A T

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ABSTRACT
An improved process is provided for the simultaneous conversion of a plurality of adjoining parallel ends of an organic polymeric fibrous material to a carbonaceous fibrous material. The parallel warp ends are provided and maintained during at least a portion of the conversion process an an integral tape possessing a high degree of structural integrity by the presence of a weft pick interlaced therewith in a sateen weave construction which forms a substantial number of the parallel warp ends as described. When the resulting carbonaceous tape is incorporated in a matrix material to form a composite article, the presence of the weft pick therein produces no substantial diminution in the composite properties.

13 Claims, 8 Drawing Figures
**Fig. 2**

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**Fig. 4**

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**Fig. 8**

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**Inventors:**

Kenneth S. Burns
George R. Ferment
Roger C. Waugh
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**Inventors:**
- Kenneth S. Burns
- George R. Ferment
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PROCESS FOR THE PRODUCTION OF CARBONACEOUS TAPES

BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon carbon fibers. The terms "carbon" fibers or "carbonaceous" fibers are used herein the generic sense and include graphite fibers as well as amorphous carbon fibers. Graphite fibers are defined herein as fibers which consist essentially of carbon and have a predominant x-ray diffraction pattern characteristic of graphite. Amorphous carbon fibers, on the other hand, are defined as fibers in which the bulk of the fiber weight can be attributed to carbon and which exhibit an essentially amorphous x-ray diffraction pattern. Graphite fibers generally have a higher Young's modulus than do amorphous carbon fibers and in addition are more highly electrically and thermally conductive.

Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites, and graphic carbon fibers theoretically have among the best properties of any fiber for use as high strength reinforcement. Among these desirable properties are corrosion and high temperature resistance, low density, high tensile strength, and high modulus. Uses for carbon fiber reinforced composites include aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles.

As is known in the art, numerous procedures have been proposed in the past for the conversion of various organic polymeric fiberous materials to a carbonaceous form while retaining the original fibrous configuration essentially intact. Such procedures have in common the thermal treatment of the fibrous precursor in an appropriate atmosphere or atmospheres which is commonly conducted in a plurality of heating zones, or alternatively in a single heating zone wherein the fibrous material is subjected to progressively increasing temperatures. Both batch and continuous processing techniques have been proposed. From the commercial standpoint those processes which are capable of functioning on a continuous basis are generally considered to be the most attractive. However, many of the prior art continuous conversion techniques have been inherently limited to the processing of a single end of fibrous precursor at a given time. Such techniques while offering the advantages of possible automation, still suffer the disadvantage of limited productivity.

Additionally techniques have been proposed wherein a plurality of ends of a fibrous precursor may be simultaneously processed. See for instant the process of commonly assigned U.S. Ser. Nos. 865,332, filed Oct. 10, 1969, of Kenneth S. Burns and William M. Cooper (now abandoned) wherein a multiplicity of strands of polymeric fiberous materials are simultaneously stabilized prior to subsequent carbonization; and 874,731, filed Nov. 7, 1969, (now U.S. Pat. No. 3,723,157), of Melvin L. Druin wherein a plurality of multifilament bundles capable of undergoing graphitization are simultaneously graphitized and subsequently coated. While such genetically defined processes offer substantial advantages over prior art batch and continuous processes, fiber handling difficulties may occasionally arise. For example, if one of the fibrous ends undergoing treatment should be defective, the breakage of the same while being passed through one of the heating zones frequently results in catastrophic failure of the process. The operation of the process must be terminated, the oven or ovens cooled, and the broken end re-united or replaced. Also, precise handling of the plurality of ends is essential if substantial end crossovers are to be eliminated and a uniform width of the plurality of the ends maintained.

One technique heretofore proposed for the simultaneous conversion of a substantial number of fibrous ends to a carbonaceous form has involved the thermal treatment of a fibrous precursor while in the form of a woven cloth. See, for instance, Belgian Pat. Nos. 720,947 and 726,761, as well as U.S. Pat. Nos. 3,541,582 for representative disclosures of the processing of cloth precursors. While fibrous assemblages in cloth form commonly offer advantages with respect to the maintenance of structural integrity throughout the thermal treatment, a permanent crimp is commonly imparted to the filaments and the single filament tensile properties of the fibers present within the cloth have tended to be adversely influenced. Additionally a high degree of fiber loading within a composite article is commonly impossible because of the inability of the cloth to form compact plies within the same. The weft threads in the cloth further appear to produce an overall reduction in the composite physical properties.

It is an object of the invention to provide an improved process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material while in the form of a tape to a carbonaceous fibrous material.

It is an object of the invention to provide an improved process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material to a carbonaceous fibrous material while in the form of a tape of enhanced structural integrity.

It is an object of the invention to provide an improved process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material wherein catastrophic process failure resulting from the breakage of an end is effectively eliminated.

It is an object of the invention to provide an improved process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material to a carbonaceous fibrous material while in the form of a tape wherein splits and crossovers are substantially eliminated.

