United States Patent

[11] 3,607,059

[72] Inventors **Louis A. Joo;**
Frank E. Snodgrass, both of Johnson City, Tenn.

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[73] Assignee **Great Lakes Carbon Corporation**
New York, N.Y.

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[54] **PROCESS FOR THE MANUFACTURE OF FILAMENTARY CARBON PRODUCTS**
6 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **23/209.1,** 23/209.4, 8/115.5
[51] **Int. Cl.** **C01b 31/07**
[50] **Field of Search** 23/209.1, 209.4; 8/115.5

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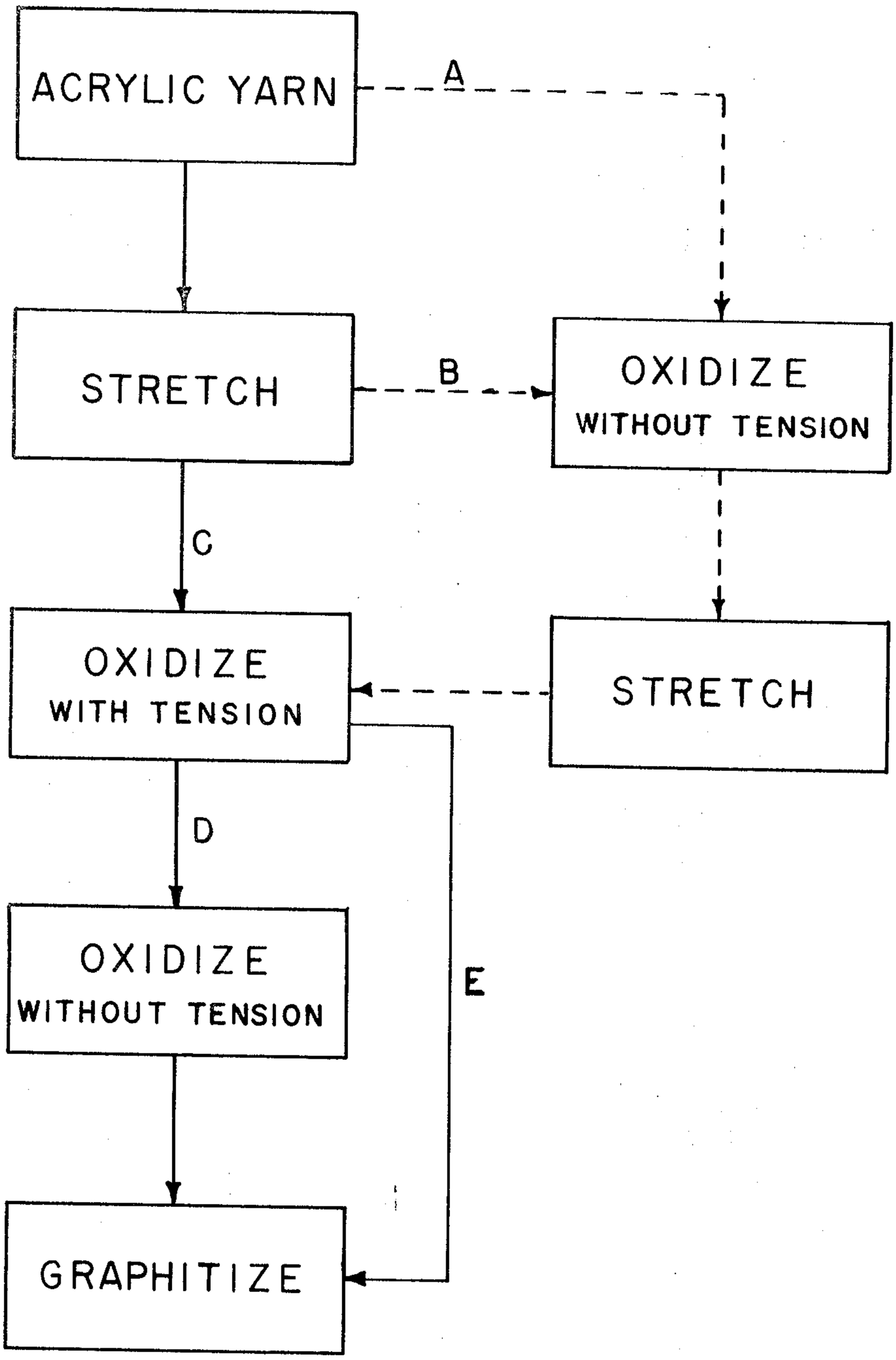
Primary Examiner—Edward J. Meros
Attorney—Donald R. Cassady

ABSTRACT: Process for the manufacture of carbon and graphite filamentary products from polyacrylonitrile filamentary material wherein said filamentary material is subjected to a preliminary tension-free noncombustive partial oxidation and thereafter stretched to introduce or restore orientation in the polymer strands prior to being oxidized under tension followed by carbonization in a nonoxidizing atmosphere at a temperature of at least 700° C.



INVENTORS.
LOUIS A. JOO
FRANK E. SNODGRASS

PROCESS FOR THE MANUFACTURE OF FILAMENTARY CARBON PRODUCTS

THE PRIOR ART

Due to the promising properties of carbon and graphite fibers in aerospace applications, there has been developed during this decade numerous processes for the manufacture of these useful fibers from a number of polymeric filamentary materials including regenerated cellulose and copolymers of polyacrylonitrile. The present invention concerns itself strictly with the processing of these polyacrylonitrile copolymers to carbon and graphite forms.

There is already available in the art a number of processes which will carry out this conversion more or less successfully. These processes are based on the capacity of these copolymers to be oxidized to an infusible state, a sine qua non requirement which renders feasible the drastic heat treatment that must follow for conversion to carbon and to graphite. Thus, the more desirable prior art processes call for the partial noncombustive oxidation of the polymer to an infusible state and for the subsequent carbonization of the modified polymer at temperatures of at least 700° C. in a nonoxidizing atmosphere. Graphitization may also be carried out under similar conditions at higher temperatures, if graphite yarn or filament is desired. Known variations of these treatments involve the use of tension during the actual oxidation, carbonization or graphitization process. Available processes also are applicable to continuous yarn or filament for continuous or batch-wise conversion.

The use of tension during the oxidation of polyacrylonitrile copolymer (PAN) filamentary material, while desirable and necessary for the production of high modulus carbon fibers in a continuous process as opposed to a batch approach, gives rise to insuperable difficulties. Thus commercially available domestic PAN fibers do not develop an infusible skin during oxidation and tend to fuse during that process even at lower temperatures where the rate of oxidation is so limited as to render the processing time uneconomical. The undesirable tendency to fuse is accentuated by the use of tension necessary to preserve the orientation introduced into the yarn or filament prior to oxidation. As the filamentary material passes on the set of grooved rolls which maintain the tension required to preserve orientation, the compacting or "ironing" effect of these rolls produces a material in which the individual filaments are fused together, thus yielding a weak, brittle, nongraphitic product.

THE OBJECTS OF THE INVENTION

An object of this invention therefore is to provide a method which will allow the continuous oxidation under tension of acrylic filamentary material which cannot presently be so treated. Another object is to increase the supply of acrylic filamentary material that can be successfully converted to carbon and graphite without losing its filamentary structure.

THE SUMMARY OF THE INVENTION

These and other objects that shall become apparent upon the description of the processes of this invention, have been unexpectedly accomplished by introducing or restoring the orientation required for high modulus and strength to acrylics which have already been partially oxidized without significant tension. It has been found that this can be done to an extent such that no fusion takes place upon further oxidation under tension. In other words, partially oxidized acrylics can be stretched or restretched to introduce or to restore the orientation required for high modulus of elasticity and high strength. Interestingly, this stretching can be carried out without damaging the fiber structure.

THE DETAILED DESCRIPTION OF THE INVENTION

Better comprehension of the processes presently disclosed can be achieved by referring to the flowsheet illustrated in the accompanying drawing.

In a conventional process for conversion of acrylic yarn or filament, the material is first stretched at about 100° C., for instance in hot water or steam. It is then oxidized under tension, usually in air, at a temperature within the range of about 200° to 250° C. for an effective period of about 1 to 2 hours. This is followed by a batch oxidation in a flowing oxidizing atmosphere at similar temperatures for a period of about 5 to 15 hours. This batch oxidation is performed on fibers that are free from mechanical tension. The oxidized fibers are then graphitized at high temperature in a nonoxidizing atmosphere. If nongraphitic carbon fibers are desired, the postoxidative treatment of the fibers may be stopped at temperatures as low as 700° C. This conventional process is schematized on the drawing by the path which passes through lines C and D of the flowsheet. In another conventional process, illustrated on the flowsheet by the path passing through lines C and E, the duration of the oxidation under tension may be increased and the subsequent batch oxidation operation is eliminated.

These basic processes are improved as disclosed in this specification by treating the yarn according to the paths which must follow either lines A or B on the drawing.

In improvement A, the unstretched yarn is first subjected to a partial oxidation without tension followed by a stretching operation before the conventional single or two-stage oxidation and the graphitization operations are performed. The preliminary oxidation process of this improvement is carried out in air at a temperature of about 200°–250° C. for about 1 to about 8 hours; the stretching step is carried out in a boiling water environment. The partially oxidized filament is stretched up to about 200 percent of its original length. This improvement is illustrated by the path which follows line A of the flowsheet. In another embodiment, improvement B, the yarn is first stretched according to the basic process of the art, up to about 150 percent of its original length, but the single or two-stage oxidation and the graphitization step are preceded by an oxidation without significant tension followed by a restretching of the yarn, up to about 200 percent of its original length. The path which goes through line B in the drawing schematizes this approach.

The improved processes of the invention are further illustrated in a more quantitative manner by the examples that follow. In studying these, it should be kept in mind that they are not intended to limit the invention beyond the scope of the claims which follow this specification.

