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(54) **NONLINEAR AROMATIC POLYAMIDE FIBER OR FIBER ASSEMBLY AND METHOD OF PREPARATION.**

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(73) Proprietor: **THE DOW CHEMICAL COMPANY**
2030 Dow Center
Abbott Road
P.O. Box 1967
Midland
Michigan 48640-1967 (US)

(72) Inventor: **MCCULLOUGH, Francis, P., Jr.**
104 Fir Drive
Lake Jackson, TX 77566 (US)
Inventor: **SNELGROVE, R., Vernon**
Route 1, Box 112
Damon, TX 77430 (US)
Inventor: **GOSWAMI, Bhuvenesh, C.**
200 Strawberry Lane
Clemson, SC 23631 (US)
Inventor: **HALL, David, M.**
855 Terrace Acres Drive
Auburn, AL 36830 (US)

(74) Representative: **Smulders, Theodorus A.H.J., Ir. et al**
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
NL-2587 BN 's-Gravenhage (NL)

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Description

The invention resides in a nonlinear fiber or fiber assembly and method of preparation according to the preamble of claims 1, 9 and 19 and known, for instance from US-A-4 756 941. The fibers are derived from aromatic polyamide precursor fibers having imparted thereto a substantially permanently set nonlinear or crimped configuration capable of a reversible deflection of greater than 1.2 times the length of the nonlinear fibers when measured at ambient temperature and which possess a percent bending strain value of less than 50. The fibers also possess improved tenacity over mechanically crimped fibers of the prior art.

The state of the art generally discloses the manufacture of fibers from polymeric compositions such as polyacrylonitrile (PAN) by the conventional technique of spinning the fibers which can then be collected into multifiber assemblies, such as tows, and can thereafter be oxidatively stabilized. Such fibers may then be subjected to a carbonizing procedure to provide the fibers with a nonlinear configuration.

The prior art also discloses linear aromatic polyamide fibers having a high tensile strength. To provide such fibers with a certain degree of electrical conductivity and a "graphitic" nature required the application of elevated temperatures to obtain a high degree of carbonization. However, the fibers produced from such a high temperature treatment are very brittle and incapable of standing up to stress, such as a repeated bending of the fibers, particularly when they have been subjected to a temperature above 700 °C.

U.S. Patent No. 4,120,914 discloses the preparation of highly crimped fibers of poly(p-phenylene terephthalamide) which, as a result of the crimping, suffer mechanical damage resulting in an appreciable decrease in fiber tenacity. The crimping is performed by a steam stuffer box crimper.

Stuffer box crimping results in the production of sharp V-type bends in the fibers such that the outer portion of the fiber bend is damaged due to a severe stress and the underside of the fiber bend is damaged due to severe compression. These sharp bends therefore are the cause of severely weakened portions in the fiber, including fibrillation. These fibers suffer an increase in bending strain, leading to unacceptable fiber breakage, especially with fibers that are relatively rigid, stiff and brittle, or that are subsequently heat treated.

In an article by Hall et al. entitled, "Effects of Excessive Crimp on the Textile Strength and Compressive Properties of Polyester Fibers," in Journal of Applied Polymer Science, Vol. 15, pp. 1539-2544 (1971), there is described the effect of forming sharp crimps in polyester fibers as well as other man-made fibers. Excessive crimping, such as is found in V-type crimps, leads to surface damage of the fibers and a reduction in tenacity and elongation properties, i.e., fiber breakage when the fiber is placed under tension.

U.S. Patent No. 4,752,514 to Windley photographically illustrates the damage to aromatic polyamide fibers resulting from stuffer box crimping.

U.S. Patent No. 4,401,588 to Turner discloses a process for making an active carbon fabric from an aramid fabric by heating the fabric to a temperature of from 850 °C to 950 °C in an inert atmosphere.

U.S. Patent No. 3,560,135 to Han discloses that heating mechanically crimped aromatic polyamide fibers to a temperature of from 257 °C to 400 °C for a time period of from 1 to 10 minutes increases their hydrolytic durability and solvent resistance. However, there is a loss in tenacity, as a result of the crimping and the presence of fibrils.

U.S. Patent No. 4,193,252 to Sheppherd et al. discloses the making of partially carbonized and carbon (graphitic) fibers from stabilized rayon. It has been found that the partially carbonized and carbonized rayon fibers do not retain their reversible deflection, easily break under tension, and lose their crimp or kinks at relatively low temperatures or under tension. More importantly, the fibers are flammable.

U.S. Patent No. 4,642,664 to Goldberg et al. discloses the use of partially carbonized aromatic polyamides for use as conductors in electrical devices. However, only linear fibers that have been heat treated to a temperature above 400 °C are disclosed in the patent.

European Patent Application No. 0199567, published October 29, 1986, entitled, "Carbonaceous Fibers with Spring-Like Reversible Deflection and Method of Manufacture," by McCullough et al., discloses nonlinear carbonaceous fibers derived from polymeric precursor fibers such as polyacrylonitrile. These fibers may be utilized to form fiber blends with the nonlinear aromatic polyamide fibers of this invention.

U.S. Patent No. 4,756,941 teaches the use of nonlinear fibers derived from a stabilized polyacrylonitrile or petroleum or coal tar spun fiber in carpet bachings in order to provide a more effective antistatic carpet. These nonlinear fibers are prepared by imparting a nonlinear configuration to the starting fiber and heating the fibers at a temperature of above 200 °C. These fibers can be blended with nylon fibers. No reference is made to a starting material consiting of aromatic polyamide fibers.

The problem underlying the present invention is the provision of nonlinear fibers having an improved tenacity over mechanically crimped fibers of the prior art. Further, the fibers of the invention are distinguishable over the carbonaceous fibers derived from polyacrylonitrile based fibers by possessing

greater relative strength and abrasion resistance. Also, fibers made from an aromatic polyamide, such as p-aramid, are liquid crystals. The term "liquid crystals" herein applies to organic compounds which are in an intermediate or mesomorphic state between a solid and a liquid.

The term "uniform diameter" when used herein relates to the diameter of the fiber as drawn prior to crimping. Although the fiber may contain minute variations, which are common during normal fiber processing operations, such slight variations can be disregarded in determining the uniformity in fiber diameter.

The term "crimp" or "crimped portions" as utilized herein, refers to nonlinear portions, kinks, bends or waviness that is imparted to the fibers. The crimped fibers of the invention include different configurations such as sinusoidal, coil-like or a combination thereof.

The term "nonlinear" as used herein applies to fibers or fiber structures that are crimped, as hereinbefore defined, but that are free of sharp V-shaped bends or fibrils.

It should be understood that the reversible deflection of a nonlinear fiber comprises two components, pseudoelongation and fiber elongation. Pseudoelongation results from an elongation of the nonlinear configuration of the fiber, while fiber elongation is the elongation to fiber break after the fiber has been made linear.

More specifically, the term "pseudoextensibility" as used herein applies to the elongation of nonlinear fibers as the result of crimps and/or false twists therein when the fiber is straightened to its linear configuration.

The sharpness of the crimp can be quantified in terms of its bending strain. The term "bending strain" as used herein is as defined in Physical Properties of Textile Fibres, W.E. Morton and J.W.S. Hearle, The Textile Institute, Manchester, 1975, pages 407-409. The percent bending strain on the fiber can be determined by the equation:

$$S = \frac{r}{R} \times 100$$

where S is the percent bending strain, r is the fiber radius and R is the radius of curvature of bend (crimp). That is, if the neutral plane remains in the center of the fiber, the maximum percentage tensile strain, which will be positive on the outside and negative on the inside of the bend, equals $^{r}/_{R}$ X 100 in a circular cross section of the fiber.

The term "carbonaceous fiber" is understood to mean that the carbon content of the original aromatic polyamide fiber has been increased as a result of an irreversible chemical reaction caused by heat treating the fiber.

It is understood that aromatic polyamide fibers can be carbonized or partially carbonized by heat treatment of the fibers at elevated temperatures and for a period of time to increase the carbon content of the fibers. That is, the fibers as disclosed in U.S. Patent No. 4,642,644 can be heat treated until they are partially carbonized or completely carbonized.

The term "stabilized" herein applies to aromatic polyamide fibers or fiber structures which are oxidized, in an oxidizing atmosphere, at a temperature of typically less than about 400 °C, preferably at a temperature of from 175 °C to 400 °C, for a period of time sufficient to oxidize the fibers. It will be understood that the fibers can be oxidized by chemical oxidants, rather than in an oxidizing atmosphere, at lower temperatures.

The fibers of the invention can be prepared from stabilized or nonstabilized aromatic polyamide precursor fibers.

The term "reversible deflection" or "working deflection" as used herein applies to a helical or sinusoidal compression spring. Particular reference is made to the publication, "Mechanical Design - Theory and Practice," MacMillan Pub. Co., 1975, pp. 719-748, particularly Section 14-2, pp. 721-724.

The terms "substantially permanently set" used herein applies to nonlinear aromatic polyamide fibers which have been heat treated under the conditions as set forth hereinafter until they are crimped and possess a degree of nonlinearity and, accordingly, a degree of resiliency and flexibility such that the fibers, when stretched to a substantially linear shape but without exceeding the tensile strength of the fibers, will revert to their original nonlinear shape once the tension on the fibers is released. The foregoing term also implies that the fibers can be stretched and released over many cycles without breaking the fibers.

The term "fiber structure" herein applies to a fiber tow comprising a multiplicity of filaments, a yarn, a multiplicity of entangled nonlinear aromatic polyamide fibers forming a shape reforming wool-like fluff, a batting, webbing or felt of nonwoven fibers, a knitted or woven cloth or fabric, or the like. More particularly, the fiber structure of the present invention, particularly when in the shape of a wool-like fluff, is lightweight, resilient, and compressible. The fluff, at ambient temperature, has good shape and volume retention and is

stable to numerous compression and unloading cycles without breakage of the fibers.

KEVLAR-29 (a trademark of E.I. du Pont de Nemours & Co.) is a p-aramid with a high tensile strength of 400,000 psi (2.758 GPa) but a moderate modulus of 9 X 10^6 psi (62 GPa) and an elongation to break of 4.0 percent.

KEVLAR-49 (a trademark of E.I. du Pont de Nemours & Co.) is a p-aramid with the same tensile strength as KEVLAR-29 but of a higher modulus of 18 X 10^6 psi (124 GPa) with an elongation to break of 2.5 percent.

It has now been found that aromatic polyamide fibers can be provided with a crimped or nonlinear configuration and without any sharp V-type bends, fibrils or other damage. The fibers of the invention do not exhibit any loss in mechanical properties and thus provide a novel fiber or fiber structure having new and unexpected properties and capabilities. In addition, crimped or nonlinear aromatic polyamide fibers of the invention provide superior loft and compression when in the form of a fluff as compared to fibers of the prior art that have been subjected to gear crimping or stuffer box crimping procedures in which the fibers are provided with sharp V-shaped bends or are otherwise damaged.

The process of the invention provides aromatic polyamide fibers, such as p-aramid, with at least a pseudoextensibility which is necessary for processing the fibers into a fabric. The resultant nonlinear fibers, when in the form of a yarn or wool-like fluff, have improved loft, bulkiness and friction without creating weak spots such as would occur with mechanically crimped fibers having sharp bends, fibrils and the like due to high gear pressure applied to the fibers by the gear crimping mechanism. Such fiber damage is generally exhibited by fibers having gouged out portions, severely compressed or stressed portions, fibrils, creased or crazed portions, and the like.

