United States Patent Office 3,508,874
Patented Apr. 28, 1970

3,508,874

PRODUCTION OF CARBON YARNS

Richard N. Rulison, Drummondville, Quebec, Canada, assignor to Celanese Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Jan. 12, 1968, Ser. No. 700,672
Int. Cl. C01b 31/07
U.S. Cl. 23—209.1 11 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for the production of carbon and graphite yarns wherein an acrylic yarn is passed through a liquid medium containing a dispersion of particulate carbon and then continuously dried before preoxidation and pyrolysis.

The search for industrial high performance materials is turning increasingly toward reinforced composites. Theoretically, highly carbonaceous fibers such as carbon (amorphous) and graphite fibers have among the best properties for high strength reinforcement. Among these desirable properties are high corrosion and temperature resistance, low density, high tensile strength and most importantly, high modulus. Uses for such high modulus fibers include filament windings for aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles.

Production of fibrous carbon by pyrolysis of hydrocarbon gases or by discharge between carbon electrodes has been reported. These methods, however, are obviously not suitable for large-scale production of a uniform yarn. Pyrolysis and graphitization of organic fibrous precursors appears to be the only practical industrial route to such carbonaceous fibers. Acrylic yarns have attracted particular interest as such precursors.

The general approach to the production of such carbonaceous yarns acrylic yarns comprises the sequence of preoxidizing the yarn at moderate temperatures to stabilize it against physical damage under the subsequent higher temperature treatments and then pyrolyzing the preoxidized yarn up to a temperature of about 1000–1200° C. See, for example, U.S. Patent 3,285,696; French Patent 1,430,803 and Belgian Patent 678,679. If graphitized yarns are desired, the pyrolyzed yarn is then treated at about 2000–3000° C.

Three factors, however, render the preoxidized yarn highly susceptible to damage during subsequent processing. In the first place, the preoxidation itself causes a marked loss of tensile strength in the yarn. the second factor arises from the economic consideration that this step be performed while the yarn is wound on a package or similar large batch in view of the time required for the preoxidation. Removal from this package for further processing is rendered difficult by the tendency of the filaments between each layer to stick together. Thirdly, during subsequent processing, the yarn is subjected to severe stress which results in a high incidence of flaws and breakage.

It is an object of this invention to provide carbon and graphite yarns having good tensile properties. It is a more specific object to enable the yarn to withstand high tension both during winding and processing to avoid breakage. It is still a further object to produce carbonaceous yarns having fewer flaws. Additionally this method should achieve the foregoing objects without significantly diminishing adhesion to conventional matrix materials employed in forming composites.

These objects have now been realized by the process of this invention which broadly comprises the steps of

(1) passing the acrylic yarn through a liquid medium containing a dispersion of finely divided carbon so as to coat the individual filaments with a total particulate carbon uptake of 0.5 to 20% by weight based on the weight of the yarn;

(2) continuously drying the yarn;

(3) preoxidizing the yarn at a temperature of between 200 and 400° C. for a time sufficient to attain a level of combined oxygen of between 4 and 17% by weight;

(4) pyrolzing said preoxidized yarn up to a temperature of at least 900° C.

I have surprisingly found that in addition to the increased ease of processsing and the higher flexibility of the yarns, the resultant pyrolyzed yarn has a higher average tensile strength. Although I do not wish to be limited by my theory of this improvement, it appears that my treatment results in both prevention of flaws and healing of those flaws which do develop.

It has been suggested in U.S. Patent No. 3,285,696 to pack pyrolzed acrylic yarns in graphite or carbon black for the purpose of providing an inert atmosphere during graphitization. This, technique, even if applied before or during pyrolysis, does not result in coating the individual filaments nor in any significant uptake of the particulate carbon and the above-mentioned advantages of my process are not realized. It has also been previously suggested to coat fibers or textiles with finely divided refractory metals and their compounds. While this method results in some increased flexibility, the refractory metal oxide-coated yarn produced thereby cannot readily be employed to form composites. In other words, the metal oxide coating does not adhere well to conventional matrix materials.

While the improved method of this invention is applicable to the preoxidation of all acrylic yarns, various degrees of beneficiation are realized since not all yarns have the same tendency to stickiness during the various thermal treatments. This method can however be advantageously employed to improve product quality and processability even with those acrylic precursors which have comparatively less tendency to stickiness, e.g. acrylonitrile homopolymer.

The acrylic precursor yarns suitable for use in the process of this invention can be formed in known manner from the polymerization product of from 90 to 100% by weight acrylonitrile and from 0 to 10% by weight of monomers copolymerizable therewith. Thus, either acrylonitrile homopolymer or copolymer can be employed. A multitude of such acrylic copolymers and their preparation are known to the art. For the purposes of this invention, a preferred copolymer is that formed from 93–94% acrylonitrile and 6–7% methyl acrylate. These acrylic homo- and copolymers can be formed into continuous filament yarn by various spinning procedures well known in the art.

