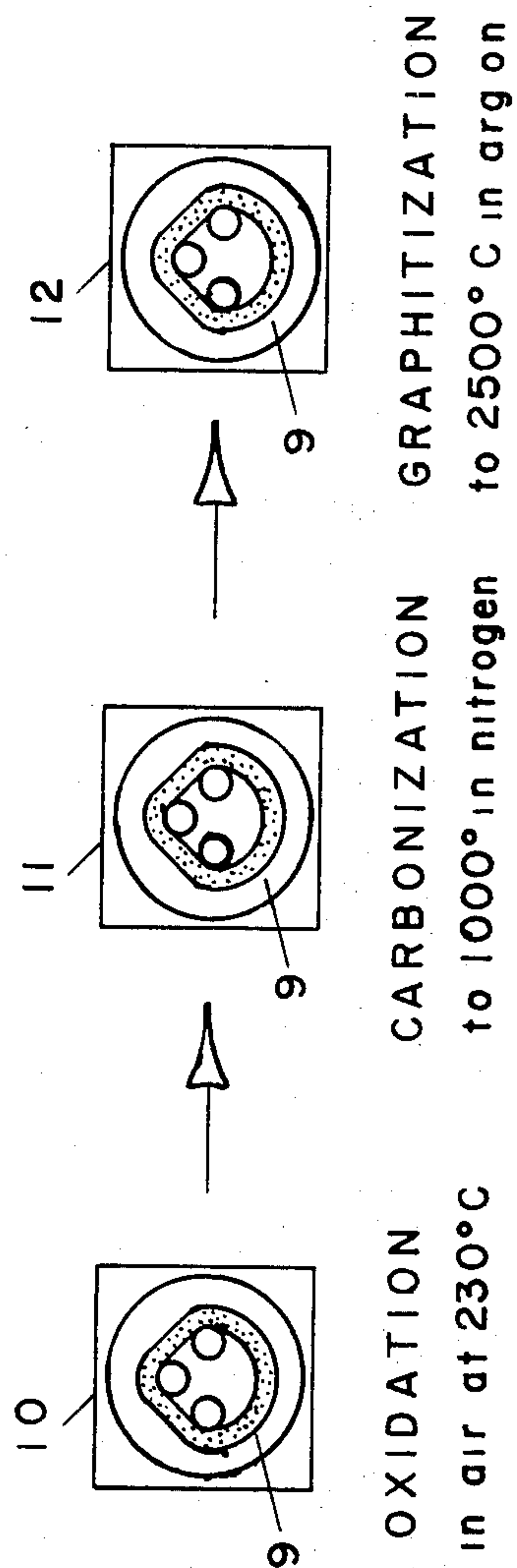
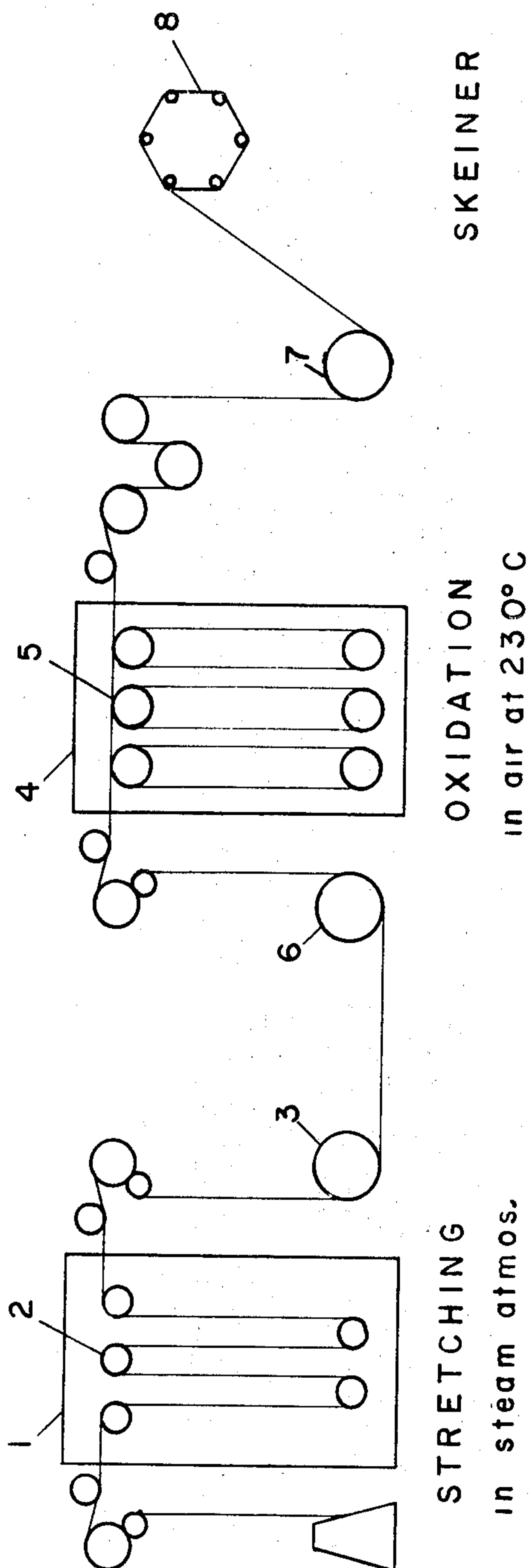


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PROCESS FOR THE MANUFACTURE OF CONTINUOUS HIGH MODULUS  
CARBON YARNS AND MONOFILAMENTS  
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## PROCESS FOR THE MANUFACTURE OF CONTINUOUS HIGH MODULUS CARBON YARNS AND MONOFILAMENTS

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6 Claims

### ABSTRACT OF THE DISCLOSURE

Carbon fiber yarns or monofilament in continuous lengths are produced by subjecting conventional polyacrylonitrile yarns or monofilaments to a two-stage process consisting of a continuous stage carried out under tension and a discontinuous skein stage in which no tension is employed. In the tension stage, the continuous yarn is stretched in steam and then oxidized in air about 230 to 250° C. for one hour while travelling from an input to an output roller set at substantially the same yarn feed rate. The yarn is then formed into skeins and subjected consecutively to further oxidation, carbonization and, if desired, graphitization—the last two steps being carried out in non-oxidizing media.

Carbon yarns or monofilaments may thus be obtained in lengths of 2000 yards or more with tensile strengths of up to about  $300 \times 10^3$  p.s.i. and Young's moduli of up to about  $80 \times 10^6$  p.s.i.

### THE PRIOR ART

Due to the constantly increasing demand for filamentary carbon structures employed as reinforcement in the composite materials used in aerospace vehicles, the art devoted to the manufacture of these carbon structures has been developing at a great pace. Thus, it is now feasible to convert all sorts of carbonaceous textile materials to carbon filament, yarn or cloth, although practical considerations generally limit the choice of raw material for the manufacture of said carbon structures to cellulosic and polyacrylonitrile fibers. As the present invention is not concerned with the processing of cellulosic fibers, the specific art dealing with that shall not be reviewed in any great detail inasmuch as any facet of it that is relevant to the transformation of polyacrylonitrile (PAN) fibers to carbon fibers is already embodied into the parallel PAN conversion art.

The processing of PAN fibers beyond ordinary textile practice began with Houtz (Textile Research Journal, Nov. 1950, pp. 797–798), Barrett (U.S. Pat. 2,789,915 and 2,913,802), Wilkinson (U.S. 3,027,222) and Crawley (U.S. 3,125,404), who demonstrated that the oxidation of PAN fibers rendered them infusible, thus giving them the structural stability to undergo the further heat treatments that could already successfully convert material infusible fibers to fire-resistant or to carbon fibers.

Oxidized PAN fibers were converted to carbon fibers around 1960 by Shindo (Studies in Graphite Fiber, Report #317 of the Government Research Industrial Institute, Osaka, Japan—1961) and Tsunoda (U.S. 3,285,686). Shindo, recalling the high theoretical melting point on PAN and its tendency to decompose below that melting point, realized that PAN fiber had "adequate properties for the production of graphite fiber." Once this basic oxidation and carbonization process had been taught, further improvements quickly followed through the application of conventional textile polymer, cellulose and

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graphite art to this newly available substrate. For instance, it was noted that the application of various amounts of stress at different stages of the process strengthens the fibers by aligning the molecules, orienting the fibers and preventing the spatial disorganization and weakening caused by shrinking and release of non-carbon substances in the course of heat treatment. PAN fibers were thus stretched beyond commercial practice for maximum alignment, as other conflicting textile properties were no longer of interest; stress was applied during oxidation and during part or all of the carbonization, sometimes at the lower temperatures and sometimes at the very high graphitization temperatures. In this manner, the teachings of Edison (U.S. 485,615), Fujisaki (U.S. 3,080,209), Turkat (U.S. 3,394,880 and 3,375,308), Spry (German 1,226,925) and Cranch (U.S. 3,313,597) were incorporated into the basic oxidation-carbonization process of Shindo to provide carbon fibers of greater strength and higher modulus. Various other specific improvements were offered by Shindo, Otani (Carbon 3, pp. 31–38—1965) and Miyamichi (Sen-i Gakkaishi 21 (12), p. 26, FIGS. 3 and 4), who showed that limiting the maximum temperature of heat treatment could lead to a maximization of tensile strength at the expense of the modulus of elasticity. Still, at that point of development, no one could conveniently produce high strengths, high modulus carbon fibers from PAN in lengths greater than a few feet.

### OBJECTS OF THE INVENTION

Accordingly, an object of this invention is to produce carbon and graphite fibers of high modulus and tensile strength in the form of yarns and monofilaments of great lengths capable of being handled in conventional textile manner. Another object is to provide a semi-continuous process which will permit the manufacture of said carbon monofilaments and yarns. Still another object is to render possible the manufacture of carbon fiber-resin composites of various shapes by providing the possibility of winding the reinforcing carbon fiber yarn or monofilament continuously on an appropriate form before embedding said wound fiber into a resin matrix.

### SUMMARY OF THE INVENTION

These and other objects which shall become apparent in the course of the detailed description of the invention that shall be made, have been accomplished by a two-stage process in which PAN fiber yarn or monofilament is first stretched beyond commercial textile practice to obtain maximum orientation and tenacity and is then subjected to a partial oxidation while being maintained under tension. The partially oxidized material is then formed into skeins and subjected in this stress-free state to a further oxidation, followed by carbonization in a non-oxidizing atmosphere to the desired temperature maximum which can provide any carbon fiber within the range of maximum strength to maximum modulus.

### DETAILED DESCRIPTION

A clear idea of the process may be obtained by referring to the flow sheet presented in the accompanying figure. This flow sheet and diagrams are merely illustrations and are not intended to supply mechanical operating detail. According to this flow sheet, which represents one of the embodiments of the process of the invention, the filament or yarn is first passed through a stretching chamber I across a series of guiding and supporting rollers to a winder 3. Steam is fed through the chamber and the rollers and winder are geared so that the desired amount of stretch is effected without causing the yarn to break. The stretched yarn is then allowed to pass through an oxidation chamber 4 across a number of rollers 5 sufficient to keep all yarn segments separate and to insure



the proper residence time in the hot air that is constantly sweeping through the chamber. The speeds of the input roller 6 and output roller 7 are kept substantially equal in terms of length of yarn by unit time, an arrangement which results in the maintenance of tension by prevention of shrinking. After a treatment in the order of one hour at 230° C. in this continuous oxidation chamber, the yarn is wound on a skeiner 8 and the skeins 9 are placed in another chamber 10 in which the yarn is further subjected to sweeping 230° C. air until the non-combustive oxidation of the yarn is completed. The skeins of oxidized yarn are then transferred to a furnace 11 in which the yarn is converted into carbon by raising the temperature to, for instance, 1000° C. in about 1 hour in flowing nitrogen. The carbonized yarn may also be graphitized by placing the skein in another furnace 12 and subjecting them to a heat treatment in the order of 30 minutes at 2800° C. in a non-oxidizing atmosphere.

The continuous carbon fiber yarn or filament of this invention is produced from any polyacrylonitrile fiber having a conventional acrylonitrile unit content of at least about 85%. The fiber may have been formed with spinneret or by stretching extruded sheets of the polymer until they fragment longitudinally into separate fibers. The actual fibers used in the conversion process are either in the form of yarn made conventionally from twisted staple fibers or in the form of monofilaments, extruded and processed in lengths of the order desired in the final carbon form. Although treatment conditions can be adapted to satisfactorily convert any type of yarn or filament, the preferred material is clean, uniform in shape and composition, and possesses the highest tenacity and smallest fiber denier that the art can produce.

Although the production of acrylic fiber by spinning always involves some post-spinning stretching which operates to increase the tenacity of the filament, it is evident that unless specifically prepared for maximum tenacity, a given commercial product will generally be capable of undergoing further stretching. This is due to textile practicalities which dictate that other characteristics be considered, in addition to tenacity, if the material is to be used as a textile material. For the purpose of this invention however, the polyacrylonitrile fiber should be stretched beyond commercial practice to its limit, if this has not already been done. The fiber can be stretched most conveniently in steam, boiling water or air to at least 150% of its commercial length. This heating of fiber to a temperature above the glass transition temperature and below the fusion point of the polymer accompanied as it is by the stretching induced by appropriately coordinated rollers on which the yarn is carried and advanced in a continuous manner results in a two to threefold increase in the modulus of the ultimate carbon fiber yarn. The operation is carried out rather quickly, the yarn being passed over a number of free or driven rollers such that, for instance, a length of not less than 30 feet of yarn is in the stretching chamber at any time and is stretched in a number of stages in about 2 minutes.

The stretched PAN yarn or filament is then oxidized. The operation is carried out in a chamber or cabinet in which the material is subjected, while under tension, to the action of a heated gas. This gas may be selected from air, oxygen or any of a number of other oxidizing gases. The rate of oxidation achieved is determined by temperature selected, the accessibility of the polymer, i.e. the cross-sectional area and shape of the fiber, and of course the chemical nature of the particular PAN polymer treated. Some of these factors, as well as the purging efficiency, also affect the maximum usable oxidizing temperature. In fact, if the PAN materials is not well purged at this stage, its linear structure rapidly breaks down to yield a fused char.

The oxidizing process just discussed may be effectively carried out in a forced air convection oven with several hundred yards of yarn or filament wrapped over several

pairs of driven rolls, with the yarn input rate being substantially equal to the yarn output rate. This arrangement and regime creates tension which prevents contraction and attendant loss of orientation and modulus. Within the limitations already disclosed, it has been found preferable to carry out the present operation at a temperature within the range of about 220 to about 250° C. for a period of one to two hours of residence in the chamber which varies of course inversely to the actual temperature employed.

It should be noted here that certain PAN fibers should be subjected to a preliminary surface oxidation at a temperature lower than those just mentioned with a strong oxidizing agent either in a gaseous or liquid media. This pretreatment with a material such as nitric oxide, nitrogen dioxide and so on, renders the surface of the fibers less fusible and thus better suited to oxidation under tension.

The partially oxidized PAN fiber material is then wound into skeins on conventional equipment and the conversion process is continued. The skeins, each consisting of a loosely wound length of yarn or monofilament of 500 or 600 meters or more, are placed in an oven or furnace and subjected to a further sweeping with an oxidizing gas such as air or oxygen at a temperature within the range of about 220 to about 250° C., preferably about 230° C. The operation is carried out for a period of about 5 to 15 hours resulting in the production of a "completely oxidized" PAN fiber, i.e. one in which no carbon has been lost and little overall weight change has occurred. On further treatment, this completely oxidized fiber does not shrink or lose much weight.

After oxidation, the skeins of oxidized PAN fiber are carbonized, i.e. the cross-linked polyacrylonitrile polymer is converted to an essentially pure carbon structure. This operation may be carried out in the oven used for the skein oxidation or, if not possible, in an oven capable of reaching and maintaining the necessary temperature. The operation consists essentially in heating the fiber to a temperature in the vicinity of 1000° C. and in sweeping the skeins with a non-oxidizing gas such as nitrogen or hydrogen during the heating and cooling cycle. Efficiency of purging here is not as critical as in the oxidation step, its only function being to prevent redeposition of volatiles on the carbon fibers. Shrinking of the fiber takes place during this operation, but no significant loss of modulus may be attributed to this contraction. The overall heating and cooling cycle in the operation is relatively rapid. The heating is carried out typically at the rate of 10 to 20° C. per minute and the cooling conditions are not critical.

Although the somewhat amorphous carbon fibers thus produced possess excellent useful properties, they may be further treated to maximize either their tensile strength or their modulus or both and to yield ultimately graphite fibers. The heat treatment is carried out in furnace or kiln under an inert atmosphere, preferably nitrogen, argon or helium. The transformation at this stage is rapid and does not require any great purging. Neither are heating and cooling rates critical. The maximum temperature of the treatment has a definite effect on the final strength of the fiber, there being a given temperature for each PAN polymer fiber at which maximum strength is obtained. Tensile strength may thus be maximized, but at the expense of modulus of elasticity. This occurs typically between 1000 and 1700° C. Modulus, on the other hand, may be optimized by maximizing the final treatment temperature to 2500+° C. and by conventionally stretching the graphite fiber during this heat treatment.

The following examples will serve to illustrate further the practice of the invention. They are not to be interpreted as limitations beyond those set by the claims that follow this specification.



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## EXAMPLE 1

The raw material employed is a type G Courtelle<sup>1</sup> yarn, marketed by Courtaulds Ltd. and made from a 3 denier 4-inch staple fiber with 4 turns per inch twist and about 800 filaments per yarn. The yarn is first continuously stretched in steam to 250% of its original length. It is then oxidized at 250° C. for 1 hour in a forced air convection oven with sufficient tension being maintained by roller adjustment so that shrinking of the yarn is kept to less than 5%. The partially oxidized yarn is wound into skeins, each skein consisting of a continuous length of yarn of about 2000 feet. The skeins are further oxidized for 15 hours at 230° C., again in a forced air oven but without tension. The oxidized yarn skeins are then loosely placed in a kiln and the temperature is raised to 1000° C. in 4 hours while the kiln is being continuously swept with nitrogen. The kiln is allowed to cool under inert atmosphere and the carbon yarn is removed for testing or for further processing. In this manner, useful amorphous carbon yarn can be obtained in continuous lengths that have an average tensile strength of 150,000 p.s.i. and an average Young's modulus of  $23 \times 10^6$  p.s.i.

## EXAMPLE 2

The properties of a carbon yarn as produced by the method of Example 1 may be further improved by heat treating the yarn at higher temperatures. The yarn, for example may be graphitized by placing it in a kiln and raising the kiln temperature to graphitization level while maintaining a non-oxidizing atmosphere. Typically, the temperature is brought from the ambient level to 2500° C. in about 90 minutes and is kept at that level for 30 minutes. The rate of temperature increase is not critical and is dependent on the kiln's capacity. A nitrogen or argon atmosphere is maintained until the equipment has once again cooled to ordinary levels.

A graphite fiber may thus be obtained from starting material having the properties described in Example 1, that measures  $6.2 \times 10^{-8}$  inch<sup>2</sup> in cross-section and constitutes a yarn having tensile strength of  $216 \times 10^3$  p.s.i. (1" gauge length) and  $300 \times 10^3$  p.s.i. ( $\frac{1}{16}$  gauge length) with a modulus of  $51 \times 10^6$  p.s.i.

## EXAMPLE 3

A repetition of the operations of Examples 1 and 2 on the same type of material, with the exception that the continuous oxidation is carried at 230° C. for 2 hours instead of at 250° C. for 1 hour, leads to graphite yarn with a tensile strength of  $204 \times 10^3$  p.s.i. (1" gauge length) and  $300 \times 10^3$  p.s.i. ( $\frac{1}{16}$  gauge length), with a modulus of  $52 \times 10^6$  p.s.i.

## EXAMPLE 4

Orlon<sup>2</sup> tow, made of continuous 3 denier polyacrylonitrile monofilaments, is oxidized with air at 250° C. under tension for a period of 2 hours. The oxidation is continued without tension for 15 hours at 230° C. in air. The material is then carbonized in nitrogen with the temperature being increased to 1000° C. in about two hours.

<sup>1</sup> Registered trademark.

<sup>2</sup> Registered trademark.

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Graphitization follows for 30 minutes at 2800° C. under nitrogen.

There can thus be obtained crystalline carbon fibers having a tensile strength of about 250,000 p.s.i. and a modulus about  $90 \times 10^6$  p.s.i.

It is evident that, because of the great variety in composition and properties possessed by available polyacrylonitrile fiber, many variables of the process of this invention can be manipulated by the man skilled in the art to achieve the type of product desired. These changes can be made however without departing from the scope of the claims which are:

What is claimed is:

1. In a process for the manufacture of carbon and graphite filament and yarn which comprises stretching a precursor poly-acrylonitrile filamentary material in stream to at least 150% of its initial length, subjecting the stretched material to a non-combustive oxidation process, and carbonizing the oxidized material in a non-oxidizing atmosphere at a temperature of at least 700° C., the improvement consisting of:

(a) performing the stretching process in a continuous manner on continuous lengths of polyacrylonitrile filament and yarn, and

(b) carrying out the non-combustive oxidation of the stretched material in a two-stage operation consisting of: a heat treatment at a temperature selected from the range of about 20° to 25° C. in a flowing oxidizing atmosphere for an effective period of about one to two hours, said treatment being carried out while the filamentary material passes through a kiln in a continuous manner and under sufficient mechanical tension to substantially prevent shrinkage; and a subsequent heat treatment of the filamentary material in batch lots at a temperature selected from within the range of about 200 to 250° C. in a flowing oxidizing atmosphere for a period of about 5 to 15 hours, said subsequent treatment being carried out on fiber and yarn free from mechanical tension.

2. The process of claim 1 wherein the carbonized filamentary material is further heat treated to a temperature of at least 1500° C., in an inert atmosphere.

3. The process of claim 1 wherein the polyacrylonitrile precursor is subjected to a preliminary oxidation treatment at a temperature below its effective softening point.

4. The process of claim 1 wherein the oxidizing atmosphere consists of air.

5. The process of claim 1 wherein the first stage non-combustive oxidation is carried out during an effective period of one hour at 250° C.

6. The process of claim 1 wherein the filamentary material is treated in continuous lengths of at least 2000 feet.

## References Cited

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EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

23—209.4

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,533,743 Dated October 13, 1970

Inventor(s) R. Prescott and I. W. Orr, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, under the title, delete "Jonesboro" and insert  
---Johnson City---.

Column 1, line 54, delete "Barrett" and insert ---Barnett---.

Column 2, line 15, delete "3,394,880" and insert  
---3,294,880---.

Claim 1, sub-paragraph (b), line 28, change "20°" to ---200°---.  
same line, change "25°" to ---250°---.

SIGNED AND  
SEALED  
DEC 29 1970

**(SEAL)**

**Attest:**

**Edward M. Fletcher, Jr.**  
**Attesting Officer**

**WILLIAM E. SCHUYLER, JR.**  
**Commissioner of Patents**