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(54) **Carbonaceous fibers with spring-like reversible deflection and method of manufacture.**

(57) A unique partially carbonized or substantially completely carbonized, resilient, fiber, yarn or fiber tow having a spring-like structural configuration and a reversible deflection of greater than 1.2:1 is prepared from a carbonaceous precurser materials which is stabilized and then heat treated to a temperature sufficient to impart a spring-like structural configuration to the fiber. Such fibers, yarn or fiber tow is optionally knitted or woven into a cloth which can then be deknitted and carded, garnetted or otherwise defibrilated to produce a resilient web-like fluff or wool-like material having the spring-like structural configuration. Electrical conductivity and a fused benzoidal structural configuration to the surface of the fiber, can optionally be obtained by carbonization of the fibers at a temperature of up to 3000°C at any stage after the spring-like structural configuration is set in the fiber.

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CARBONACEOUS FIBERS WITH SPRING-LIKE REVERSIBLE DEFLECTION AND METHOD OF MANUFACTURE

The invention resides in a resilient fiber or fiber assembly derived from a stabilized carbonaceous precursor material having imparted thereto a spring-like structural configuration capable of reversible deflection of greater than about 1.2 times the length of the fiber when in a relaxed condition.

The carbonaceous fiber of the present invention is provided with a substantially permanent, non-linear, resilient, elongatable, spring-like structural configuration, e.g. of a substantial coil-like, sinusoidal or other multi-curvilinear configuration having no sharp or acute angular bends in the fiber. The spring-like structural configuration and the resilient, elongatable, characteristics of the fiber allows for a dimensional change of the fiber from a relaxed condition (ie. spring-like configuration) to an elongated, stretched, and substantially linear state, or any degree there-in-between, in which the fiber is under tension. When placed under tension, the fiber can be extended at least 1.2 times, typically from 2 to 4 times, the length of the fiber in its relaxed non-deflected spring-like configuration. The spring-like fiber can thus be deflected (elongated or stretched) to a substantially linear shape or configuration. If the modulus of elasticity of the fiber per se is not approached or exceeded, that is to say the fiber is not put under tension beyond that necessary to straighten the fiber to a substantially linear shape, the fiber is capable of returning from the linear to its relaxed spring-like shape over many cycles of stress elongation and relaxation without either breaking or substantially altering the dimensions or physical structure of the fiber.

The prior art has generally taught the manufacture of filaments from pitch based (petroleum and/or coal tar) compositions by the conventional technique of melt spinning the composition into continuous filaments which can then be stabilized by oxidation. Such filaments are taught to be useful per se. Alternatively, the continuous filament may be chopped or stretch-broken into what the art refers to as a "staple" fiber. Such "staple" fiber can be converted into a yarn by drafting, drawing and/or twisting, (referred to as spinning in the industry). The continuous filaments can also be made into a tow formed from a plurality of continuous mono-filaments. The resulting yarn or threads are used per se or may be woven into cloth-like articles and used as such. Alternatively, a woven article may be carbonized to produce a graphite or graphite-like cloth. In addition, a tow per se, may be carbonized, without weaving the tow into a cloth, and thereafter used as a reinforcement material for synthetic resinous materials e.g. "pre-preg", and the like.

In a somewhat similar manner it has been taught that polyacrylonitrile (PAN) can be wet spun into filaments; the filaments assembled into filament tow; the filaments or tow stabilized by oxidation; the filaments or tow made into staple by chopping or stretch breaking; the staple spun into yarn; the yarn knitted or woven into a cloth or fabric; and, if desired, the resulting fabric carbonized at a temperature of greater than 1400°C. These materials, in their pre-carbonized woven state, have been used as a non-combustible reinforcing material for metallized fire fighting suits. In their unwoven carbonized form, these materials have also been used as a reinforcement material for synthetic resinous materials such as golf club shafts, and the like.

In preparing uncarbonized conventional polymeric textile yarns for knitting, weaving or other textile manufacture, it is the usual practice in the industry to pinch crimp a fiber tow and thus sharply crimp-set the individual fibers of the tow (placing sharp or acute angular bends into the fiber). Such textile treatment has the same effect if used on a stabilized carbonaceous precursor yarn or tow, i.e. severe and sharp angular crimps are imparted to the yarn causing entanglement among the individual fibers of the yarn and thus assisting in maintaining or fixing the short staple fibers in the yarn as well as imparting bulk properties to the yarn. However, when the procedure for the manufacture of ordinary textile yarn is followed and a yarn made from a carbonaceous precursor material is crimped and then carbonized, usually at a temperature above about 1000°C and, more practically, at a temperature of 1400°C and above, the resulting carbonized yarn becomes very brittle. That is to say, the yarn cannot be harshly handled or sharply creased, e.g. knitted or woven unless the knitting or weaving is done with great care and under highly controlled processing conditions. By the same token, such a knitted or woven yarn cannot be readily deknitted, garnetted or carded without breaking the fibers in the yarn into small segments. As a result of such brittleness, a knitted fabric cannot be deknitted without special care and such a deknitted yarn cannot thereafter be carded to convert the fibers in the yarn into a wool-like fluffy material without causing severe destruction, i.e. breakage, of the fibers. The resulting short and broken fibers do not have sufficient length or crimp to produce a well entangled fluff.