Preferably the acrylic yarn is highly molecularly oriented by drawing under suitable conditions. Such methods of orientation are disclosed, for example, in U.S. Patents Nos. 2,455,173; 2,948,581; and 3,122,412. Molecular orientation is a very difficult property to quantify of measure. Tenacity, an easily measurable property, is considered a related, thougth not exact measure, of molecular orientation. For the purposes of this specification it will be so measured. In a preferred embodiment, the tenacity of the precursor acrylic yarns of this invention should be at least 3 grams per denier, and preferebly, at least 4 grams per denier.

Any form of particulate carbon can be used in the process of this invention. The two most preferred forms are powdered graphite and carbon black.

The nature of the dispersing medium is not critical. For example water, lower alcohols, mineral spirits, and other low molecular weight liquid hydrocarbons can readily be employed. The preferred dispersing medium is isopropanol.

The particulate carbon should be present in an amount from 2% to 8% by weight based on the total weight of the dispersion. The optimum amount depends on, inter alia, the nature of the dispersing medium. In water, the preferred weight is 4% particulate carbon. Other factors influencing the optimum content of particulate carbon are the specific acrylic precursor, the processing speed, and the nature of the subsequent processing conditions. In addition to the amount of particulate carbon on the yarn, the distribution is equally important in insuring the production of uniform yarn.

Continuous drying, as compared to batch drying, of the dispersion-treated acrylic yarn increases the amount of residual particulate carbon on the yarn during and after preoxidation. Moreover, it promotes more uniform distribution of the particulate carbon. This continuous drying treatment can be performed in numerous ways, most conveniently by passing over a steam-heated roll or through a heated tube. The residence time should be about 5 seconds to 1 minute, depending on total yarn denier, the liquid used and the temperature.

Numerous preoxidation procedures are disclosed in the art. In a preferred mode of operation according to the process of this invention, the yarn is wound around a core constructed of a material that will not be destroyed or compressed by the heat exposure or by the stress developed by the highly oriented yarn upon heating. An aluminum core has been especially well suited for this purpose. Other suitable core materials include carbon, graphite, stainless steel, ceramics and the like. When employing an acrylic precursor, the preoxidation should preferably be in air at a temperature of between 240–300° C. for a time sufficient to attain a level of combined oxygen between 4–17% by weight and preferably 6 to 17% by weight.

The pyrolysis can be conducted in any of several known methods. See for example U.S. Patent 3,285,696, Belgian Patent 678,679 and French Patent 1,430,803.

If graphite fibers are desired, the pyrolyzed fibers of my invention can be graphitized in several ways. They can be passed through a graphite tube furnace at 2000–3000° C. which can conveniently be arranged in series with the pyrolysis tube. Other methods include resistance graphitization as described in U.S. Patent 3,313,597, or flame graphitization according to the method of copending application S.N. 614,811 filed Feb. 9, 1967, now abandoned.

Example I illustrates a preferred embodiment of this invention. Example II illustrates the importance of the graphite treatment of this invention. Example III illustrates the criticality of the yarn being impregnated with an aqueous colloidal dispersion of graphite as opposed to dry powdered graphite. Example IV illustrates the criticality of first drying the graphite-impregnated yarn before preoxidation.

EXAMPLE I

A 100 meter length of a 750 filament yarn of a copolymer of acrylonitrile and methyl acrylate in the proportions of approximately 93/7 respectively, is employed as the precursor yarn. This yarn is passed continuously under about 10 grams tension through an aqueous colloidal dispersion of graphite (4% by weight) for an immersion time of about 0.1 second. Excess dispersion is wiped off by passing the saturated yarn upwardly through a series of five ceramic pins. Thereafter, the wet impregnated yarn is continuously passed to a drying roll heated to within the range of 105–110° C. The dried yarn is then wound on to a 3 inch diameter aluminum tube under 150 grams tension and the tube is placed in a heated

air oven for the preoxidation treatment. The preoxidation schedule consists of 16 hours at 200° C., 1 hour rise to 270° C. and two hours at 270° C. The tube of yarn is then removed from the oven and allowed to cool.

The stabilized yarn is then pyrolyzed by passing it continuously through a resistance-heated metal tube which is ½ inch in diamter and is 48 inches long. The yarn enters and leaves the tube chamber through 1 mm. diameter orifices to keep out air and the tube is flushed constantly in the top end by the flow of 300 cc./min. of argon. Tension on the yarn is maintained at 100 grams. The tube wall temperature is about 600° C. over the upper 12 inch of length and about 1200° C. over the lower 36 inches. The resulting pyrolyzed yarn is graphitized in nitrogen by passing it continuously under 100 grams tension through a graphite tube heated to 3000° C. for an exposure time of ½ minute.

At all stages following the treatment with the aqueous colloidal dispersion of graphite, the yarns are flexible and non-sticky. This is reflected in trouble-free winding and unwinding and handling over rolls without yarn breakage. Moreover the treated yarn could sustain very high tensions in processing, as high as 700 grams during the above pyrolysis treatment and 500 grams during the above graphitization treatment, indicating low mechanical sensitivity to processing.

The following table indicates single filament denier and tensile properties of the yarn at the several stages of the process.

TABLE I

Yarn stage	Filament denier	Tenacity (g./d.)	Initial modulus (g./d.)
Precursor	1.6	4.8	6
Preoxidized	1.6	1.3	65
Pyrolyzed	0.8	8.6	1,140
Graphitized	0.7	9.2	2,670

EXAMPLE II

The process of Example I is repeated except that the graphite treatment is omitted. Following the preoxidation step, no more than a few inches of the yarn could be unwound from the spool without severe damage due to sticking between yarn wraps.

EXAMPLE III

The process of Example I is repeated except that a very fine commercial graphite powder in a dry form is substituted for the aqueous colloidal graphite dispersion in the precursor yarn dip. The dry impregnation of powdered graphite resulted in only about 0.5% pick-up of graphite on the yarn. Following the preoxidation step, it was difficult to unwind the preoxidized yarn from the spool without damage due to sticking between yarn wraps. Following the pyrolyzed step, the yarn was quite stiff and could not be subjected successfully to the graphitization step due to frequent breakage of the yarn under the standard tension of 100 grams. The filament of the pyrolyzed yarn cannot be separated from the yarn bundle for testing due to excess sticking between filaments,

EXAMPLE IV

An acrylonitrile homopolymer yarn is passed through a solution containing 4% by weight graphite dispersed in water. One portion of this yarn is directly wound on a core, over-dried and preoxidized. The resulting yarn has an average residual graphite content of 3% and this graphite is poorly distributed. A second portion of the yarn passed through this solution is first dried on a steam-heated roll. It is then wound on the same core and subjected to the same preoxidation conditions. The resultant yarn has a residual graphite content of 7% by weight and this graphite is well distributed. Processing of the latter yarn proceeds much better than that of the former yarn.

Numerous variations of the above-described process

will be apparent to one skilled in the art within the spirit of the present invention.

What is claimed is:

1. In the process for converting acrylic yarns to carbonaceous yarn by means of the preoxidation and pyrolysis of said yarn, the improvement which comprises passing said acrylic yarn prior to preoxidation through a liquid medium containing a dispersion of finely divided carbon so as to coat the individual filaments with a total particulate carbon uptake of about 0.5–20% by weight based on the weight of the yarn, and then continuously drying said yarn.

2. A process according to claim 1 wherein said preoxidation is effected while the yarn is wound on a core which is stable to high temperature and stress.

3. A process according to claim 1 wherein said acrylic yarn is formed from the polymerization product of from 90 to 100% by weight acrylonitrile and from 0 to 10% by weight of a monomer copolymerizable therewith.

4. A process according to claim 1 wherein said acrylic yarn is formed from the polymerization product of 93–94% acrylonitrile and 6–7% methyl acrylate.

5. A process according to claim 1 wherein the particulate carbon is powdered graphite.

6. A process according to claim 1 wherein the particulate carbon is carbon black.

7. A process according to claim 1 wherein said liquid medium is an aqueous medium.

8. A process according to claim 1 wherein said liquid medium is isopropanol.

9. A process according to claim 1 wherein said particulate carbon is present in the liquid medium in an amount of from 2 to 8% by weight based on the total weight of the dispersion.

10. A process according to claim 1 wherein said acrylic yarn has a tenacity of at least 3 grams per denier.

11. A process according to claim 1 wherein said pyrolysis is effected in a continous manner with the yarn under high tension.

References Cited

UNITED STATES PATENTS

2,799,915	7/1957	Barnett et al.	
3,235,323	2/1966	Peters.	
3,242,000	3/1966	Lynch.	
3,281,261	10/1966	Lynch	23—209.1 X
3,285,696	11/1966	Tsunoda	23—209.1
3,305,315	2/1967	Bacon et al.	23—209.1

EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

23—209.4

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,508,874 Dated April 28, 1970

Inventor(s) Richard N. Rubinson

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

In column 4, Table I, under the column entitled "Initial modulus", "6" in the first line should read --66--.

Signed and sealed this 28th day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents