N72 29529

NASA CR-120902



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HOUGH LABORATORY

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center

Contract NAS 3-14325

1 Report No	2. Government Accession No.	3. Recipient's Catalog	No		
CR-120902					
4 Title and Subtitle IMPROVEMENT OF CHEMICAL VAPOR PRODUCTION OF LARGE DIAMETER	DEPOSITION PROCESS FOR CARBON BASE MONOFILAMENTS	5 Report Date November 1971 6. Performing Organiz	ration Code		
7 Author(s) R. L. Hough R. D. Richmond		8 Performing Organiz	ation Report No		
		10. Work Unit No.			
9. Performing Organization Name and Address		114-03-23			
708 Rice Street		11. Contract or Grant	No		
Springfield, Ohio 45505		NAS 3-14325			
12 Sponsoring Agency Name and Address NATIONAL AERONAUTICS & SPACE	ADMINISTRATION	13 Type of Report an Contractor Rep Nov. 1970 to N	d Period Covered Port Pov. 1971		
Washington, D. C. 20546		14 Sponsoring Agency	Code		
15. Supplementary Notes Project Manager, David L. McD NASA Lewis Research Center, C	anels, Materials & Structures Divisi leveland, Ohio	on,			
16 Abstract Research was conducted to dev mole % elemental boron, in th deposition process. The obje critical process variables an modified to allow these varia permitted reduction in scatte been synthesized in the 3.0 t 552,000 psi for ultimate tens	elop large diameter carbon monofilam e 2.0 to 10.0 mil diameter range usi ctive of this program was to gain an d their effect on fiber properties. bles to be studied. Improved contro r of properties of the monofilaments o nearly 6.0 mil diameter range havi ile strength and up to 30.0 × 10 ⁶ ps	ent, containing 2 ng the chemical v understanding of Synthesis equipm 1 of synthesis va . Monofilaments ng measured value i for elastic mod	5 to 35 apor the lent was riables have s up to ulus.		
17. Key Words (Suggested by Author(s)) Carbon, Monofilaments, Compos Chemical Vapor Deposition, Re	ites, Fibers inforcement 18. Distribution Statemen Unclassified -	nt unlimited			
19 Security Classif. (of this report)	20 Security Classif. (of this page)	21. No. of Pages	22. Price*		
Unclassified	Unclassified	46	\$3.00		

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* For sale by the National Technical Information Service, Springfield, Virginia 22151

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SUMP!ARY

A research program was conducted to further develop large diameter carbon based monofilament in the 51 to 254μ (2 to 10 mil) diameter range using the chemical vapor deposition process. This process had been demonstrated as feasible in a previous NASA sponsored program. The effort was directed toward gaining an increased understanding of the critical processing variables and the role played by each on fiber properties. One finding was that the substrate quality and uniformity as received from the supplier is an important variable regulating fiber quality. Undesirable variations in substrate surface texture were found for nearly 50% of the substrate. Corrective measures are now being taken by the supplier. Such variations induce strength limiting defects (nodules) into the fiber structure. These defects effectively mask any improvements being made in other fiber synthesis parameters, as plating atmosphere, synthesis speed, and synthesis temperature. Another important finding is that fiber modulus appears to decrease as either synthesis temperature and/or synthesis speed are increased. A simple relationship does not appear to exist. Indeed, it may well be that maximum values exist for these variables which, if exceeded, totally cancel any effects of variable change for the other synthesis parameters. There does appear to be an increase in modulus attending a boron content increase which, in turn, correlates with the effect of a combined decrease in both synthesis speed and temperature.

The improvement of processing parameters was demonstrated in a corollary monofilament production program. Monofilaments synthesized during the previous study were limited to continuous lengths of up to 61 meters (200 feet). During one production program, continuous lengths were extended to 1646 meters (5400 feet). The scatter in ultimate tensile strength was reduced. Average strength increased from 207,000 N/cm² (300,000 psi) to nominal 242,000 N/cm² (350,000 psi); the maximum tensile strength observed went from 373,000 N/cm² (541,000 psi) during the previous investigation to 381,000 N/cm² (552,000 psi). Maximum fiber diameter was increased from a nominal 102µ (4 mils) to nearly 152µ (6 mils). Modulus was also increased to nearly 21×10^6 N/cm² (30 × 10⁶ psi). These represent the highest values yet achieved for these fibers. However, synthesis parameters were not found which can produce all these property values simultaneously in one fiber. Also, these values could not be consistently reproduced.

Synthesis speeds can now reach 12.9×10^{-3} mps (2.54 fpm) for 84μ (3.3 mil) diameter fiber. This represents a 338% increase over synthesis speed achieved under the previous effort.

Additional research is required to relate the critical processing variables such that higher strength, higher modulus, larger diameter fibers can be reproducibly formed.

I. INTRODUCTION

As the performance requirements for aerospace propulsion systems increase, a corresponding need develops for increasing materials capabilities. One area of materials development involves improving the high temperature capabilities of metals and ceramics which are intended for use in turbine engines. Fibrous reinforcements which both strengthen and stiffen metals and ceramics are being considered for achieving these desired improvements. Reinforcements based on carbon are particularly attractive in this respect because of the inherent high strength-to-weight ratio. Carbon and graphite yarns composed of multistrands of small diameter fibers have been available. However, such fibers can be easily damaged by deletrious interaction between the metal or ceramic and the fiber during the fabrication process. Subsequent end use of the resulting composite may further damage these small fibers because of their fragile nature. Larger diameter carbon based monofilament would be considerably more stable in this respect.

One promising approach to synthesizing continuous large diameter filaments is chemical vapor deposition. This approach involves the decomposition of a gaseous atmosphere at or near a substrate to achieve a solid deposit. This synthesis normally begins with a core material in the form of a tiny continuous fiber, such as fine tungsten wire or carbon fiber. This core is used as a nucleus upon which the required filament material is vapor deposited.

The feasibility of synthesizing high strength continuous carbon based monofilament by chemical vapor deposition upon a carbon substrate was established under a previous NASA contract (Reference 1). These filaments were synthesized by chemical vapor deposition utilizing a "hot wire" apparatus. A 1.3 mil carbon substrate was drawn through the apparatus at a rate of 3.8 $\times 10^{-3}$ mps (0.75 fpm). Carbon was preferable over other substrates, as tungsten, since it did not react with the deposited material and, therefore, did not interfere with initial nucleation and growth of the pyrolytic fiber. Monofilaments were synthesized to lengths of up to 61 meters (200 feet) and to diameters of 76 to 100μ (3.0 to 4.0 mils). The highest ultimate tensile

strength measured was 372,000 N/cm² (541,000 psi), and an elastic modulus of up to 19.1×10^6 N/cm² (27.7 × 10^6 psi).