It is another object of the invention to provide an improved process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material wherein the warp ends are maintained in position by at least one weft pick in the substantial absence of the impairment of the linear configuration and tensile properties of the warp ends.

It is another object of the invention to provide an improved process for the conversion of a plurality of adjoining ends of an organic polymeric fibrous material to an integral carbonaceous tape which is capable of a high degree of compaction and fiber loading when utilized as a reinforcing medium in a composite article.

It is another object of the invention to provide an improved process for producing a woven carbonaceous tape which when utilized as a reinforcing medium
yields a composite article of enhanced physical properties.

It is a further object of the invention to provide in a preferred embodiment an improved process for producing carbonaceous tapes from a fibrous acrylic precursor.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the detailed description which follows, and the appended claims.

SUMMARY OF THE INVENTION

It has been found in a process for the simultaneous conversion of a plurality of adjoining ends of an organic polymeric fibrous material capable of undergoing conversion to a carbonaceous fibrous material while in the form of a tape to a carbonaceous fibrous material wherein the ends are continuously passed in the direction of their length through a series of heating zones while substantially suspending therein to form a fibrous product which contains at least 90 per cent carbon by weight, that improved results are achieved by providing the fibrous material during at least a portion of the conversion process in the form of a tape of sateen weave construction consisting of at least 32 adjoining substantially parallel linear warp ends capable of undergoing conversion to a carbonaceous fibrous material essentially coextensive with the length of the tape and a weft pick interfaced therewith at a plurality of points capable of maintaining the substantially parallel relationship of the warp ends which substantially float at least four of the warp ends prior to each additional interlacing point in the main body of the tape as the warp ends are traversed, the weft pick being provided at a tension sufficient to prevent the linear configuration of the warp ends is substantially unimpaired and at a frequency of about 0.1 to 8 picks per inch of the tape.

The preferred organic polymeric fibrous material is an acrylic polymer comprising at least about 85 mol per cent of acrylonitrile units and up to about 15 mol per cent of one or more monovinyl units copolymerized therewith. In a preferred embodiment of the process the organic polymeric tape is provided in the sateen weave construction throughout the conversion process.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged plan view of a portion of precursor tape of a 4 × 4 sateen weave construction suitable for use in the present process.

FIG. 2 is the numerical weaving pattern for the tape of FIG. 1.

FIG. 3 is an enlarged plan view of a portion of precursor tape of an 8 × 8 sateen weave construction suitable for use in the present process.

FIG. 4 is the numerical weaving pattern for the tape of FIG. 3.

FIG. 5 is an enlarged plan view of a portion of precursor tape of a 16 × 16 sateen weave construction suitable for use in the present process.

FIG. 6 is the numerical weaving pattern for the tape of FIG. 5.

FIG. 7 is an enlarged plan view of a portion of precursor tape having a weave construction not in accordance with that employed in the present process and is presented for comparative purposes.

FIG. 8 is the numerical weaving pattern for the tape of FIG. 7 and is presented for comparative purposes only.

DESCRIPTION OF PREFERRED EMBODIMENTS

The tape which is converted to a carbonaceous fibrous material possesses a sateen weave construction (as described in detail hereafter) during at least a portion of the conversion process which includes at least 32 adjoining substantially parallel linear warp ends.

The warp ends are composed of an organic polymeric fibrous material capable of conversion to a carbonaceous fibrous material. The warp ends may be conveniently selected from those fibrous materials which are recognized as being suitable for thermal conversion to a carbonaceous fibrous material. For instance, the warp ends may be derived from organic polymers such as an acrylic polymer, a cellulose polymer, a polyanide, a polybenzimidazole, polyvinyl alcohol, pitch, etc. As discussed hereafter, acrylic polymeric materials are particularly suited for use in the formation of the warp ends employed in the present process. Illustrative examples of suitable cellulose materials include the natural and regenerated forms of cellulose, e.g. rayon. Illustrative examples of suitable polyamide materials include the aromatic polyamides, such as nylon 6T, which is formed by the condensation of hexamethylene diamine and terephthalic acid. An illustrative example of a suitable polybenzimidazole is poly-2,2'-m-phenylene-5,5'-bienzimidazole.

An acrylic polymeric material prior to thermal stabilization may be formed primarily of recurring acrylonitrile units. For instance, the acryl polymer should contain not less than about 85 mol per cent of acrylonitrile units with not more than about 15 mol per cent of monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monomers. A particularly preferred acryl polymeric material is an acrylonitrile homopolymer, or a closely relate acrylonitrile copolymer (i.e. contains at least about 95 mol per cent of acrylonitrile units and up to about 5 mol per cent of one or more monovinyl compounds copolymerized with acrylonitrile.

The warp ends may be provided in a variety of physical configurations. For instance, the warp ends may assume the configuration of continuous lengths of multifilament yarns, tows, strands, cables, or similar fibrous assemblages. In a preferred embodiment of the process the warp ends are a continuous multifilament yarn.