The prior art also generally discloses carbonized filaments having a high tensile strength or a high surface area. Such filaments are of a highly "graphitic" nature and necessitate the utilization of high temperatures to obtain a high degree of carbonization. However, the filaments produced by such a high temperature treatment are very brittle and incapable of standing up to stress such as repeated bending of the filaments, particularly when they have been subjected to a temperature above about 1000°C, and more so when they have been subjected to a temperature of above about 1400°C. Exemplary of a high temperature treatment of filaments derived from stabilized mesophase pitch can be found in U.S. Patent No. 4,005,183 where the oxidation stabilized (at a temperature of from 250° to 400°C) fibers are made into a yarn having a low (below normal absorptive carbon) surface area and a Young's modulus within the range of from 1 to 55 million psi (7 - 380 GPa).

Another technique for making a fabric panel is described in U.S. Patent No. 4,341,830 in which a tow of acrylic filaments is oxidized under tension, at a temperature of from 200° to 300°C, crimped in a stuffer box (thus imparting a pinch type crimp), made into staple fibers, spun into a yarn which is then knitted into a cloth panel and heat treated, ie. carbonized, in an inert atmosphere at a temperature of 1400°C. The so carbonized cloth panels are assembled into a stack and the stack placed into a carbon vapor furnace for deposition of carbon onto and into the stack. This treatment is carried out by passing a carbonaceous gas, i.e. methane, through the stack while inductively heating the stack to a temperature of 2000°C to cause carbon to be deposited onto and into the stack and thus produce a carbonaceous body having a matrix of the knitted panels. However, the yarn made by this process has been found, by Comparative Example A, to be very brittle and cannot be subjected to repeated acute angular stress bending, such as would occur if the cloth panel were deknitted and carded, without severe breakage of the fibers.

Definitions

The term "fiber" or "filament" interchangeably refers to a fine threadlike body or structure of a natural or synthetic material in the conventional usage. Included herein are filaments made by melt spinning a pitch based composition such as petroleum or coal tar, or fibers which are made by wet spinning a synthetic resinous material such as polyacrylonitrile.

The term "fiber assembly" as used herein refers to a multiplicity of filaments commonly referred to in the textile industry as a tow or yarn. Fiber assemblies are made of common polymeric textile fibers or filaments, but are also applicable to carbonaceous fibers or filaments which have been stablized and treated in accordance with the following teaching and examples.

The term "spring-like", "spring-like structure", or "spring-like structural configuration" are interchangeably used herein to designate a fiber, yarn or tow that is physically deformed from a substantially linear configuration into a coil-like, sinusoidal, or other multi-curvilinear form or configuration having no acute angular bends.

The term "tow" herein refers to an assembly of a plurality of continuous filaments in which the number of filaments are identified by the designation nK wherein n is a numerical value in increments of 1000 filaments.

The term "staple" refers to a non-continuous strand of threads or fibers which may be "spun" (drafted, drawn and/or twisted) into yarns or threads which are used in the textile industry in forming woven and/or knitted articles.

The term "stabilized" herein applies to fibers or tows which have been oxidized at a specific temperature, typically less than about 250°C for PAN fibers, provided it is understood that in some instances the fibers are oxidized by chemical oxidants at lower temperatures.

The term "yarn" herein applies to a continuous strand of twisted filaments, threads or fibers. The term "spun yarn" refers to continuous strands of staple fibers which have been drafted, drawn and/or twisted into threads or yarns.

The term "carding" herein refers to a pro- cedure in which a yarn is combed or brushed with a toothed apparatus, e.g. a wire tooth brush, to effect at least a partial alignment of the staple fibers into an entangled web or sliver.

The term "garnetted" herein refers to a process for reducing various textile waste materials to fiber by passing them through a machine called a garnett, which is similar to a card.

The term "knitting" herein includes single Jersey knit, Rib knit, Pearl knit, Interlock knit, Double knit, and similar methods of knitting a fiber, yarn or tow into a cloth.

The term "reversible deflection" or "working deflection" is used herein as it applies to a helical or sinusoidal compression spring. Particular reference is made to the publication "Mechanical Design - Theory and Practice", MacMillan Publ. Co., 1975, pp 719 to 748; particularly Section 14-2, pages 721-24.

"Hooke's Law" herein refers to the stress applied to stretch or compress a body which is proportional to the strain or alteration in length so provided, as long as the limit of elasticity is not exceeded.

Carbonaceous precursor starting materials which have the capability of forming the spring-like structural configuration fiber of the invention are selected from starting materials such as pitch (petroleum or coal tar), polyacetylene, polyacrylonitrile (PANOX or GRAFIL), polyphenylene, SARAN (Trade Mark), and the like. The carbonaceous precursor material should have some degree of skeletal orientation, i.e. have substantial concentrations of oriented, fused, benzenoid structural moieties or moieties which are capable of conversion, on heating, to fused benzenoid or equivalent skeletal orientation at or near the surface.

