are examples of calculations made during this investigation.

Drawdown Ratio. This ratio is defined and derived later. All samples were extruded using a dope concentration of 17.1% by weight at 50°C. Figure 11 shows a dope density of 0.961 gr/cm<sup>3</sup> under these conditions. The spinneret holes are circular with an average diameter of 118 microns. Table III shows the total denier at the feed roll was usually 200 and the average denier per filament was therefore 50. The drawdown under these conditions was calculated as

Table VII

## DATA OF FIBER DIMENSIONS

| Sample No. | 0*   | Filar Eyepiece Divisions |      |      |      |      |      |      |      |      |      |      |      |      |      |  |
|------------|------|--------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|--|
|            |      | 1                        | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 11   | 12   | 13   | 15   | 16   | 17   |  |
| 1          | 0.98 | 3.88                     | 2.46 | 2.95 | 2.12 | 3.64 | 2.67 | 3.03 | 2.63 | 2.09 | 2.80 | 2.45 | 2.39 | 2.96 | 2.51 |  |
| 2          | 1.01 | 3.68                     | 2.11 | 3.07 | 2.04 | 3.38 | 2.66 | 3.35 | 1.63 | 1.93 | 2.66 | 2.30 | 2.01 | 3.40 | 2.17 |  |
| 3          | 0.96 | 3.79                     | 2.19 | 2.79 | 2.47 | 3.30 | 2.52 | 3.20 | 2.48 | 2.45 | 3.10 | 1.98 | 2.30 | 2.65 | 2.25 |  |
| 4          | 0.83 | 3.20                     | 2.37 | 3.57 | 2.00 | 3.67 | 2.79 | 3.68 | 2.25 | 2.45 | 3.95 | 2.63 | 2.17 | 2.69 | 2.64 |  |
| 5          | 0.99 | 4.01                     | 2.48 | 2.49 | 2.00 | 3.59 | 2.11 | 3.22 | 2.52 | 2.22 | 2.45 | 1.71 | 2.67 | 2.49 | 1.97 |  |
| 6          | 0.98 | 3.81                     | 1.88 | 2.77 | 2.38 | 3.53 | 2.46 | 2.56 | 2.29 | 1.95 | 3.19 | 2.38 | 2.39 | 3.30 | 2.41 |  |
| 7          | 0.92 | 3.79                     | 2.12 | 3.19 | 2.31 | 3.11 | 2.60 | 2.98 | 2.59 | 2.47 | 2.98 | 2.41 | 1.86 | 3.24 | 2.72 |  |
| 8          | 0.95 | 2.93                     | 2.46 | 3.12 | 2.18 | 3.41 | 2.32 | 3.21 | 2.07 | 2.26 | 2.60 | 2.13 | 2.47 | 2.88 | 2.17 |  |
| 9          | 1.02 | 3.65                     | 2.34 | 3.22 | 2.02 | 3.53 | 2.31 | 3.17 | 1.67 | 2.32 | 2.29 | 2.25 | 2.65 | 2.25 | 2.16 |  |
| 10         | 1.07 | 2.94                     | 2.43 | 2.89 | 2.47 | 3.61 | 2.58 | 2.28 | 1.94 | 2.39 | 3.32 | 2.56 | 2.35 | 2.72 | 1.83 |  |
| 11         | 0.75 | 2.81                     | 2.17 | 2.88 | 2.33 | 3.73 | 2.14 | 2.87 | 1.64 | 2.25 | 3.57 | 2.42 | 2.28 | 2.78 | 1.95 |  |
| 12         | 0.96 | 2.91                     | 2.10 | 3.17 | 1.73 | 3.63 | 2.18 | 2.43 | 2.32 | 2.09 | 3.22 | 2.46 | 2.45 | 2.34 | 2.02 |  |

\*Special dry spun PAN fiber sample

1 Division = 17.7 microns

Samples 10 and 14 were not measured

Table VIII

POROSIMETRY DATA

| Sample No.                    | 1  | 2    | 3     | 4     | 5     | 6     | 7     | 8     | S.S.* |
|-------------------------------|--|------|-------|-------|-------|-------|-------|-------|-------|
| Sample Wgt.<br>(mg)           | 6.45   | 7.38 | 27.60 | 19.27 | 13.19 | 14.01 | 15.28 | 49.46 | 30.05 |
| Pressure<br>Reading<br>(psig) | Scale Reading (cm <sup>3</sup> ) x 10 <sup>4</sup> |      |       |       |       |       |       |       |       |
| 0                             | 2  | 2.5  | 1     | 0     | 0     | 2     | 1     | 4     | 20    |
| 10                            | 3  | 3    | 3     | 2     | 1     | 4     | 2     | 11    | 55    |
| 25                            | 4  | 3    | 5     | 5     | 3     | 6     | 5     | 18    | 99    |
| 50                            | 4  | 4    | 6     | 5.5   | 5     | 7.5   | 6     | 21    | 112   |
| 100                           | 5  | 4    | 8     | 6     | 10    | 9     | 6     | 22    | 115   |
| 200                           | 7  | 4    | 10    | 6     | 19    | 12    | 8     | 23    | 116   |
| 300                           | 9  | 4    | 11    | 6     | 28    | 15    | 10    | 24    | 116   |
| 400                           | 12   | 4    | 12    | 6     | 37    | 18    | 11    | 24    | 116   |
| 500                           | 14   | 5    | 13    | 7     | 46    | 21    | 12    | 25    | 117   |
| 600                           | 16   | 5    | 15    | 7     | 54    | 24    | 14    | 26    | 117   |
| 800                           | 20   | 6    | 17    | 8     | 69    | 29    | 16    | 26    | 117.5 |
| 1000                          | 24   | 6    | 20    | 8     | 78    | 34    | 19    | 27    | 118   |
| 1400                          | 34   | 6    | 26    | 9     | 96    | 40    | 24    | 29    | 118.5 |
| 1800                          | 38   | 7    | 31    | 10    | 108   | 46    | 29    | 31    | 119   |
| 2200                          | 42   | 8    | 37    | 11    | 118   | 50    | 34    | 32.5  | 119.5 |
| 2600                          | 48   | 8    | 43    | 12    | 126   | 54    | 39    | 34    | 120   |
| 3000                          | 52   | 9.5  | 48    | 13    | 132   | 56    | 42    | 36    | 121   |
| 3400                          | 56   | 10   | 53    | 14    | 138   | 58    | 46    | 37    | 122   |
| 3800                          | 58   | 11   | 58    | 15    | 143   | 60    | 50    | 39    | 123   |
| 4200                          | 60   | 11   | 62    | 15    | 147   | 62    | 54    | 40    | 124   |
| 4600                          | 62   | 12   | 24    | 16    | 150   | 64    | 57    | 41.5  | 125   |
| 5000                          | 65   | 12   | 72    | 16    | 154   | 66    | 59    | 42.5  | 125   |

\*Special Sample - Ether Extracted Sample of Dry Spun Polyacrylonitrile

Table IX

TGA DATA USING ATMOSPHERE OF AIR

Sample: Ether Extracted Dry Spun PAN Fiber

Temperature: 230°C

| Time (minutes) | Purge Gas Rate (CFH) | Weight |
|----------------|----------------------|--------|
| 0              | 2                    | 10.61  |
| 10             | 2                    | 10.57  |
| 20             | 2                    | 10.50  |
| 30             | 2                    | 10.48  |
| 40             | 2                    | 10.48  |
| 50             | 2                    | 10.43  |
| 60             | 2                    | 10.40  |
| 70             | 2                    | 10.37  |
| 80             | 4                    | 10.37  |
| 90             | 4                    | 10.37  |
| 100            | 4                    | 10.37  |
| 110            | 4                    | 10.37  |
| 120            | 4                    | 10.37  |
| 130            | 4                    | 10.37  |
| 140            | 4                    | 10.37  |

