

1

2

3,671,192 METHOD OF STABILIZING ACRYLIC POLYMER FIBERS PRIOR TO GRAPHITIZATION

Herbert M. Ezekiel, Dayton, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force

No Drawing. Filed May 28, 1968, Ser. No. 732,514

The portion of the term of the patent subsequent to Jan. 18, 1972, has been disclaimed

Int. Cl. C01b 31/07

U.S. Cl. 23-209.1

9 Claims

ABSTRACT OF THE DISCLOSURE

A method of stabilizing acrylonitrile polymer fibers prior to carbonization or direct graphitization is described. The method comprises the step of heating the fibers at 265-290° C., preferably at 275° C., in an oxidizing atmosphere for, for example, about 3-7 hours, in a manner such as to dissipate the heat of reaction and allow controlled oxidation. The stabilization step when followed by graphitization of a polymer fiber or yarn at a temperature within the range of 1800-3200° C. leads to a graphite fiber of high tensile strength, high modulus of elasticity, and a fiber of improved graphitic character.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without payment to me of any royalty thereon.

BACKGROUND OF THE INVENTION

The present invention deals with the stabilization of acrylonitrile polymer fibers and more particularly acrylonitrile polymer yarns. The invention is particularly concerned with such stabilization as a step prior to the subsequent graphitization of the fibers or yarns.

There has been an increasing demand for materials of construction of high strength to weight ratio and high modulus to weight ratio for use in aerospace vehicles and devices; particularly for materials which, additionally, have good thermal stability. Specifically, there has been a demand for improved reinforcing fibers to be embodied in structural composites which form the components of the leading edges of high speed aircraft, the nose cones or heat shields for re-entry vehicles, rocket engine components, and the like.

Graphite and other carbon forms have already been used in reinforcing agents in such structures, and, in particular, have been used in the form of graphite strands or fibers in the reinforcement of composite materials for aerospace structures. Such fibers have been made in a number of ways. An early type of fiber comprised "Whiskers" resulting from the partial oxidation of natural gas. Another early type of carbon fiber was made by the carbonization of strands of cellulosic material such as strands of cotton. As the plastic field developed many of the new synthetic polymers were substituted for cotton with advantage. Simple carbonization of such fibers, however, led to the production of very weak fibers with practically no resistance to mechanical stresses. Research was then directed to the improvement of the physical properties of the fibers.

An almost invariable practice in the art has been for multiple step, particularly three step, treatment of synthetic polymer yarns. The three step treatment can be defined as: first, a stabilization step which can include oxidation, cross-linking, cyclization, and other well-known polymer reactions and degradations for the temperature range involved; second, a carbonization step which converts the altered high molecular weight polymer fiber to a fiber

consisting of a highly carbonaceous residue with as much as several percent each of various elements such as hydrogen, oxygen, nitrogen, and phosphorus depending upon the original polymer nature, the time and temperatures involved in the carbonization process, and the mode of stabilization preceding carbonization; and, third, a graphitization step.

The terms "stabilization" and "stabilized" are used herein to describe fibers which have been treated so as to be particularly suitable for graphitization without rupturing or forming large voids or hollow structures during the process. Such stabilized fibers are normally characterized by their increased oxygen content, their uniformity of color in cross sections thereof, and by the integrity of the fibers at all processing stages (that is, they don't stick together).

Graphitization is referred to by the practitioners of this art in the sense of a high temperature treatment, usually above 2000° C.; and it is commonly recognized that this treatment has the effect of yielding materials of almost pure carbon but that the product may or may not be truly graphitic in the crystallographic sense and that the precursor polymer has a pronounced bearing on the degree of graphitic character that one may expect from the treatment. Thus, certain polymers, such as polyvinyl chloride, are called "graphitizing" and others, such as polyvinylidene chloride and polyacrylonitrile, are called "non-graphitizing."

In addition to the division of the graphitization process into these three general steps or temperature ranges the first two steps usually incorporate a gradual heating of the fibers by either utilizing slowly increased temperatures and sometimes holding the fiber at the maximum temperature for that step or utilizing a series of temperatures within the particular step and holding the fibers for various times at each of these temperatures. Thus, French Patent 1,430,803 (Jan. 24, 1966) teaches that polyacrylonitrile fibers are oxidized in the first of a three step process by heating the fiber at about 220° C. for 24 hours in an oxidizing atmosphere, while holding the yarns under tension. Such low temperature pretreatment of the fiber in an oxidizing atmosphere is designed to prepare, or stabilize, the fiber for subsequent carbonization although the patent does not specifically state such a purpose. The patent also describes carbonization processes for these fibers which require 24 to 66 hours for the gradual heating to the maximum carbonization temperature of 1000° C. Similarly, U.S. Patent 3,107,152 teaches that flexible fibrous graphite may be produced from cellulosic material by slowly heating the material to about 400° C. during 6 to 30 hours, followed by a heating schedule of about 5 hours to reach a temperature of 900° C. and a subsequent graphitization step.

As indicated above, the workers in the art have stabilized synthetic polymer fibers in a number of ways prior to a second step of carbonizing the fibers at some relatively intermediate temperature and a third step of graphitizing the carbonized fiber at some relatively high temperature.

Despite these improvements in the art, however, the need continues for high strength, high modulus reinforcing fibers for the preparation of structural composites.

OBJECTS

It is, therefore, an object of this invention to provide a method for the improvement of the pre-treatment, or stabilization, of acrylonitrile polymer fibers prior to subjecting the latter to carbonization or graphitization.

It is a further object to stabilize such fibers, preferably in the form of yarn, in a manner such that, upon subsequent direct graphitization of the fibers, fibers of improved graphitic character are formed.

SUMMARY OF THE INVENTION

I have now found that the foregoing and related objects can be attained by the method of stabilizing acrylic polymer fibers which comprises the step of heating said fibers at 265–290° C., preferably at 275° C., in an oxidizing atmosphere. I prefer that the fiber be in the form of a yarn and that it be treated in a fashion which will approximately hold the fiber at its original length or cause it to stretch a few percent of its length during stabilization. This latter can be accomplished by using a tension selected to suit the particular yarn or, conveniently, by winding the yarn on a cylinder at a specific, uniform tension.

As indicated previously, the invention finds unique advantage when used as a step prior to the step of direct graphitization. With respect to direct graphitization, I describe in a copending application filed the same date herewith the direct graphitization of a stabilized acrylonitrile polymer fiber by rapidly bringing the stabilized fiber to a high temperature in the range of 1800–3200° C., that is without going through any intermediate gradual or prolonged increase in temperature as an intermediate step. Thus, one can obtain a fiber of improved graphitic character by (1) stabilizing the acrylic fiber by the method of this invention and (2) rapidly bringing the stabilized fiber to a high temperature by my new improved method of direct graphitizing stabilized fibers as disclosed and covered in my said copending application.

The temperature range of 265–290° C. is fairly critical. I believe the superior stabilization results achieved in that temperature range may be due to (1) the attainment of a relatively high temperature without effecting any significant exothermic decomposition reactions in the acrylic polymer as generally occur at various temperatures above 200° C. depending on the precise acrylic polymer, the size of the polymer sample, and the heat dissipation characteristics of the sample package and the heating method; (2) the effecting of complete stabilization throughout the diameter of the fiber in a reasonably short time (in contrast to times required at 220° C.), for example, in about 7 hours for yarns comprised of 3.75 denier filaments and in about 3–5 hours for yarns comprised of 1.2–2.1 denier filaments; (3) the attainment of a favorable degree of oxidation, or oxygen pick-up (typically about 10–20 percent by weight) concurrent with the other reactions, especially cyclization and aromatization, which are believed to occur under these conditions; (4) and the attainment of a highly favorable balance between the degree of oxidation of the polymer and the amount of rigidization of the fiber structure (due to cross-linking or analogous processes) which, during a graphitization step, stabilizes the fiber against rupture, pore or void formation, and the like while still imparting to it the strength necessary to allow a wide range of tensions to be used during graphitization. I believe that this last item above allows me to impart to the fiber a higher degree of orientation during the graphitization than is possible with samples stabilized at either lower temperatures (such as 220° C.) or at higher temperatures (such as 300° C.) and it has been shown that a wide range of tensile properties and fiber densities can be achieved by the different tensioning weights and temperatures used with yarns stabilized in this fashion.

The acrylonitrile polymer fibers and yarns used in the method of the invention can be homopolymers, copolymers, terpolymers, graft polymers, and the like of acrylonitrile. I prefer acrylonitrile homopolymers and copolymers such as the copolymer of acrylonitrile and methyl acrylate. In the case of copolymers, for example, these may include nonacrylic constituents. For example, I prefer the copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and the like copolymers which include about 85 percent or more acrylonitrile units. Typical of such polymers are those sold, for example, under the trademarks "Courtelle" and "Dralon T."