Preferred precursor materials are prepared by melt spinning or wet spinning in a manner to yield a monofilament or multi-filament assembly. The filaments are stabilized by oxidation or dehydrochlorination and then converted into a yarn, tow, or a woven cloth or knitted cloth by any of a number of commercially available techniques.

According to a first aspect of the present invention, there is provided an article derived from a stabilized, carbonaceous precursor material, said article comprising a partially carbonized or substantially completely carbonized fiber and being characterised in that the fiber has a spring-like structural configuration with a reversible deflection ratio of greater than about 1.2:1. Usually the fiber has a diameter of 4 to 20 micrometers.

According to a second aspect of the present invention, there is provided a method of forming a fiber with reversible deflection from a stabilized, carbonaceous precursor material, comprising the steps of imparting a spring-like shape to the stabilized fiber, heating the fiber having said spring-like shape in a relaxed state under non-oxidizing conditions and at a temperature sufficient to impart a temporary setting of a spring-like structural configuration to the fiber, and/or heating the fiber having said spring-like shape in a relaxed state under non-oxidizing conditions to a temperature sufficient to impart a permanent setting of a spring-like structural configuration to the fiber.

In accordance with the present invention a unique article is prepared from such a carbonaceous precursor material which is made into a fiber, yarn or tow of fibers, stabilized and then provided with a spring-like structural configuration, imparting to the fiber flexible, resilient, elongatable and deflectable characteristics, without altering the spring-like configuration of the fiber over many cycles of elongation and contraction. Fibers made from PAN are generally oxidation stabilized at a temperature of from 200°C to 250°C and typically have a nominal diameter of from 10 to 20 micrometers. Fibers made from mesophase pitches are oxidation stabilized at a temperature of from 250° to 400°C, preferably at a temperature of from 300° to 390°C, as described in U.S. Patent No. 4005183. Fibers made from SARAN (Trade Mark) are stabilized by dehydrochlorination in which the SARAN fiber loses its thermoplastic nature and begins to take on a thermoset-like behavior. It will be understood that fibers having a somewhat larger diameter of, for example, 30 micrometers may be employed where stiffer fibers are desired, depending upon the particular end use to which such heavier and stiffer fibers are to be applied.

A multiplicity of continuous fibers are associated into a tow which is then stabilized by oxidation in conventional manner. The stabilized tow (or staple yarn made from chopped or stretch-broken fiber staple) is thereafter, and in accordance with the present invention, formed into a coil-like structural configuration as, for example, by winding the tow on a cylindrical rod or mandrel, or is formed into a sinusoidal form or other multi-curvilinear form by knitting the tow or yarn into a fabric or cloth (recognizing that other fabric forming and coil forming methods can be employed). It is convenient to form the sinusoidal structure on a standard textile knitting machine (e.g. Flat bed knitting machine, or a tubular knitting machine) or in a rounded tooth gear-box that will not impart any sharp or acute angular bends to the fibers. The coil-like or sinusoidally shaped fiber, tow or the knitted cloth is thereafter heat treated at a temperature of from 150°C to 1550°C. At a temperature of above about 250°C, the fiber, tow or cloth is heat treated in an inert atmosphere. If the desired end product requires subsequent mechanical treatment, ie. carding or deknitting of the fabric, it is preferable to subject the fiber, tow or cloth to a temperature below about 550°C in an inert atmosphere.

At a temperature of from 150°C to 550°C, the fibers are provided with a temporary set and have not yet acquired the high degree of brittleness associated with "graphite" fibers. However, when the fibers are initally treated in the upper range of temperatures of from 550°C to 1550°C, the fibers are, ab initio, provided with a permanent set. Such permanent set is accompanied by some degree of orientation and brittleness which can lead to breakage of some fibers during subsequent treatment of the fibers, particularily if the treatment is carried out with short staple fibers which are highly entangled. It has been found that when the spring-like fiber is formed from continuous filaments, temperatures as high as 1550°C can be used since the filaments are not entangled with one another (as in a staple fiber or yarn) and the mechanical treatment necessary to prepare a wool-like fluff is not as severe in the separation of such continuous filaments.

It is especially critical that, if a spring- like configuration is imparted to the fiber or fiber tow by a rounded gear tooth crimp or by wrapping around a rod or mandrel, the fiber not be heated to a temperature above about 275°C, while under tension. Above this temperature, the fiber begins to loose weight and shrink in coilure diameter and the tension resulting from such shrinkage and weight loss causes nonannealable stress cracks and weak points in the fiber.