Table X  
TGA DATA USING ARGON ATMOSPHERE

| Sample No.<br>Time (minutes) | 1       | 3       | 5       | 6       | Extra*  |
|------------------------------|---------|---------|---------|---------|---------|
| 0                            | 7.90    | 10.30   | 8.83    | 11.20   | 11.50   |
| 10                           | 7.90    | 10.28   | 8.78    | 11.10   | 11.45   |
| 20                           | 7.90    | 10.28   | 8.72    | 11.10   | 11.42   |
| 30                           | 7.90    | 10.23   | 8.67    | 11.05   | 11.40   |
| 40                           | 7.90    | 10.22   | 8.62    | 11.02   | 11.40   |
| 50                           | 7.90    | 10.20   | 8.61    | 11.02   | 11.40   |
| 60                           | 7.89    | 10.17   | 8.56    | 11.01   | 11.40   |
| 70                           | 7.88    | 10.15   | 8.51    | 11.00   | 11.40   |
| 80                           | 7.88    | 10.14   | 8.49    | 11.00   | 11.40   |
| 90                           | 7.86    | 10.10   | 8.46    | 11.00   | 11.40   |
| 100                          | 7.86    | 10.08   | 8.41    | 11.00   | 11.40   |
| 110                          | 7.82    | 10.06   | 8.40    |         | 11.37   |
| 120                          | 7.80    | 10.04   | 8.37    |         | 11.35   |
| 130                          | 7.80    | 10.02   | 8.37    |         | 11.32   |
| 140                          | 7.78    | 10.01   | 8.37    |         | 11.29   |
| 150                          | 7.78    | 10.00   | 8.35    |         | 11.25   |
| 160                          | 7.78    | 10.00   | 8.35    |         | 11.23   |
| 170                          | 7.77    | 9.99    | 8.34    |         | 11.22   |
| 180                          | 7.75    | 9.98    | 8.34    |         | 11.18   |
| 190                          | 7.75    | 9.97    | 8.32    |         | 11.15   |
| 200                          | 7.70    | 9.96    | 8.30    |         | 11.12   |
| Temperature Range<br>(°C)    | 223-225 | 225-225 | 220-220 | 220-228 | 225-225 |

\*Special dry spun PAN sample, ether extracted.

$$\begin{aligned} \text{D.D.} &= \frac{(9000)(p)(c)(A)}{\text{dpf}_B} \\ &= \frac{(9000)(.961)(.171)(3.1416)(.118)^2}{(50)(4)} \\ &= 0.32 \end{aligned}$$

Total Denier. The weight in grams per 9000 meters for a fiber consisting of any number of filaments. Total Denier was measured by weighing a 90 cm length of the fiber

$$\text{Total Denier(grams)} = (\text{weight of 90 cm})(1 \times 10^4)$$

For example: 90 cm of sample 1 weighed 4.7 milligrams

$$\text{Total Denier} = (0.0047)(1 \times 10^4) = 47 \text{ grams}$$

Average Denier Per Filament. The average total denier of a fiber divided by the number of filaments in the fiber.

For sample 1:

$$\text{dpf} = 47/4 = 1.75 \text{ grams}$$

Stretching Ratio. The ratio of the linear speed of yarn on the takeup roll divided by the velocity of yarn on the feed roll. Measurement of the feed roll and takeup roll speed is usually taken to determine the stretching ratio. However, to eliminate the possibility of slippage, the stretching ratio was based on fiber deniers as follows:

$$\text{Stretching Ratio} = \frac{\text{Feed roll denier}}{\text{Takeup roll denier}}$$

For sample 1:

$$\text{Stretching Ratio} = \frac{199}{47} = 4.25$$

Relaxation Length Shrinkage. The shrinkage due to the relaxation operation was based on fiber deniers as:

$$\text{Length Shrinkage (\%)} = 100X \frac{\text{fiber denier after relaxation} - \text{fiber denier before relaxation}}{\text{fiber denier after relaxation}}$$

Fiber from sample 1 was relaxed and relabeled as sample 10. The percent shrinkage in length for sample 10 is therefore,

$$\text{Length Shrinkage} = \frac{56-47}{56} = 16.1\%$$

Void Fraction. The following equation was used:

$$\text{Void Fraction} = 1 - \frac{(\text{dpf})(4)}{(9 \times 10^5)(\rho)(\pi)(\text{diameter})^2}$$

where: dpf = bone dry denier per filament

$\rho$  = density of pure, void free polymer. This value was assumed to be  $1.20 \text{ gr/cm}^3$

diameter = average filament diameter, cm .

For Sample 1:

$$\begin{aligned} \text{Void Fraction} &= 1 - \frac{(11.75)(4)}{(9 \times 10^5)(1.20)(3.1416)(61.1 \times 10^{-4})^2} \\ &= 1 - 0.37 \\ &= 0.63 \end{aligned}$$

Tenacity. The area compensator accessory was used on the Instron Tensile Tester. The denier was dialed prior to each sample and tenacity read directly from the chart paper.

Elongation. The chart speed on the Instron unit was set at 50 cm/min while the cross head speed was 10 cm/min. The gage length was 16.7 cm. The % elongation was calculated using:

$$\begin{aligned} \% \text{ Elongation} &= \frac{\text{chart distance from initial upswing to break}}{(5)(16.7)} \\ &= \frac{\text{chart distance}}{83.5} \end{aligned}$$

For Sample 1:

Three pulls resulted in chart distances of 5.8, 6.2, and 9.8 cms.

$$\% \text{ Elongation} = \frac{5.8}{83.5} = 6.9\%, \quad \frac{6.2}{83.5} = 7.4\%, \quad \text{and} \quad \frac{9.8}{83.5} = 11.7\%$$

$$\text{The average Elongation} = \frac{6.9 + 7.4 + 11.7}{3} = \frac{26.0}{3} = 8.7\%$$

Average Stiffness. The average stiffness was calculated at the break point as follows:

$$\text{Average Stiffness} = \frac{\text{breaking tenacity}}{\text{breaking elongation}}$$

For Sample 1:

$$\text{Average Stiffness} = \frac{1.75 \text{ gr/den}}{.087} = 20.1 \text{ gr/den}$$



Average Yield Stress. Read directly from chart paper since accessory was used which compensated for the denier dialed in prior to testing.

Average Yield Strain. Calculated in a manner similar to elongation except the chart distance was measured from the initial upswing to the yield point.

For Sample 1:

Three pulls resulted in chart distances of 1.4, 1.5 and 1.6 cms.

$$\% \text{ Elongation to Yield} = \frac{1.4}{83.5} = 1.7\%, \frac{1.5}{83.5} = 1.8\%, \frac{1.6}{83.5} = 1.9\%$$

$$\text{The average yield strain} = \frac{1.7 + 1.8 + 1.9}{3} = \frac{5.4}{3} = 1.8\%$$

Initial Modulus. The initial modulus was calculated as the initial linear slope of the stress strain curve.

$$\text{Initial Modulus} \left( \frac{\text{gr}}{\text{den}} \right) = \frac{\text{change in tenacity}}{\text{fractional elongation}}$$

Weight Loss. TGA analysis of sample 1 indicated:

$$\text{initial weight} = 7.90 \text{ mg}$$

$$\text{weight at 100 minutes} = 7.80 \text{ mg}$$

$$\text{percent weight loss} = \frac{7.90 - 7.86}{7.90} \times 100 = 0.51\%$$

Safety Data

The solvent, N-N dimethylformamide, is moderately toxic and has a threshold limit value of 20 ppm<sup>(16)</sup>. The material fortunately has the relatively high boiling point of 153°C and is generally non-corrosive. Adsorption through the skin may be harmful, so gloves were worn whenever contact was necessary. The explosive limits for DMF are: L.E.L. = 2.2% and U.E.L. = 15.2% by volume at 100°C.

Determination of PAN Concentration in PAN/DMF Dope

The following procedure was used to determine the percentage by weight of PAN in PAN/DMF dope.

1. A cleaned dish is heated at 200°C for one hour.
2. The dish is placed in a dessicator with dry sodium silicate crystals for 30 minutes.
3. Weigh dish to nearest 0.0001 grams and weight is recorded as weight A.
4. Approximately 3 grams of filtered dope are added to the dish which is then reweighed to the nearest 0.0001 grams. Weight is recorded as weight B.
5. Dish is placed in a vacuum oven for two hours at 200°C.
6. Place dish in dessicator for 30 minutes.
7. Reweigh dish to nearest 0.0001 grams and record as weight C.

Calculation:  $\text{weight \% PAN} = \frac{\text{weight C} - \text{weight A}}{\text{weight B} - \text{weight A}} \times 100$

Notes:

1. Drying time was determined by changes in results with one, two and three hours of drying time. Larger quantities of dope will require longer drying time.

2. Tongs should be used whenever dish is handled.

3. Figure 10 shows the concentration of dope before and after filtration. The results indicated that the concentration of PAN increased approximately 0.2 weight percent during filtration since a closed system was not used.

Determination of PAN/DMF Dope Density

Procedure used is as follows:

1. Place jar of dope in a 25°C constant temperature bath for two hours.

2. A 25 ml graduated cylinder (subdivisions of 0.2 ml) was washed and dried in a vacuum oven at 100°C for one hour.

3. The cylinder was placed in a dessicator containing dry sodium silicate crystals for 30 minutes.

4. The cylinder was weighed to nearest 0.0001 grams and the weight recorded as A.

5. Slowly pour approximately 18-20 ml of cooled filtered dope into the graduated cylinder. Use caution in pouring since air is entrapped if done too quickly. If air bubbles exist, the sample must be discarded.

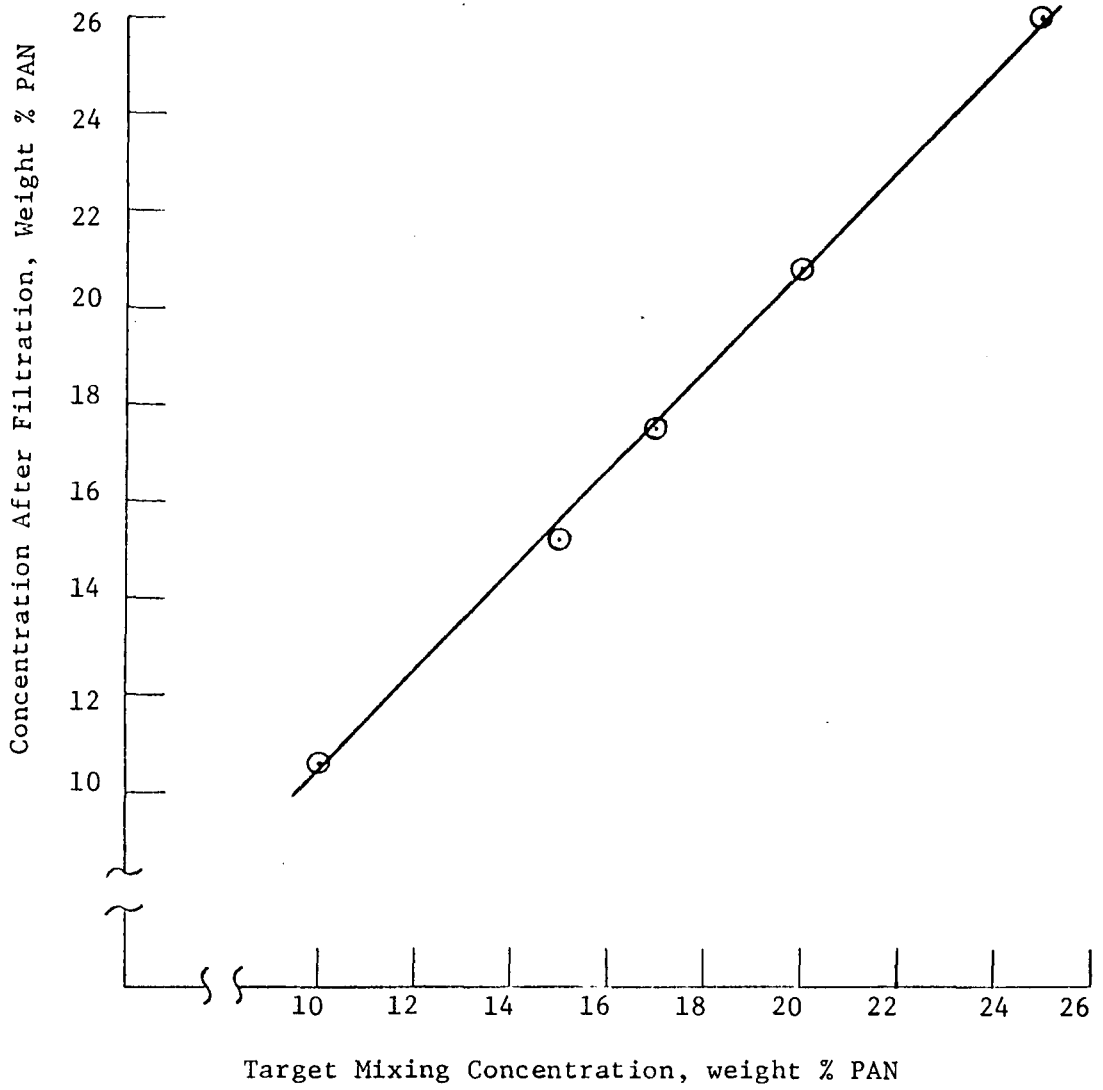


Figure 10. Loss of Solvent During Dope Filtration

6. Immediately read the volume of dope to the nearest 0.1 ml and record as volume A.

7. Reweigh the filled cylinder quickly to the nearest 0.0001 grams and note as weight B.

8. Place the cylinder in an oven at  $50^{\circ}\text{C} \pm 1^{\circ}\text{C}$  for 30 minutes.

9. Remove cylinder and quickly observe volume and reweigh. Record as volume B and weight C.

$$\text{Calculation: Density at } 27^{\circ}\text{C (gr/cc)} = \frac{\text{weight B} - \text{weight A}}{\text{volume A}}$$

$$\text{Density at } 50^{\circ}\text{C (gr/cc)} = \frac{\text{weight C} - \text{weight A}}{\text{volume B}}$$

Notes:

1. It is presumed that the initial concentration of dope is known.

2. Due to the high boiling point of DMF, only minute quantities of DMF were lost during the heating at  $50^{\circ}\text{C}$ . For example, the concentration at  $25^{\circ}\text{C}$  was measured gravimetrically to be 15.10% and calculated to be 15.11% due to a loss of 0.0163 grams, which was assumed to be solvent only, during the heating period.

Therefore concentration was assumed constant.

3. Tongs should be used to handle all apparatus.

A plot of density as a function of concentration is shown in Figure 11.

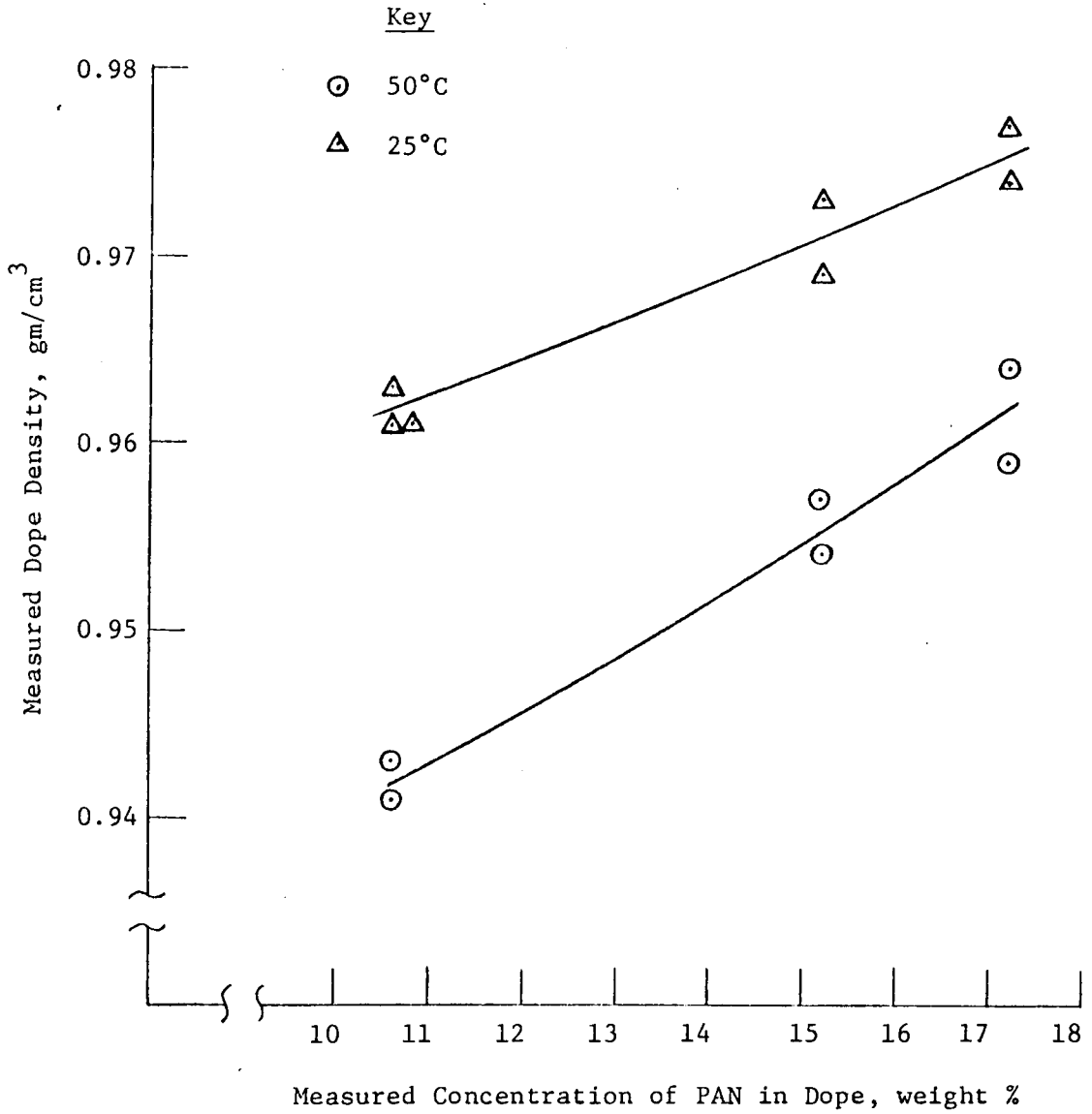


Figure 11. Density versus Concentration of PAN/DMF Spinning Dope

Derivation of Spinning Drawdown Ratio

Drawdown is defined as the ratio of the speed of bone dry solids at the feed roll to the velocity of the solids at the spinneret face. It will be assumed that the dope stream does not swell or contract at the spinneret hole exit.

- DD = Drawdown ratio (dimensionless)
- S = Feed roll speed (meters/minute)
- $D_B$  = Bone dry total denier (grams)
- $dpf_B$  = Bone dry denier per filament (grams) =  $\frac{D_B}{N}$
- N = Number of spinneret holes or filaments per end
- $\rho$  = Density of dope at the spinneret hole ( $\frac{gr}{cc}$ )
- c = Concentration of dope (weight fraction)
- A = Area of one spinneret hole ( $mm^2$ )
- $W_s$  = Weight rate of solids flow  
=  $(D_B)(S)/9000$  [grams/minute]
- $W_d$  = Weight rate of dope flow  
=  $(D_B)(S)/(9000)(C)$  [grams/minute]
- $V_j$  = Average velocity of dope at the spinneret face  
=  $W_d/(N)(\rho)(A) = (D_B)(S)/(9000)(c)(N)(\rho)(A)$  [meters/min]
- DD =  $\frac{\text{velocity of bone dry solids at feed roll}}{\text{velocity of bone dry solids at spinneret face}}$

Note: Assuming no slippage between the yarn and feed roll, the velocity of solids at the feed roll will be taken as the feed roll speed. Since the dope is homogeneous, the velocity of dope through

the spinneret hole is the same as the solids velocity through the hole. Therefore,

$$DD = \frac{S}{V_j} = S / \frac{(D_B)(S)}{(9000)(c)(N)(\rho)(A)}$$

or

$$DD = \frac{(9000)(\rho)(c)(A)}{dpf_B} \quad \text{or} \quad \frac{(9000)(N)(\rho)(A)(C)}{D_B}$$

Therefore drawdown is dependent on the density of dope, concentration of solids in the dope, size of the spinneret hole, and the denier per filament.

#### Concentration of DMF in DMF/Water Solutions

The following procedures were used to determine the concentration (weight percent) of DMF in the coagulation bath solution of DMF and water:

1. Samples were prepared of various concentrations of DMF in DMF/distilled water solutions. Four of these samples kept in 2 ounce eyedropper bottles and stored under refrigeration.

2. Table XI shows the refractive index measured with the prepared standards. Figure 12 shows the refractive index as a function of the concentration of DMF.

3. Whenever a sample was to be measured the refractometer would be calibrated with distilled water to read 1.3325.

4. An eyedropper was used to place the sample on the refractometer sample plate.



Table XI

CALIBRATION DATA FOR REFRACTOMETER

| <u>Weight % Water Prepared in DMF</u> | <u>Refractive Index Measured</u> |
|---------------------------------------|----------------------------------|
| 0.0                                   | 1.4273                           |
| 10.0                                  | 1.4244                           |
| 20.0                                  | 1.4186                           |
| 20.9                                  | 1.4182                           |
| 25.0                                  | 1.4153                           |
| 40.0                                  | 1.4035                           |
| 40.8                                  | 1.4017                           |
| 41.4                                  | 1.4008                           |
| 50.0                                  | 1.3919                           |
| 60.0                                  | 1.3807                           |
| 70.0                                  | 1.3679                           |
| 71.2                                  | 1.3670                           |
| 80.0                                  | 1.3561                           |
| 100.0                                 | 1.3325                           |

Constants:

|                        | <u>DMF</u> | <u>Water</u> |
|------------------------|------------|--------------|
| $\rho$ (gr/cc) at 25°C | 0.9445     | 1.0000       |
| $n_D$ at 25°C          | 1.4269     | 1.3325       |