The warp ends may optionally be provided with a twist which tends to improve the handling characteristics. For instance, a twist of about 0.1 to 5 tpi and preferably about 0.3 to 1.0 tpi, may be utilized. Also, a false twist may be used instead of or in addition to a real twist. Alternatively, one may select bundles of fibrous material which possess essentially no twist.

The warp ends may be drawn in accordance with conventional techniques in order to improve their orientation. For instance, acrylic warp ends may be preliminarily drawn by stretching before or after incorporation in the tape while in contact with a hot shoe at about 140° to 160°C. Additional representative drawing techniques are disclosed in U.S. Pat. Nos. 2,455,173; 2,948,581; and 3,122,412. It is recommended that acrylic warp ends selected for use in the
process be initially drawn to a single filament tenacity of at least about 3 grams per denier. If desired, however, the warp ends may be more highly oriented, e.g. drawn up to a single filament tenacity of about 7.5 to 8 grams per denier, or more.

The weft pick is preferably also composed of an organic polymeric fibrous material which is capable of undergoing carbonization without the destruction of its original fibrous configuration. If desired, however, the weft pick may be initially provided as a previously stabilized organic polymeric fibrous material, a carbonaceous fibrous material, or other fibrous material capable of withstanding the carbonization temperatures. Alternatively, a weft pick may be selected which is incapable of withstanding the highly elevated temperatures required to complete carbonization and/or graphitization of the warp ends. For instance, the weft pick may be formed from a cellulosic material such as cotton which will impart dimensional stability to the warp ends through the stabilization step, but which is incapable of withstanding a subsequent heat treatment step.

The weft pick may be provided in a variety of physical configurations. For instance, the weft pick may assume the configuration of a multifilament yarn, tow, strand, cable, or similar fibrous assemblage. In a preferred embodiment of the process the weft pick is a continuous multifilament yarn having a total denier equal to or less than that of the continuous multifilament yarn warp ends. Preferably the total denier of a multifilament acrylic yarn weft pick prior to thermal stabilization is below about 400, e.g. about 100 to 300, total denier. In a particularly preferred embodiment of the process the total denier of the weft pick is about 0.2 to 0.5 times the total denier of a warp end. A minor amount of twist may be beneficially provided in a multifilament yarn weft pick which improves the handling characteristics during weaving. For instance, the weft pick may be provided with a twist of about 0.1 to 5 tpi (preferably 0.1 to 3 tpi), and most preferably about 0.2 to 0.7 tpi. If a twist is utilized in the warp ends it is recommended that any twist employed in the weft pick be to a lesser degree so that the weft pick may readily assume a more flattened configuration when in contact with warp ends.

It is essential that the weft pick utilized in the formation of the tape lacks a tendency to undergo excessive shrinkage during heat treatment (described hereinafter) which imparts a puckering to the warp ends and thereby interferes with the flat configuration of the tape. In a preferred embodiment of the process the weft pick is hot drawn at least about 3 times its as-spun length to increase its orientation and is subsequently relaxed (e.g. 5 to 40 per cent of drawn length) prior to incorporation in the precursor tape so that its tendency to undergo shrinkage is minimized.

The fibrous material utilized as the warp ends and weft pick may optionally be provided in intimate association with one or more catalytic agents capable of enhancing the rate of the thermal conversion to a carbonaceous fibrous material.

The fibrous organic polymeric tape utilized as the precursor in the process of the present invention during at least a portion of its thermal conversion to a carbonized form is provided in a highly unbalanced sateen weave construction. A "sateen weave construction" is defined as a woven construction possessing a substantial number of floats which run fillingwise (i.e. weftwise). The term "float" is used in its usual sense and indicates that a plurality of substantially perpendicular strands present within the construction are being passed over or skipped in the absence of interlacement. The tape is unbalanced in that the numerical proportion of warp ends to filling picks per square inch present within the same is substantially greater than 1:1, e.g. about 4:1 to 100:1, or more, and preferably about 15:1 to 30:1. The tape comprises at least 32 adjoining substantially parallel linear warp ends. Commonly, the tape comprises about 32 to 500 adjoining warp ends; however, even a substantially larger number of warp ends can be employed, e.g. 1,000 or more. The warp ends are essentially coextensive with the length of the tape. The weft pick present within the tape of sateen weave construction is provided at a frequency of about 0.1 to 8 picks per inch of said tape, and preferably at a frequency of about 1 to 3 picks per inch of said tape. Since the weft pick is provided at a relatively low frequency, and preferably as a continuous length, it may intersect the edge of the tape at an angle other than exactly ninety degrees unlike common woven fabrics. The exact angle of intersection with the edge of the tape is influenced by the pick frequency, and the width of the tape (i.e. number and total denier of the warp ends).

The sateen weave construction of the tape is such that the weft pick is interlaced with the warp ends at a plurality of points capable of maintaining the substantially parallel relationship of the warp ends which are in an adjoining relationship in the form of a flat tape with contact being made between contiguous warp ends. The weft pick is provided under a tension sufficient that the linear configuration of the warp ends present within the tape is substantially unimpaired. Additionally, any crimp which is present in the tape components should be present in the weft pick and not in the warp ends.