It is of course to be understood that the fiber, tow or yarn may be initially heat treated at the higher temperature range (550°C-1000°C for knitted fabric of staple yarn and up to 1550°C for knitted fabric made of continuous filament tows) so long as the heat treatment is conducted while the fiber is in a relaxed state (spring-like configuration) under an inert, non-oxidizing atmosphere. As a result of the higher temperature treatment, a permanent set spring-like structural configuration is imparted to the fiber. The resulting fibers, tow or yarn having such spring- like structural configuration may be used per se, or in the case of a knitted cloth, may be deknitted to form a sinusoidal or other multi-curvilinear yarn or tow. In either event the yarn, tow or the cloth per se may then be further subjected to a carding or garnetting operation or any of a number of other methods of mechanical treatment known in the art to create an entangled wool-like fluffy material in which, the fibers are separated into an entangled mass of fibers and in which the individual fibers retain their spring-like configuration.

For certain applications, it is preferred that the fibers of the invention have a density of less than 2.5 gm/cm^3 and/or a Young's modulus of from 7 to 380 GPa.

The fibers, tow, or yarn, or the knitted cloth or the wool-like fluff produced by a heat treatment at a temperature of no higher than about 550°C, in a relaxed state (which has placed a temporary set spring-like configuration into the fibers, yarn, tow or thread) may then be further heat treated in a relaxed state and under a non-oxidizing atmosphere to a temperature of from 550°C to 1500°C to impart not a permanent set, spring-like structural configuration to the fiber. At a temperature above 1550°C and up to about 3000°C, various lower degrees of electrical resistivity are imparted to the fibers, such resistivity being preferably less than about 10^{10} ohm-cm. A fused conjugated (benzenoidal) structural configuration is imparted to the fibers, at least at their outer surface, due to the heat treatment of the fibers at these higher temperatures. A more extensive developement of the fused benzoidal structure occurs as the heat treatment is carried out at the higher temperatures, particularily at a temperature of from 1000-1550°C. In the case of PAN fibers, the diameter of the fibers is reduced when treated at a higher temperature up to about 1550°C. Although higher temperature treatment results in a gradually increasing brittleness, the fibers still retain their spring-like configuration. The carbonaceous precursor materials are of a nature believed to lose their non-carbon moieties upon heating and form a conjugated bond structure within the carbon to carbon backbones which are believed to convert to an aromatic, fused, ring-like form of the graphitic nature carbons.

Preferably, when the spring-like structural configuration in the fiber is formed by knitting a staple spun yarn into a cloth, the knitted cloth is not heated to a temperature above 1000°C, preferably not above 550°C, prior to carding when a wool- like fluffy material is desired in order to avoid fiber breakage, since at temperatures much above about 1000°C, the fibers become too brittle to survive the mechanical forces of disentanglement necesssary to produce the wool-like fluffy material. However, with careful handling and with improved handling techniques, brittle fibers produced at the higher temperatures of above 1000°C may still be useful as, for example, a structural reinforcement material for various synthetic resinous materials, as a filler material for rendering synthetic resinous materials antistatic, as electrical conductors (e.g. automobile ignition systems), as a thermal insulating material, or the like.

While it is desirable to limit the heat treatment of the staple yarns and threads during for mation of the spring-like structural configuration as noted above if further mechanical treatment is proposed, the same is not as critical when continuous filament tows are to be formed into the spring-like structural configuration. Thus, continuous filaments may be heat treated to a temperature of about 1550°C and still be carded to prepare a wool-like fluffy product.

The stabilized fibers, yarn or tow, when heat-set into the desired spring-like structural configuration, e.g. by knitting, and thereafter heating at a temperature of from 550°C to 1550°C retain their resilient and reversible, deflectable characteristics in accordance with Hooke's Law. If the yarn or tow has been knitted and heat treated at a temperature between 550°C. and 1000°C to "perm-set" the spring-like configuration in the yarn or tow, it may then be de-knitted, carded, garnetted or otherwise mechanically treated to convert the deknitted yarn or tow to an entangled wool-like fluffy material which still retains a resilience similar to that found in wool.

A predetermined length of fiber, yarn or tow made into a spring-like structural configuration in accordance with the above described manner will exhibit a reversible deflection in excess of 1.2 times, generally greater than twice, of its relaxed, non-elongated, spring-like configuration. Stated another way a fiber, yarn or tow which has been provided with a permanently set spring-like configuration can be stretched or elongated to a length of at least 1.2 times of its coiled, i.e. contracted, relaxed spring-like structural configuration length. By controlling the structural configuration, e.g. by controlling the knitting parameters such as the number of loops per unit length or the number of turns on a rod or mandrel, it is of course understood that a greater extension or elongation of the spring-like fiber, yarn or tow is possible. The tightness or looseness of the non-linear, coil or curl in the fiber, e.g. the loops per centimeter in a knitted cloth, therefor governs the extent of the elongation of the spring-like fiber, yarn or tow. Thus, the reversible deflection could be much greater than twice the length of a fiber yarn or tow when in a relaxed state, spring-like configuration.

In a preferred embodiment, an assembly, e.g. a bundle of fibers is obtained, by spinning a carbonaceous precursor material into a fiber, stabilizing the fiber assembling a multiplicity of mono-filaments or fibers into a tow, and knitting the tow into a cloth. After knitting, the fibers in the cloth are "set", i.e. temporarily formed into a coil-like or sinusoidal structure, by treating the knitted cloth at a temperature of from 150°C to 550°C. Preferably, the fibers in the knitted cloth are formed into a permanently set, spring-like structure at a temperature of from 550°C to 1550°C and most preferably at a temperature of less than 100°C, under an inert atmosphere and in a relaxed condition. The fibers in the knitted cloth may then be carbonized at a temperature in excess of 1000°C to impart other desirable properties into the fibers, noted hereinabove.

Likewise, if a wool-like fluff is desired, the fiber tow having the spring-likle configuration or even the knitted fabric, may be carded, garnetted, or otherwise mechanically treated either before or after treatment at a temperature of less than 1550°C, preferably less than 1000°C., and most preferably at a temperature of below about 650°C, when preparing a wool-like, fluffy material. If a higher electrical conductivity in a fiber is desired, the perm set (550 to 1000°C) fiber, tow or cloth can be further heat treated to a temperature above 1000°C, e.g. up to 3000°C. As previously noted, fibers treated at a temperature above 1550°C become extremely brittle and do not readily lend themselves to a deknitting, carding or garnetting treatment. Accordingly, such carding and/or garnetting treatment should be accomplished prior to heat treatment to temperatures above 1000°C for staple yarn, tows, or threads and prior to heat-treatment to a temperature of up to 1550°C for continuous fiber or fiber tows.

Fibers made from carbonaceous precursor materials normally have a surface area of from 0.5 to 1600 m^2/gm, preferably less than 15m^2/gm when produced according to the procedures set forth above. However, it is known that such fibers can have imparted to them a surface area of greater than this by rapidly heating the fibers to a high temperature thereby converting the non-carbon moieties to gases which, on leaving the fiber, disrupt the surface. Other techniques known in the art for producing high surface area, high porousity fibers include oxidation of the fiber surface. Such high porousity fibers can be prepared from the materials of the present invention by the same techniques after the spring-like structural configuration has been imparted into the fibers.

It is also to be understood that after formation of the spring-like structural configuration into the fiber, the continuous fibers or the yarns or threads of staple fiber may be chopped into discrete lengths and made in to non-woven products employing present day techniques for preparing such non-woven products.

Exemplary of the products which can be produced by the technique of the present invention are set forth in the following examples:

<u>Example 1</u>

An oxidation (at a temperature of about 250°C) stabilized polyacrylonitrile PANOX (R.K. Textiles) continuous 3K or 6K tow (ie. 3000 - 6000 fibers per tow) having nominal single fiber diameters of 12 micrometers, was knitted on a flat bed knitting machine into a cloth having from 3 to 4 loops per centimeter. Portions of this cloth were heat set at the temperatures set forth in Table I over a 6 hour period and under an inert atmosphere of nitrogen. When the cloth was deknitted, it produced a tow which had an elongation or reversible deflection ratio of greater than 2:1. The deknitted tow was cut into various lengths of from 5 to 25 cm, and fed into a Platts Shirley Analyzer. The fibers of the tow were separated by a carding treatment into a wool-like fluff, that is to say, the resulting product resembled an entangled wool-like mass or fluff in which the fibers had a high interstitial spacing and a high degree of interlocking as a result of the coiled and spring-like configuration of the fibers. The fiber lengths of each such treatment were measured and the results of these measurements set forth in Table I.

TABLE I

Run #	Fiber Staple Length (cm)	Heat Treatment °C	Stitches/ cm	Tow Size	Range of Fiber Lengths (cm)	Length of majority of Fibers (cm)
1	15	550	4	3K	4 - 15	13 - 15
2	5	550	4	3K	2.5 - 5	2.5 - 5
3	10	650	3	6K	5 - 10	7.5 - 10
4	10	950	3	6K	4 - 9.5	7.5 - 9.5
5	20	750	3	6K	7.5 - 19	15 - 19
6	25	950	4	6K	7.5 - 23	19 - 23

Example 2

A fabric was knitted from a 3K or 6K PANOX (R.K. Textiles) continuous stabilized filament tow on a Singer flat bed knitting machine and heat treated at the temperatures set forth in Table II and under an inert atmosphere of nitrogen. The fabric was then deknitted and the tow having a spring-like structural configuration fed directly into a carding machine. The resulting wool-like mass was collected onto a rotating drum and had sufficient integrity to enable it to be easily handled. The length of the fibers ranged from 2 to 15 cm. The wool-like mass treated at a temperature of 950°C was highly conductive and had a resistance of less than 75 ohms at any probe length taken at widely separated distances up to 60 cm in the wool-like mass.

TABLE II

Run #	Fiber Staple Length (cm)	Heat Treatment °C	Stitches/cm	Tow Size	Range of Fiber Lengths (cm)
1	7.5	550	4	3K	2.5 - 7.5
2	10	650	3	6K	2.5 - 10
3	15	650	3	6K	2.5 - 13
4	20	950	3	6K	2 - 15
5	25	950	3	6K	2 - 12.5

Example 3

A 3K PANOX stabilized tow was knitted on a Singer flat bed knitting machine at a rate of 4 stitches/cm and was then heat treated at a temperature of 950°C and under an inert atmosphere of nitrogen. The cloth was deknitted and the tow (which had a coil elongation or reversible deflection ratio of greater than 2:1) cut into 7.5 cm lengths. The cut yarn was then carded on a Platt Minature Carding machine to produce a wool-like fluff having fibers ranging from 3.5 to 6.5 cm in length with an average length of about 5 cm. The wool-like fluff had a high electrical conductivity over any length of up to 60 cm tested.

Example 4

In a similar manner to Example 3 a portion from the same knitted cloth was heat treated at a temperature of 1550°C and under an inert atmosphere of nitrogen. The cloth itself and the deknitted tow had a very high electrical conductivity. On carding 15 cm lengths of cut tow, a fluff was obtained which had fibers of lengths 2.5 to 9.5 cm with average lengths of 5 cm. Thus, carding of a deknitted, continuous filament tow, fabric which has been subjected to a temperature of above 1000°C is still capable of producing a wool-like fluffy product.

Comparative Example A

A staple 2 ply singles 10's stabilized polyacrylonitrile PANOX yarn was knitted into a tubular sock at a rate of 4 loops per cm and thereafter heat treated at a temperature of 1550°C under an inert atmosphere of nitrogen and the yarn was then cut into 10 cm lengths. The cut yarn was carded in a carding machine. The resulting product was collected with difficulty. Only short fibers having a length of from 0.5 to 1.25 cm were obtained along with a high level of dust. The difficulty of fiber recovery resulted from the high degree of twist and fiber entanglement which is typically found in spun yarns. Similar results were obtained when this example was repeated starting with a similar spun yarn sample of Grafil-01 obtained from Hysol-Grafil Ltd., Coventry, England.

Example 5

A series of runs were made to determine the effect various heat treatment temperatures had on the fibers. A significant property was the specific resistivity of the fibers. To determine such property, numerous samples of an oxidation stabilized polyacrylonitrile yarn having a density of from 1.35 to 1.38 g/cm^3 yarn was assembled into 3K and 6K tows. The tows (identified as PANOX and manufactured by RK Textiles of

Heaton-Norris, Stockport, England), were knitted into a plain jersey flat cloth having from 3 to 4 stitches per cm, respectively. The cloth was thereafter heat treated at various temperatures under an oxygen-free nitrogen pad in an incremental heat control quartz tube furnace. The temperature of the furnace was gradually increased from room temperature to about 550°C. over a three hour period with the higher temperatures being achieved by 50°C increments every 10-15 min. The material was held at the desired temperature for about 1 hour, the furnace opened and allowed to cool while purging with nitrogen. Representative of the furnace temperatures at the above preset incremental temperature schedule is that for a 6K yarn and shown in Table III following:

TABLE III

Time	Temp. °C
0720	200
0810	270
0820	300
0830	320
0840	340
0850	360
0900	370
0905	380
0935	420
0950	450
1005	500
1010	550
1025	590
1035	650
1045	700
1100	750
1400	750

The specific resistivity of the fibers was calculated from measurements made on each sample using a measured average of six measurements, one made from fibers removed at each corner of the sample and one made from fibers removed from each edge, approximately at the middle of the sample. The results are set forth in Table IV following:

TABLE IV

Final Temp. in °C	% wt. loss	Log Specific Resistivity
500	-	4.849
550	33	-
600	-	2.010
650	34	-
700	-	-
750	37	- 1.21
850	38	- 2.02
900	42	- 2.54
950	45	- 2.84
1000	48	- 3.026
1800	51	- 3.295

The carbonized and permanently set fibers of the invention, when treated at temperatures sufficiently high to render the fibers electrically conductive and yet sufficiently low where the fibers still exhibit resilient, flexible, and non- brittle characteristics, are particularly suitable for blending with standard carpet fibers or yarn to produce a yarn having static dissipation properties. Such a carpet/yarn blend may incorporate at least 0.25 weight percent carbonized fibers in the carpet yarn. The weight ratio of synthetic carpet fibers to carbonized fibers is preferably greater than 100:1 to 200:1. A carpet employing the carbonized fibers of the invention exhibited static discharge properties to 0 percent of an applied electrostatic charge in less than 1 second.

Example 6

Monsanto 1879 nylon (trilobal) staple was blended with 0.5 percent by weight of a conductive fiber prepared in accordance with the present invention. The conductive fiber was prepared by heating an oxidatively stabilized polyacrylonitrile multifilament fiber tow which had been knitted into a cloth, heat treated at about 1500°C, de-knitted and cut into staple approximately 18 cm in length. The blended staple was carded and the resulting sliver was pin drafted three times, recombination ratios were 10:1, 3:1, and 5:1, respectively. The resulting drafted sliver was spun into a single ply yarn with an average twist of about 4.75. The majority of the carbonaceous fiber was broken into lengths much smaller than the original 18 cm lengths, resulting in a large loss of carbonaceous fiber from that originally included in the singles spinning process. The resulting carbonaceous fiber containing singles yarn was plied with a nylon yarn made in the same fashion but containing no carbonaceous fiber. The 3.00/2 ply yarn which was heat set on a Suessen heat setting apparatus was thereafter tufted into a 1/8 inch (3 mm) gauge, 27 on (765 gm), 9.5 mm pile height carpet (a cut loop form) with approximately 3 stitches per cm. The ratio of carbonaceous fiber to yarn containing no carbonaceous yarn in the tufting operation was 1:5, respectively. A portion of the carpet was backed with a commercial non-conductive latex carpet backing. The resulting carpet was tested for static discharge properties by charging the carpet to 5000 volts while in an atmosphere having a relative humidity of less than 20 percent. The static charge was dissipated to 0 percent of original charge in less than one second, and some of the samples discharged in less than 1/2 second. The standard for the industry is a discharge to 0 percent in 2 seconds or less.

This example illustrates that temperatures above about 1000°C. can be employed in heat-setting the spring-like structural configuration into the carbonaceous fiber tow, but that at temperatures above 1000°C much embrittlement occurs and the fibers resulting were inefficiently used, being lost as short fibers not incorporated into the yarn when drafted with normal carpet staple to prepare singles.

Example 7

In another example 100 grams of the same precursor acrylonitrile fiber tow as described in Example 6 was used. However, the precurser fiber was heat treated after knitting at a temperature of 950°C. All other aspects of handling the carbonaceous material were the same. The carbonized fiber was blended with 45 kg of the Monsanto 1879 nylon yarn as in Example 6. The resulting yarn contained 0.02 percent carbonized fibers which were substantially evenly distributed throughout the yarn. The yarn was tufted to prepare a carpet in a similar manner to Example 6. Thus, each tufted end has the carbonized fibers. Results were similar to the results obtained in Example 6.

Knitted yarn or fiber tows which have been heat treated to a temperature above 1000°C, and thus been rendered electrically conductive, have also found special utility in the manufacture of electrodes for a non-aqueous secondary energy storage device such as described in U.S. Application Serial No. 558,239 filed December 5, 1983, entitled Energy Storage Device by F.P. McCullough and A. F. Beale, Jr., as well as Application Serial No. 678,186 filed December 4, 1984, entitled Secondary Electrical Energy Storage Device and Electrode Therefor.

Example 8

In another experiment tows made by deknitting a flat stock cloth in which the tow was a stabilized polyacrylonitrile precursor of the indicated filament count which had been heat-set at the indicated temperatures prior to deknitting. Tow lengths were measured for resilient deflection by adding known weights to the tow portion and the intermediate and the final deformations as well as the final non-resilient elongation deflection measured. The results are set forth in Table V.

TABLE V

Sample Description	a	b	c	d	e	f	g	h	i
Heat Treat. °C.	650	650	650	650	170	300	525	1550	950
Relaxed Length (mm)	106	92	122	107	137	145	109	63	77
Weight Added (gm)	DEFLECTION (mm)								
0	0	0	0	0	0	0	0	0	0
0.275	16	33	25	31	38	55	51	22	29
0.901	54	101	75	71	69	111	131	57	81
1.526	83	140	87	98	66	116	167	82	108
2.107	99	163	116	105	66	115	187	94	119
2.468	110	172	128	115	61	116	196	104	126
2.943	119	186	133	119	60	118	201	114	132
Stretched*	216	256	208	187	98	157	249	185	276
Relaxed**	0	6	1	0	49	25	14	0	0

(a) Panox 6K tow with 0.4 twists/cm. as plain jersey with 3-4 picks/cm.

(b) Panox 3K tow with no twist, plain jersey knit with 4-5 picks/cm.

(c) Hysol-Grafil-01, 6K tow with no twist knitted as Interlock with 3 picks/cm.

(d) Grafil-01 knitted as interlock with 3 picks/cm.

(e) Panox 6K tow with 0.4 twists/cm knitted as plain jersey with 3-4 picks/cm.

(f) Panox 6K tow with 0.4 twists/cm knitted as plain jersey with 3-4 picks/cm.

(g) Panox 6K tow with 0.4 twists/cm, knitted as plain jersey with 3-4 picks/cm.

(h and i) Panox 3K tow with no twist, plain jersey knit with 4-5 picks/cm.

* Fully stretched to structure length

** All load removed coil returns to relaxed state

Comparative Example B

To illustrate the effect of tension on the fibers during setting of the spring-like configuration, a 6K tow of Panox continuous fibers was roll-wrapped onto a 8 mm quartz rod. The wound tow was heat treated according to the schedule as set forth in Example 5, Table III to a final temperature of 300°C while holding the ends of the wrapped tow secure. The heat treatment set a spring-like configuration into the tow. However, the fibers were very stiff and the tow was removed from the rod with difficulty. Many of the fibers broke on removal. This tow did not have the same resilience as tows which had been heat set in a relaxed knitted configuration. If the same procedure is employed but the spring-like tow is heated to a temperature of 350°C, much greater breakage occurs even before removal.

The latter procedure was repeated and the heat treated material (350°C) after being carefully removed from the rod, was heated while in a relaxed state slowly to about a temperature of 650°C to determine whether any annealing would occur. None did. The resultant coil was brittle and had no resiliency.

However, if the wrapped coiled tow was removed from the rod prior to reaching 275°C and a smaller diameter rod inserted to maintain the integrity of the spring-like shape, heating in this "relaxed" state resulted in a spring like tow having substantially the same properties as the aforedescribed deknitted tows and/or yarns.

CLAIMS

1. An article derived from a stabilized, carbonaceous precursor material, said article comprising a partially carbonized or substantially completely carbonized fiber and being characterised in that the fiber has a spring-like structural configuration with a reversible deflection ratio of greater than about 1.2:1.

2. An article as claimed in Claim 1, wherein the fiber has a diameter of from 4 to 20 micrometers.

3. An article as claimed in Claim 1, wherein said reversible deflection ratio is greater than 2:1.

4. An article as claimed in any one of the preceding claims, wherein said fiber has a specific electrical resistivity of less than 10^{10} ohm-cm.

5. An article as claimed in any one of the preceding claims, wherein said fiber has a density of less than 2.5 gm/cm^3, and/or a Young's modulus of from 7 GPa to 380 GPa.

6. An article as claimed in any one of the preceding claims, wherein said fiber has a surface area of from 0.5 to 1600 m^2/gm.

7. An article as claimed in Claim 6, wherein said fiber has a surface area of less than 15 m^2/gm.

8. A wool-like fluff comprising a multiplicity of fibers as claimed in any one of the preceding claims, said fibers having a specific resistivity of less than 10^{10} ohm-cm and a resistance of less than 75 ohms at a probe distance of 60 cm when measured across the wool-like fluff.

9. A method of forming a fiber with reversible deflection from a stabilized, carbonaceous precursor material, comprising the steps of imparting a spring-like shape to the stabilized fiber, heating the fiber having said spring-like shape in a relaxed state under non-oxidizing conditions and at a temperature sufficient to impart a temporary setting of a spring-like structural configuration to the fiber, and/or heating the fiber having said spring-like shape in a relaxed state under non-oxidizing conditions to a temperature sufficient to impart a permanent setting of a spring-like structural configuration to the fiber.

10. A method as claimed in Claim 9, wherein said stabilized fiber is heated to a temperature of from 150°C to 550°C to impart said temporary setting of a spring-like structural configuration to the fiber.

11. A method as claimed in Claim 9 or Claim 10, wherein said stabilized fiber is heated to a temperature of from 550°C to 1550°C to impart said permanent setting of a spring-like structural configuration to the fiber and wherein said fiber, upon deflection, conforms to Hooke's law.

12. A method as claimed in any one of Claims 9, 10 and 11, including the step of assembling the stabilized fiber into a fiber tow, imparting said spring-like structural configuration to the fiber tow, and heating the fiber tow in said relaxed condition to a temperature of from 550° to 1550°C to impart said permanent setting of a spring-like structural configuration to the fiber tow.

13. A method as claimed in Claim 11 or Claim 12, including the step of heating the permanently set fiber in a non-oxidizing atmosphere at a temperature up to 3000°C to render the fiber electrically conductive.

14. A method as claimed in any one of Claims 11 to 13, including the step of imparting said spring-like structural configuration to a stabilized fiber tow by winding the tow around a cylindrical rod or mandrel, heating the wound fiber tow to a temperature of from 150°C. to 300°C in a non-oxidizing atmosphere, unwinding the fiber tow from the cylindrical rod or mandrel, and heating the fiber tow, in a relaxed condition, and in an inert atmosphere, to said temperature of from 550° to 1550°C to form a partially carbonized or substantially completely carbonized fiber tow having a reversible deflection ratio of greater than 1.2:1.

15. A method as claimed in any one of Claims 11 to 13, including the step of imparting said spring-like shape ~~to~~ a stabilized fiber tow by knitting the tow into a cloth, heating the cloth to a temperature of from 150°C to 550°C to impart said temporary set to the fibers in the cloth, deknitting the cloth, and heating the fiber tows from the deknitted cloth to a temperature of from 550°C to 1000°C to impart a permanent setting of a spring-like structural configuration to the fiber tows.

16. A method as claimed in Claim 10, including the step of imparting said spring-like shape to the stabilized fiber tow by knitting the tow into a cloth, heating the cloth to a temperature of from 150°C to 550°C, deknitting the cloth and mechanically treating the deknitted fiber tow to form a wool-like fluff.

17. A method as claimed in Claim 16, including the step of heating the wool-like fluff at a temperature of less than 1000°C to render the fibers in the fluff electrically conductive.

18. A method as claimed in Claim 16 or Claim 17, including the step of heating the electrically conductive fiber tow to a temperature of greater than 1000°C to render the fibers more highly electrically conductive, and incorporating the electrically conductive fibers into a synthetic resinous material.

19. A method as claimed in any one of Claims 9 to 18, wherein the carbonaceous precurser material, on heating, forms fused benzenoid or equivalent skeletal orientation at or near the surface.