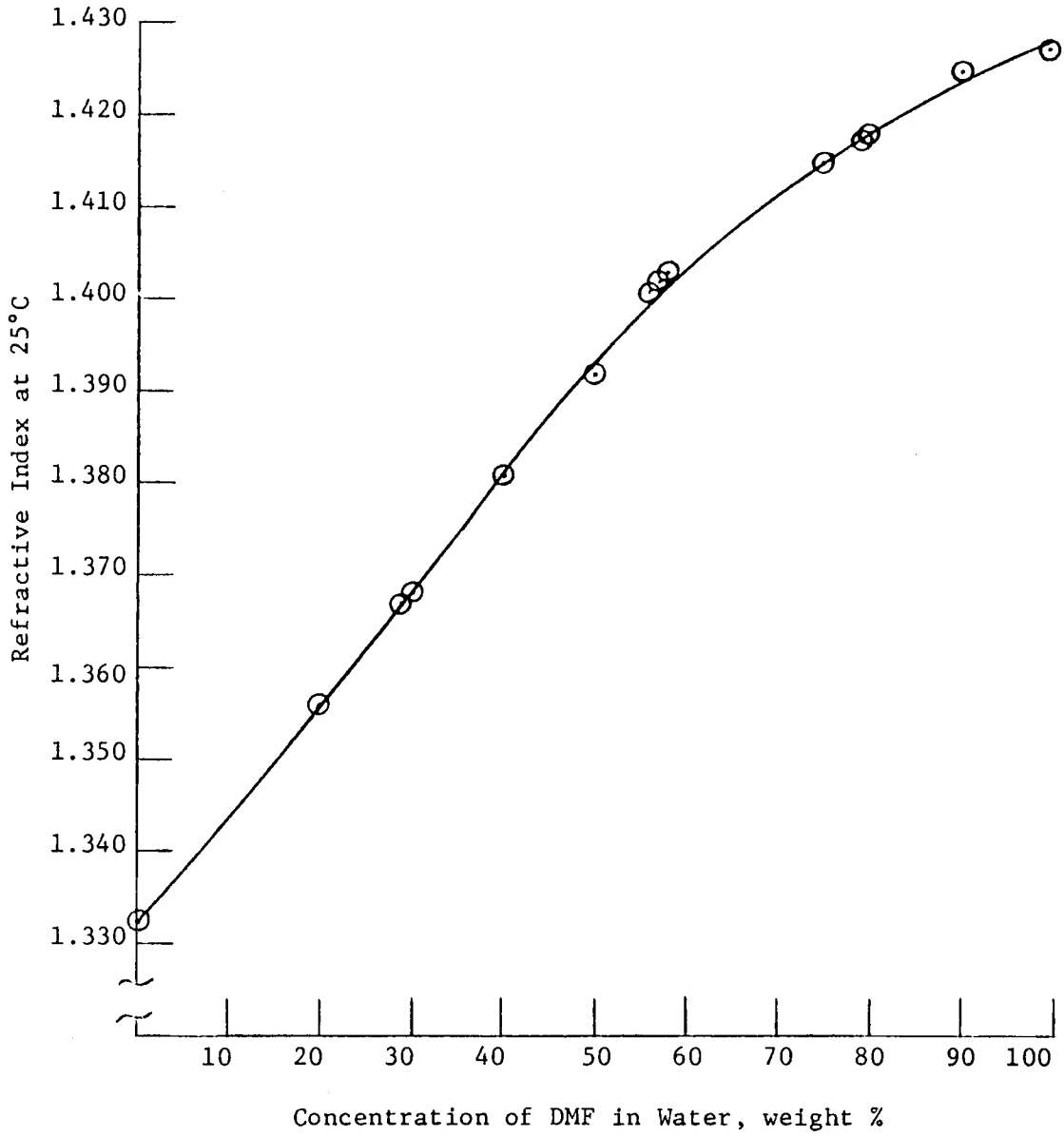


Figure 12. Refractive Index versus Concentration of DMF in Water Solutions

5. The sample plate was cleaned with distilled water and Kim-Wipes between each sample.

#### Calibration of Zenith Metering Pump

Zenith metering pumps are positive displacement gear pumps used for accurately metering viscous materials. Model 1/4B-4391 was used and is the smallest capacity pump available. Conversations with personnel at Zenith Products Company, revealed that inaccurate delivery rates may occur at speeds of less than 5 rpm if a large pressure drop exists across the pump. As a safeguard, therefore, a pressure gauge was installed on the discharge line and the pressure placed on the dope reservoir was continually adjusted to be close to the discharge line pressure. The 42 tooth pump gear was driven by a smaller 32 tooth gear mounted on the motor drive shaft which allowed higher motor speeds to be used.

The metering accuracy was measured using the following procedure:

1. A 17.1% (by weight) dope was extruded from the spinneret until the dope was bubble free.
2. Dope was then collected in a clean tared beaker for 10 minutes.
3. During the collection period, a hand held tachometer was used to measure the rpm of the 42 tooth drive gear several times.  
(see note)

4. The pump speed was changed and dope collected in a similar manner for four different speeds covering the range of speeds expected to be used. The reservoir pressure was increased at the higher delivery rates to minimize any pressure drop across the pump.

5. The collected dope samples were dried overnight at 200°C.

6. The beaker was reweighed to determine the amount of residue remaining.

7. The volumetric delivery rate of 17% dope at 50°C was then calculated as follows:

$$\text{volumetric delivery rate } \left( \frac{\text{cc}}{\text{min}} \right) = W / (C) (\rho) (T)$$

where:

W = weight of residue in grams

C = concentration of dope solids as weight fraction = 0.171

$\rho$  = dope density at 50°C = 0.96 gr/cc

T = collection period = 10 minutes

8. The pump delivery rate could be calculated using:

$$\text{delivery rate (cc/rev)} = \frac{\text{volumetric delivery rate } \left( \frac{\text{cc}}{\text{min}} \right)}{\text{pump speed (rev/min)}}$$

Note: An aluminum adapter was made to fit the tachometer spindle which fit over the rectangular end of the gear arbor which protrudes from the center of the drive gear.

Table XII shows the results of the metering pump calibration and Figure 13 shows the pump delivery rate as a function of the pump speed.

Table XII

ZENITH DOPE PUMP CALIBRATION DATA [Model 1/4B-4391]

|                              |        |        |        |        |
|------------------------------|--------|--------|--------|--------|
| Sample Number                | 1      | 2      | 3      | 4      |
| Measured Pump Speed (rpm)    | 5.1    | 6.8    | 9.3    | 12.0   |
| Residue weight (grams)       | 1.3126 | 1.8412 | 2.3600 | 3.1479 |
| Volumetric delivery (cc/min) | 0.803  | 1.127  | 1.445  | 1.928  |
| Pump delivery rate (cc/rev)  | 0.157  | 0.166  | 0.155  | 0.161  |

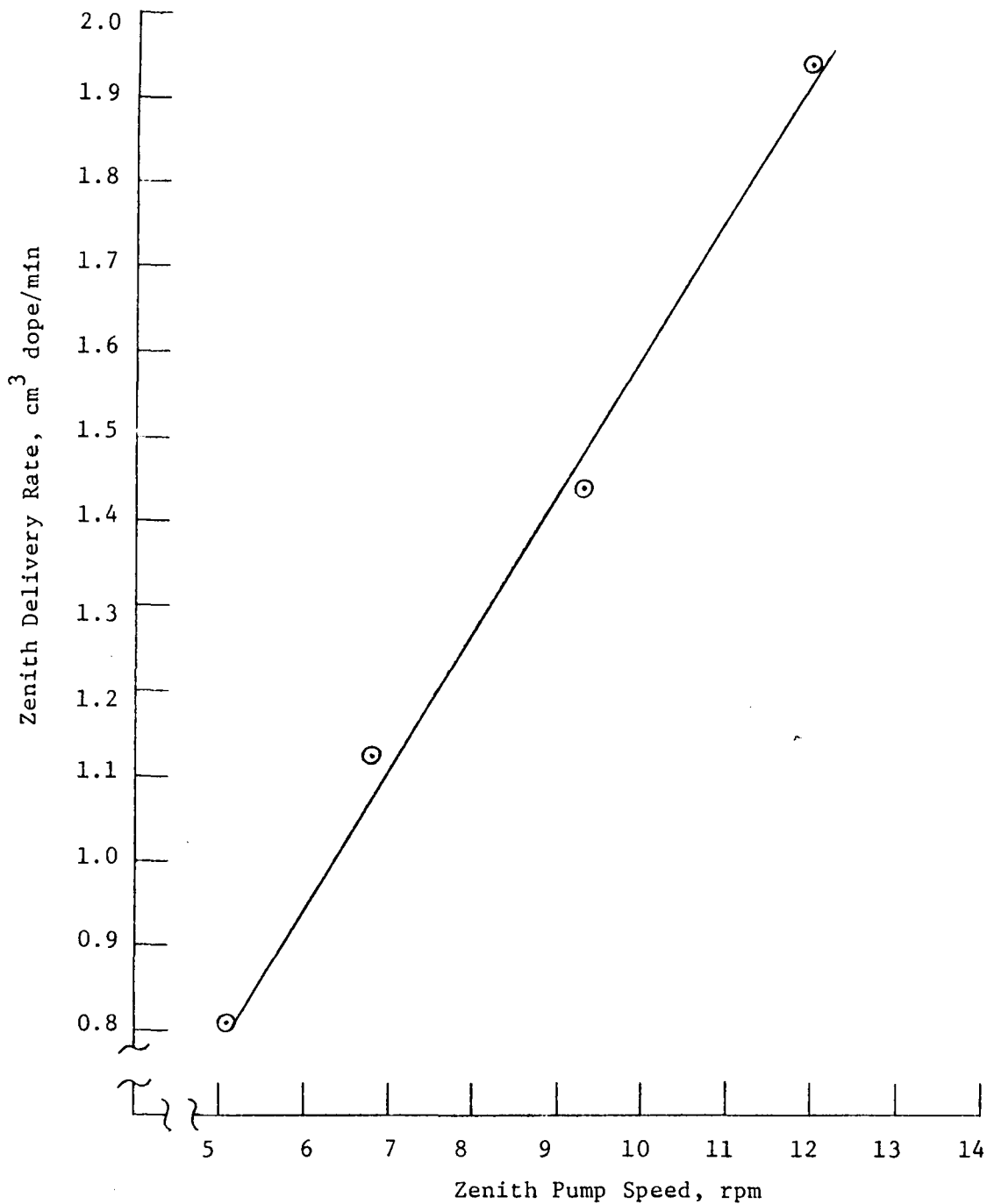


Figure 13. Zenith Pump Delivery Rate at Various Speeds (RPM)

### Materials

Materials used in this project are as follows:

N,N-Dimethyl Formamide. Reagent Grade. Purchased from Fisher Scientific Company, Fair Lawn, New Jersey. Catalog Number D-119. Used as solvent for polyacrylonitrile powder.

Polyacrylonitrile Powder. Two pounds of PAN polymer powder. Intrinsic viscosity of 2.18. Donated by Celanese Research Company, Summit, New Jersey. Used for extrusion into fibers.