EXAMPLE 1

Orlon(R)

(R)—Registered trademark PAN staple yarn was stretched in boiling water to 210 percent of its original length. It was then passed through a conventional continuous oxidation unit on a pair of driven grooved rolls. After an effective residence time of 1 hour in air at 230° C., the yarn was fused and unfit for further processing.

EXAMPLES 2 and 3

The stretched PAN staple yarn of example 1 was formed into skeins hung loosely in a chamber and oxidized in a flowing current of air at 195° C. for 4 hours. It was subsequently restretched in steam at 96° C. to 130 percent of its resulting length and oxidized in air for 2 hours in a conventional continuous unit. The yarn remained unfused. After further oxidation with tension (example 2) and without tension (example 3) for a period of 16 hours at 220° C., the yarn was carbonized and graphitized in argon to a maximum temperature of 2,500° C.

Both products were unfused and possessed the following properties:

Example	16-hour oxidation p.s.i.	Tensile Strength p.s.i.	Modulus of Elasticity p.s.i.
2	under tension	253,000	$48.8=10^6$
3	no tension	190,000	51.1×10^6

EXAMPLES 4 to 10

Orlon staple acrylic yarn was preoxidized in loose skeins at 220° C., in the manner already described, for various lengths of time, restretched to different degrees in boiling water and processed further under tension as in example 2. The results of these variations as well as the variations themselves are tabulated below:

Example	Pre-oxidation time (hours)	Percent restretched	Tensile strength ($\times 10^3$ p.s.i.)	Modulus of elasticity ($\times 10^6$ p.s.i.)
4	2	20	148	59.5
5	2	40	273	72.6
6	4	20	203	60.8
7	4	40	164	61.1
8	8	20	138	52.9
9	8	40	148	50.2
10	16	(1)		

[1] Not handleable.

It becomes apparent from this data that restretching is effective only when a certain degree of oxidation has been achieved, and that beyond that point it will cause damage in the yarn structure with consequent loss of strength.

EXAMPLE 11

Unstretched Orlon staple acrylic yarn was preoxidized in skein form for 4 hours at 220° C. and subsequently stretched in boiling water to 200 percent of its original length. It was then processed as in example 2 to a graphitized product possessing a tensile strength of 108×10^3 p.s.i. and a modulus of 62.2×10^6 p.s.i.

It can be seen therefore that great advantages are derived from the preoxidation and the subsequent stretching which constitute the essence of the present contribution to the art. It will also be apparent to those skilled in the art that the actual extent and conditions of these processes may vary without departing from the scope of the invention as summarized by the following claims.

1. In a process for the manufacture of carbon and graphite filament and yarn which comprises subjecting a precursor polyacrylonitrile filamentary material (a) to a continuous noncombustive oxidation process carried out under mechanical tension and (b) to a carbonization stage in a nonoxidizing atmosphere at a temperature of at least 700° C., the improvement which consists in first subjecting the filamentary material to a preliminary substantially tension-free noncombustive partial oxidation in air at a temperature within the range of about 200°–250° C. for a duration within the range of about 1 to 8 hours followed by stretching of the partially oxidized filamentary material by up to about 200 percent of its original length in a boiling water environment.

2. In a process for the manufacture of carbon and graphite filament and yarn which comprises subjecting a precursor polyacrylonitrile filamentary material (a) to a noncumbustive oxidation process consisting of a continuous phase carried out under tension and a secondary batch phase carried out without tension, and (b) to a carbonization stage in a nonoxidizing atmosphere at a temperature of at least 700° C., the improvement which consists in first subjecting the filamentary material to a preliminary substantially tension-free noncombustive partial oxidation in air at a temperature within the range of about 200°–250° C. for a duration within the range of about 1 to 8 hours followed by stretching of the partially oxidized filamentary material by up to about 200 percent of its original length in a boiling water environment.

3. The process of claim 1 wherein the entire sequence of operations is preceded by the stretching of the original filamentary material in an H_2O environment at about 100° C. to about 150 percent of its original length.

4. The process of claim 1 wherein the preliminary tension-free noncombustive oxidation process is carried out in air at a temperature of about 220° C. during a period of about 4 hours.

5. The process of claim 2 wherein the preliminary tension-free noncombustive oxidation process is carried out in air at a temperature of about 220° C. during a period of about 4 hours.

6. The process of claim 2 wherein the entire sequence of operations is preceded by the stretching of the original filamentary material in an H_2O environment at about 100° C. to about 150 percent of its original length.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,607,059 Dated September 21, 1971

Inventor(s) Joo, Louis A. and Snodgrass, Frank E.

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

Col. 2, Example 1 should read:

Example 1

Orlon(R) PAN staple yarn was stretched in boiling water to 210% of its original length. It was then passed through a conventional continuous oxidation unit on a pair of driven grooved rolls. After an effective residence time of one hour in air at 230°C., the yarn was fused and unfit for further processing.

(R) - Registered trademark

Col. 2, line 72 "$48.8=10^6$ " should read --48.8×10^6--.

Signed and sealed this 21st day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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