In accordance with the present invention there is provided an aromatic polyamide fiber having a crimped or nonlinear configuration, an aspect ratio of greater than 10:1, and a bending strain value of less than 50 percent as determined by the equation:

$$S = \frac{r}{R} \times 100$$

In accordance with another aspect of the invention, there is provided a fibrous structure comprising a multiplicity of aromatic polyamide fibers having a nonlinear configuration and a bending strain value of less than 50 percent as determined by the equation:

$$S = \frac{r}{R} \times 100$$

In accordance with a further aspect of the invention, there is provided a process for making nonlinear, aromatic polyamide fibers, comprising the steps of imparting a nonlinear configuration to the fibers, heating said fibers at a temperature of above 200 °C to provide said fibers with a reversible deflection ratio of greater than 1.2:1 when measured at ambient temperature and a bending strain value of less than 50 percent.

The fibers of the invention also provide for an improved tenacity over mechanically crimped fibers. The tenacity of the fibers is at least about

$$0.018 \ \frac{N.s^2}{m}$$

per 0.000111 g/m (18 g/dn), preferably from 0.018 to

$$0.025 \ \frac{N.s^2}{m}$$

per 0.000111 g/m (18 to 25 g/dn) or greater.

Fibers of the invention will maintain their reversible deflection when measured at ambient temperature. Fibers, when measured at a temperature in excess of 100 °C and up to 130 °C, still maintained their reversible deflection characteristics. However, reversible deflection of the fibers when measured at the higher temperature of 100 °C to 130 °C will depend on the particular aromatic polyamide that is selected and other physical characteristics, such as fiber diameter. The higher temperatures are those which the nonlinear fibers of the invention will commonly encounter in any washing or fiber treatment operation.

Advantageously, the fibers of the invention are substantially free of variations in fiber diameter at each bend portion thereof. In particular, the fibers have not more than a 15 percent variation, i.e. reduction, in fiber diameter over the length of the fiber.

The fibers of the present invention provide an improvement over present state of the art aromatic polyamide fibers which have been subjected to standard gear crimping or stuffer box crimping techniques. The prior crimping techniques generally result in fibrillation and/or other damage to the fiber, as mentioned herein before, at the sites of the crimp or bend as well as a substantial variation in fiber diameter of greater than 15 percent. These factors result in a weakening of the fiber and thus affect the performance of the fiber during processing and when placed in an environment where the fiber is subject to repeated bending or flexing. The loss of fiber properties becomes even more pronounced when the weakened or damaged fibers are subsequently heat treated.

Fibers that are substantially weakened at the bent portions due to conventional crimping techniques exhibit a bending strain value of greater than 50 percent. If attempts are made to decrease the bending strain value by mechanical crimping with rounded crimps, such as may be produced by a round gear tooth crimping mechanism, there is a corresponding loss in the reversible deflection ratio. Gear crimping with flat faced gears usually results in the production of fibers exhibiting greater damage, particularly fibrillation, and thus these fibers have a bending strain value which is substantially greater than 50 percent and generally as high as about 80 percent.

In accordance with another embodiment of the invention the crimped or nonlinear fibers of the invention may be blended with the carbonaceous fibers of the afore-mentioned European Patent Publication Serial No. 0199567 or with the carbonaceous fibers of U.S. Patent No. 4,868,037. The combination of carbonaceous fibers and nonlinear polyamide fibers in yarn permits the manufacture of fabrics which are resistant to chemical attack, which possesses good abrasive strength and a loft which permits the permeation of air.

It has been found that the physical characteristics of the crimped or nonlinear fibers of the invention can be better controlled than the state of the art fibers that are produced with the use of standard gear crimping or stuffer box crimping techniques, particularly where these standard techniques are applied to fibers of larger diameters or fiber tows having a larger number of fibers and/or larger diameter fibers.

The graph provided herein illustrates the improvement in tenacity and elongation of KEVLAR-29 when treated according to the invention.

According to the invention, an aromatic polyamide precursor fiber is formed into a crimped or nonlinear configuration with the fiber exhibiting a substantially uniform diameter along its length. The nonlinear precursor fiber is then heated, preferably without applying any tension or stress to the fiber, at an elevated temperature. The so-formed crimped or nonlinear fiber is thereby provided with a substantially permanent set and a reversible deflection ratio of greater than 1.2:1, preferably 2:1, when measured at ambient temperatures, a bending strain value of less than 50 percent, preferably less than 30 percent, and is free of any sharp V-shaped bends and/or fibrils.

Alternatively, the fibers can be simultaneously provided with a crimped or nonlinear configuration and heat treated at a temperature higher than 200 °C to provide the fibers with a substantially permanent set. Preferably, heat setting is conducted in a water-free atmosphere.

Specific examples of aromatic polyamides include polyparabenzamide and polyparaphenylene terephthalamide. Polyparabenzamide and their processes of preparation are disclosed in U.S. Patent Nos. 3,109,836; 3,225,011; 3,541,056; 3,542,719; 3,547,895; 3,558,571; 3,575,933; 3,600,350; 3,671,542; 3,699,085; 3,753,957; and 4,025,494. Polyparaphenylene terephthalamide (p-aramid) is available commercially as KEVLAR, a trademark of E.I. du Pont de Nemours, and processes of preparing the same are disclosed in U.S. Patent Nos. 3,006,899; 3,063,966; 3,094,511; 3,232,910; 3,414,645; 3,673,143; 3,748,299; 3,836,498; 3,827,988; among others. Other wholly aromatic polyamides are (poly(2,7-phenanthridone)-terephthalamide), poly(paraphenylene-2,6-naphthalamide), poly(methyl-1,4-phenylene) terephthalamide Additional specific examples of wholly aromatic polyamides are disclosed by P.W. Morgan in "Macromolecules," Vol. 10, No. 6, pp. 1381-90 (1977).

The aromatic polyamide fibers of the invention are provided with a substantially permanently set nonlinear configuration when heated in a nonlinear configuration, for example, a coiled or sinusoidal configuration, at a temperature above 200 °C, preferably at a temperature of from 200 °C to 550 °C, and more preferably at a temperature of from 200 °C to 420 °C in a water free atmosphere. The time period of heating the fiber depends on the temperature, diameter of fiber, type of aromatic polyamide polymer used, etc. A more permanent heat set is imparted when the fibers are heated at higher temperatures to thereby increase the carbon content, although it will be understood that the fibers become more brittle as the temperature is increased above 500 °C.

Stabilized or nonstabilized aromatic polyamide fibers which are heat treated, in a nonlinear configuration and in an inert atmosphere result in a fiber with a substantially permanent set and higher tenacity as compared to fibers which are heat treated in oxygen or air. It is preferable to do this heat treatment in a substantially unstressed condition.

The fibers of the invention have a substantially uniform diameter, especially in the bent portions, and preferably have a sinusoidal or coil-like configuration or a more complicated structural configuration of a combination of the two. The precursor fibers are typically formed by conventional methods into a fiber having a nominal diameter of from 4 to 25 microns and an aspect ratio of greater than 10:1.

The fibers are collected as an assembly of a multiplicity of continuous fibers in tows. The tows, optionally, may then be stabilized in the conventional manner such as described in U.S. Patent No. 4,642,664. The tows (or staple yarn made from chopped or stretch broken fiber staple) are thereafter formed into a substantially uniform coil-like and/or sinusoidal form by knitting or weaving the tow or yarn into a fabric or cloth. The so-formed knitted fabric or cloth is thereafter heat treated at the hereinbefore stated temperatures, in an inert atmosphere or in air for a period of time sufficient to produce an internal modification of the polymer structure such that the fiber is substantially irreversibly heat set into a nonlinear configuration exhibiting a reversible deflection of greater than 1.2:1 when measured at ambient temperature. The heat treatment be conducted while the nonlinear fibers are in a relaxed or unstressed condition. Greater improvement in physical properties are found with fibers which are simultaneously formed into a nonlinear configuration and heat treated, particularly when heat treated in a water free atmosphere.

As a result of the heat treatment of the knitted cloth, a substantially permanently set coil-like or sinusoidal configuration or structure is imparted to the fibers, fiber tow or yarn which are free of sharp V-type bends and/or fibrils and which exhibits a reversible deflection of greater than 1.2:1 when measured at ambient temperature. The resulting deknitted tows or yarn, or even the cloth per se, may then be subjected to other methods of treatment known in the art, such as garnetting (to create an opening), a procedure in which the fiber structure is separated into an entangled mass of a multiplicity of nonlinear, curly fibers in the form of a wool-like fluffy material wherein the individual fibers retain their coil-like or sinusoidal configuration yielding a shape reforming mass of the entangled fibers of considerable loft.

The fibers when substantially permanently set in accordance with the present invention into the desired nonlinear structural configuration retain their resilient and reversible deflection characteristics when measured at ambient temperature and, preferably, will retain their reversible deflection when measured at a temperature of about 130 °C.

It was found that fibers, when heat treated to a temperature of from 525 °C to 625 °C for a period of time of from 2 to 3 minutes, had an increase of carbon content from about 70.6 percent to about 75 percent. Although these fibers had a higher carbon content, they were still nongraphitic.

The fibers of the invention may be blended with other synthetic or natural fibers including, for example, nongraphitic carbonaceous fibers. Other fibers may be used in an amount of up to 90 percent by weight, based on the total weight of the fibers, so as to obtain the benefits of abrasion resistance from the aromatic polyamide fibers as well as the handle of the other fibers The blended fibers are advantageously used in protective clothing, such as fire fighting garments. The nonlinearity and increased tenacity of the fibers of the invention greatly improves the conditions for manufacture of the fibers into the desired end products since there are fewer fiber breaks and since the nonlinearity of the fibers provides for a substantial increase in loft. The substantially permanently set crimped or nonlinear fibers improve the bending strain value of the fibers and thus the compressibility of the fibers when in the form of a wool-like fluff or batting.

It is to be further understood that, if desired, the fibers may have imparted to them an electrically conductive property by heating the fibers, or fiber structure, to a temperature above 700 °C in a nonoxidizing atmosphere as described in the aforementioned U.S. Patent No. 4,642,664.

The process of the present invention results in nonlinear aromatic polyamide fibers which are free of many defects with weaken the fibers. It has been found that mechanical gear crimping or stuffer box crimping of aromatic polyamide fibers by standard methods result in damage to the fibers at the bent portions of the fibers, i.e., at the portions where the fiber is doubled back on itself as is the case in the use of a stuffer box, or where the fiber is compressed between the gears of a gear crimping mechanism. Such damage becomes more pronounced when the fibers are subsequently heat treated.

Crimped or nonlinear fibers of the invention when heat treated at a temperature of 300 °C or 500 °C for 10 minutes were found to be substantially uniform in diameter and free of damage and/or fibrils at their crimped or bent portions.

Fibers that were subjected to mechanical gear crimping at a higher pressure, after they have been heat treated at temperatures of 300 °C and 500 °C for 10 minutes exhibited substantially greater damage at the bend portions of the fibers as a result of the higher pressure and heat treatment. These fibers showed

severe flattened and distorted portions, and many were torn, broken or fibrillated.

Example 1

A continuous 0,167 g/m (1500 denier) tow of KEVLAR-29, an aromatic polyamide, was stabilized pursuant to the same process described in U.S. Patent No. 4,642,664. The tow, containing 1000 fibers, was knitted on a circular knitting machine into a cloth having from 3 to 4 loops per cm. The cloth was heat set at a temperature of 227 °C for a time period of 20 minutes. 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 length 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 in which the fibers had a high interstitial spacing and a high degree of interlocking as a result of the coiled configuration of the fibers. A similar result was achieved with KEVLAR-49 fibers.

Example 2

An approximately 0.167 g/m (1500 denier) tow of stabilized p-aramid fibers, containing 1000 fibers, was knitted on a circular knitting machine at a rate of 4 stitches/cm and was then heat treated at a temperature of 425 °C in a nitrogen atmosphere for 10 minutes. The cloth was deknitted and the tow (which had an elongation or reversible deflection ratio of greater than 2:1) was cut. The cut tow was then carded on a Plat Miniature carding machine and mixed with the carbonaceous fibers of Patent No. 4,869,951 to produce a wool-like fluff.

