

Jan. 5, 1971

W. G. D. CARPENTER ET AL

3,552,923

PRODUCTION OF CARBON FIBERS

Filed June 26, 1967

2 Sheets-Sheet 1

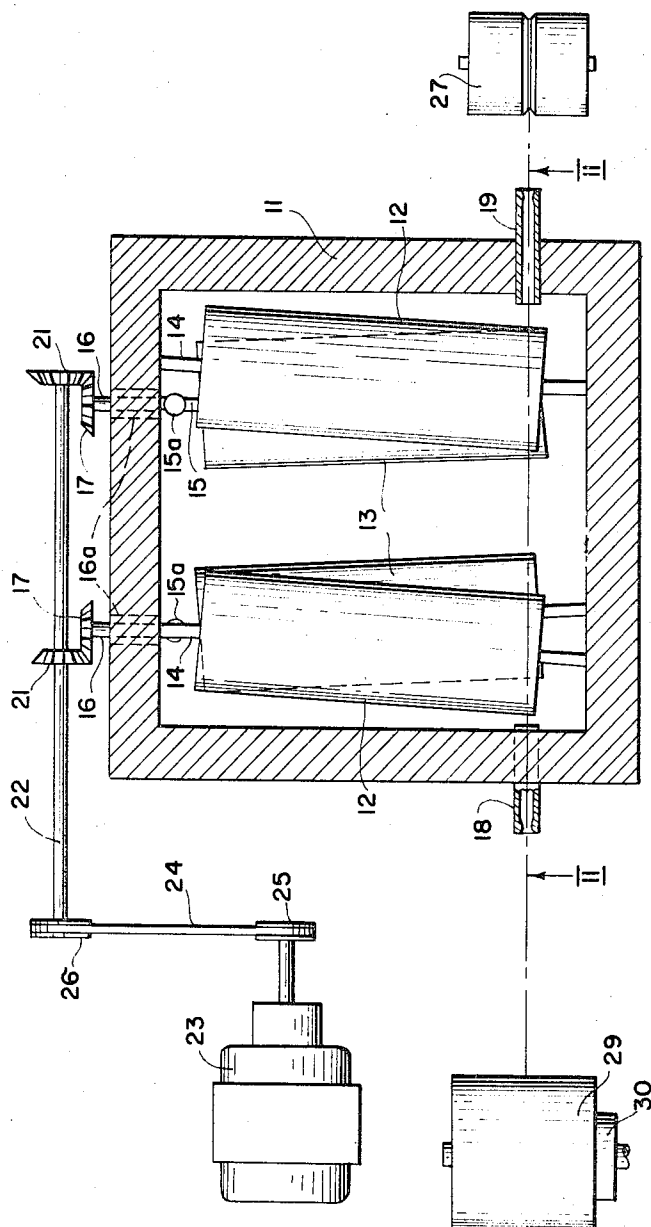


FIG. 1

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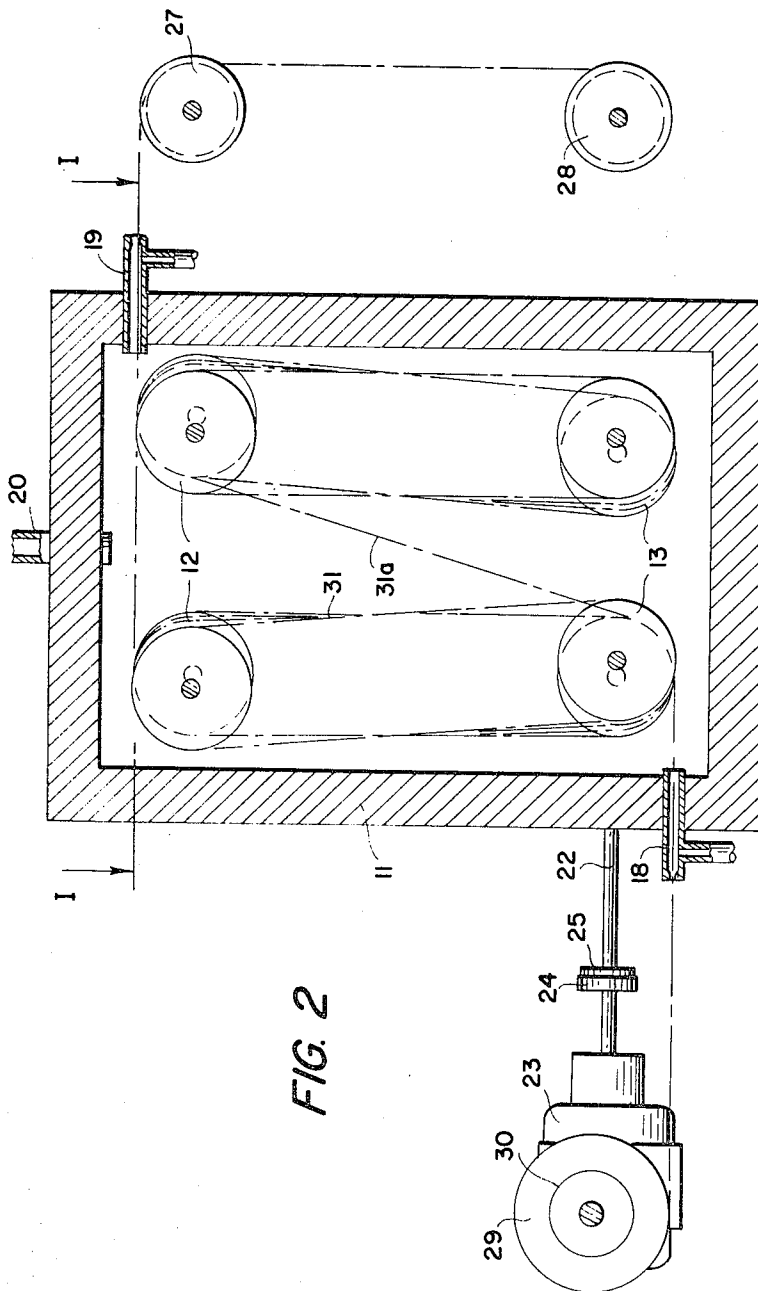


FIG. 2

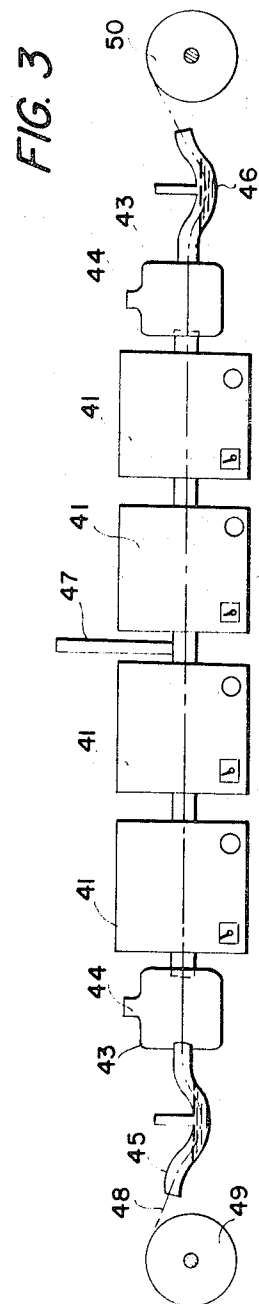


FIG. 3

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PRODUCTION OF CARBON FIBERS

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Filed June 26, 1967, Ser. No. 648,916

Claims priority, application Great Britain, June 28, 1966, 28,879/66

Int. Cl. C01b 31/07

U.S. Cl. 23—209.1

5 Claims

ABSTRACT OF THE DISCLOSURE

Apparatus and process for the production of continuous lengths of carbon fibers of high strength and high Young's modulus from fibers of organic polymer material. The apparatus comprises a supply spool for the polymer fiber, brake means for the supply spool, and oxidizing oven including means to support and drive the fiber through the oven at a pre-determined rate and to hold the fiber taut to control its length, take-up means for the take-up means, a carbonizing furnace for carbonizing the oxidized fiber, a supply spool for supplying oxidized fiber to the carbonizing furnace, and take-up means for collecting carbonized fiber from the carbonizing furnace. A process for the production of the carbon fiber comprises oxidizing the polymer fiber in the oxidizing atmosphere of an oven through which the fiber is passed, holding the fiber under tension throughout the oxidizing step such that the fibers do not shrink, continuing oxidation for a time such that substantially complete penetration of oxygen is achieved throughout the fiber, and carbonizing the oxidized fibers by passing the fibers from a supply spool through a furnace in which the fiber is carbonized in a non-oxidizing atmosphere, the fibers being permitted to shrink during the carbonization step.

This invention relates to a process and apparatus for the continuous production of carbon fibers having high Young's modulus.

United Kingdom Patent Nos. 1,110,791; 1,148,874; 1,166,251; and 1,166,252, disclose various processes for the conversion of fibers of an organic polymer such as polyacrylonitrile, polyamide, aromatic polyester, and polyvinyl alcohol into high strength and high Young's modulus carbon fibers and as a result of these processes carbon fibers having these desired characteristics have been produced.

The essential feature of said processes is that the fiber, at some stage of the process, is under tension opposing a tendency to shrink lengthwise; the tension may be sufficient to reduce or eliminate lengthwise shrinkage or to stretch the fiber.

In one particular and important process, fibers of an organic polymer from which carbon fibers can be produced are oxidized whilst held under tension and subsequently carbonized in a nonoxidizing atmosphere at a temperature of at least 1000° C. with or without tension; during oxidation the tension applied to the fibers is desirably at least sufficient to prevent lengthwise shrinkage of the fibers and the duration of the oxidation is preferably sufficient to permit complete permeation of oxygen throughout the structure of the fibers.

To enable the maximum advantage to be taken of the high strength and high Young's modulus characteristics of fiber produced in accordance with the disclosures of the above applications it is desirable that such fiber should

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be available in continuous lengths as understood in the textile context.

The object of the present invention is to provide a process and apparatus for the production of high strength and high Young's modulus carbon fiber in continuous lengths suitable for use in a filament winding machine from fibers of a type e.g. polyacrylonitrile, in which the linear molecules can be cross-linked, for example by oxidation by heating at below their melting point in an oxidizing atmosphere, or, if the polymer fiber is of a type having no melting point, heating in an oxidizing atmosphere at a temperature which allows oxidation to proceed in a controlled manner, and which upon subsequent carbonizing in a non-oxidizing atmosphere yield carbon fibers which are highly crystalline with the C axis of the graphite crystallites preferentially aligned normal to the fiber longitudinal axis.

In the general and preferred form of the processes of the applications referred to above there may be three steps:

- (1) Oxidation whilst the polymer fiber is under tension,
- (2) Carbonizing in a non-oxidizing atmosphere with or without tension applied to the fiber, and
- (3) Subsequent heat treatment in a non-oxidizing atmosphere to a temperature higher than the carbonizing temperature.

A process for the production of continuous lengths (as understood in the textile context) of carbon fibers having high strength and high Young's modulus from fiber of polymeric material of the type referred to above which may be in the form of a tow or yarn comprises, according to the present invention:

- (1) An oxidizing step in which a continuous length of fibers passing from an external supply into an oxidizing atmosphere in an oven where it is heated at a temperature within the range of 200–250° C. travels between supporting and driving means within the oven which support and drive the fibers, the fibers being held throughout the oxidizing step under tension sufficient to reduce or prevent their shrinkage or to elongate them and whereby each unit length of fiber remains in the oven for the required period, to achieve substantially complete penetration of oxygen throughout the material of the fiber, and,

- (2) a carbonizing step in which the oxidized fibers pass from a supply spool through a furnace or series of furnaces in which a non-oxidizing atmosphere is maintained and in which the temperature is raised to and held at a carbonizing temperature of about 1000° C. and is drawn on to a take-up spool outside the furnace, the fibers being permitted to shrink during the carbonization step.

It is preferred that the fiber is held under sufficient tension to restrict lengthwise shrinkage to not more than 10 percent or to stretch the fiber to not more than 20 percent of its original length prior to oxidizing.

Also, the invention may comprise a third step in which the fibers after oxidation and carbonizing treatment as disclosed above are heated in a non-oxidizing atmosphere at a temperature higher than the carbonizing temperature and in the range 1000°–3000° C.

The third step may be carried out with the carbonized fiber wound on a spool, for example the take up spool of the carbonizing step since the carbonized fiber does not shrink appreciably during the heat treatment. Alternatively the third step may be carried out continuously by passing the fiber through a graphite tube furnace.

The duration of the oxidizing step is a function of the type of fiber used, its diameter, the nature of the oxidizing atmosphere and the temperature in the oven. Thus for 1½ denier Courtelee a polyacrylonitrile fiber containing minor proportions of other constituents, which has a

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diameter of 12 microns the fiber is maintained at 220° C. for about 3 hours or more if the atmosphere is air and for 30–60 minutes if the atmosphere is commercial oxygen.

In a particular example according to the invention for the continuous oxidation of Courtele the fiber is fed under very accurately controlled tension to two large diameter, rotating rollers or drums placed one above the other with their axes slightly inclined to each other on the well known textile thread advancing principle.

Both drums are enclosed in a well insulated chamber which can be maintained at 220° C. and through which air preheated to 220° C. can be circulated.

The surfaces of any such supporting drums or rollers should be sufficiently smooth to avoid damage to the fiber and may advantageously be made of polished carbon or graphite.

The lower drum is rotatably driven from outside the chamber at a speed which ensures that each unit length of fiber remains in the heated chamber for 3½ hours after which it is spooled on a standard "take up" unit driven through a magnetic clutch which ensures the fiber being kept under sufficient tension to prevent slippage on the main drums.

Also, the fiber is fed from a supply spool which is braked, for example by means of a magnetic clutch, which controls the tension at the supply to the internal drums and prevents slippage of the fiber on the drums.

The process and apparatus for the carbonizing step are dictated by shrinkage of the fiber, its varying mechanical properties and the gas evolution by the polymer as the carbonizing step proceeds. In the case of 1½ denier Courtele which has been subjected to the oxidizing step the oxidized fiber is heated to 1000° C. to convert it substantially to carbon and there is about a 50 percent reduction in weight as volatile degradation products are given off as gas evolution takes place. The gas evolution mainly occurs at a steady rate within the temperature range of 300° C. to 750° C. Also, within the temperature range 350° C. to 500° C. the fiber undergoes major structural change and the mechanical properties of the degrading fiber are poor. During the carbonizing step a 10–12 percent longitudinal shrinkage of the fiber which has been fully oxidized in the oxidation step occurs.

To permit the required shrinkage to occur during the carbonizing step the rotation of a supply spool for the carbonizing step may be lightly controlled through a magnetic brake and the take up spool is driven at a speed which is governed by the total duration of the passage of any one portion of fiber through the furnace.

To take into account the gas evolution and degradation characteristics of the fiber during the carbonizing step the heating is controlled so that the temperature is raised to 1000° C. in as short a time as is compatible with obtaining the required high strength and high Young's modulus of the fiber.

One form of apparatus for the continuous production of high strength high Young's modulus carbon fibers according to the invention is illustrated by the accompanying diagrammatic drawings of which:

FIG. 1 is a sectional plan on the line I—I of FIG. 2, and

FIG. 2 is a sectional side elevation in the line II—II of FIG. 1 of a furnace arrangement for heating the fibers in an oxidizing atmosphere, and,

FIG. 3 is a general side view showing a furnace arrangement for carbonizing and further heat treating the fibers.

Referring first to FIGS. 1 and 2, the furnace comprises a typical well heat insulated hollow box structure 11. Two pairs of equal diameter upper and lower fiber advancing rollers 12, 12 and 13, 13, respectively are supported for rotation within the furnace 11. The upper rollers 12, 12 are parallel to each other and supported with their axes of rotation in a plane parallel to that con-