Polyacrylonitrile Fiber. One cone of PAN Homopolymer Yarn. Donated by Celanese Research Company, Summit, New Jersey. Used to establish and compare oxidation conditions on thermogravimetric analyzer.

Nitrogen. Oil pumped. Minimum purity is 99.7 weight percent. Supplied by Industrial Gas, Bluefield, West Virginia. Used to pressurize dope reservoir.

Washer. Hard gray fiber washer. Purchased from Penn Fiber and Specialty Company, Philadelphia, Pennsylvania. Used to seal spinneret assembly and discarded after use.

Micromesh Screen. Micronic rating of 10. 304 stainless steel. Purchased from Kressilk Products, Inc., Elmsford, New York. Used as final filter in spinneret assembly and discarded after use.

Filters, A. 25 x 100 mesh wire cloth and 40 x 150 mesh wire cloth with micronic ratings of 100 and 60 respectively. Plain Dutch

Weave. 304 stainless steel. Purchased from National-Standard Company, Corbin, Kentucky. Used as first and second stage filtering media respectively.

Filters, B. ED-349-48 filter paper. Composed of compressed wood fibers. Purchased from Eaton Dikeman Company, Mt. Holly Springs, Pennsylvania. Used as third stage filter media.

Filters, C. Cotton Batting. Trade name CCE-30. Purchased from Barhardt Manufacturing Company, Charlotte, North Carolina. Used as fourth stage filter media.

Filters, D. Cotton, sheeting. 4 ounce. Purchased from Lamport's Company, Cleveland, Ohio. Used on each side of filter paper or cotton batting to secure the filtering media.

#### Apparatus

The apparatus used in this project are described as follows:

Constant Speed Control Unit with Motor. Model 4420. 120 volts range 0-3000 rpm. Supplied by Cole Parmer Instrument and Equipment Company, Chicago, Illinois. One unit was used as the feed roll drive and another unit for takeup roll drive.

Motor. Model B-2420C-40L. One sixth h.p., 73 inch pounds torque, 2.6-52 rpm. Manufactured by B&B Motor Control Corporation, New York, New York. Used to drive Zenith Metering Pump.

Controller. Model SA12. Obtained from B&B Motor Control Corporation, New York, New York. Used to control motor speed for



Zenith pump drive.

Heating Tape. Electrothermal Heating Tape. 120 v. Used to heat dope in discharge line from Zenith pump.

Variac. Powerstat voltage regulator, type 3PN116, 0-140 volts. Manufactured by Superior Electric Company, Inc., Bristol, Connecticut. Used to control voltage to dope line heating tape.

Galvanometer. Model 9B. Manufactured by Technique Associates, Division of West Instrument Corporation, Schiller Park, Indiana. Used with thermocouple to read dope temperature just prior to spinneret.

Thermocouple. Copper-Constantin, Manufactured by Marlin Manufacturing Corporation, Cleveland, Ohio. Used to measure dope temperature just prior to spinneret.

Glass Trays. 7" x 11" x 2" deep, Model 411 with two quart capacity. Manufactured by Anchor Hocking Ovenware Company. One used as coagulation bath and another for stretching bath.

Constant Temperature Controller. Model AC-505. Temperature range = 38°-288°C. 120 volts. Copper-constantin thermocouple included. Manufactured by Blue M Electric Company, Blue Island, Illinois. Used to measure temperature of coagulation bath and control the heating tape surrounding the bath.

Heating Cord. Cal-cord 400. Flexible. Temperature limit 400°C. Rating of 120 watts, 120 volts. Manufactured by Glas-Col. Used to heat coagulation bath.

Tachometers, Hand, A. Range 0-1000 rpm with 0.2 rpm subdivisions. Distributed by Hasler-Tel Company, Inc., New York, New York. Used to check the rotational speeds of feed roll and takeup roll.

Tachometers, Hand, B. Range 0-100 rpm with 0.05 rpm subdivisions. Distributed by Hasler-Tel Company, Inc., New York, New York. Used to check the rotational speed of Zenith Metering Pump.

Guides and Rollers. Various configurations. Aluminum oxide composition. Purchased from Heany Industries, Scottsville, New York. Used to guide yarn through baths and onto feed roll.

Metering Pump. Model 1/4B-4391. All wetted parts 440-C stainless steel. 42 tooth drive gear. Speed range 0-250 rpm. Purchased from Zenith Products Company, West Newton, Massachusetts. Used to pump and meter dope from the reservoir to the spinneret.

Mercury Intrusion Porosimeter. Aminco-Winslow Catalog Number 5-7107. Manufactured by American Instrument Company, Silver Spring, Maryland. Property of the Metals and Ceramics Engineering Department, Virginia Polytechnic Institute and State University. Used to measure the pore size and distribution of selected fiber samples.

Thermogravimetric Analyzer. Model 950. Manufactured by E. I. du Pont de Nemours and Company, Instrument Products Division, Wilmington, Delaware. Property of Chemical Engineering Department, Virginia Polytechnic Institute and State University. Used for

thermal analysis of selected fiber samples.

Spinning and Stretching Apparatus. Figure 14 shows the overall layout of the spinning and stretching units. The spinning unit consisted of the dope reservoir, pump drive motor, metering pump, and spinneret support mounted on a 30" x 30" slab of 1" thick pressed particle board. Sufficient space remained on the slab to place the galvanometer used to read the dope temperature thermocouple, the coagulation bath temperature controller, and the variace used to control the heating tape for dope temperature control. Figure 15 is an exploded view of the spinneret assembly and Figure 16 shows the dimensions of the spinneret holes. The spinneret contained four holes having a diameter of approximately 0.005". Figure 17 is an exploded view of the Zenith Metering Pump.

The stretching unit consisted of two motor supports, supports for the feed roll guides, and supports for rollers used to guide the yarn through the bath mounted on a 30" x 30" slab of 1" thick pressed particle board. A hotplate having a 12 inch square heating surface was used to heat the water.

The feed roll and takeup roll were controlled with constant speed control units. The feed roll and takeup roll were both 1 1/2" dia. x 6" long cylinders made of aluminum and machined to fit on the drive shaft of the constant speed motors.

Dope was poured into the reservoir and forced to the Zenith metering pump by pressurizing the reservoir with nitrogen. A

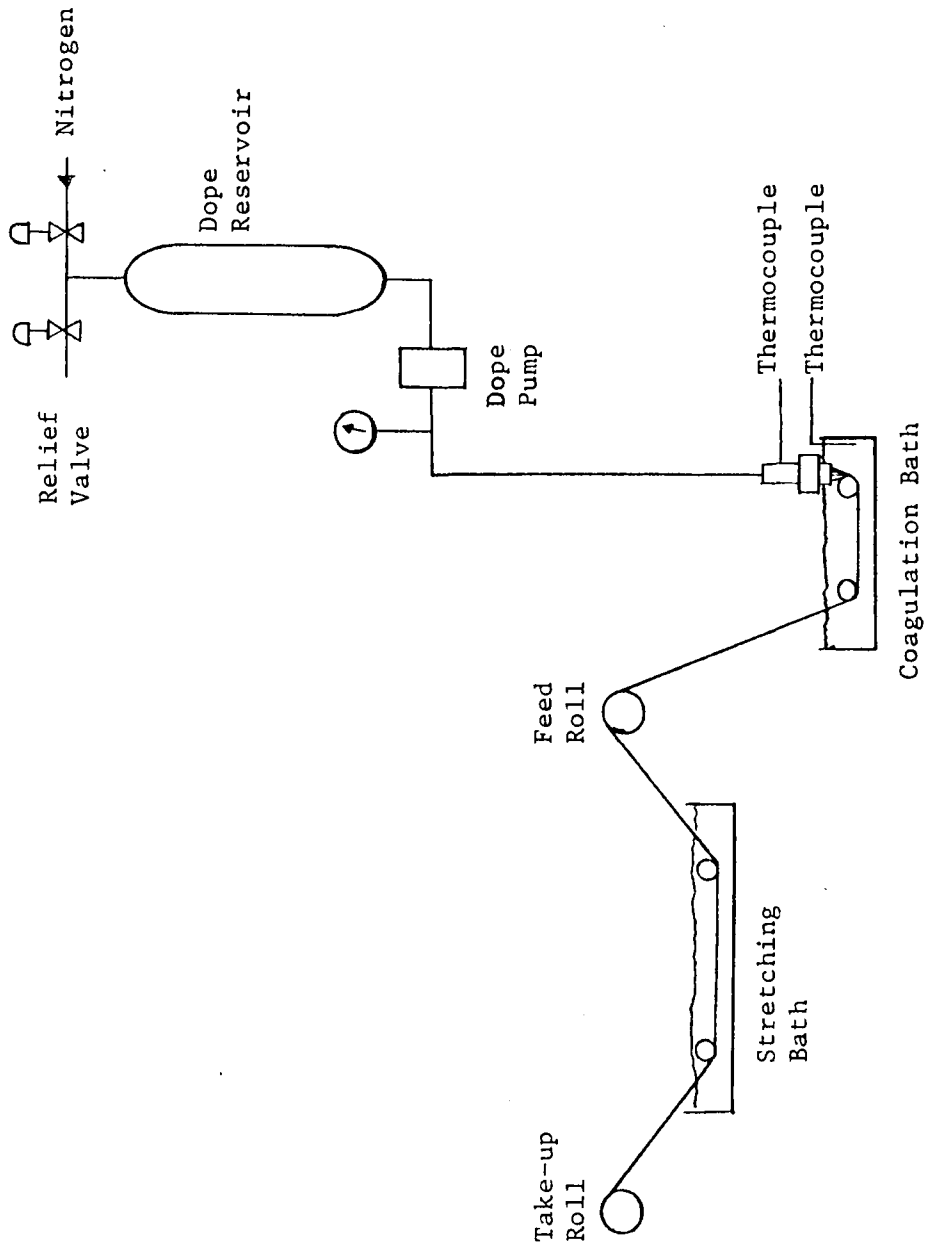


Figure 14. Schematic Layout of Spinning and Stretching Apparatus

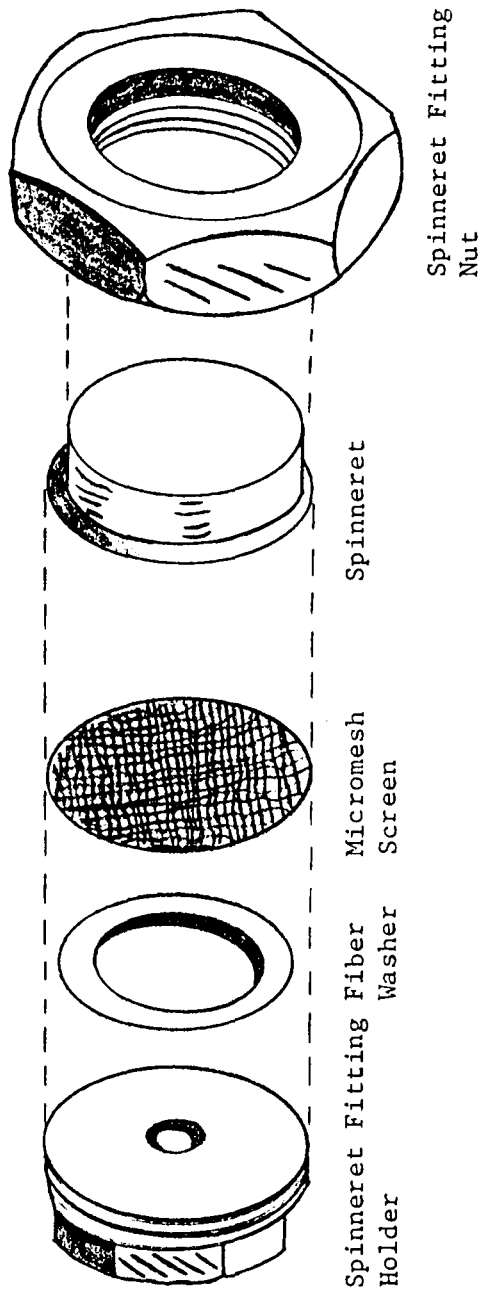


Figure 15. Spinneret Assembly

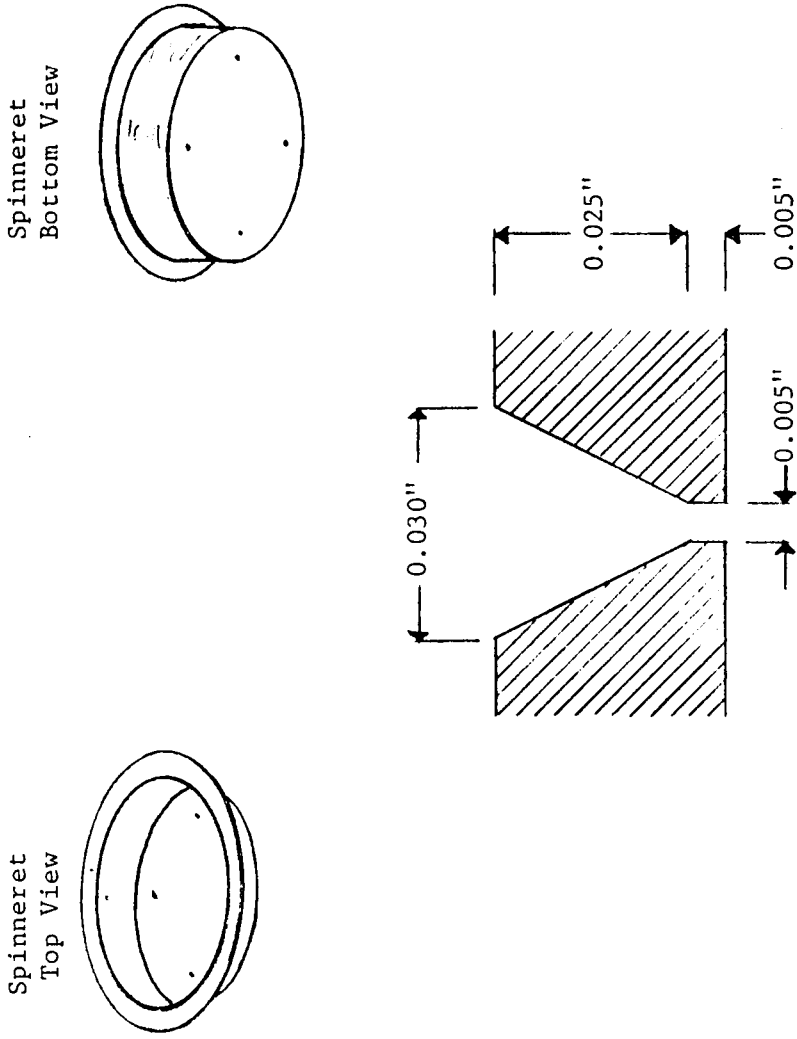


Figure 16. Spinneret Hole Configuration and Dimensions

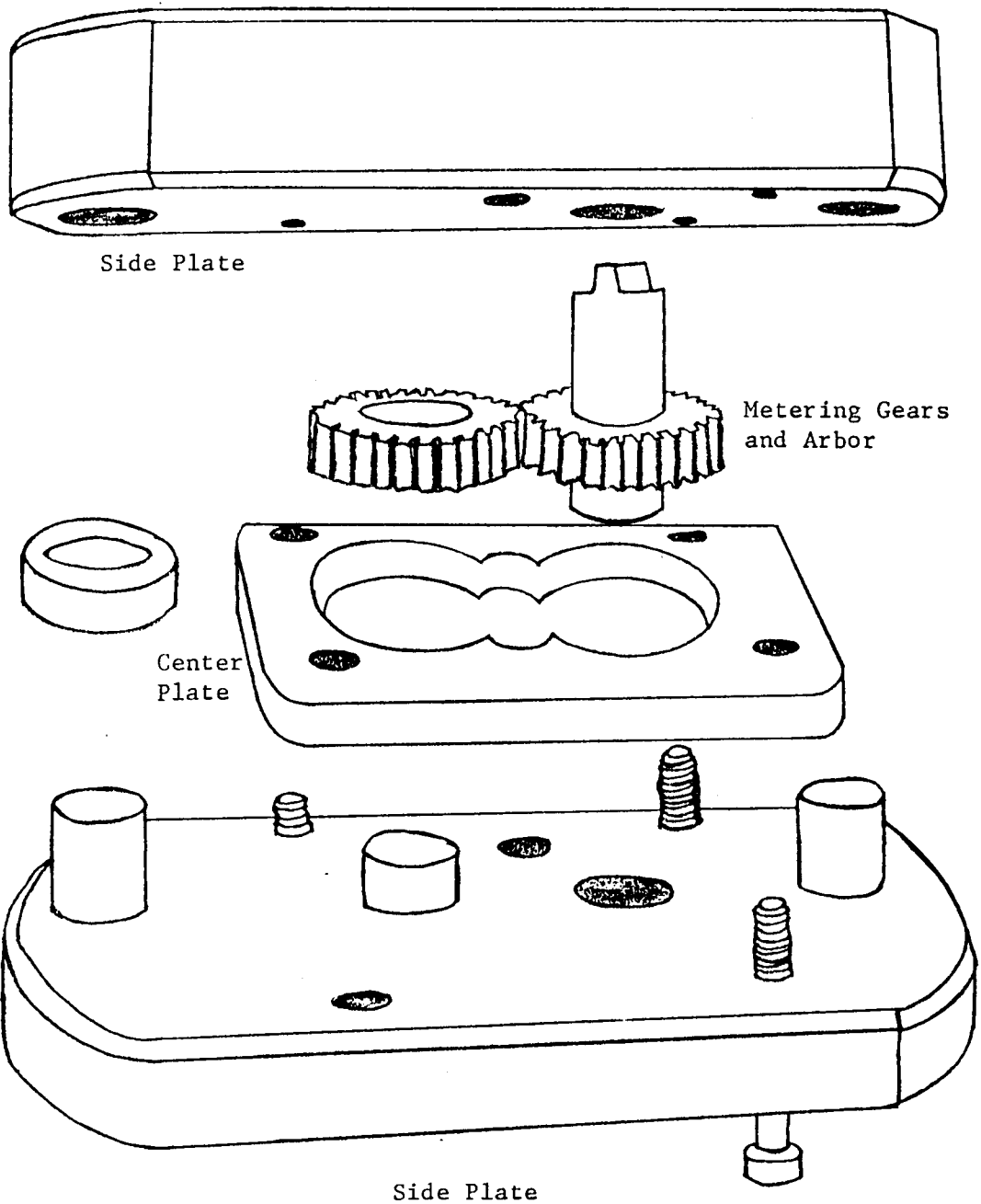


Figure 17. Assembly View of Zenith Dope Pump

regulator was used to adjust the pressure from the nitrogen supply cylinder. As recommended by the manufacturer, the pressure on the dope reservoir was adjusted to match the dope pressure in the discharge line to ensure accurate metering rates. From the pump, dope flowed to the spinneret and extruded into the coagulation bath. The solidified fibers traveled under two rollers in the coagulation bath and was wound around the variable speed feed roll. The yarn was wrapped four times around the feed roll to ensure no slippage. For each wrap, the yarn would contact approximately  $3/4$  of the feed roll circumference and then pass through offset back guides which would prevent the parallel wraps from overlapping. This arrangement ensured constant yarn speed from the coagulation bath and prevented slippage when the takeup roll speed was changed.

After the feed roll, the yarn passed to the takeup roll at the far end of the stretching bath. Rollers were placed on stainless steel rods to guide the yarn through the boiling water. High draw ratios could be achieved only when these rollers were loose and easily rotated. The elevation of the feed roll and takeup roll was adjusted to minimize the amount of contact between the yarn and rollers. The yarn would break frequently unless the yarn contacted less than  $1/4$  of the roller circumference.

Filtering Apparatus. Figure 18 shows the filter assembly. Dope was forced, using nitrogen, through various filter media held by the filter assembly. The filter media was cut into  $1\ 1/2$ "



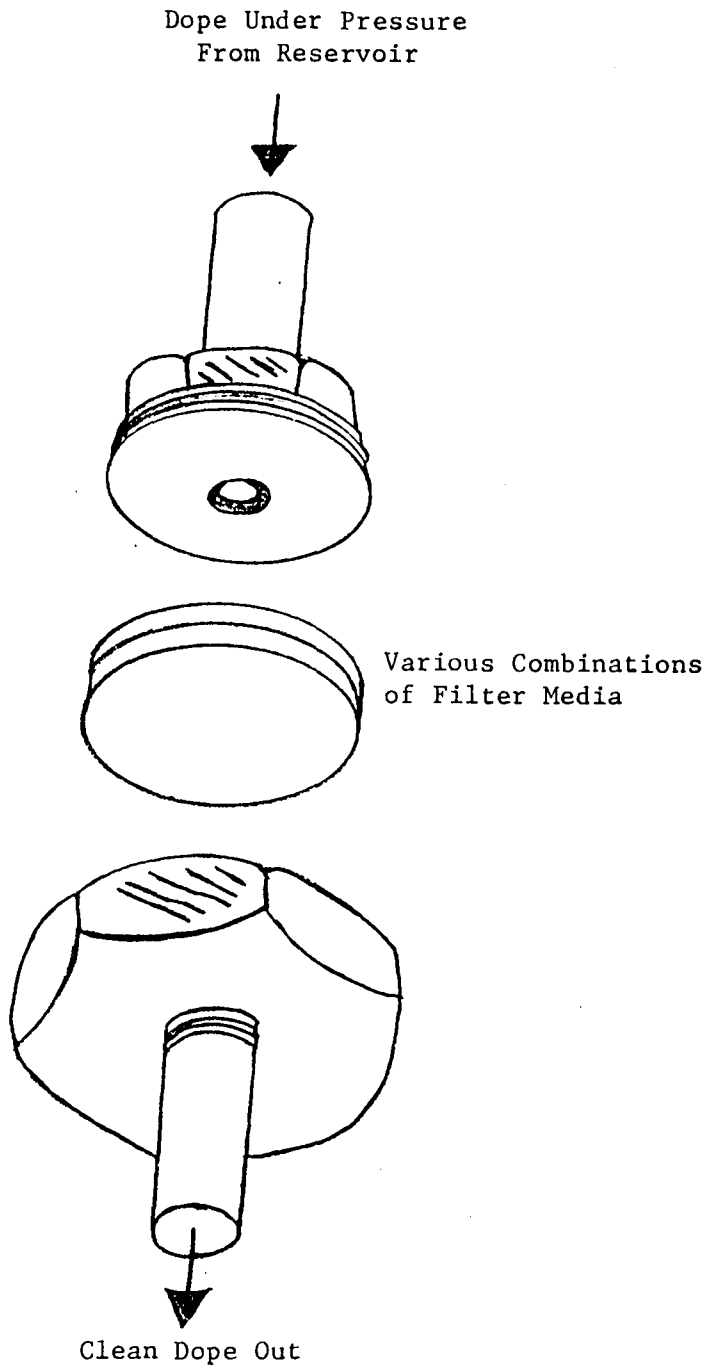