The fluff may be densified by needled punching, treated with a thermoplastic binder such as a polyester binder, or the like, to form a mat or felt-like structure having fire resistance and good abrasion strength.

Example 3

The wool-like fluff of Example 2 was fabricated into a thermal jacket employing about 200 g of the fluff as the sole filler for the jacket. The jacket had an insulating effect similar to that of a down (feather) filled jacket having from 425g to 710g of down as the insulating fill. If desired, the fibers may be blended with other natural or polymeric linear or nonlinear fibers including, for example, nylon, rayon polyester, cotton, wool, and the like, or carbonaceous nongraphitic fibers.

Example 4

A circular knit fabric composed of non-stabilized p-aramid fibers was placed in a laboratory tube furnace under a nitrogen purge. The sample was heated to a temperature of 250 °C and held for 10 minutes. The sample was then cooled under nitrogen and removed. The fabric, when opened, contained fibers having a sinusoidal shape which could not be pulled out at ambient temperatures, i.e., the fibers had a substantially permanent set and could not be forced into a linear configuration by stretching of the fibers.

Example 5

A 0.167 g/m (1500 denier) tow of stabilized p-aramid fibers, containing 1000 fibers, was non-mechanically crimped in a relaxed state while simultaneously heated to a temperature of 275 °C under a nitrogen purge. The heat treatment was conducted over a period of 10 minutes. When cooled, the tow was opened. The fibers contained a heat set sinusoidal crimp which could not be removed by stretching the fiber or by heating with a conventional hair dryer.

Example 6

The textile properties of various fiber samples of nonlinear fibers of the present invention, as described in Example 1 and derived from KEVLAR-29 were determined on an Instron Tensile Tester Series 4201 in lots of ten and the average result taken. The following settings were used:

Load Cell - "C"
Maximum Load - 22.7 kg
Gauge Length - 22.5 cm

Chart Speed - 5 mm/min
Cross Head Speed - 5 cm/min
Initial Mounting Tension - sufficient to straighten out the yarn
Temperature and Relative Humidity - 70 °C and 65%

The stress (tenacity) values at break were calculated by normalizing the load by denier (linear density) of the original yarn. The yarn linear density was found to be 1000.

Elongation (change in length) reading was given automatically on the digital readout of an Instron Tensile Tester. Extension (percent) at break was then calculated by change in length divided by gauge length multiplied by 100.

The values for each sample are shown in the following Table I and illustrated in the graph.

The samples prepared were:

K-29 (air): Fibers of the invention, derived from KEVLAR-29, were heat treated in air;

K-29 (N_2): Fibers of the invention, derived from KEVLAR-29, were heat treated in nitrogen only; and

K-29 (stab.→N_2): Fibers of the invention, derived from KEVLAR-29, were stabilized in air at a temperature of 217 °C and then heat treated in a nitrogen atmosphere.

The fibers had an amplitude of $2\frac{1}{2}$ mm and 120 coils per meter (three crimps per inch).

Table I

Tenacity (*0.001 Ns^2/m per 0.000111 g/m) ((g/dn))			
Treatment (°C)	K-29 (air)	K-29 (N_2)	K-29 (stab.→N_2)
20 (gear crimped virgin)	16.76		
20 (virgin)*	27.84	27.84	27.84
207		21.68	
217	23.21		
270			23.16
305	22.87	19.92	
315			23.39
402	14.21	16.46	16.75
503		6.64	
509	0.73		6.75
522	1.55		
605			0.25
g/dn = grams/denier			

*non-heat treated

Example 7

Following the procedure of Example 1, nonlinear fibers of the invention derived from KEVLAR-49 were tested. The results are shown in the following Table II.

The nonlinear fibers of the invention had superior mechanical properties over nonlinear fibers which were mechanically crimped. A sharp deterioration of the properties of the fibers occurred when the heat treatment temperature was raised above 500 °C.

Table II

Tenacity (*0.001 Ns^2/m per 0.000111 g/m) ((g/dn))			
Treatment (°C)	K-49 (air)	K-49 (N_2)	K-49 (stab.→N_2)
20 (virgin)*	25.11	25.11	25.11
213	24.92		
217	23.21		
260		17.29	
305	18.33	18.84	
315		21.57	
402	11.53	13.26	14.51
503		9.65	
509	1.69		5.15
522			1.09
610			0.25
g/dn = grams/denier Fibers heated above 525 °C were carbonaceous.			

*non-heat treated

Claims

1. A nonlinear fiber having bends or crimps, and an aspect ratio of greater than 10:1, characterized in that the fiber is a nonlinear aromatic polyamide fiber having a bending strain value of less than 50 percent as determined by the equation:

$$S = \frac{r}{R} \times 100$$

where S is the percent bending strain, r is the fiber radius and R is the radius of curvature of bend or crimp.

2. The fiber of Claim 1, having a reversible deflection ratio of greater than 1.2:1 when measured at ambient temperature.

3. The fiber of Claim 1, wherein said nonlinear fiber is substantially permanently set and has a reversible deflection ratio of greater than 1.2:1 when measured at a temperature of 130 °C.

4. The fiber of Claim 1, 2 or 3, having a bonding strain value of less than 30 percent.

5. The fiber of any one of claims 1-4, having a tenacity of at least about

$$0.018 \ \frac{Ns^2}{m}$$

per 0.000111 g/m (18 g/dn (grams per denier)).

6. The fiber of any one of claims 1-5, having not more than a 15 percent variation in the diameter of the fiber at the bends or crimps.

7. The fiber of any one of claims 1-6, wherein said fiber is substantially free of sharp V-type bends and fibrils.

8. The fiber of any one of claims 1-7, wherein said fiber is partially carbonized.

9. A fibrous structure comprising a multiplicity of nonlinear fibers having bends or crimps, characterized in that the fibers are nonlinear aromatic polyamide fibers having a bending strain value of less than 50 percent as determined by the equation:

$$S = \frac{r}{R} \times 100$$

where S is the percent bending strain, r is the fiber radius and R is the radius of curvature of bend or crimp.

10. The fibrous structure of Claim 9, having a reversible deflection ratio of greater than 1.2:1 when measured at ambient temperature.

11. The fibrous structure of Claim 9, wherein said nonlinear fiber is substantially permanently set and has a reversible deflection ratio of greater than 1.2:1 when measured at a temperature of 130 °C.

12. The fibrous structure of Claim 9, 10 or 11, having a bending strain value of less than 30 percent.

13. The fibrous structure of any one of Claims 9 to 12, having a tenacity of at least about

$$0.018 \ \frac{Ns^2}{m}$$

per 0.000111 g/m (18 g/dn).

14. The fibrous structure of any one of Claims 9 to 13, having not more than a 15 percent variation in the diameter of the fiber at the bends or crimps.

15. The fibrous structure of any one of Claims 9 to 14, wherein said fiber is substantially free of sharp V-type bends and fibrils.

16. The fibrous structure of any one of Claims 9 to 15, wherein said fiber is partially carbonized.

17. The fibrous structure of any one of Claims 9 to 16, comprising a blend of said nonlinear aromatic polyamide fibers with other fibers selected from natural fibers, synthetic fibers and nonlinear carbonaceous fibers.

18. The fibrous structure of any one of Claims 9 to 17, wherein said multiplicity of polyamide fibers are in the form of a tow or yarn, a wool-like fluffy mass of entangled fibers, a nonwoven batting, felt or web, or a knitted or woven cloth or fabric.

19. A process for making nonlinear fibers, comprising the steps of imparting a nonlinear configuration to the fibers, and heating said fibers at a temperature of above 200 °C to provide said fibers with a reversible deflection ratio of greater than 1.2:1 when measured at ambient temperature characterized in that the starting fibers are aromatic polyamide fibers, and that fibers are provided having a bending strain value of less than 50 percent as determined by the equation:

$$S = \frac{r}{R} \times 100$$

where S is the percent bending strain, r is the fiber radius and R is the radius of curvature of bend or crimp.

20. The process of Claim 19, wherein said fibers are heated at a temperature of from 200 °C to 550 °C.

21. The process of Claim 19, wherein the fibers are substantially permanently heat set in a nonaqueous atmosphere and are free of any sharp V-type bends or fibrils.

22. The process of Claim 19, 20 or 21, wherein said fibers are heated in a relaxed condition and without tension.

23. The process of any one of Claims 19 to 22, having not more than a 15 percent variation in the diameter of the fiber at the bends or crimps.

Patentansprüche

1. Eine nicht lineare Faser, die Biegungen oder Kräuselungen aufweist, und ein Längenänderungsverhältis größer als 10:
1 hat,
dadurch gekennzeichnet,
daß die Faser eine nicht-lineare aromatische Polyamidfaser ist, die einen Beugespannungswert von weniger als 50 Prozent aufweist, wie festgelegt durch die Gleichung

$$S = \frac{r}{R} \times 100$$

wobei S die prozentuale Beugespannung ist, r der Radius der Faser und R der Krümmungsradius der Biegung oder der Kräuselung.

2. Die Faser nach Anspruch 1 mit einer reversiblen Durchbiegungsrate größer als 1,2:1, gemessen bei Umgebungstemperatur.

3. Die Faser nach Anspruch 1, wobei besagte nicht-lineare Faser eine hochgradig dauerhafte Verformung erhalten hat und eine reversible Durchbiegungsrate größer als 1,2:1, wenn bei einer Temperatur von 130 °C gemessen.

4. Die Faser nach Anspruch 1, 2 oder 3 mit einem Beugespannungswert von weniger als 30 Prozent.

5. Die Faser nach jedem der Ansprüche 1 bis 4, mit einer Zugfestigkeit von wenigstens ungefähr 0,018 Ns^2/m pro 0,000111 g/m (18 g/dn (Gramm pro Denier)).

6. Die Faser nach jedem der Ansprüche 1 bis 5, die nicht mehr als 15 Prozent Variation im Faserdurchmesser an den Krümmungen oder Kräuselungen aufweist.

7. Die Faser nach jedem der Ansprüche 1 bis 6, wobei besagte Faser im wesentlichen frei ist von scharfen V-Typ ähnlichen Knicks und Fibrillen.

8. Die Faser nach jedem der Ansprüche 1 bis 7, wobei besagte Faser teilweise carbonisiert ist.

9. Eine faserige Struktur, die eine Vielzahl nicht linearer Fasern umfaßt, die Knicks oder Kräuselungen aufweisen,
dadurch gekennzeichnet,
daß die Fasern nicht-lineare aromatische Polyamidfasern sind,
mit einem Beugespannungswert von weniger als 50 Prozent,
wie durch die Gleichung

$$S = \frac{r}{R} \times 100$$

festgelegt wird, wobei S der prozentuale Beugespannungswert ist, r der Radius der Faser und R der Krümmungsradius der Biegung oder der Kräuselung.

10. Die faserige Struktur nach Anspruch 9 mit einer reversiblen Durchbiegungsrate größer als 1,2:1, gemessen bei Umgebungstemperatur.

11. Die faserige Struktur von Anspruch 9, wobei besagte nicht-lineare Faser hochgradig dauerhaft verformt ist und eine reversible Durchbiegungsrate größer als 1,2:1 aufweist, wenn bei einer Temperatur von 130 °C gemessen.

12. Die faserige Struktur von Anspruch 9, 10 oder 11 mit einem Beugespannungswert von weniger als 30 Prozent.

13. Die faserige Struktur von jedem der Ansprüche 9 bis 12 mit einer Zugfestigkeit von wenigstens ungefähr 0,18 Ns^2/m pro 0,000111 g/m (18 g/dn).

14. Die faserige Struktur von jedem der Ansprüche 9 bis 13, die nicht mehr als 15 Prozent Variation im Faserdurchmesser an den Knicks oder Kräuselungen aufweist.

15. Die faserige Struktur jeder der Ansprüche 9 bis 14, worin besagte Faser im wesentlichen frei ist von scharfen V-Typ ähnlichen Knicks oder Fibrillen.

16. Die faserige Struktur von jedem der Ansprüche 9 bis 15, worin besagte Faser teilweise carbonisiert ist.

17. Die faserige Struktur von jedem der Ansprüche 9 bis 16, die eine Mischung von besagten nicht linearen aromatischen Polyamidfasern mit anderen Fasern, ausgewählt aus natürlichen Fasern, synthetischen Fasern und nicht linearen kohlenstoffhaltigen Fasern umfaßt.

18. Die faserige Struktur von jedem der Ansprüche 9 bis 17, worin besagte Vielzahl der Polyamidfasern in der Form von einem Kabel oder Garn vorliegen, einer wolleähnlichen flauschigen Masse von verworrenen Fasern, einer nicht gewebten Watte, Filzes oder Gewebes oder eines gestrickten oder gewebten Tuchs oder Stoffs.

19. Ein Verfahren zur Herstellung nicht linearer Fasern, umfassend die Schritte der Verleihung einer nicht linearen Konfiguration der Fasern, einer Erhitzung besagter Fasern auf eine Temperatur von über 200 °C, um besagte Fasern mit einer reversiblen Durchbiegungsrate von größer als 1,2:1 zu versehen, wenn bei Umgebungstemperatur gemessen,
dadurch gekennzeichnet,
daß die Startfasern aromatische Polyamidfasern sind und die Fasern mit einem Beugespannungswert von weniger als 50 Prozent versehen werden, wie durch die Gleichung

$$S = \frac{r}{R} \times 100$$

determiniert wird, wobei S die prozentuale Biegeverformung ist, r der Radius der Faser und R der Krümmungsradius der Biegung oder Kräuselung.

20. Verfahren nach Anspruch 19, wobei besagte Fasern bei einer Temperatur von 200 °C bis 550 °C erhitzt werden.

21. Verfahren nach Anspruch 19, wobei die Fasern hochgradig dauerhaft hitzeverformt sind in einer wasserfreien Atmosphäre und frei sind von jeglichen scharfen V-Typ ähnlichen Knicks oder Fibrillen.

22. Verfahren nach Anspruch 19, 20 oder 21, worin besagte Fasern unter relaxierten Bedingungen und ohne Spannung erhitzt werden.

23. Verfahren nach einem der Ansprüche 19 bis 22, wobei die Fasern nicht mehr als 15 Prozent Variation im Durchmesser an den Krümmungen oder Kräuselungen aufweisen.

Revendications

1. Fibre non-linéaire présentant des plis ou des frisures et un rapport d'aspect supérieur à 10:1, caractérisée par le fait que la fibre est une fibre de polyamide aromatique non linéaire présentant un pourcentage de contrainte par pliage inférieur à 50 pour-cent tel que déterminé par l'équation:

$$S = \frac{r}{R} \times 100$$

où S est le pourcentage de contrainte par pliage, r est le rayon de la fibre et R est le rayon de courbure du pli ou de la frisure.

2. Fibre selon la revendication 1, présentant un taux d'élasticité réversible supérieur à 1,2:1 lors d'une mesure à la température ambiante.

3. Fibre selon la revendication 1, ladite fibre non-linéaire étant texturée de façon pratiquement permanente et présentant un taux d'élasticité réversible supérieur à 1,2:1 lors d'une mesure à une température de 130 °C.

4. Fibre selon les revendications 1, 2 ou 3, présentant un pourcentage de contrainte par pliage inférieur à 30%.

5. Fibre selon l'une quelconque des revendications 1 à 4, présentant une résistance d'au moins environ 0,018 Ns^2/m pour une fibre de 0,000111 g/m (18 grammes par denier).

6. Fibre selon l'une quelconque des revendications 1 à 5, ne présentant pas plus de 15 pour-cent de variation du diamètre de la fibre aux plis ou aux frisures.

7. Fibre selon l'une quelconque des revendications 1 à 6, ladite fibre étant pratiquement exempte de plis vifs de type V et de fibrilles.

8. Fibre selon l'une quelconque des revendications 1 à 7, ladite fibre étant partiellement carbonisée.

9. Structure fibreuse comportant une multiplicité de fibres non linéaires présentant des plis ou des frisures, caractérisée par le fait que les fibres sont des fibres de polyamide aromatique non linéaires présentant un pourcentage de contrainte par pliage inférieur à 50 pour-cent tel que déterminé par l'équation:

$$S = \frac{r}{R} \times 100$$

où S est le pourcentage de contente par pliage, r est le rayon de la fibre et R est le rayon de courbure du pli ou de la frisure.

10. Structure fibreuse selon la revendication 9, présentant un taux d'élasticité réversible supérieur à 1,2:1 lors d'une mesure à la température ambiante.

11. Structure fibreuse selon la revendication 9; ladite fibre non linéaire étant texturée de façon pratiquement permanente et présentant un taux d'élasticité réversible supérieur à 1,2:1 lors d'une mesure à une température de 130 °C.

12. Structure fibreuse selon l'une des revendications 9, 10 ou 11, présentant un pourcentage de contrainte par pliage inférieur à 30 pour-cent.

13. Structure fibreuse selon l'une quelconque des revendications 9 à 12, présentant une résistance d'au moins environ 0,018 Ns^2/m pour une fibre de 0,000111 g/m (18g/dn).

14. Structure fibreuse selon l'une quelconque des revendications 9 à 13, ne présentant pas plus de 15 pour-cent de variation en diamètre de la fibre aux plis ou aux frisures.

15. Structure fibreuse selon l'une quelconque des revendications 9 à 14, ladite fibre étant pratiquement exempte de plis vifs du type V et de fibrilles.

16. Structure fibreuse selon l'une quelconque des revendications 9 à 15, ladite fibre étant partiellement carbonisée.

17. Structure fibreuse selon l'une quelconque des revendications 9 à 16, comportant un mélange desdites libres de polyamide aromatique non linéaires avec d'autres libres choisies parmi des fibres naturelles, des fibres synthétiques et des fibres carbonées non linéaires.

18. Structure fibreuse selon l'une quelconque des revendications 9 à 17, dans laquelle ladite multiplicité de fibres de polyamide se présentant sous forme d'une mèche ou d'un fil, d'une masse duveteuse laineuse de fibres emmêlées, de nappe, de feutre ou de voile non tissé ou de tricot tricoté ou de tissu tissé.

19. Procédé de fabrication de libres non linéaires, comportant les étapes consistant à donner une configuration non linéaire aux libres, puis à chauffer lesdites libres à une température supérieure à 200 °C pour donner auxdites libres un taux d'élasticité réversible supérieur à 1,2:1 lors d'une mesure à la température ambiante, caractérisé par le fait que les libres de départ sont des fibres de polyamide aromatique et que l'on donne aux fibres un pourcentage de contrainte par pliage inférieur à 50 pour-cent tel que déterminé par l'équation:

$$S = \frac{r}{R} \times 100$$

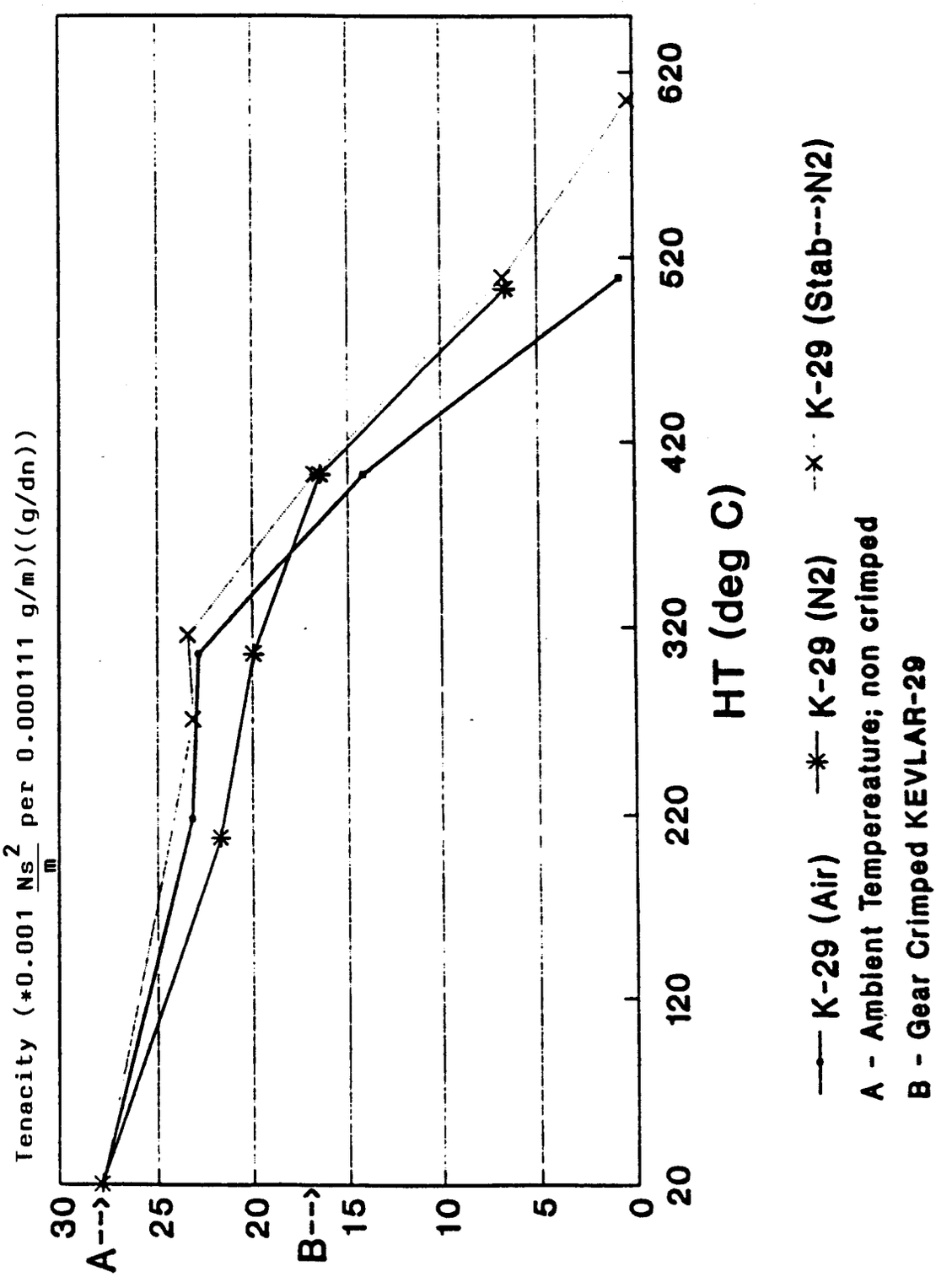
où S est le pourcentage de contrainte par pliagé, r est le rayon de la fibre et R est le rayon de courbure des plis ou des frisures.

20. Procédé selon la revendication 19, dans lequel lesdites fibres sont chauffées à une température allant de 200 °C à 550 °C.

21. Procédé selon la revendication 19, dans lequel les fibres sont traitées à chaud de façon pratiquement permanente sous atmosphère non aqueuse et sont exemptes de tous plis vifs de type V ou de fibrilles.

22. Procédé selon l'une des revendications 19, 20 ou 21 dans lequel lesdites fibres sont chauffées en condition relaxée et sans tension.

23. Procédé selon l'une quelconque des revendications 19 à 22 ne présentant pas plus de 15 pour-cent de variation dans le diamètre des fibres aux plis ou aux frisures.


Tenacity (*0.001 Ns2/m per 0.000111 g/m)((g/dn))
A-->
B-->
30
25
20
15
10
5
0
20
120
220
320
420
520
620
HT (deg C)
K-29 (Air)
K-29 (N2)
K-29 (Stab-->N2)
A - Ambient Tempereature; non crimped
B - Gear Crimped KEVLAR-29