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taining the parallel axes of rotation of the lower rollers 13, 13. The latter are parallel to each other but are skewed with respect to the parallel axes of the upper rollers 12, 12 as shown. This arrangement is well known as a thread or fiber advancing technique in the textile art. The upper rollers 12, 12 are supported for rotation by shafts 14, 14 which engage bearings (not shown) in the side walls of the furnace 11. The lower rollers 13, 13 are similarly supported by shafts 15, 15 which at their one ends engage bearings (not shown) in the side wall of the furnace but at their other ends are connected through universal joints (not shown) to drive shafts 16, 16 which extend through gas sealed bearings 16a, 16a and bevel wheels 17, 17. Air inlets are provided at 18, 19 and a gas outlet at 20. The bevel wheels 17, 17 are of the same diameter and engage corresponding bevel wheels 21, 21 on a common drive shaft 22 which is driven by a motor 23 through a belt 24 and pulleys 25, 26. A guide pulley 27 is mounted adjacent the air inlet 19 externally of the furnace 11 and parallel to a take up roller 28. The take up roller 28 is driven through a magnetic clutch by a take up motor (not shown) as will later be described. A supply spool 29 is supported for rotation several feet from the inlet 18 and is controlled through a magnetic clutch 30.

In practice a length of fiber tow 31 in this case Courtele (registered trademark) a polyacrylonitrile fiber is wound onto the drums 12, 12 and 13, 13 by a conventional winding technique with the drums supported on a spacing frame (not shown) and the ends of the tow are tied so that there is minimum slack in the tow. The fiber tow is wound to pass onto the lower left hand drum 13, up and over the upper left hand drum 14 and down and under the lower left hand drum 13. It is then continuously looped around both left hand drums 13, 14 in a series of elongated loops each succeeding loop being spaced from the preceding loop. In practice there are thirty such loops before the tow reaches those ends of the left hand drums 13, 14 adjacent the bevel wheels 17, 17. The tow then passes from the lower left hand drum 13 to the upper right hand drum 14, as shown at 31a, and similar succeeding loops are passed over the right hand upper and lower drums 12 and 13 until the tow approaches those ends of the right hand drums 12 and 13 remote from the bevel wheels 17, 17. The frame carrying the loaded drums is then placed in the furnace and the necessary connections made to the bevel wheels 17, 17. The ends of the tow are now untied and the one end is fed through the air inlet 19, over the guide roller 27 and joined to the take up spool 28. The other end of the tow is fed through the air inlet 18. It is then secured to the free end of a length of fiber tow 31b which passes from the supply spool 29. The drive motor which drives the spool 28 and the motor 23 are now switched on and any slack which may have developed in the tow is taken up until the magnetic clutch 30 slips. The furnace is now closed and air is supplied through the inlets 18 and 19. The furnace is now brought up to a temperature of 220° C. The drums 12, 12, 13, 13 are all driven at the same speed by the motor 23 and as oxidation of the fibers takes place shrinkage of the fiber tow is prevented by the nature of its engagement over the drums 12, 12 and 13, 13. By the time the fiber tow is drawn through the air inlet 19 oxidation will be complete and there will be no tendency for further shrinkage of the fibers to occur. As a result the only power required of the take up motor driving the spool 28 is that required for winding on the tow and maintaining the fiber under tension. With this arrangement the desired tensioning of the fibers during oxidation is achieved by preventing the shrinkage which would otherwise occur.

FIG. 3 shows four separately controlled furnaces 41—41 through which extends a graphite lined aluminous porcelain tube 42. The two ends of the tube 42 lead into gas supply chambers 43, 43 having inlets 44, 44 for nitrogen gas. Mercury seals 45, 46 lead from the gas supply

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chambers 43, 43. A gas vent 47 leads from the center region of the tube 42. A tow of fiber 48, which has been oxidized under tension in the apparatus disclosed above with reference to FIGS. 1 and 2, is fed from a supply spool 49 (which may comprise the take up spool 31 used at FIG. 2) through the seal 45, the left hand gas chamber 43, the tube 42, right hand gas chamber 43, and seal 46 and onto a driven take up spool 50.

In operation nitrogen gas is supplied through the inlets 44 and the temperature gradient in the tube 42 is controlled by the settings of the furnaces 41—41 and is raised to a carbonizing temperature of about 1000° C. as near to the inlet end of the tube as is practicable commensurate with obtaining the required high strength and high Young's modulus fibers. As many furnaces and as long a length of furnace tube are preferable since this increases the rate at which carbon fibers can be produced. To permit shrinkage of the oxidized fiber to take place during the carbonizing step the supply spool 49 is allowed to rotate freely or is lightly controlled through a magnetic brake to allow stretching and the take up spool 50 is driven at a speed which is governed by the total duration of the passage of any one portion of fiber through the furnace.

Further heat treatment of the carbonized fibers may be completed within the furnace arrangement shown by raising the temperature towards the outlet end of the tube 42 to above the carbonizing temperature in some cases up to 1500° C. Further heat treatment up to 3000° C. may be carried out by the addition of one or more graphite tube furnaces.

In a practical process a tow of 1½ denier fibers of Courtele (registered trademark) was drawn through an oxidizing oven as described with reference to FIGS. 1 and 2. The fiber tow was prevented from shrinking and oxidized in air at a temperature of 220° C.

The oxidized fiber tow was then drawn into the carbonizing and further heat treatment furnace arrangement shown at FIG. 3. The tow was first carbonized by passing it through the temperature gradient in the furnaces from about 300° C. to 1000° C. in 45 minutes in an atmosphere of white spot (oxygen free) nitrogen and then passing it through a temperature gradient of 1000° C. to 1480° C. in additional furnaces over a period of 25 minutes.

Three separate tows of similar polyacrylonitrile fibers were treated in this manner and the results obtained were as follows:

Mean ultimate tensile strength 320,000 lb. per sq. in.
Mean Young's modulus parallel to the fiber longitudinal axes 30.6×10^6 lb. per sq. in.

The fiber advancing rollers 12, 12 and 13, 13 may be made of or surfaced with carbon or graphite and it is also advantageous to line the interior walls of the carbonizing furnace tube with carbon or graphite.

It is to be noted that the term polyacrylonitrile fibers is

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used by those skilled in this art to include copolymers or terpolymers of acrylonitrile with other monomers e.g. methyl methacrylate or vinyl acetate, either alone or to which have been added polymers compatible with them for example phenolic resins or Friedel-Crafts condensates. It is in this sense that the term polyacrylonitrile fibers is used throughout the specification.

We claim:

1. A process for the production of continuous lengths of carbon fibers of high strength and high Young's modulus from carbonizable polymeric organic fibers comprising: continuously introducing a continuous length of carbonizable polymeric organic fiber from an external supply under tension into an oven containing an oxidizing atmosphere maintained at a temperature of from 200 to 250° C.; winding the fiber around at least one pair of fiber advancing members located in said oven a plurality of times to form a plurality of loops in engagement with said fiber advancing members, tension developed in said loops as the fiber attempts to shrink causing said loops to grip said members whereby shrinkage of the fiber is restrained; moving said fiber advancing members to advance the fiber through the oven; continuously removing the fiber from the oven at a rate such that each unit length of fiber is held in said oven for a time sufficient to achieve at least substantially complete penetration of oxygen throughout the body of the fiber to oxidize the fiber while the fiber is held under tension in the oxidizing atmosphere; and carbonizing the oxidized fiber by continuously passing the oxidized fiber through a carbonizing furnace in which a non-oxidizing atmosphere is maintained at a temperature sufficient to carbonize the oxidized fiber, the fibers being permitted to shrink during carbonizing.

2. A process according to claim 1 wherein the fiber is elongated during its passage through said oven to not more than 20% of its length prior to oxidizing.

3. A process according to claim 1 wherein shrinkage of the fiber passing through said oven is restricted to not more than 10% of its length prior to oxidizing.

4. A process according to claim 1 wherein the carbonized fibers are heated in a non-oxidizing atmosphere at a temperature above the carbonizing temperature and within the range 1000–3000° C.

5. A process according to claim 1 wherein the fiber comprises polyacrylonitrile.

References Cited

UNITED STATES PATENTS

3,011,981	12/1961	Soltes	23—209.1X
3,313,597	4/1967	Cranch et al.	23—209.1X
3,399,252	8/1968	Hough et al.	23—209.3
3,412,062	11/1968	Johnson et al.	23—209.1X

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U.S. Cl. X.R.

23—209.4