Figure 18. Drawing of Filtration Apparatus

diameter circles and held in place by screwing the bottom and top pieces together.

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WET SPINNING OF POROUS POLYACRYLONITRILE FIBERS  
AND AFFECT ON FIBER OXIDATION

by

William Finley Speer, Jr.

(ABSTRACT)

A spinning apparatus was built to investigate the wet spinning technique for production of porous polyacrylonitrile fibers. Dimethylformamide was used as the solvent and a 17% by weight dope was extruded through a spinneret having four 118 micron diameter holes.

It was found that porous fibers could be produced with reasonable physical properties. Fiber porosity was increased with lower solvent concentration in the precipitation bath and higher bath temperatures. The fibers were particularly porous when low stretching ratios were used and the yarn was not allowed to relax during exposure to elevated temperatures. PAN fibers are stretched to improve the molecular orientation along the fiber axis while relaxation is generally used to improve the elastic properties. It appears that processing conditions can be changed to yield fibers with adequate properties for handling but with greater pore volume.

Pore volume does not appear to be directly correlated with the oxidation rate of the fibers. Experimental fibers containing pores did show generally a faster initial weight loss rate but some inconsistencies were found. The sample with greatest measured pore

volume had a substantially higher weight loss and percentage weight loss rate than other experimental fibers and a commercial dry spun fiber. The effect of operating conditions on fiber properties and porosity were found to be in agreement with the literature.

It was recommended that the precision of the Thermogravimetric Analysis, for fibrous sample, be determined to provide some explanation perhaps of the inconsistencies found during the oxidation experimentation.