Processing variables investigated included gas composition, heating current, and fiber velocity. With the equipment available, none of these variables could be controlled to the degree which appeared necessary. The best monofilaments were synthesized by alloying the carbon with nominally 25 to 35 mole per cent elemental boron. Other alloying agents, as silicon or aluminum, did not prove satisfactory. Unalloyed carbon fibers were relatively weak, having maximum measured tensile strengths of ca. 110,000 N/cm² (160,000 psi). Figure 1 displays maximum strength vs. modulus for this carbon and carbon alloy fiber developed under this initial work.

The experimental high for monofilaments developed during this program is displayed in Figures 2 and 3, wherein strength vs. modulus and specific strength vs. specific modulus are recorded respectively. Comparative values for selected fibers are also displayed in these figures. The position of the experimental high lies above the curve for the pyrolytic graphite whiskers of Bourdeau (Reference 2). This suggests that the microstructure of the filaments is rather unusual and, in some respects, may resemble a high temperature glass because of the high strength coupled with only moderate modulus values.

These large diameter fibers may be more amenable to composite fabrication because of the larger size compared to fine diameter fibers in yarns. For example, coatings can be applied to these fibers which actually increase strength as shown in Reference 3. Coatings on these fibers and other fibers, as boron and silicon carbide, have also been discussed elsewhere (Reference 4). These fibers may well be amenable to incorporation methods for forming metal matrix composites which are too severe for finer diameter fibers.

While the synthesis of these interesting monofilaments was demonstrated under the previous NASA sponsored program, the achievement of production quality control and an understanding of the factors which might lead to higher synthesis rate and fiber diameter while maintaining fiber quality was not fully developed. A considerable portion of the difficulty was believed to arise from insufficient control of gas flows and CVD reactor power. Thus,



Figure 1 - Previous Experimental Monofilament Properties (Ref. 1)



Figure 2 - Comparison of U.T.S. vs. E for Various Fibers



Figure 3 - Specific Strength vs. Specific Modulus for Various Fibers

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in the current program, considerable emphasis has been placed on adequate control and surveillance of these parameters.

Accordingly, the objectives of this reported effort have been to:

- 1. Reduce scatter in fiber properties;
- 2. Increase fiber synthesis rate; and
- 3. Increase fiber diameter.

The first of these objectives is the most difficult to achieve. Once fiber synthesis conditions are defined which provide superior fibers having reproducibly higher strengths, comparatively simple expedients can be used to increase fiber diameter and fiber synthesis rate. Such expedients would include increases per line in plating stage length and number of plating stages.

The first phase of this program was devoted to building and modifying equipment to control and monitor the process. The second phase consisted of using this equipment, which allowed the process variables to be controlled sufficiently to attempt to isolate and study their effects, and to optimize the process. This optimization was demonstrated in a separate contract calling for the production of 12,192 meters (40,000 feet) of monofilament. The results of this production contract are also described in this report.

II. FIBER DEPOSITION PROCESS

The developmental effort under this program was directed toward studying variables which might lead to reduced fiber property scatter, higher fiber synthesis rate, and larger fiber diameter. Such variables include plating gas control and distribution, CVD reactor power control, and fiber synthesis velocity. An additional variable found during this program was the condition of the carbon substrate as received from the supplier.

A. MATERIALS

Processing materials include carbon monofilament utilized as a deposition substrate and various gases employed in the plating atmosphere. The

substrate used is carbon monofilament obtained from the Great Lakes Carbon Corporation. This material has the following vendor stated properties:

Diameter	Nominal 1.3 mils
Tensile Strength	100,000 psi
Modulus	4.8 × 10 ⁶ psi
Density	1.65 g/cc

The various precursor gases and the vendors' stated purity are as follows:

- Hydrogen and argon carrier and diluent gases are obtained from local vendors with stated purities of 99.99% and 99.9995% respectively;
- 2. Hydrocarbon gases are obtained from Matheson Gas Products having minimum purities of 98.0%; and
- 3. Borane material is obtained from the Callery Chemical Company having minimum 99.0% purity.

B. APPARATUS

The processing apparatus utilized in this development program is essentially a series of long cylinders (Figure 4) through which the substrate material is drawn by means of a motor driven take-up spool. The number of cells was varied in this program between three and five. A simple braking device on the supply spool provides proper substrate tension. The ends of each cylinder are sealed by mercury filled capillaries which allow passage of the fiber while preventing interchange of plating gases and air.

The chemical vapor deposition reaction is initiated by the "hot wire" method. The substrate is drawn through the mercury seals which also serve as electrical contacts. It is then resistively heated to the required deposition temperature by application of controlled electrical power. The main factors which control the deposition process include:

1. Plating gas distribution and control;

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- 2. CVD reactor power for controlling temperature; and
- 3. Fiber synthesis velocity control.
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Figure 4 - Production Line Schematic

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C. CVD PROCESS PROCEDURE

1. Plating Gas Distribution and Control

Laminar flow elements with a manufacturers' stated accuracy of 0.5% of full scale are used without further calibration to monitor gas flow. These elements have ranges of 1.0 to 10.0 lpm referenced to air. We examined the utilization of NPN piezotransistors as a means for transducing the output of these flow elements. We found that the transistors are too temperature sensitive for use in our specific application. We have, therefore, employed the direct and more reliable expedient of utilizing differential manometers, readable to 0.025 cm (0.01 inches). Gases can be mixed and distributed to various stages of the synthesis line under close monitoring. Thus, under controlled variations, the relationship of flow rate and gas composition on fiber properties can be established. Nominally 450 - 500 ml/min argon, 300 to 400 ml/min hydrogen, 80 - 110 ml/min C_2H_4 , and 3 - 5 ml/min $(C_2H_5)_3B$ flowed through each cell.

2. CVD Reactor Power for Controlling Temperature

The installation and check-out of automatic power controllers was completed during this program. CVD reactor power control is obtained to within ± 1 ma of the setting range 100 - 150 ma. The power controls use magnetic amplifiers which operate the primaries of high voltage (2000 - 2500 volts) transformers feeding rectifier and filter banks. A solid state feedback loop senses current output and adjusts the current level in the control circuit of the magnetic amplifiers to compensate for any spurious drifting effects.

Substrate temperature is measured using a micro-optical pyrometer manufactured by the Pyrometer Instrument Company. Measurement accuracy and repeatability are conservatively estimated at ± 50 °C or less. Temperature is spot-checked and not measured regularly. One reason for this is that the plating cells walls become clouded during prolonged experimentation. Accurate

visual measurements then become impossible. A second reason is that a pronounced temperature gradient exists in the plating cells, making reported temperatures highly position dependent.

3. Fiber Synthesis Velocity Control

The velocity at which the fibers are synthesized, on the range of 0 to 12.7×10^{-3} mps (0 - 2.5 fpm), is controlled in incremental steps by inserting synchronous motors of various speeds into the take-up mechanism. This results in considerable accuracy in maintaining a fixed velocity. For somewhat less accurate synthesis velocities, a D.C. servo motor is employed. A simple traverse mechanism, utilizing a double helix cam, is coupled to the take-up spool drive to automatically lay up the fiber across the spool.

Static deposition experiments can be performed utilizing the plating cells at zero fiber velocity. Under such conditions, a thermal gradient generally does not develop. Thus, these experiments, if successful, can be utilized to examine the effects of deposition temperature on the growth rate, morphology, composition of the fibers, and mechanical properties of the fiber. To accomplish this, the deposition cells can be operated while heating the motionless substrate at various fixed temperatures. Fiber diameter can be controlled by varying total deposition time. In static experiments, plating gas atmosphere is the same as in continuous synthesis experiments.

D. MONOFILAMENT EVALUATION

Fibers synthesized during this program are examined for diameter and surface smoothness. General toughness in handling and tensile tests further classify the fibers. Synthesis parameters may then be altered based upon an engineering judgment of the quality of the fiber and a new experiment performed. When considered pertinent, fiber samples are examined for modulus, density, and elemental composition.

1. Diameter and Surface Smoothness

Fiber diameter and surface smoothness are assessed by optical microscopy at 400×. A Unitron inverted metallurgical microscope having a filar micrometer eye-piece is used for this purpose. For diameter measurement, the fiber is backlighted with an adjustable intensity lamp to produce a sharp profile. The filar micrometer is then adjusted to obtain three diameter readings and the results averaged. Surface smoothness is determined visually by observing the regularity of reflected light profile and by slowly moving the fiber in the field of view to detect nodules. Fibers having an excessive number of nodules are always weak. Higher strength fibers appear to have some latitude in surface texture ranging from glassy smooth to slightly irregular.

2. Density

Fiber density is determined by flotation. Two liquids of different densities, one having a density less than the fiber and one having a density greater than the fiber, are mixed in such proportion that a nominal 6 mm (1/4 inch) length of fiber will remain suspended therein after settling for 10 to 15 minutes. A precision hydrometer is then used to determine the liquid and, hence, fiber density. Liquid mixtures, as xylene and 2, 3-dibromopropanol are suitable for this purpose.

3. Preliminary Bend Testing

Experienced personnel can roughly classify fibers by simple manipulations, including bending the fibers over a finger tip, looping the fiber and observing the loop radius at fracture, etc. Such elementary tests quickly assess general fiber quality and serve to screen fibers which are sufficiently strong and defect free so as to merit more rigorous testing methods.

4. Ultimate Tensile Strength

Material which appears promising in preliminary bend tests is tensile tested. Tensile tests are conducted by conventional load cell methods using a ten pound load cell coupled to a Statham transducer. Loading rate is 0.127 cm/min (0.05 in/min) on a 0.64 cm (0.25 in) gauge length. The testing is performed in a horizontal mode. The sample is affixed with epoxy to aligned 0.089 cm (0.035 in) diameter tungsten rods which extend from the traverse and from the load cell. The epoxy is fast cured by heating the tungsten rods with match flames held near the joint area.

5. Modulus

Modulus is determined by the dynamic "vibrating reed" technique. A length of the sample fiber $(2.54 \text{ cm} \pm 0.03 \text{ cm} \text{ or } 1.0 \text{ inch } \pm 0.01 \text{ inch})$ is affixed at one end to a magnetic transducer driven by the amplified sine wave from an audio-frequency generator. The generator is calibrated by the Lissajous Figure method. The frequency is recorded at which maximum vibration occurs for the free end of the fiber. The fiber is glued to the transducer with household type cement. Diameter is measured by microscopy and density by flotation.

The modulus is determined from the relationship (Reference 5):

$$M = \frac{f^2 1^4 \rho}{7.58 d^2}$$

where

1 = length (in.) M = elastic modulus (psi) f = resonant frequency (Hertz) ρ = density (lb/in³) d = fiber diameter (inches)

Using this method, boron filament was found to have a modulus of 40×10^6 N/cm² (58 × 10⁶ psi), which is in agreement with accepted range of values.

6. Chemical Analysis

A limited number of filament samples were analyzed for boron content by Galbraith Laboratories, Knoxville, Tennessee. Galbraith Laboratories did attempt to analyze for carbon and hydrogen, but the analytical procedure did not give satisfactory results. The only elements present in the plating gas atmosphere are carbon, boron, hydrogen, and argon. Since only carbon and boron produce refractory solids, an analysis for boron content should yield carbon content by difference.

III. RESULTS AND DISCUSSION

This program was directed toward studying variables which might lead to reduced scatter in fiber strength and modulus, higher fiber synthesis rate, and larger fiber diameter. Such variables include plating gas control and distribution, CVD reactor power control for controlling temperature, fiber synthesis velocity, and substrate quality. Under the previous NASA sponsored program (Reference 1), the synthesis of large diameter carbon based monofilament was demonstrated. However, the achievement of quality control and an understanding of the factors which might lead to higher synthesis rate and fiber diameter, while maintaining fiber quality, was not fully developed.

A. SUBSTRATE PROBLEMS

The most detrimental problem found during this program was the condition of the carbon substrate as received from the supplier. Surface defects on the substrate can cause nodules in the CVD fiber. Fiber defects involved anomalies such as spheres, gouges, cracks, etc. A defect population density exceeding an average of nominally 0.5 per equivalent diameter length of fiber was considered unacceptable. We found that nearly 50% of the substrate footage was defective in this respect. The supplier was alerted to this problem and greater quality control has been assured for future material.

Surface nodules limit the effective tensile strength of the fibers. Figure 5 displays a tensile fracture occurring at a nodule under a stress of 144,000 N/cm² (209,000 psi). Such fractures generally initiate at the nodule and propagate across the entire fiber. Fractures which occur where large nodules are not observed (Figure 6) sometimes break part way into the fiber then follow axially down the fiber before continuing across the fiber cross-section. Improved tensile strength can be obtained either by etching the surface to reduce imperfections or by eliminating the nodule source. Various post treatments performed during this program suggest that an etchant atmosphere of argon-oxygen at 1100°C (2012°F) will increase fiber strength for nodulated fibers from an average U.T.S. of $197,000 \text{ N/cm}^2$ (285,000 psi) to an avarage U.T.S. of 230,000 N/cm² (334,000 psi). To perform the etching, we utilized a nominal 2.54 cm (1 inch) hot wire cell in atmospheres consisting of argon first bubbled through water, hydrogen first bubbled through water, or argon-oxygen mixtures. Volume percentages of oxygen in argon included: 1%, 2-1/2%, 7-1/2%, 16%, and 21%. Etching temperatures included: 900°C, 1000°C, and 1100°C. Volumetric flow rates ranged from 700 to 800 ml/min. In addition, a propane-air flame was utilized as an etchant method. Best results were obtained at 1100°C using the argon-oxygen etchant[\]at 16 vol. % oxygen in argon flowing at 780 ml/min.

While etching appears to have some merit, preliminary research had already shown that very smooth fibers could have strengths in excess of $345,000 \text{ N/cm}^2$ (500,000 psi). Thus, the elimination, rather than the moderation by etching, of nodules appears to hold greatest promise in attaining high strength fibers.

The source of the nodules was traced to the first deposition cell by using careful microscopic examination of the fiber emerging from each deposition cell. The thermal gradient normally encountered in "hot wire" CVD methods was highest in this cell due to the difference in electrical resistivities between the substrate carbon and the CVD boron-carbon material. High thermal gradients are potential sites at which pyrolytic soots can form in the gas phase and migrate to the growing fiber or to the electrode area, thus forming nucleation centers for nodular growths on the filament. We found that a pre-coating of the initial substrate with either pyrolytic



Figure 5 - Fracture at Nodule 114,000 N/cm² (209,000 psi) (400×)



Figure 6 - Higher Strength Fracture 285,000 N/cm² (413,000 psi) (400×)

carbon or boron-carbon alloy reduces this excessive thermal gradient, thus controlling nodule formation initiated by pyrolytic soots.

We found that clean cell operation could be obtained in the pre-treatment cell by plating with the boron-carbon atmosphere which is the same as is used in the remaining plating cells. Using the "controlled thermal gradient" concept, it then appeared that fiber strengths approaching 290,000 N/cm^2 (400,000 psi) could be more consistantly attained.

Periodically, we continued to experience the appearance of nodules. Initially, we attributed these nodules to air or traces of water vapor residue existing in the plating cells or lines adjacent to these cells and caused by inadequate line purging after cell cleaning or after gas line modifications. This indeed can occur, and we now believe that we understand the necessary procedures for eliminating nodule formation traceable to these factors. We continued to observe the appearance of nodules in what appeared to be a totally random manner. Again a microscopic tracing of the source of these nodules was performed by examining the fiber sequentially before and after it entered each processing cell. We found a correspondance between the visually determined population density of nodules on the product fiber and minute "dirt" particles which existed on the substrate carbon fiber prior to deposition.

Under microscopic examination, we found that some spools of carbon substrate appear clean (Figure 7) while others are obviously "dirty". We experimented with a hydrogen pre-treatment cell to clean the substrate prior to any deposition. During production runs, we found that this cell could remove traces of unknown volatiles from the fiber surface when operated at 1300° to 1450° C (2372° to 2642° F). After over 50 hours running time, the pre-treatment cell walls contained traces of a grey to off-white film of undetermined composition. However, surface defects could not be removed even at temperatures to 1600° C (2912° F) in hydrogen.

The defects are observed to assume several forms. These are:

1. Numerous tiny spheroids embedded at or near the fiber surface and frequently residing in a short channel grooved into the fiber surface (Figures 8 and 9). Such defects are by far the



Figure 7 - Clean Carbon Substrate (400×)



Figure 8 - Numerous Spheroid Defects (400×)



Figure 9 - Spheroid Defect Lying in Grooved Channel (400×)



Figure 10 - Large Spheroid Defect (400×)

most plentiful.

- 2. Rarer large spheroids (Figure 10).
- 3. Rarer surface pits (Figure 11).
- 4. Rarer gouged out short channels with the "gouged" material lying aligned with the channel and apparently fused to the fiber surface (Figure 12).

We are microscopically examining the first few turns of substrate taken from each spool prior to use. Only experience will indicate whether this is a sufficiently valid "screening" procedure. Other potential suppliers of substrate have stated that "at present, it would not be feasible to produce this material in an economical manner." (Reference 6).

The imperfect surface condition on random samples of the substrate carbon monofilament has been mentioned to the supplier, Great Lakes Carbon Corporation. The supplier is very cooperative in replacing "defective" substrate material. The carbon monofilament defects are believed by the supplier to arise from filtering aids used in processing the precursor fiber. They are working on substrate improvements in the following areas (Reference 7):

- 1. Increased backwound length
- 2. Splices
- 3. Improved surface smoothness
- 4. Diameter uniformity

Length improvement attained by early 1971 resulted in over 80% of the 33μ (1.3 mil) filament having backwound (rewound) lengths over 610 meters (2,000 feet). An unfortunate side effect appears to exist in which longer filament synthesis is attended by a decrease in fiber uniformity.

Surface smoothness improvements to be made by the Great Lakes Carbon Corporation include:

- 1. Modifications in precursor preparation techniques;
- Altering filter media in precursors preparation and in spinning;
- Enclosing the spinning cell to avoid dust contamination at extrusion;



Figure 11 - Pit Defect (400×)



Figure 12 - Gouged-Out Defect (400×)

4. Improved graphite lined furnaces; and

5. "Clean room" operation.

Diameter uniformity has been improved at Great Lakes Carbon Corporation by modification in filament take-up geometry. This has resulted in a drop from $\pm 10\%$ to $\pm 5\%$ in short-term electrical resistance variation.

In summary, we believe that the nodule problem has been isolated and is definable as follows:

- Nodules occur because of residual air or moisture in the plating cells. Air leaks or improper purging after line clean-up operations are responsible. Operating procedure can correct this potential nodule source.
- 2. Nodules arise when excessive thermal gradients exist in the plating cells. Pyrolytic soots form and migrate to the growing fiber surface or to the electrode contact area where they form nucleation centers for nodular growth. By utilizing a pre-coat stage and by avoiding excessive plating temperatures, this source for nodules can be controlled.
- 3. Nodules can arise from nucleation centers which pre-exist on the carbon substrate in the form of volatile contamination as lubricants, finger oils, etc. This contamination can be effectively reduced by pre-heating the substrate in hydrogen at from 1300° to 1450°C (2372° to 2642°F).
- 4. Nodules arise from substrate surface defects. These defects may assume such observed forms as tiny spheroids embedded in the fiber surface, surface pits, or gouged out channels. Such nodule sources can only be eliminated by improved techniques for manufacturing the carbon substrate.

B. PLATING GAS CONTROL

During this program, attempts were made to systematically vary the composition of the plating gas. The critical variable appears to be the ratio of boron to carbon in the plating gases. An approximate mole ratio of boron to carbon of 1:66 was utilized throughout this program. This ratio is based upon interpreting the laminar flow element readings. Any attempt to change this ratio produced negative results. The plating atmosphere consisted of approximately 51% argon, 38% hydrogen, 11% ethylene, and .2 - .4% triethyl borane. An increase in the boron-to-carbon ratio produces highly nodulated fibers of low quality. Any decrease in the boron to carbon ratio produces smaller diameter and considerably weakened fiber. Deviations from the 1:66 ratio of only 2% caused these problems. The general range of flow rate was 3 to 5 lpm, and the range of ratio of boron to carbon studied was 1:60 to 1:100.

C. INTERDEPENDENCE OF CELL TEMPERATURES FOR QUALITY CONTROL

To obtain monofilament having reproducible properties, it is important to control temperature. A series of continuous experiments was performed in an attempt to define the degree of sensitivity of three main plating cell temperatures with respect to current variations. The temperatures were varied by changing the current level supplying each cell (Table I). It was found that cell temperatures varied primarily only in the first 0.305 meters (12 inches) of each cell. Beyond this length, the plating action is such that temperatures remain relatively constant. In addition, it is evident that changes in the operating temperature of the first plating cell have a more pronounced effect on the downstream cell temperatures than do changes in the heating current supplying these downstream cells. The results of these experiments suggest that cell current must not vary beyond a nominal ± 1 , ma. for reproducible temperature profiles.

D. FIBER DIAMETER AND SYNTHESIS SPEED

Both fiber drawing speed and fiber diameter can be increased by an increase in fiber synthesis temperature, and/or by increasing the synthesis line length.

A series of experiments was performed to relate fiber strength, fiber

diameter, and boron content with changes in fiber drawing speed and heating current. Fiber drawing speed was varied from 4.1×10^{-3} to 5.5×10^{-3} mps (0.8 to 1.08 fpm). Heating currents which control fiber temperature were also varied and measured. Temperature itself was not measured for two reasons. First, clouding can and does frequently occur on the deposition cell walls, making pyrometer measurements inaccurate. Second, heating current regulation has been found to be a convenient means for regulating temperature dependent reactions. Thus, a higher current implies a higher temperature, while a lower current gives lowered temperatures. These experiments were performed utilizing the boron to carbon ratio of 1:66 in the plating gas as discussed in Section III. B.

Several important results are evident from these experiments as displayed in Table II. First, heating current increases (and hence temperature increases) do increase fiber diameter at a given drawing speed. Second, the concentration of boron in the fiber changes even though the plating gas composition and flow rate remain the same. The boron concentration found in the fiber appears to be a function of heating current and is hence temperature dependent. Lowering the heating current gives rise to higher boron content in the fiber.

The interrelation of these variables appears to be rather complex and requires further study. However, we do not believe that these parameters can be varied without limitations imposed by a degradation in fiber quality. For example, the effect of the concentration of boron in the carbon alloy strength is not at present understood. An increase in values for the above reported synthesis variables can affect boron concentration in the fiber. It has been our experience that, for the variables of temperature, gas concentration, and gas flow.rate, the synthesis temperature most strongly affects fiber composition. Upper bounds may, therefore, exist for these parameters beyond which fiber quality is seriously impaired as diameter is increased. An acceptable alternative for increasing diameter at a given synthesis speed is to increase production line length.

Because of the apparently detrimental effect of higher temperatures on fiber quality, we decided that the drawing speed could most readily be

increased by increases in apparatus length. Accordingly, a third plating cell was added to the two cell system. The first cell was utilized as a cleaning, pre-coating cell, utilizing the same plating gases as the remaining cells. The remaining two were standard plating cells.

With this system, samples were run with a maximum diameter of nominally 107μ (4.25 mils), an average tensile strength of 256,000 N/cm² (371,000 psi), a maximum strength of 274,000 N/cm² (397,000 psi), and a drawing speed of 5.5×10^{-3} mps (1.08 fpm). Maximum velocity of this system was 8.1×10^{-3} mps (1.6 fpm), resulting in a diameter of 99.8 μ (3.93 mils), an average tensile strength of 214,000 N/cm² (311,000 psi), and a maximum strength of 297,000 N/cm² (431,000 psi).

Finally, a fourth cell was added at the beginning of the synthesis line. This cell functions as a hydrogen precleaning cell to condition the substrate prior to plating. Using this system, fiber as large as 151μ (5.96 mils) has been synthesized, and tensile strengths of over 345,000 N/cm² (500,000 psi) have been measured. Figures 13, 14, and 15 show the diameter build-up as a function of distance along each of the three plating cells for a drawing speed of 12.9×10^{-3} mps (2.54 fpm). This represents the maximum speed at which this system has been operated.

We feel that, while the fiber is in the high temperature, inert atmosphere environment of this pretreat cell, any dirt, oils, moisture, or other contaminants and possible nodule precursors not an integral part of the substrate itself are burned off. The three main cells are then utilized entirely as plating cells, and the effective length of the system is thereby increased. Consequently, the speed has been increased without sacrificing fiber diameter or properties.

E. STATIC DEPOSITION STUDY

We also began static deposition experiments to examine the effects of deposition temperature on the growth rate, morphology, and composition of the





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fibers. In these experiments, temperature could be measured with an optical pyrometer because the deposition cells did not become severely clouded. Reduced wall clouding probably resulted from a reduced or limited development of a thermal gradient which always forms in continuous filament synthesis. To accomplish this objective, we operated one of the deposition cells while heating the motionless substrate at temperatures of from 1000 to $1400^{\circ}C$ (1832 to $2552^{\circ}F$) in $100^{\circ}C$ ($212^{\circ}F$) increments. Fibers were synthesized by varying the total deposition time at each temperature such that equal diameters would be formed. When fiber samples were successfully grown to nearly the same diameters at these various temperatures, they were evaluated, if possible, for:

- 1. Growth rate at given temperature
- 2. Presence of nodules
- 3. Toughness in handling
- 4. Tensile strength

During these experiments, we expected to at least partially answer such fundamental questions as:

- 1. Is it advisable to operate the deposition process at a virtually zero temperature gradient or does a moderate thermal gradient facilitate the formation of higher strength material?
- 2. Is there an optimum deposition temperature, and, if so, is it optimum because of a trade-off in growth rate as opposed to an increasing population density of nodules, or is it optimum because boron content is very dependent upon temperature?

We believed that answers to these questions could pave the way for advanced second generation fiber production line designs and to major strides in improved fiber performance characteristics.

Initial experiments were performed using cell lengths of nominal 1 meter (40 inches) to 1.2 meters (48 inches). The results of these initial studies show that static deposition was unsuccessful due to filament breakage and nonuniform diameter. Table III illustrates the experimental results.

1. Filament Breakage

Filament breakage occurs at the electrodes during static deposition experiments designed for isothermal plating conditions.

As the filament diameter increases, higher and higher current is required to maintain a given temperature. This is done by manually increasing current while observing the temperature of a fixed point on the fiber with an optical pyrometer. As this current is increased, any area of the fiber which does not increase in size must carry a progressively higher current density. Such areas do exist very near each electrode. The stagnant gas layer very close to the electrodes does not provide sufficient migration of plating gas so that fiber growth is uniform within these tiny areas. The result is that a fraction of a millimeter of fiber length must carry an increasing current density and, therefore, becomes progressively hotter. At about 200 ma., this uncoated or thinly coated carbon substrate weakens and breaks.

We found that, if we would move the filament forward approximately 0.254 $\times 10^{-3}$ meters (one inch) during the experiment, we could expose the smaller substrate at one end of the cell to the plating gas, thus building up the diameter. At the opposite electrode, a larger fiber would then be contacting the electrode. After a short interval, we could then move the filament backward approximately 0.127×10^{-3} meters (one-half inch), thus reimmersing the somewhat enlarged fiber in the mercury electrode while not exposing the initial substrate at the opposite electrode. Utilizing this approach, we could drive the heating current to 315 ma. before again experiencing fiber breakage near the electrodes. The maximum deposition temperature attainable under this heating current limitation is 1200°C (2192°F) for a one minute duration. This current level is considerable above the maximum 135 ma. used in fiber production. The development of an appreciable thermal gradient does not occur in the static deposition mode compared to a continuous deposition process. Consequently, a larger total surface area and total mass of material must be maintained at temperature. Heat loss by radiation is probably high, obeying the fourth power law. Even though the maximum temperature in a continuous process may exceed that in the isothermal static experiments, the total heat

loss appears greater for the static tests, at least for static deposition temperatures of 1200°C (2192°F) and above.

2. Non-Uniform Static Fiber Diameter

A second problem encountered in static deposition was a non-uniform diameter in the fiber. The fiber diameter was found to be larger near the plating gas, inlet than at the gas exhaust. We believe that this is caused by a change in the plating gas composition as it proceeds through the long deposition cell. A non-uniform diameter specimen does not allow us to obtain meaningful isothermal information.

3. Temperature Dependence of Growth Rates

The expedient of shifting the fiber during static deposition enables us to go from a heating current maximum of 200 ma. to slightly over 300 ma. Accurate shifting of the fiber becomes very difficult for deposition times of anything less than 60 seconds. We, therefore, assembled a modified apparatus using a shorter static span in which we attempted to exceed 300 ma. and eliminate the requirement to shift the filament during deposition. To accomplish this, we plated a section of substrate at a lower temperature for a sufficient time to build the diameter to several mils. We then drew the enlarged fiber through the apparatus and plated a second section to increase the diameter to several mils. This produced a spacing between the two plated sections which remained uncoated, with a length somewhat less than the span between plating cell electrodes. The fiber was then repositioned so that the uncoated length lay within the span between electrodes while the enlarged sections projected out from each electrode, away from the stagnant gas layers surrounding these electrodes. In this manner, we were able to avoid excessive fiber heating near each end. Our use of the shorter deposition length produced more consistant results though breakage and non-uniform diameters still existed as problems. Table IV illustrates the data from these additional tests.

In these experiments, we found that it is necessary to "flash" the substrate to a higher temperature to initiate deposition, thus circumventing the normal deposition induction period. Consequently, some error is introduced into the calculated deposition rates, particularly for experiments of short duration. However, the tabulated values do show the expected increase in deposition rate with temperature. It is also interesting to note the appearance of nodules in the temperature range 900 to 1100°C (1652 to 2012°F), coupled with an apparent disappearance at 1200°C (2192°F). This phenomenon is not understood at present.

4. Results

The temperatures utilized in the static deposition experiments were not higher than those found in continuous synthesis, the dwell time was sufficiently long such that the fiber appeared too brittle. Shorter dwell times could not be used because the fiber diameter would be too small. In addition, the fiber is larger at the gas inlet than at the exhaust. We, thus, found that the dynamic conditions that exist in a continuous synthesis experiment are not easy (possibly even impossible) to duplicate under static conditions. This immediately suggests that a rather complex chemical reaction, involving the formation of intermediates, is a vital part in attaining high performance multicomponent fiber.

F. MODULUS PROBLEMS ARISING FROM INCREASING SYNTHESIS SPEED

Modulus improvement was one of the objective goals of this program. Modulus is usually considered a relatively invariant property of vapor deposited fibers, but we observed an evident drop in modulus found in production run fibers. We, therefore, began a survey to determine the cause for this unexpected modulus decrease. One of the major changes occurring in our processing methods during this study involved strong emphasis upon increasing production velocity. We, therefore, decided to examine velocity as a possible suspect variable. Results of this examination indicate that modulus decreases as either temperature and/or velocity are increased. A simple relationship does not appear to exist. Indeed, it may well be that maximum values exist for these variables which, if exceeded, totally cancel any effects of variable change for the other synthesis parameters. There does appear to be an increase in boron content attending a modulus increase which, in turn, correlates with the effect of a combined decrease in both velocity and temperature. Typical parameters are shown in Table V.

We began an additional study of the effects of various increases and decreases in temperatures, speeds, and gas flows and their effect on modulus (Table VI). This study was near the end of the program, and we were not able to determine boron content with respect to these variables.

At a synthesis speed of 8.0×10^{-3} mps (1.5 fpm), we obtain acceptable results for tensile strength and diameter by slightly reducing cell current. We believe that this one speed, 8.0×10^{-3} mps (1.5 fpm), is only an interim plateau and that higher speed capability is entirely possible. We are presently working at the 12.9×10^{-3} mps (2.54 fpm) level and have tested modulus up to 17.9×10^{6} N/cm² (26 × 10⁶ psi), but the results are not yet consistent and reproducible. For example, one isolated fiber had a measured modulus of slightly over 20.7 × 10⁶ N/cm² (30 × 10⁶ psi) and an average U.T.S. of nominal 242,000 N/cm² (350,000 psi). However, this was not reproducible.

G. BORON CONTENT OF MONOFILAMENT

Selected monofilaments were analyzed for boron content during this program. Results for these analyses are displayed in Tables II and V. We found that we could not arbitrarily modify boron content by the obvious expedient of varying the plating gas mixture. Any deviation from a boron to carbon ratio in the gases from the approximate ratio of 1:66 yielded poor quality fiber. However, the boron content can be made to vary. Boron content is a dependent variable evidently associated in a complex relationship to the variables of filament drawing speed and heating current which in turn controls the deposition temperature. An additional relationship also appears to exist between boron content and filament strength and modulus. While these relationships were discovered during this program, they could not be defined in a systematic manner because of time limitations. However, certain trends appear evident. First, there appears to be a relationship between an increase in boron and corresponding increases in both filament strength and modulus. Second, the boron content appears to increase as filament drawing speed and/ or heating current are decreased. Thirdly, boron content cannot be effectively changed by altering plating gas concentration.

H. FILAMENT PROPERTY SCATTER REDUCTION

One objective of this program was quality control which is expressed in terms of reduced filament property scatter. In order to accomplish this objective, it is important that processing variables be studied, optimized and controlled. During this program, the main variables that received attention were quality control of the substrate, improved control and distribution of the plating gases and control and repeatability of heating current.

As a demonstration of the optimization of these variables, during this research program a separate production program was conducted for synthesizing nominally 12,192 meters (40,000 feet) of large diameter monofilament having a nominal diameter in the 76 μ to 102 μ (3.0 to 4.0 mil) range and with a diameter variation of only ±2.5 μ (±0.1 mil) within a single spool. Minimum continuous lengths for this separate program were 61 meters (200 feet) with a maximum continuous length reaching 1650 meters (5400 feet). Modulus for these production fibers was spot checked and found to be 13.8 × 10⁶ ±1 N/cm² (20 × 10⁶ ±1 psi), but after reducing the velocity, it was raised to 19.3 × 10⁶ ±1 N/cm² (28 × 10⁶ ±1 psi). The data obtained from these tensile tests on this production run showed an average strength of 232,800 N/cm² (337,600 psi) with a standard deviation of 34,500 N/cm² (50,100 psi). The production data is summarized in Table VII.

The reduction in scatter for tensile strength was significantly improved. Figure 16 is a histogram displaying the reduced tensile strength scatter for these production fibers which resulted from the optimization of



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processing variables under the research contract. By comparison, Figure 17 displays typical tensile strength distribution of filaments synthesized under the previous research program (Reference 1). Although the number of tests was smaller in the first program, the trend of strength improvement and reduced scatter can be seen.

Improvements were achieved during this contract with respect to the previous referenced program. The average ultimate tensile strength increased to nominal 242,000 N/cm² (350,000 psi) from a previous average somewhat below 207,000 N/cm² (300,000 psi). Highest measured strength increased from 373,000 N/cm² (541,000 psi) to 381,000 N/cm² (552,000 psi). Modulus remained essentially the same with the experimental high value increasing from 19×10^6 N/cm² (28 × 10⁶ psi) to 21 × 10⁶ N/cm² (30 × 10⁶ psi). Average diameter increased from nominal 76µ (3.0 mils) to nominal 86µ (3.4 mils) with high values increasing from nominal 102µ (4 mils) to nearly 152µ (6 mils). Synthesis velocity was also increased from 3.8 × 10⁻³ mps (0.75 fpm) to nearly 12.9 × 10⁻³ mps (2.54 fpm).





The primary conclusions reached during this program are:

1. The CVD method for producing carbon-based fibers can be utilized to synthesize fibers having experimental U.T.S. values ranging up to 381,000 N/cm² (552,000 psi); modulus values to nearly 21×10^6 N/cm² (30 $\times 10^6$ psi); and diameters to nearly 152μ (6 mils). These represent the highest values yet achieved for these fibers. However, synthesis parameters are not at present known which can produce these properties simultaneously in the same fiber. Thus, the highest modulus filament had only a U.T.S. of ca. 242,000 N/cm² (350,000 psi), while the highest strength fiber had a modulus of ca. 18.6×10^6 N/cm² (27 $\times 10^6$ psi).

2. Synthesis speeds can now reach 12.9×10^{-3} mps (2.54fpm) for 84μ (3.3 mil) diameter fiber. This represents a 338% increase over synthesis speed achieved under the previous contractural effort.

3. Filament quality control has been improved. Scatter in the measured ultimate tensile strength has been reduced, and the average tensile strength has been increased from 300,000 psi to nominal 350,000 psi.

4. A major processing variable which masks all other variable optimization studies was found to be the carbon substrate quality and uniformity as received from the supplier. Numerous defects can and do occur in various lots for this substrate. Quality control procedures have been instigated by the supplier as a result, in part, of the findings of this research program.

5. The composition of the plating gas atmosphere was optimized during this program. The optimum boron to carbon ratio in this atmosphere appears to be nominally 1:66. A deviation from this ratio of only 2% results in reduced fiber quality.

6. It was discovered that the strength and modulus appear to be variables dependent upon boron concentration. Boron concentration is in turn a variable dependent upon filament drawing speed and temperature. The interrelationship of these variables appears to be rather complex, however, and additional research is required to optimize synthesis conditions.

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TABLE I

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EFFECTS OF CURRENT CHANGES ON TEMPERATURE (°C)

Plating <u>Cells</u>	Production Currents	5 ma . <u>Increase</u>	5 ma Decrease
1 Intake	1125°	1275°	990°
Middle	1000	975	1000
Exhaust	950	945	925
2 Intake	1160	1110	1160
Middle	1000	975	1000
Exhaust	950	960	955
3 Intake	1075	1060	1070
Middle	975	980	975
Exhaust	950	945	940

EFFECTS OF CURRENT CHANGES ON TEMPERATURE (°F)

Plating Cells	Production Currents	5 ma . Increase	5 ma Decrease
l Intake	2057°	2327°	1814°
Middle	1832	1787	1832
Exhaust	1742	1733	1697
2 Intake	2120	2030	2120
Middle	· 1832	1787	1832
Exhaust	1742	1760	1751
3 Intake	1967	1940	1958
Middle	1787	1796	1787
Exhaust	1742	1733	1724

TABLE II

RELATIONSHIP OF DRAWING SPEED TO HEATING CURRENT AND FIBER STRENGTH AND DIAMETER (SI Units)

	Heating	Current			
Speed $(mps \times 10^{-3})$	Stage 1 (ma)	Stage 2 (ma)	Fiber Dia. (µ)	U.T.S. $(N/cm^2 \times 10^3)$	Boron (Wt.%)
4.07	175	140	88.2 - 94.8	140 - 187	28.68
2.29	100		80.5	215 - 267	31.99
4.07	85	90	86.3 - 92.6	180 - 268	33.12
3.82	92	92	94.8	139 - 284	35.83; 36.11
5.48	100	105	95.9		33.12; 33.51
8.48	100	125	101.3	•	30.56; 30.62
8.48	100	135	102.8		30.79; 30.26

(English Units)

Speed (fpm)	Heating Stage 1 (ma)	Current Stage 2 (ma)	Fiber Dia. (mils)	U.T.S. <u>(psi × 10³)</u>	Boron (Wt.%)
0.8	175	140	3.47 - 3.73	151 - 271	28.68
0.45	100		3.17	312 - 387	31.99
0.8	85	90	3.39 - 3.64	261 - 389	33.12
0.75	92	92	3.73	202 - 412	35.83; 36.11
1.08	100	105	3.77		33.12; 33.51
1.08	100	125	3.99		30.56; 30.62
1.08	100	135	4.05		30.79; 30.26

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	haust psi			230.			17.5						149.
10 ³)	Near Ex N/cm ²			115.8			12.1						102.5
.T.S. (×	Inlet psi	126 77.8	67.2	84.			120.		81.4			261.	130.
	Near N/cm ²	86.9 53.6	46.2	57.9			82.7		56.1			180.	88.6
	xhaust (mils)			2.83	3.04	3.23	2.36			2.60		3.17	4.62
iameter	Near E			72.0	77.3	82.1	60.0			66.1		80.6	117.4
Final D:	Inlet (mils)	3.48	3.38	4.74	5.32	4.71	3.48	2.22	3.07	2.71	2.67	4.51	6.01
	Near (µ)	88.5	86.0	120.5	135.0	119.6	88.5	56.5	78.1	68.8	67.9	114.5	152.7
trate	neter (mils)	1.31	1.31	1.31	1.31	1.31	1.31	1.31	1.31	1.28	1.28	1.28	1.28
Subs	Diam (µ)	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	32.6	32.6	32.6	32.6
	ature (°F)	1832	1832	1832	1832	1832	2012	2192	2192	2192	2192	1742- 1832	1742- 1832
	Temper (°C)	1000	1000	1000	1000	1000	1100	1200	1200	1200	1200	950- 1000	950- 1000
Total	Time (min)	2.5	2.25	5.8	6.0	5.8	1.85	.48	1.0	1.5	2.2	10.	8.

TABLE III

INITIAL STATIC TEST RESULTS

TABLE IV

STATIC TEST GROWTH RATES (SI Units)

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Temp. (°C)	Time (Min)	Final Dia. (µ)	Coating Thickness (µ)	Growth Rate (µ/min)	Remarks
800.	10.0	54.7	10.9	1.09	Smooth surface, brittle
800	15.0	65.4	16.3	1.09	Smooth, brittle
900	6.5	72.2	19.6	3.00	Nodules, brittle
1000	3.5	114.6	41.2	11.75	Nodules, brittle
1000	5.3	120.7	44.0	8.28	Nodules, brittle
1100	2.0	94.9	31.0	15.5	Many nodules, brittle
1200	0.5	64.4	15.7	31.5	Smooth, brittle

(English Units)

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Temp. (°F)	Time (min)	Final Dia. (mils)	Coating Thickness (mils)	Growth Rate (mils/min)	Remarks
1472	10.0	2.15	.43	.043	Smooth surface, brittle
1472	15.0	2.57	.64	.043	Smooth, brittle
1652	6.5	2.84	.77	.118	Nodules, brittle
1832	3.5	4.53	1.62	.463	Nodules, brittle
1832	5.3	4.75	1.73	. 326	Nodules, brittle
2012	2.0	3.73	1.22	.61	Many nodules, brittle
2192	0.5	2.53	.62	1.24	Smooth, brittle

TABLE V

TEMPERATURE AND VELOCITY DEPENDENCE OF MODULUS (SI Units)

	mps		Cell Temp. (°C)				ρ	Е
Sample	$\times 10^{-3}$	<u>Wt.% B</u>	<u>#1</u>	#2	#3	<u>(µ)</u>	g/cc	$N/cm^2 \times 10^6$
1	12.9	25.74	1100	1120	1065	87.9	1.93	13.5
2	12.9	25.88	1175	1125	1065	88.2	1.92	14.3
3	6.46	29.28	1140	1070	1040	107.8	1.89	15.3
4	12.9	26.05	1300	1195	1020	82.6	1.92	16.1
5	7.62	31.17	1035	1035	1000	97.8	1.93	17.9

(English Units)

			Cell	l Temp.	(°F)		ρ	E
Sample	fpm	Wt.% B	#1	#2	#3	<u>mils</u>	<u>lbs/in³</u>	<u>psi × 10⁶</u>
1	2.54	25.74	2012	2048	1949	3.46	.0698	19.4
2	2.54	25.88	2147	2057	1949	3.47	.0694	20.5
3	1.27	29.28	2084	1858	1904	4.25	.0684	21.9
4	2.54	26.05	2372	2183	1868	3.25	.0694	23.1
5	1.5	31.17	1895	1895	1832	3.85	.0698	25.6

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TABLE VI

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MODULUS-INCREASING EXPERIMENTS

Diameter Modulus	$psi \times 10^6$	7.8	10.5	23.0	26.1	25.5	25.3	29.2	21.3	30.4	25.0
	$N/cm^2 \times 10^6$	5.4	7.2	15.9	18.0	17.6	17.5	20.1	14.7	21.0	17.2
	mils	2.92	2.86	3.00	2.88	3.61	3.34	3.34	3.34	3.39	3.17
	(1)	74.2	72.6	76.2	73.2	91.7	84.8	84.8	84.8	86.1	80.5
<u>Velocity</u> mps	fpm	1.26	1.26	1.26	1.26	1.26	1.5	1.5	1.5	1.5	2.0
	× 10 ⁻³	6.41	6.41	6.41	6.41	6.41	7.63	7.63	7.63	7.63	10.16
Plating Cells Current (ma)	#3	92	92	92	92	98	98	98	100	98	98
	#2	06	06	06	06	92	92	94	96	94	94
	1#					06	06	06	06	06	06
Pretreat Current	(ma)		120	120	120	122	120	120	120	120	120
	Example	1	2	3	4	Ŋ	9	7	8	6	10

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TABLE VII

PRODUCTION RUN PROPERTIES (Runs over 500 feet)

Lot	Run	Len	gth	Diam	eter	Average U.T.S. $\times 10^3$
<u>No.</u>	No.	Meters	Feet	<u>μ</u>	mils	N/cm ² psi
1000	P-100	. 603	1,977	89	3.51	255 . 370
	P-121	170	557	88	3.45	232 337
	P-124	304	999	89	3.50	230 333
1010	P- 87	376	1,234	87	3.44	286 415
	P-103	246	808	87	3.44	235 341
	P-111	226	743	88	3.45	245 356
	P-128	229	752	87	3.44	259 376
	P-132	175	574	87	3.44	216 314
	P-134	174	570	87	3.43	223 323
1020	P-122	248	814	87	3.43	223 324
	P-125	776	2,545	87	3.43	238 345
	P-126	430	1,411	87	3.43	266 386
1030	P-105	371	1,218	87	3.42	214 311
	P-116	201	660	86	3.40	259 376
	P-129	311	1,020	87	3.41	244 354
	P-130	302	990	87	3.42	229 332
1040	P- 77	172	565	86	3.40	286 415
	P- 78	946	3,104	86	3.40	261 379
	P- 86	372	1,221	86	3.40	240 348
1050	P- 79	906	2,971	86	3.39	217 315
	P- 81	320	1,051	86	3.37	227 329
	P- 89	515	1,691	86	3.39	248 360
1060	P- 88	- 626	2,053	86	3.38	263 382
	P-127	547	1,796	86	3.37	250 362
1070	P- 97	584	1,915	85	3.34	248 360
	P-118	546	1,790	84	3.30	228 330
	P-144	213	700	86	3.39	239 346

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