Typical comonomers that can be used are: styrene, 75

alphanethyl styrene, vinyl toluene, vinyl xylene, vinyl naphthalene, vinyl diphenyl, vinyl methylnaphthalene, vinyl acetate, vinyl chloride, acrylamide, dimethylacrylamide, methacrylonitrile, methyl methacrylate, ethyl acrylate, vinylidene chloride, vinylidene cyanide, phenyl vinyl ether, vinyl methyl phthalate, vinyl methyl maleate, vinyl butyl succinate, ethylene, propylene, butylene, amylene, decylene, etc.

Polymers containing 50% or more acrylonitrile can be used for the purpose of this invention depending on the particular properties desired in the ultimate product. However, for maximum strength properties it is desirable to have at least 65% acrylonitrile and preferably at least 85% acrylonitrile in the starting polymer material.

From the disclosures made herein it should be clear that this invention is successful because provision is made to cope with a well-known phenomenon of acrylonitrile polymers. Usually the buildup of exothermic heat from the oxidation reactions in the polymer sample mass generates a temperature rise which exceeds the so-called "explosive exotherm" temperature of the particular polymer or copolymer, at which time the sample generally rapidly decomposes to a charred mass. In the practice of this invention, provision should be made to dissipate the heat of reaction so as to allow for controlled oxidation. For example, the sample mass or thickness may be kept small so that air circulation serves this purpose. An alternate method is the winding of single or thin layers of the sample on a metal tube which tends to conduct excess heat away as well as expose the yarn to the circulating air to some degree.

The acrylonitrile polymer fibers are subject to this problem over a wide range of temperatures, at least as low as 220° C. In terms of the advantages of this method of stabilization, improved materials are obtained by utilizing a stabilization temperature range made available because provision is made for the dissipation of the heat of reaction.

In referring to "oxidizing atmosphere" it is intended that various atmospheres can be used which contain oxygen in such a concentration that the oxidation can be controlled as described herein under the conditions used. Generally atmospheres containing 5–50% oxygen can be used under appropriate conditions, with the remainder of the atmosphere being an inert gas such as nitrogen, argon, helium, etc. Preferably the atmosphere is air.

Suitable tensions on the fibers or yarn during the stabilization step are not critical, although the tension sometimes appears to influence the properties of the stabilized yarn. If the yarn is held under tension by suspended weights or forces along the yarn axis, the weight will be dictated by the requirements for attaining the desired yarn length at the end of the stabilization process. If, on the other hand, the convenient laboratory process of winding the yarn on a cylinder is used, the original elongation and tenacity (strength) properties of the polymer fiber affect both the tensions that can be used on the fiber during stabilization and the orientation that can be incorporated in the stabilized fiber. It is best to avoid placing the yarn under an initial wound tension which is too near the breaking point of the yarn because expansion of the tube upon which the yarn is wound might increase the tension, during the heating step, to beyond the breaking point. It will be apparent that some fibers may be very much weaker than others and it may be necessary to test a specific fiber or yarn before a suitable tension is selected. Generally speaking, increased fiber diameters, increased number of strands, and increased amounts of twist permit high tensions without breaking of the fibers.

Example I

A polyacrylonitrile homopolymer yarn consisting of 120 filaments (each 3.75 denier) with no twist is wound on an aluminum tube in a single layer at a tension pro-

vided by a 60 gram riding pulley from which a 200 gram weight is suspended. The tube is placed in a circulating air oven for 7 hours at 275° C. A length of the resulting stabilized yarn is then passed through a vertical induction furnace susceptor in an argon atmosphere at 2800° C. under a tension provided by suspending 50 grams from the yarn. The yarn is moved at ½ inch per minute and the hot zone of the susceptor is about ½ inch resulting in the yarn being exposed to the 2800° C. temperature for about one minute. The single filament tensile strength of the resulting fibers is about 265,000 lbs. per square inch and the initial modulus is 61,000,000 lbs. per square inch. X-ray diffraction studies show that the yarn has a high degree of graphitic character.

Example II

The foregoing example is repeated except that the high temperature step is carried out under 100 gram tension and the final temperature is 2500° C. The resulting single filament tensile strength is 277,000 lbs. per square inch and the initial modulus is 52,000,000 lbs. per square inch.