The weft pick is interlaced with the warp ends in such a manner that it substantially floats at least four of the warp ends prior to each additional interlacing point in the main body of the tape, i.e. the central portion of the tape with the possible exclusion of the selvage. More specifically, the weft pick floats from about four to 16, or more, of the warp ends prior to each additional interlacing point in the main body of the tape as the warp ends are traversed. As the weft pick passes between adjoining warp ends in the main body of the tape at an interlacing point, an additional float preferably of like length is begun on the opposite face of the tape. Accordingly, floats of at least four warp ends are substantially present upon each face of the main tape body. Such floats maintain the warp ends as an integral tape of controlled lateral integrity. In the particularly preferred embodiment of the process the weft pick floats about eight of the warp ends prior to the next interlacing point. While standard weaving equipment is commonly incapable of producing a sateen weave construction wherein more than 16 warp ends are floated, this fact should not limit the maximum float utilized in the process to 16 warp ends. It should be recognized, however, that the structural integrity of the tape tends to be reduced if the float greatly exceeds 16 warp ends, e.g. up to about 50 warp ends.

The lengths of the floats utilized in the sateen weave construction in the main body of the tape need not be identical provided at least four of the substantially par-
allel linear warp ends are skipped prior to each addi-
tional point of interlacement. It is preferred, however,
that floats of substantially uniform length (i.e. naturally
balanced in weft direction) be used throughout a given
sateen weave construction. Such substantially uniform
float lengths aid in imparting transverse symmetry to
the resulting tape which enhances its ability to maintain
a flat configuration as the carbonization reaction pro-
gresses. The intersection points are preferably varied
between successive weft interlacements. Accordingly,
as will be apparent to those skilled in weaving technol-
ogy, the counter (i.e. step or move) of the sateen weave
construction may commonly be from about one to 10,
or more, and is preferably one.

The tape of sateen weave construction utilized in the
present process can be formed by conventional weav-
ing techniques as will be apparent to those skilled in
weaving technology. For instance, the warp ends may
be beamed, and the weft pick subsequently inserted at
appropriate intervals utilizing a narrow fabric loom.
Care, of course, must be taken to insure that the ten-
sion exerted upon the weft pick is insufficient to impair
the substantially linear configuration of the warp ends.

In a preferred embodiment of the process the tape of
sateen weave construction (as previously described) is
provided with a selvage which is capable of aiding the
structural integrity of the weave. Such selvage may be
positioned upon each edge of the main body of the tape
and is of a relatively narrow width. For instance, the
selvage may be formed by converting the sateen weave
construction created by the weft pick to a plain weave
construction as the pair of warp ends at each edge of
the tape are traversed. Such a selvage of relatively nar-
row width has been found helpful in retaining the weft
pick at substantially the same location as initially
woven, and does not deleteriously influence composite
properties to any significant degree.

The heating temperatures, heating atmospheres, and
residence times utilized in the present process to pro-
duce carbon fibers may be in accordance with thermal
conversion techniques heretofore known in the art.
The plurality of adjoining ends of an organic polymeric
fibrous material while in the form of a tape are con-
verted to a carbonaceous fibrous material by continu-
ous passage in the direction of their length through a
series of heating zones while substantially suspended
therein to form a fibrous product which contains at
least 90 per cent carbon by weight. The organic poly-
meric fibrous tape during at least a portion of its ther-
mal conversion to a carbonaceous fibrous material is
provided in the form of a highly unbalanced tape of a
sateen weave configuration (as heretofore described).
In a preferred embodiment of the process the organic
polymeric fibrous tape is provided in the sateen weave
configuration throughout its thermal conversion to a
carbonaceous fibrous material. Alternatively, the sa-
teen weave tape configuration may be formed subse-
cquent to an initial thermal stabilization treatment.
Additionally, the sateen weave tape configuration may be
optionally retained while the tape is passed through any
or all of the following (1) a graphitization zone, (2) a
surface treatment zone wherein the surface character-
istics of the fibrous product are modified so as to en-
chance its bonding characteristics to a matrix material,
and (3) a resin impregnation zone.

The stabilization heating zone is commonly provided
at a temperature of about 200° to 400°C, depending
upon the composition of the tape. As will be apparent
to those skilled in the art, the atmosphere provided in
the stabilization heating zone may be varied. For in-
stance, a cellulosic precursor is commonly stabilized in
(1) an oxygen-containing atmosphere or (2) in an inert
or non-oxidizing atmosphere, such as nitrogen, helium,
argon, etc. Additionally, precursors such as an acrylic
polymer, a polyamide, a polybenzimidazole, or polyvi-
nyl alcohol are commonly stabilized in an oxygen-
containing atmosphere. Air may be conveniently se-
lected as the oxygen-containing atmosphere for use in
the process. When the stabilization treatment is con-
ducted in an oxygen-containing atmosphere, it is com-
monly termed a "preoxidation" treatment.

The stabilization heating zone is substantially closed
in order to facilitate the confinement and withdrawal of
off gases and/or the maintenance of an appropriate at-
mosphere. When a non-oxidizing atmosphere is desired
within the heat treatment chamber, the strands may pass
through a seal as they continuously enter and leave the
heat treatment chamber in order to exclude oxy-
gen.

The stabilization of fibers of acrylonitrile homopoly-
mers and copolymers in an oxygen-containing atmo-
sphere involves (1) an oxidative cross-linking reaction
of adjoining molecules as well as (2) a cyclization reac-
tion of pendant nitrile groups to a condensed dihydroy-
pyridine structure. While the reaction mechanism is
complex and not readily explainable, it is believed that
these two reactions occur concurrently, or are to some
extent competing reactions.

The cyclization reaction involving pendant nitrile
groups which occurs upon exposure of an acrylic fi-
brous material to heat is generally highly exothermic
and, if uncontrolled, results in the destruction of the fi-
brous configuration of the starting material. In some
instances this exothermic reaction will occur with ex-
plorative violence and result in the fibrous material being
consumed by flame. More commonly, however, the fi-
brous material will simply rupture, disintegrate and/or
coalesce when the critical temperature is reached. As
the quantity of comonomer present in an acrylonitrile
co-polymer is increased, a fibrous material consisting of
the same tends to soften at a progressively lower tem-
perature and the possible destruction of the original fi-
brous configuration through coalescence of adjoining
fibers becomes a factor of increasing importance. The
"critical temperature" referred to herein is defined as
the temperature at which the fibrous configuration of
a given sample of acrylic fibrous starting material will
be destroyed in the absence of prior stabilization.

In a preferred embodiment of the invention the acryl-
ic starting material exhibits a critical temperature of
at least about 300°C, e.g. about 300° to 330°C. In
addition to visual observation, the detection of the cri-
tical temperature of a given acrylic fibrous material may
be aided by the use of thermoanalytical methods such
as differential scanning calorimeter techniques, where-
by the location and magnitude of the exothermic
reaction can be measured quantitatively.

The stabilized acrylic warp ends (1) retain essentially
the same fibrous configuration as the starting material,
(2) are capable of undergoing carbonization, (3) are
black in appearance, (4) are non-burning when sub-
jected to an ordinary match flame, and (5) commonly
contain a bound oxygen content of at least about 7 percent by weight as determined by the Unterzaucher analysis.

In a preferred embodiment of the process the sateen tape (hereinafter described) is stabilized in accordance with the processing conditions of commonly assigned U.S. Ser. Nos. 749,957, filed Aug. 8, 1968, and 865,332, filed Oct. 10, 1969 (now abandoned) which are herein incorporated by reference.

The carbonization heating zone is commonly provided with an inert or non-oxidizing atmosphere at a temperature of at least about 900°C (e.g. 900°C to 1,600°C). Suitable inert atmospheres include nitrogen, argon, helium, etc. During the carbonization reaction elements present in the continuous length of fibrous material other than carbon, e.g. nitrogen, hydrogen and oxygen are substantially expelled until the warp ends contain at least 90 percent carbon by weight, and preferably at least 95 percent carbon by weight.

An optional graphitization zone is commonly provided with an inert or non-oxidizing atmosphere at a more highly elevated temperature of about 2,000°C to 3,100°C.

A longitudinal tension may optionally be applied to the tape while passing through the carbonization and/or graphitization heating zones in accordance with techniques known in the art.

In a preferred embodiment of the process the carbonization and graphitization of a stabilized acrylic sateen tape may be conducted by the continuous passage of the same through a single heating apparatus, such as the heater of an induction furnace, provided with a temperature gradient in accordance with the teachings of commonly assigned U.S. Ser. No. 777,275, filed Nov. 20, 1968 (now abandoned), which is herein incorporated by reference. A partially preferred susceptor for use in the production of carbonaceous fibrous materials while in tape form is disclosed in commonly assigned U.S. Ser. No. 46,675, filed June 16, 1970 (now U.S. Pat. No. 3,656,910), which is herein incorporated by reference.

The carbonaceous tape, whether formed of amorphous or graphitic carbon, can next optionally be passed through a surface treatment zone wherein its ability to bond to a matrix material is enhanced. Any conventional surface treatment technique may be selected. Additionally, the tape (preferably following surface treatment) can optionally be passed through a coating zone wherein it is impregnated with a resinous matrix-forming material, e.g. an epoxy resin.

During the stabilization and carbonization steps of the present process it is common for the width of the tape to diminish due to controlled shrinkage as elements other than carbon are expelled. A flat tape configuration is nevertheless retained.

The tape undergoing treatment in the present process is continuously passed in the direction of its length through each of the heating zones (e.g. a stabilization zone and a carbonization zone). If desired, the forward movement of the tape may be terminated between heating zones and the tape collected upon a support where it is stored prior to additional processing. It is recommended, however, that the heating zones be aligned in close proximity and the tape continuously passed from one zone to another without termination of the forward movement. Various rolls, or other guides may be employed to direct the movement of the tape as will be apparent to those skilled in fiber technology.

The following examples are provided as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

In the examples of various sateen weave constructions in accordance with the present invention were continuously passed in the direction of their length through (1) a pretreatment zone, (2) a stabilization zone, (3) a heating zone provided with a temperature gradient wherein both carbonization and graphitization were carried out, (4) and a surface treatment zone. Following resin impregnation composite articles incorporating the resulting graphite tape as fibrous reinforcement were formed.

Each tape was produced by initially beaming 200 warp ends of a dry spun acrylonitrile homopolymer, and inserting a neat pick by use of a Fletcher narrow fabric loom. Each warp end consisted of about 385 continuous filaments having a total denier of about 775, and was provided with a twist of about 0.5 turns per inch. The 200 warp ends were aligned in adjoining parallel contact to form a flat tape having a width of 4 inches. Prior to incorporation in the tape the warp ends had been hot drawn to a single filament tenacity of about 4 grams per denier.

The pretreatment of the acrylonitrile homopolymer tape was conducted in accordance with the teachings of commonly assigned U.S. Ser. No. 17,962, filed Mar. 9, 1970 (now abandoned). The tape was continuously passed through an oven containing circulating air provided at about 220°C while under a longitudinal tension sufficient to permit a 16 percent reduction in length brought about by shrinkage for a residence time of about 300 seconds.

The stabilization (i.e. preoxidation) was conducted in accordance with the teachings of commonly assigned U.S. Ser. No. 865,332, filed Oct. 10, 1969 (now abandoned). The tape was continuously passed through an oven containing circulating air maintained at about 265°C, while under a longitudinal tension sufficient to maintain a constant length for a residence time of about 175 minutes. The preoxidized tape was black in appearance, retained its initial fibrous configuration essentially intact, was non-burning when subjected to an ordinary match flame, and contained a bound oxygen content of 10 percent by weight as determined by the Unterzaucher analysis.

The preoxidized tape was continuously passed through a heating zone of an induction furnace provided with a nitrogen atmosphere and a temperature gradient in accordance with the teachings of commonly assigned U.S. Ser. No. 777,275, filed Nov. 20, 1968 (now abandoned). The hollow graphite susceptor of the induction furnace was formed in accordance with the teachings of commonly assigned U.S. Ser. No. 46,675, filed June 16, 1970 (now U.S. Pat. No. 3,656,910). The temperature gradient within the heating zone raised the tape from room temperature (i.e. about 25°C) to a temperature of 800°C in approximately 50 seconds after entering the susceptor, from 800°C to 1,600°C in approximately 25 seconds to produce a carbonized tape, and from 1,600°C to 2,750°C in approximately 50 seconds where it was maintained ±50°C for about 40 seconds to produce a graphitized tape. A longitudinal tension of 70 pounds (i.e. about
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150 grams per warp end) was exerted upon the tape as it passed through the heating zone of the induction furnace. The warp ends and weft picks substantially retained their original fibrillar configuration following carbonization and graphitization and exhibited a specific gravity of about 2.0. The tape exhibited a predominant x-ray diffraction pattern characteristic of graphitic carbon when subjected to x-ray analysis. The graphite tape was next surface treated to modify its surface characteristics by continuous passage through a heating zone provided with an atmosphere of molecular oxygen in an inert carrier gas. The surface treated tape was collected by winding upon a package.

Tensile and interlaminar shear strength test bars were formed employing the surface treated tape as a fibrous reinforcing medium in a resinous matrix. The tensile test bars had dimensions of 8.5 inches x 0.5 inch x 0.03 inch, and the interlaminar shear strength test bars had dimensions of 8 inches x 0.25 inch x 0.125 inch. The composite articles were formed by immersing strips of the tape in a liquid epoxy resin-hardener mixture provided at about 70°C, removing excess resin, placing a plurality of the strips of the impregnated tape in a fixed stop matched die mold, and curing for 40 minutes at 93°C. With minimal pressure, 80 minutes at 93°C, at a pressure of 100 psi, and 150 minutes at 200°C at a pressure of 100 psi, cooling the resulting bars to room temperature, trimming the same, and cementing tabs to the ends of the bars for use in an Intron tester. Twelve plies of the tensile test bars, and 24 plies of the tape were utilized in the interlaminar shear strength test bars. The resinous matrix material used in the formation of the composites was provided as a solventless system which contained 100 parts by weight epoxy resin and 88 parts by weight of anhydride curing agent. The tensile strength and the horizontal interlaminar shear strength of the resulting composites were determined. The tensile strength was determined employing a modified ASTM D638 procedure utilizing fiberglass tabs to avoid clamp damage. Precise alignment of the bars was obtained prior to setting the clamps. The horizontal interlaminar shear strength of the composite was determined by short beam testing of the fiber reinforced composite according to the procedure of ASTM D2344-65T as modified for straight bar testing with a 4:1 span to depth ratio.

EXAMPLE I

The acrylonitrile homopolymer tape having a double faced 8 float filling sateen weave construction as illustrated in FIG. 1 was employed. Representative warp ends are identified at A and representative weft picks at B. The weft pick was formed from approximately 100 continuous filaments of acrylonitrile homopolymer having a total denier of about 200 and a twist of 0.5 turns per inch. The weft pick was provided at a frequency of 2 picks per inch of tape. The counter for the weave was one. The weave pattern for the tape is illustrated in FIG. 2. The appearance of a number within a box of the weave pattern indicates that the corresponding warp end is present upon the surface of the woven tape. The absence of a number within a box of the weave pattern indicates that a weft pick is present upon the surface of the woven tape. A plain weave construction was employed when the weft pick traversed the pair of warp ends adjacent each edge of the tape.

Following stabilization (i.e. preoxidation) the tape width had decreased to 2.8 inches. Following carbonization and graphitization the width of the tape had decreased to 2.4 inches. The average single filament tensile properties (20 breaks tested) of the warp ends following graphitization and prior to surface treatment were 10 grams per denier tenacity, and 3,250 grams per denier Young's modulus. The resulting composites exhibited an average tensile strength of 70,000 psi, and an average horizontal interlaminar shear strength of 7,300 psi.

EXAMPLE II

The acrylonitrile homopolymer tape having a double faced 8 float filling sateen weave construction as illustrated in FIG. 3 was employed. Representative warp ends are identified at A and representative weft picks at B. The weft pick was formed from approximately 100 continuous filaments of acrylonitrile homopolymer having a total denier of about 200 and a twist of 0.5 turns per inch. The weft pick was provided at a frequency of 2 picks per inch of tape.

The counter for the weave was one. The weave pattern for the tape is illustrated in FIG. 4. The appearance of a number within a box of the weave pattern indicates that the corresponding warp end is present upon the surface of the woven tape. The absence of a number within a box of the weave pattern indicates that a weft pick is present upon the surface of the woven tape. A plain weave construction was employed when the weft pick traversed the pair of warp ends adjacent each edge of the tape.

Following stabilization (i.e. preoxidation) the tape width had decreased to approximately 2.9 inches. Following carbonization and graphitization the width of the tape had decreased to approximately 2.5 inches. The average single filament tensile properties (20 breaks tested) of the warp ends following graphitization and prior to surface treatment were 10.2 grams per denier tenacity, and 3,200 grams per denier Young's modulus. The resulting composites exhibited an average tensile strength of 95,000 psi, and an average horizontal interlaminar shear strength of 8,700 psi.

EXAMPLE III

The acrylonitrile homopolymer tape having a double faced 8 float filling sateen weave construction similar to that illustrated in FIG. 3 was employed. The weft pick was formed from approximately 200 continuous filaments of acrylonitrile homopolymer having a total denier of about 400 and a twist of 4.5 turns per inch. The weft pick was provided at a frequency of 6 picks per inch of tape.

The counter for the weave was one. The weave pattern for the tape is illustrated in FIG. 4. The appearance of a number within a box of the weave pattern indicates that the corresponding warp end is present upon the surface of the woven tape. The absence of a number within a box of the weave pattern indicates that a weft pick is present upon the surface of the woven tape. A plain weave construction was employed when the weft pick traversed the pair of warp ends adjacent each edge of the tape.

Following stabilization (i.e. preoxidation) the tape width had decreased to 2.9 inches. Following carbon-
The acrylonitrile homopolymer tape having a double faced 16 float filling sateen weave construction as illustrated in FIG. 5 was employed. Representative warp ends are identified at A and representative weft picks at B. The weft pick was formed from approximately 100 continuous filaments of acrylonitrile homopolymer having a total denier of about 200 and a twist of 0.5 turn per inch. The weft pick was provided at a frequency of 4 picks per inch of tape. The count for the weave was one. The weave pattern for the tape is illustrated in FIG. 6. The appearance of a number within a box of the weave pattern indicates that the corresponding warp end is present upon the surface of the woven tape. The absence of a number within a box of the weave pattern indicates that a weft pick is present upon the surface of the woven tape. A plain weave construction was employed when the weft pick traversed the pair of warp ends adjacent each edge of the tape.

Following stabilization (i.e. preoxidation) the tape width had decreased to approximately 2.9 inches. Following carbonization and graphitization the width of the tape had decreased to approximately 2.5 inches. The average single filament tensile properties (20 breaks tested) of the warp ends following graphitization and prior to surface treatment were 10 grams per denier tenacity, and 3,309 grams per denier Young’s modulus. The resulting composites exhibited an average tensile strength of 105,000 psi, and an average horizontal interlamellar shear strength of 8,400 psi.

For comparative purposes an acrylonitrile homopolymer tape employing identical warp ends was processed as heretofore described in the absence of any form of weaving. More specifically, the warp ends were maintained in parallel in the form of a flat tape which lacked a weft pick interlaced therewith. The average single filament tensile properties (20 breaks tested) of the warp ends following graphitization and prior to surface treatment were 11.5 grams per denier tenacity, and 3,200 grams per denier Young’s modulus. The resulting composites exhibited an average tensile strength of 90,000 psi, and an average horizontal interlamellar shear strength of 8,800 psi. A comparison of the composite properties indicates that the presence of the weft pick within composites reinforced by carbonized sateen tapes formed in accordance with the present process results in no substantial diminution of composite properties. Additionally, the present process offers significant fiber handling advantages.

For comparative purposes a woven acrylonitrile homopolymer tape was formed in a plain weave construction and processed as heretofore described. The warp ends were in adjoining contact throughout the process. The weave construction is illustrated in FIG. 7. Representative warp ends are identified at A and representative weft picks at B. The weft pick was formed from approximately 200 continuous filaments of acrylonitrile homopolymer having a total denier of about 400 and a twist of 4.5 turns per inch. The weft pick was provided at a frequency of 2 picks per inch of tape. The counter for the weave was one. The weave pattern for the tape is illustrated in FIG. 8. The appearance of a number within a box of the weave pattern indicates that the corresponding warp end is present upon the surface of the woven tape. The absence of a number within a box of the weave pattern indicates that a weft pick is present upon the surface of the woven tape. Following stabilization (i.e. preoxidation) the tape width had decreased to 3.15 inches. Following carbonization and graphitization the width of the tape had decreased to 2.4 inches. The average single filament tensile properties (20 breaks tested) of the warp ends following graphitization and prior to surface treatment were 8.6 grams per denier tenacity, and 3,300 grams per denier Young’s modulus. The resulting composite exhibited an average tensile strength of 46,000 psi, and an average horizontal interlamellar shear strength of 7,200 psi. A comparison of composite properties indicates a substantial diminution of composite properties results when the reinforcing tape is formed in the plain weave construction.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. In a process for the simultaneous conversion of a plurality of adjoining ends of a multifilament acrylic fibrous material capable of undergoing conversion to a carbonaceous fibrous material selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer containing at least about 85 mol per cent of acrylonitrile units and up to about 15 mol per cent of one or more monovinyl units copolymerized therewith, while in the form of a tape to a carbonaceous fibrous material wherein said ends are continuously passed in the direction of their length through a series of heating zones while substantially suspended therein to form a fibrous product which contains at least 90 per cent carbon by weight, the improvement which comprises providing said fibrous material during at least the stabilization portion of the said conversion process in the form of a tape of sateen weave construction consisting of at least 32 adjoining substantially parallel linear multifilament warp ends of fibrous material essentially coextensive with the width of said tape and a weft pick which initially is provided prior to stabilization as a multifilament acrylic yarn having a total denier below about 400 interlaced therewith at a plurality of points capable of maintaining and substantially parallel relationship of said warp ends which substantially floats at least 4 of said warp ends prior to each additional interlacing point in the main body of said tape as said warp ends are traversed, said weft pick being provided under a tension sufficient that said linear configuration of said warp ends is substantially unimpaired and at a frequency of about 0.1 to 8 picks per inch of said tape.
2. An improved process according to claim 1 wherein said warp ends are an acrylonitrile homopolymer.
3. An improved process according to claim 1 wherein the composition of said weft pick is substantially identical to that of said warp ends.
4. An improved process according to claim 1 wherein said fibrous material is provided in the form of said tape of sateen weave construction while being passed through a stabilization zone and a carbonization zone.
5. An improved process according to claim 1 wherein said fibrous material is provided in the form of said tape of sateen weave construction while being passed through a stabilization zone, a carbonization zone, and a graphitization zone.
6. An improved process according to claim 1 wherein said fibrous material is provided in the form of said tape of sateen weave construction while being passed through a stabilization zone, a carbonization zone, and a surface treatment zone.
7. An improved process according to claim 1 wherein said warp ends are continuous multilament yarns exhibiting a twist of about 0.1 to 5 turns per inch.
8. An improved process according to claim 7 wherein said weft pick possesses a twist of about 0.5 turn per inch.
9. An improved process according to claim 1 wherein said tape of sateen weave construction includes 32 to 500 adjoining substantially parallel linear warp ends.
10. An improved process according to claim 1 wherein the total denier of said weft pick is equal to or less than that of each of said warp ends.
11. An improved process according to claim 1 wherein said weft pick possesses a twist of about 0.1 to 3 turns per inch.
12. An improved process according to claim 1 wherein said weft pick substantially floats from about 4 to 16 of said warp ends prior to each additional interlacing point in the main body of said tape as said warp ends are traversed.
13. An improved process according to claim 1 wherein said weft pick is provided at a frequency of about 1 to 3 picks per inch of said tape.

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