Process for producing carbon fibers.

Priority: 17.09.81 US 303185

Date of publication of application: 30.03.83 Bulletin 83/13

Publication of the grant of the patent: 04.06.86 Bulletin 86/23

Designated Contracting States: DE FR GB

References cited:
FR-A-2 450 294
US-A-3 705 236

Proprietor: UNION CARBIDE CORPORATION
39 Old Ridgebury Road
Danbury Connecticut 06817 (US)

Inventor: Schulz, David Arthur
20935 Mastick Road
Fairview Park Ohio 44126 (US)
Inventor: Brookstein, David Stuart
83 Booth Street
Needham Heights Massachusetts (US)

Representative: McCall, John Douglas et al
W.P. THOMPSON & CO. Coopers Building
Church Street
Liverpool L1 3AB (GB)

The file contains technical information submitted after the application was filed and not included in this specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).
Description

The invention relates to a process for producing carbon fibers and in particular to a process for cleaning the fibers.

Generally, the conventional process for producing a polyacrylonitrile (PAN) or pitch derived carbon fiber comprises the steps of spinning a fiber from PAN or mesophase pitch, infusibilizing the spun fiber by heating it in air, and carbonizing the infusible fiber by heating it in an inert gaseous environment. It is common practice to refer to the infusibilizing step as a "thermosetting step" and the infusible fiber is referred to as a "thermoset fiber".

Generally, high quality commercial carbon fibers are made from PAN and mesophase pitch. In commercial practice, several thousand fibers are spun and combined into a bundle referred to as "yarn". The pitch yarn comprises a plurality of pitch fibers whereas PAN yarn comprises a plurality of PAN fibers. The subsequent operations are carried out on the yarn to produce a carbon yarn comprising a plurality of carbon fibers. A mesophase pitch yarn typically can have 2,000 fibers. Each fiber typically has a diameter of about 14 μm or less.

It has been found that during the commercial production of mesophase pitch derived carbon yarn hot spots developed within a pitch yarn during the thermosetting step and as a result individual fibers melted or softened before they became thermoset. These fibers tended to adhere to other fibers and the yarn became stiff and brittle. The mechanical properties of the carbon yarn produced under such circumstances are relatively poor.

The U.S. Patents No. 4,275,061 and No. 4,276,278 relate to methods for overcoming these problems which can arise during the thermosetting operating. Generally, these methods feature depositing graphite or carbon black particles on the surfaces of the pitch fibers prior to the thermosetting step.

The presence of carbon black particles during the thermosetting step improved the quality of the carbon yarn obtained but resulted in a new problem. Many commercial uses of carbon yarn take the form of composites. The presence of the particles on the carbon fibers of the carbon yarn resulted in poor end products for certain composites.

The search for a process for removing the particles from the fibers started with a review of the prior art and an evaluation of conventional methods.

The prior art method of cleaning objects with ultrasonic vibrations was found to be satisfactory for cleaning and removing particles from the fibers but presented serious drawbacks. Conventional ultrasonic cleaning is carried out by having an ultrasonic source of mechanical energy in a liquid medium containing the object to be cleaned. The liquid medium communicates the ultrasonic vibrations from the ultrasonic source to the object. The art teaches that the ultrasonic cleaning is accomplished by the phenomena called "cavitation" and a liquid medium is required to produce cavitation.

One problem with the prior art ultrasonic cleaning as applied to cleaning yarn is that the yarn must be dried after being cleaned. It would be undesirable to ship wet yarn and it is particularly important to have dry yarn if the yarn is to be carbonized or heat treated additionally. The drying step requires an oven, energy to operate the oven, additional monitoring, and floor space in the manufacturing area. Another problem with the prior art ultrasonic cleaning as applied to cleaning yarn is that at production line speeds suitable for commercial operations, the fibers in the yarn become damaged or broken so a poor quality carbon yarn is produced.

US—A—3705236 describes a method of making carbon fibers having tensile strength improved by the application of vibrational energy during one or more heat treatment stages of the fiber production. However, the vibrational energy is disclosed only for improving the degree of orientation of the molecules and hence, the tensile strength of the fiber, and it is only disclosed as occurring during the heat treatment steps so that the amplitude of the energy vibrations applied must be lower than that which will effect breakage or damage of the fibers whilst at the elevated temperatures of the heat treatment stages. There is no suggestion in US—A—3705236 of applying vibrations of an amplitude to effect cleaning of the fibers.

After studying this problem, it was realized that the fibers uniquely lend themselves to a simple solution for cleaning the yarn.

Instead of using a liquid medium, an ultrasonic source was applied directly to the dry yarn. Surprisingly, the fibers became substantially clean and were not appreciably damaged by the heat produced.

For mesophase pitch derived fibers, the cleaning step can be carried out subsequent to the fibers being thermoset. In commercial practice, the thermoset fibers are usually subjected to a coating step and the coating or "finish" can interfere with the effectiveness of the cleaning step according to the invention.

It happens that the commercial practice for carbonizing the mesophase pitch derived thermoset yarn is advantageously carried out in two stages. The thermoset yarn is subjected to a first heat treatment at a temperature of about 1300°C in an inert atmosphere by the yarn being pulled through a heat chamber. The first heat treatment substantially removes the finish and is sometimes called in the art "precarbonization", even though it is a carbonization step. The yarn, after the first heat treatment, is much stronger and can be handled with considerably less care. Subsequently, the yarn is subjected to a second heat treatment at a temperature of from about 1500°C to about 3000°C in an inert atmosphere to produce the final product, carbon yarn.
Neither of the heat treatments remove the carbon black particles which were deposited on the fibers to improve the thermosetting step. It is preferable to use the instant cleaning step between the first and second heat treatments because the yarn is free of the finish, and because the yarn has good mechanical properties so higher speeds and more intense cleaning can be carried out.

The excellent results obtained for the mesophase derived yarn suggested the larger scope of the invention. The same cleaning operation can be used for PAN derived yarns because these yarns have performance comparable to the mesophase pitch derived yarn.

Although ultrasonic vibrations have been found to be highly effective, generally the instant invention is the use of high frequency mechanical vibrations applied directly to a substantially dry yarn or fiber.

The fiber can be mesophase pitch derived or PAN derived and preferably the mechanical vibrations are in the ultrasonic frequency range.

Of course, a yarn comprising a plurality of fibers having diameters of about 14 µm, typically about 2,000 fibers, can be used instead of a single fiber. Preferably, the cleaning step can be carried out subsequent to the first heat treatment.

Preferably, the yarn after a first heat treatment, is cleaned according to the invention immediately prior to the yarn entering into a chamber for carrying out the second heat treatment. The yarn is extended generally along a linear path and presses against the horn of an ultrasonic source with an effective force of from about 0.098 to about 0.245 Newtons. Preferably, the ultrasonic source produces mechanical vibrations having an ultrasonic frequency of about 20,000 Hertz.

The range of suitable amplitudes and frequencies of the mechanical vibrations for cleaning according to the invention can be determined easily experimentally for the particular yarn being used. Some of the factors to be considered for yarns are the degree of cleaning which is acceptable, the speed at which the yarn is to be moved, the amount of yarn damage which can be tolerated, and the economics of the cleaning operation.

Further advantages of the invention will be set forth, in part, in the following specification and, in part, will be obvious therefrom, without being specifically referred to, the same being realized and attained as pointed out in the claims hereof.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description, taken in conjunction with the accompanying drawings, in which:

The sole Figure shows a diagrammatic side view of components carrying out the instant invention. The best mode for carrying out the instant invention is shown in the Figure. A mesophase pitch derived yarn 1 which has been thermoset exits a precarbonizing unit 2 which is operating at a maximum temperature of about 1300°C. The yarn 1 has 2,000 fibers and each fiber has a diameter of about 10 µm.

Ultrasonic sources 3, 4 and 6 produce mechanical vibrations and clean the yarn 1 in accordance with the invention. The yarn 1 moves at a rate of about 20 meters per minute and has a tension of about 5.39 Newtons.

Each of the ultrasonic sources 3, 4 and 6 has a frequency of about 20,000 Hertz and is a commercially available model. Each of the horns, 7, 8 and 9 is the active output element of the respective ultrasonic sources 3, 4 and 6 and each horn has a surface about 1.3 centimeters long in contact with the yarn so that the residence time for the yarn 1 on each horn is about 0.04 second. For each of the horns 7, 8 and 9, the yarn 1 is pressed with a force of from about 0.098 to about 0.245 Newtons.

There are two important matters as to the instant invention. One is the degree of cleaning and the other is the degree of adverse influence on mechanical properties.

The yarns cleaned by the invention showed significant improvements in the absence of particles as compared to yarns not cleaned. In addition, a carbon yarn which had been cleaned according to the invention possessed tensile strength and Young's modulus comparable to those of a carbon yarn which had not been cleaned at all. This is important because it shows that the invention does not degrade these two important mechanical properties.

In a typical case, a carbon yarn made according to the invention as described for the Figure, had fibers having an average tensile strength of 2.23 GPa and an average Young's modulus of 632 GPa whereas the carbon yarn which had not been cleaned at all had corresponding average values of 2.24 GPa and 600 GPa.

A higher degree of cleaning of the yarn can be obtained for predetermined output levels of the horns by decreasing the number of ultrasonic sources and/or increasing the pressure of the yarn against the horn. Commercially available ultrasonic sources usually have preset output levels. The cleaning step was carried out in a separate experiment using a pressing force of about 0.49 Newtons for each of the three horns instead of from about 0.098 to about 0.245 Newtons. The fibers of the carbon yarn produced had a tensile strength of about 2.25 GPa and a Young's modulus of about 612 GPa. These results also compared favourably with those obtained for uncleaned yarn and show that considerable latitude exists for selecting the pressure.

It is interesting that the particles being mechanically removed from the yarn during the cleaning step according to the invention appear in the form of visible clouds in the regions of the respective horns. Removal of the particles from the cleaning region can be accomplished with a suction device or the like. The largest cloud was present at the first horn, horn 7.
When the ultrasonic sources 3, 4 and 6 were turned off, the clouds were no longer formed and the yarn developed fraying damage which seriously degraded the yarn. Actually, such fraying would be expected; however, it is surprising that when the ultrasonic sources 3, 4 and 6 are operating, the fraying does not occur.

We wish it to be understood that we do not desire to be limited to the exact details of construction shown and described, for obvious modifications will occur to a person skilled in the art.

Claims

1. A process for producing at least one carbon fiber, comprising spinning at least one fiber, thermosetting the fiber, and carbonizing the fiber by means of either one or two heat treatment steps characterized by cleaning the fiber, by subjecting the dry fiber to high frequency mechanical vibrations of an amplitude and frequency to remove particles from the surface of the fiber, subsequent to the thermosetting step, no high frequency mechanical vibrations being applied to the fiber during the or either carbonization heat treatment step.

2. A process as claimed in claim 1, characterized in that said fiber is either polyacrylonitrile derived or pitch derived.

3. A process as claimed in claim 1, characterized in that said fiber is mesophase pitch derived.

4. A process as claimed in any one of the preceding claims, characterized in that a plurality of fibers are spun and combined to form a yarn.

5. A process as claimed in any one of the preceding claims, characterized in that at least one ultrasonic source is used to produce the high frequency mechanical vibrations.

6. A process as claimed in claim 5, characterized in that said ultrasonic source has a frequency of about 20,000 Hertz.

7. A process as claimed in any one of the preceding claims, characterized in that a plurality of fibers are spun and combined to form a yarn, and at least one ultrasonic source is used to produce the high frequency mechanical vibrations.

8. A process as claimed in claim 7, characterized in that said yarn is carbonized by a first heat treatment to about 1300°C and subsequently by a second heat treatment to a temperature in the range of from about 1500°C to about 3000°C and said cleaning step is carried out between said first and second heat treatments.

9. A process as claimed in any one of claims 1 to 6, characterized in that a plurality of fibers are spun and combined to form a yarn and further comprising the step of coating a portion of the surfaces of said fibers with graphite or carbon black particles prior to said thermosetting step.

Patentansprüche

1. Verfahren zur Herstellung von wenigstens einer Kohlenstofffaser, das umfaßt:


2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Faser von Polyacrylnitril oder Pech abgeleitet ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Faser von Mesophasenpech abgeleitet ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß eine Mehrzahl von Fasern gesponnen und zu einem Garn kombiniert ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß zumindest eine Ultraschalquelle zur Erzeugung der mechanischen Hochfrequenzschwingungen verwendet wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Ultraschalquelle eine Frequenz von etwa 20.000 Hertz besitzt.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß eine Mehrzahl von Fasern gesponnen und zu einem Garn kombiniert ist und mindestens eine Ultraschalquelle zur Erzeugung der mechanischen Hochfrequenzschwingungen verwendet wird.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Garn durch eine erste Wärmebehandlung auf etwa 1300°C und eine anschließende zweite Wärmebehandlung auf eine Temperatur im Bereich zwischen 1500 und 3000°C carbonisier wird und daß der Reinigungsschritt zwischen der ersten und der zweiten Wärmebehandlung erfolgt.


Revendications

1. Procédé de production d’au moins une fibre de carbone, consistant à filer au moins une fibre, à thermodurcir la fibre et à carboniser la fibre au moyen d’une ou de deux étapes de traitement thermique, caractérisé en ce qu’il consiste à nettoyer la fibre en soumettant la fibre sèche à des vibrations mécaniques à haute fréquence, d’une amplitude et d’une fréquence éliminant des particules de la surface de la fibre, après l’étape de thermodurcissement, aucune vibration mécanique à haute fréquence n’étant appliquée à la
fibre pendant la ou chacune des étapes de traitement thermique de carbonisation.

2. Procédé selon la revendication 1, caractérisé en ce que ladite fibre dérive de polyacrylonitrile ou dérive d’un brai.

3. Procédé selon la revendication 1, caractérisé en ce que ladite fibre dérive d’un brai en mésophase.

4. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que plusieurs fibres sont filées et combinées pour former un fil.

5. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce qu’au moins une source d’ultrasons est utilisée pour produire les vibrations mécaniques à haute fréquence.

6. Procédé selon la revendication 5, caractérisé en ce que ladite source d’ultrasons possède une fréquence d’environ 20 000 hertz.

7. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que plusieurs fibres sont filées et combinées pour former un fil, et au moins une source d’ultrasons est utilisée pour produire les vibrations mécaniques à haute fréquence.

8. Procédé selon la revendication 7, caractérisé en ce que ledit fil est carbonisé par un premier traitement thermique à environ 1300°C et ensuite par un second traitement thermique à une température dans la plage d’environ 1500°C à environ 3000°C, et ladite étape de nettoyage est effectuée entre lesdits premier et second traitements thermiques.

9. Procédé selon l’une quelconque des revendications 1 à 6, caractérisé en ce que plusieurs fibres sont filées et combinées pour former un fil et en ce qu’il comprend en outre l’étape consister à enduire une partie des surfaces desdites fibres avec des particules de graphite ou de noir de carbone avant ladite étape de thermodurcisement.