Example III

Example I is repeated except that the high temperature step is carried out with the yarn under 50 grams tension and moving through a hot zone of about 3000° C. at a rate of 2 inches per minute. The resulting tensile strength of a single filament is 151,000 lbs. per square inch and the initial modulus is 40,000,000 lbs. per square inch.

Example IV

A yarn, comprising a copolymer of 94 percent acrylonitrile and 6 percent methyl acrylate and comprising 750 filaments (each 1.5 denier) with no twist, is wound on an aluminum tube in a single layer at a tension provided by a 60 gram pulley from which a 1200 gram weight is suspended and placed in a circulating air oven for 7 hours at 275° C. Portions of the yarn are then treated as indicated in Table I.

TABLE I

Temp., ° C.	Rate, in./min.	Tension, gms.	Tensile strength, lbs./sq. in.	Modulus, lbs./sq. in.
2,550	2	100	226,000	45,000,000
2,620	0.5	100	219,000	63,000,000
2,800	2	100	203,000	45,000,000
2,860	0.5	100	240,000	62,000,000

Portions of the stabilized yarn are also passed through a furnace about 22 inches long at relatively more rapid rates. Results are in accordance with Table II.

TABLE II

Temp., ° C.	Rate, in./min.	Tension, gms.	Tensile strength, lbs./sq. in.	Modulus, lbs./sq. in.
1,500	10	48	228,000	27,000,000
2,500	9	223	180,000	44,000,000
2,900	9	38	260,000	86,000,000

Example V

An 800 denier yarn (384 filaments, 0.5 turn per inch twist) made from a copolymer of 99.5 percent acrylonitrile and 0.5 percent methyl acrylate is wound on an aluminum tube under a tension provided by a 60 gram riding pulley from which a 50 gram weight is suspended. The tube is placed in a circulating air oven for 5 hours at 275° C. A length of the resulting stabilized yarn is then graphitized at 2800° C. in the manner described in Example I. A length of the stabilized yarn is similarly graphitized except at a temperature of 2215° C. The resulting single filament tests are shown in Table III. As in the case of the preceding examples, X-ray diffraction studies show the resulting yarn to have a high degree of graphitic character.

TABLE III

Graphitization temp., ° C.	Tension, gms.	Tensile strength, lbs./sq. in.	Modulus, lbs./sq. in.
2,800	100	334,000	76,000,000
2,800	150	340,000	110,000,000
2,800	50	280,000	92,000,000
2,215	50	374,000	49,000,000

Example VI

A polyacrylonitrile homopolymer yarn consisting of 120 filaments (each 3.75 denier) with no twist is wound on a high temperature glass tube (of approximately 96 percent silica content) at a tension provided by a 60 gram riding pulley from which a 50 gram weight is suspended. The tube is placed in a circulating air oven for 7 hours at 275° C. A length of the resulting yarn is then graphitized at 2520° C. and under a tension of 100 grams in the manner described in Example I. The resulting single filament tensile strength is 254,000 lbs. per square inch and the initial modulus is 54,000,000 lbs. per square inch.

Example VII

A portion of polyacrylonitrile homopolymer yarn consisting of 120 filaments (each 3.75 denier) is heated on an aluminum tube for 7 hours at 275° C. and is then carbonized. The carbonization is accomplished by passing the yarn through a three-stage furnace in an inert atmosphere such as lamp grade nitrogen at the rate of eighteen inches per minute. Each of the furnace stages or zones is approximately 6 inches in length and the zones are maintained at 430° C., 710° C., and 1000° C., respectively. A tension is maintained on the yarn by placing a light Teflon ring from which a 10 gram weight is suspended over the yarn before the pulley at the entrance of the furnace; the yarn shrinks approximately 13.4 percent during carbonization. The carbonized yarn is then graphitized in the manner described in Example I and as indicated in Table IV.

TABLE IV

Temp., ° C.	Rate, in./min.	Tension, gms.	Tensile strength, lbs./sq. in.	Modulus, lbs./sq. in.
2,700	0.5	10	92,000	63,000,000
2,450	0.5	10	149,000	67,000,000

Example VIII

The following is given to show the superior effects of the stabilization procedures followed in Examples I through VII above.

Three yarns, comprising those described in Examples I, IV and V (except that this last has a twist of 4-5 turns per inch) respectively, are each heated in single layers on aluminum tubes for 40 hours at 220° C. These yarns, thus stabilized by prior art methods, are then treated by the direct graphitization invention described in the co-pending application as indicated in Table VI:

TABLE VI

Yarn listed	Temp., ° C.	Rate, in./min.	Tension, gms.	Tensile strength, lbs./sq. in.	Modulus, lbs./sq. in.
Example:					
I	2,500	2.0	2	141,000	28,000,000
IV	2,500	2.0	2	244,000	32,000,000
V	2,530	0.5	5	123,000	37,000,000
	2,850	0.5	5	87,000	23,000,000

Some of these yarns are tested at higher tensions and are found to break immediately at the lowest weight used for direct graphitization (50 grams) in the examples above. The superiority of the invention described in the prior examples can be seen readily when processing data and resultant tensile and modulus properties are compared.

Thus the tensile strength and modulus for these fibers of Example VIII stabilized according to prior art methods at 220° C. for 40 hours are much inferior to the modulus and to the tensile strength of fibers stabilized by the process of this invention as illustrated in Examples I-VII. The fact that the tensile strengths of the fibers of Example VIII are greater than those in Example VII is explained by the fact that an intermediate carbonization step is used in Example VII while the direct graphitization process of applicant's copending application is used in Example VIII.

Example IX

The procedure of Example I is repeated a number of times using individually in place of the polymer of that example the following copolymers respectively:

Acrylonitrile-styrene 80-20

Acrylonitrile-vinyl chloride 85-15

Acrylonitrile-vinylidene chloride 90-10

Acrylonitrile-acrylamide 75-25

Acrylonitrile-methacrylonitrile 50-50

Acrylonitrile-styrene-acrylamide 80-10-10

Acrylonitrile-methyl methacrylate 60-40

Acrylonitrile-vinyl chloride-vinylidene chloride 50-25-25.

In each case improvements in the tensile strength and modulus are noted as compared to the same copolymer stabilized according to prior art method of Example VIII.

The expression "oxidizing atmosphere" as used herein is intended to include air and other atmospheres containing oxygen in a proportion to give an oxidizing effect somewhat equivalent to air.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

I claim:

1. In the process for the high temperature graphitization of acrylonitrile polymer fibers to form high tensile strength, high modulus of elasticity graphite fibers, the improvement in stabilizing said acrylonitrile polymer fibers prior to graphitization which comprises the step of oxidizing said acrylonitrile polymer fibers by initially heating said polymer fibers at 265° C.-290° C. in an oxygen-con-

taining atmosphere for a period of at least 3 hours, said oxidizing step being conducted with said polymer fibers wound on a metal tube so as to dissipate heat of reaction generated during the oxidation and thereby prevent heat build-up in said acrylonitrile polymer fibers.

2. The process of claim 1 wherein said heating is at a temperature of about 275° C.

3. The method according to claim 1 wherein said fibers are in the form of a yarn and are under tension.

4. The process of claim 1 wherein said fibers are in the form of yarn, are under tension, and said heating is continued for about 3-7 hours.

5. The process of claim 1 wherein said polymer comprises an acrylonitrile copolymer containing at least 50 percent by weight of acrylonitrile.

6. The process of claim 1 wherein said polymer comprises an acrylonitrile homopolymer.

7. The process of claim 1 wherein said polymer is a copolymer of methyl methacrylate and at least 50 percent by weight of acrylonitrile.

8. The process of claim 1 wherein said polymer is a copolymer of about 97 percent by weight acrylonitrile and about 3 percent by weight vinyl acetate.

9. The process of claim 1 wherein said polymer is a copolymer having at least 85 percent by weight of acrylonitrile.

References Cited

UNITED STATES PATENTS

2,799,915	7/1957	Barnett et al.	8-115.5 X
3,285,696	11/1966	Tsunoda	23-209.1
3,399,252	8/1968	Hough et al.	23-209.3
3,412,062	11/1968	Johnson et al.	23-209.1 UX
3,449,077	6/1969	Stuetz	23-209.1
3,508,874	4/1970	Rulison	23-209.1

FOREIGN PATENTS

911,542	11/1962	Great Britain	23-209.1
---------	---------	---------------------	----------

OTHER REFERENCES

Vosburgh: "Textile Research Journal," vol. 30, 1960, pp. 882-896.

EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

8-115.5; 23-209.2; 264-29

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,671,192 Dated June 20, 1972

Inventor(s) Herbert M. Ezekiel

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

[Column 1, line 9, "Jan. 18, 1972" should read --- Jan. 18, 1989 ---]

Signed and sealed this 22nd day of May 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents