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(54) Title: HIGH TENACITY OR HIGH LOAD BEARING NYLON FIBERS AND YARNS AND FABRICS THEREOF

(57) Abstract: High strength or load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den as well as yarns, fabrics and articles of manufacture thereof and methods for their production are provided.



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High Tenacity or High Load Bearing Nylon Fibers and Yarns and Fabrics Thereof

Field of Invention

[0001] The present disclosure relates to the preparation of improved nylon staple fiber of desirably high strength as quantified by break tenacity and tenacity at 7% and 10% elongation. Such nylon staple fiber is produced by preparing tows of relatively uniformly spun and quenched nylon filaments, drawing and annealing such tows in the presence of steam, and then cutting or otherwise converting the drawn and annealed tows into the desired high strength nylon staple fiber.

[0002] The nylon staple fiber so prepared can be blended with other fibers such as cotton staple fiber to produce yarns which are also of desirably high strength. Such yarns can then be made into fabrics and other articles of manufacture which can be advantageously lightweight, comfortable, lower cost, and durable and hence especially suitable for use in or as, for example, military apparel such as combat uniforms or other rugged use apparel.

[0003] The present disclosure also relates to non-woven composites of high tenacity nylon fiber and cellulosic or recycled synthetic or natural fiber technologies. End uses for such composites include, but are not limited to, industrial (felts/backings/filtration/insulation), apparel (inclusive of liner fabrics), footwear, bag/pack hard gear, durable and semi-durable (disposable or semi disposable) clothing or PPE, including FR (chemically treated or in combination with inherent FR fiber technologies), bio chemical, or other specialty protective wear.

Background

[0004] Nylon has been manufactured and used commercially for a number of years. The first nylon fibers were of nylon 6,6, poly(hexamethylene adipamide), and nylon 6,6 fiber is still made and used commercially as the main nylon fiber. Large quantities of other nylon fibers, especially nylon 6 fiber prepared from caprolactam, are also made and used commercially. Nylon fiber is used in yarns for textile fabrics, and for other purposes. For textile fabrics, there are essentially two main yarn categories, namely continuous filament yarns and yarns made from staple fiber, i.e. cut fiber.

[0005] Nylon staple fiber has conventionally been made by melt-spinning nylon polymer into filaments, collecting very large numbers of these filaments into a tow, subjecting the tow to a

drawing operation and then converting the tow to staple fiber, e.g., in a staple cutter. The tow usually contains many thousands of filaments and is generally of the order of several hundred thousand (or more) in total denier. The drawing operation involves conveying the tow between a set of feed rolls and a set of draw rolls (operating at a higher speed than the feed rolls) to increase the orientation of nylon polymer in the filaments. Drawing is often combined with an annealing operation to increase nylon crystallinity in the tow filaments before the tow is converted into staple fiber.

[0006] One of the advantages of nylon staple fibers is that they are readily blended, particularly with natural fibers, such as cotton (often referred to as short staple) and/or with other synthetic fibers, to achieve the advantages derivable from such blending. A particularly desirable form of nylon staple fiber has been used for many years for blending with cotton, particularly to improve the durability and economics of the fabrics made from yarns comprising blends of cotton with nylon. This is because such nylon staple fiber has a relatively high load-bearing tenacity, as disclosed in Hebel, U.S. Pat. Nos. 3,044,250; 3,188,790; 3,321,448; and 3,459,845, the disclosures of which are hereby entirely incorporated by reference. As explained by Hebel, the load-bearing capacity of nylon staple fiber is conveniently measured as the tenacity at 7% elongation (T_7), and the T_7 parameter has long been accepted as a standard measurement and is easily read on an Instron machine.

[0007] The Hebel process for preparing nylon staple fiber involves the nylon spinning, tow forming, drawing and converting operations hereinbefore described. Improvements in the Hebel process for preparing nylon staple fiber have subsequently been made by modifying the nature of the tow drawing operation and by adding specific types of annealing (or high temperature treatment) and subsequent cooling steps to the overall process. For example, Thompson in U.S. Pat. Nos. 5,093,195 and 5,011,645 discloses nylon staple fiber preparation wherein nylon 6,6 polymer, having for example a formic acid relative viscosity (RV) of 55, is spun into filaments which are then drawn, annealed, cooled and cut into staple fiber having a tenacity, T , at break of about 6.8-6.9, a denier per filament of about 2.44, and a load-bearing capacity, T_7 , of from about 2.4 to 3.2. Such nylon staple fibers are further disclosed in the Thompson patents as being blended with cotton and formed into yarns of improved yarn strength. (Both of these Thompson patents are incorporated herein by reference in their entirety.)

[0008] Nylon staple fibers prepared in accordance with the Thompson technology have been blended into NYCO yarns (generally at a 50:50 nylon/cotton ratio) with these yarns being used to prepare NYCO fabrics. Such NYCO fabrics, e.g., woven fabrics, find application in military combat uniforms and apparel. While such fabrics have generally proven satisfactory for military or other rugged apparel use, military authorities, for example, are continually looking for improved fabrics which may be lighter in weight, lower in cost and/or more comfortable but still highly durable or even of improved durability.

Summary of the Invention

[0009] The invention relates to creating a nylon staple fiber with extremely high tenacity (both break tenacity and tenacity at low elongations). The invention involves the use of a steam to allow higher draw ratios versus normal draw ratios used currently. The product is then annealed and dried under tension. The annealing/oven drying under tension helps remove excess moisture gained during steam draw. The resulting fiber break tenacity has been increased from a 7.1 gram/den average to 7.5-7.75 grams/denier range. Tenacity at 10% elongation has also increased 10-20% higher versus standard product or previously described improvements. Fabrics made from this fiber are expected to exhibit either higher strength in terms of grab and tear strength or comparable strength but up to 1.0 oz. lighter in weight.

[0010] Accordingly, an aspect of the present invention relates to high strength or load bearing nylon staple fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den.

[0011] Another aspect of the present invention related to a yarn, at least a portion of which is spun from high strength or load bearing nylon staple fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den.

[0012] In one embodiment, the yarns are made by blending these nylon staple fibers with at least one companion staple fiber.

[0013] In one embodiment, the yarns may be nylon/cotton (NYCO) yarns that can then be woven into durable, and optionally lightweight, woven NYCO fabrics which can be especially suitable for military or other rugged apparel use.

[0014] Another aspect of the present invention relates to a light weight fabric of less than 6.0 oz./yd² that meets or exceeds current military fabrics strength and tear specifications established

for fabrics that weigh $>6.0 \text{ oz./yd}^2$. The fabric is made up of a fiber blend at least a portion of which comprises high strength or load bearing nylon fiber with break tenacity greater than 7.5 g/den and a tenacity at 10% elongation of greater than 4.0g/den.

[0015] Another aspect of the present invention relates to an article of manufacture, at least a portion of which comprises high strength or load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den.

[0016] Another aspect of the present invention relates to non-woven fabric composites comprising high tenacity fiber and cellulosic or recycled synthetic or natural fiber.

[0017] In one embodiment, the high tenacity fiber used in the non-woven fabric composite comprises load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den.

[0018] Yet another aspect of the present invention related to a method for producing high strength or load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den. This method comprises the steps of melt-spinning nylon polymer into filaments, uniformly quenching the filaments and forming a tow from a multiplicity of these quenched filaments, subjecting the tow to drawing in the presence of steam, annealing under tension, and then converting the resulting drawn and annealed tow into staple fibers suitable for forming into, for example, spun yarn.

Detailed Description of the Invention

[0019] Provided by this disclosure are high strength or load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den, yarns, fabrics and other articles of manufacture, at least a portion of which are prepared from these fibers, and methods for their production.

[0020] Also provided by this disclosure are non-woven fabric composites comprising high tenacity fiber and cellulosic or recycled synthetic or natural fiber.

[0021] As used herein, the terms "durable" and "durability" refer to the propensity of a fabric so characterized to have suitably high grab and tear strength as well as resistance to abrasion for the intended end use of such fabric, and to retain such desirable properties for an appropriate length of time after fabric use has begun.

[0022] As used herein, the term blend or blended, in referring to a spun yarn, means a mixture of fibers of at least two types, wherein the mixture is formed in such a way that the individual fibers of each type of fiber are substantially completely intermixed with individual fibers of the other types to provide a substantially homogeneous mixture of fibers, having sufficient entanglement to maintain its integrity in further processing and use.

[0023] As used herein, cotton count refers to the yarn numbering system based on a length of 840 yards, and wherein the count of the yarn is equal to the number of 840-yard skeins required to weigh 1 pound.

[0024] All numerical values recited herein are understood to be modified by the term "about".

[0025] Some embodiments are based on the preparation of improved nylon staple fibers having certain specified characteristics and on the subsequent preparation of yarns, and fabrics woven from such yarns, wherein these improved nylon staple fibers are blended with at least one other fiber. The other fibers may include cellulosics such as cotton, modified cellulosics such as FR treated cellulose, polyester, rayon, animal fibers such as wool, fire resistant (FR) polyester, FR nylon, FR rayon, FR treated cellulose, m-aramid, p-aramid, modacrylic, novoloid, melamine, polyvinyl chloride, antistatic fiber, PBO (1,4-benzenedicarboxylic acid, polymer with 4,6-diamino-1,3-benzenediol dihydrochloride), PBI (polybenzimidazole), and combinations thereof. The nylon staple fibers of some embodiments can provide an increase in strength and/or abrasion resistance to yarns and fabrics. This is especially true for combination with relatively weaker fibers such as cotton and wool.

[0026] The specific characteristics of the nylon staple fibers prepared and used herein include fiber denier, fiber tenacity and fiber load-bearing capacity defined in terms of fiber tenacity at 7% and 10% elongation.

[0027] Realization of the desired nylon staple fiber material herein is based on the use in staple fiber manufacture of nylon polymeric filaments and tows having certain selected properties and processed using certain selected processing operations and conditions. Specifically, the inventors herein have found that introduction of steam between the feed and draw module and/or tension during annealing significantly reduces draw forces thus allowing the nylon supply to be drawn much further versus any dry draw process. In one embodiment of the present invention, steam is introduced into the normal nylon staple process by addition of a steam chamber between the feed and draw modules as this allows the excess water to be removed prior to annealing.

Without being limited to any particular theory, it is believed that the steam chamber adds enough heat/steam to reduce the draw force of the nylon and help localize the draw to the steam chamber and not over or at the feed roll exit. Steam can be controlled by pressure.

[0028] The nylon polymer itself which is used for the spinning of nylon filaments of the present invention can be produced in conventional manner. Nylon polymer suitable for use in the process and filaments of some embodiments consists of synthetic melt spinnable or melt spun polymer. Such nylon polymers can include polyamide homopolymers, copolymers, and mixtures thereof which are predominantly aliphatic, i.e., less than 85% of the amide-linkages of the polymer are attached to two aromatic rings. Widely-used polyamide polymers such as poly(hexamethylene adipamide) which is nylon 6,6 and poly(epsilon.-caproamide) which is nylon 6 and their copolymers and mixtures can be used in accordance with some embodiments. Other polyamide polymers which may be advantageously used are nylon 12, nylon 4,6, nylon 6,10, nylon 6,12, nylon 12,12, and their copolymers and mixtures. Illustrative of polyamides and copolyamides which can be employed in the process, fibers, yarns and fabrics of some embodiments are those described in U.S. Pat. Nos. 5,077,124, 5,106,946, and 5,139,729 (each to Cofer et al.) and the polyamide polymer mixtures disclosed by Gutmann in Chemical Fibers International, pages 418-420, Volume 46, December 1996. These publications are all incorporated herein by reference.

[0029] Nylon polymer used in the preparation of nylon staple fibers has conventionally been prepared by reacting appropriate monomers, catalysts, antioxidants and other additives, such as plasticizers, delustrants, pigments, dyes, light stabilizers, heat stabilizers, antistatic agents for reducing static, additives for modifying dye ability, agents for modifying surface tension, etc. Polymerization has typically been carried out in a continuous polymerizer or batch autoclave. The molten polymer produced thereby has then typically been introduced to a spin pack wherein it is forced through a suitable spinneret and formed into filaments which are quenched and then formed into tows for ultimate processing into nylon staple fiber. As used herein, spin pack is comprised of a pack lid at the top of the pack, a spinneret plate at the bottom of the pack and a polymer filter holder sandwiched between the former two components. The filter holder has a central recess therein. The lid and the recess in the filter holder cooperate to define an enclosed pocket in which a polymer filter medium, such as sand, is received. There are provided channels interior to the pack to allow the flow of molten polymer, supplied by a pump or extruder to travel through the pack and ultimately through the spinneret plate. The spinneret plate has an array of

small, precision bores extending therethrough which convey the polymer to the lower surface of the pack. The mouths of the bores form an array of orifices on the lower surface of the spinneret plate, which surface defines the top of the quench zone. The polymer exiting these orifices is in the form of filaments which are then directed downwards through the quench zone.

[0030] The extent of polymerization carried out in the continuous polymerizer or batch autoclave can generally be quantified by means of a parameter known as relative viscosity or RV. RV is the ratio of the viscosity of a solution of nylon polymer in a formic acid solvent to the viscosity of the formic acid solvent itself. RV is taken as an indirect indication of nylon polymer molecular weight. For purposes herein, increasing nylon polymer RV is considered synonymous with increasing nylon polymer molecular weight.

[0031] As nylon molecular weight increases, its processing becomes more difficult due to the increasing viscosity of the nylon polymer. Accordingly, continuous polymerizers or batch autoclaves are typically operated to provide nylon polymer for eventual processing into staple fiber wherein the nylon polymer has an RV value of about 60 or less.

[0032] It is known that for some purposes, provision of nylon polymer of greater molecular weight, i.e., nylon polymer having RV values of greater than 70-75 and up to 140 or even 190 and higher can be advantageous. It is known, for example, that high RV nylon polymer of this type has improved resistance to flex abrasion and chemical degradation. Accordingly, such high RV nylon polymer is especially suitable for spinning into nylon staple fiber which can advantageously be used for the preparation of papermaking felts. Procedures and apparatus for making high RV nylon polymer and staple fiber therefrom are disclosed in U.S. Pat. No. 5,236,652 to Kidder and in U.S. Pat. Nos. 6,235,390; 6,605,694; 6,627,129 and 6,814,939 to Schwinn and West. All of these patents are incorporated herein by reference in their entirety.

[0033] In accordance with some embodiments, it has been discovered that staple fibers prepared from nylon polymer having an RV value which is generally consistent with, or in some cases higher than, that generally obtained via polymerization in a continuous polymerizer or batch autoclave, when processed in accordance with the spinning, quenching, feeding and drawing in the presence of steam and annealing procedures described herein, unexpectedly exhibit increased fiber break tenacity and increased tenacity and 10% elongation as compared to standard product or previously described improvements. When such nylon staple fibers of improved tenacity are blended with one or more other fibers such as cotton staple fibers, textile yarns of improved

strength as well as lower weight can be realized. Fabrics such as NYCO fabrics woven from such yarns exhibit the advantages hereinbefore described with respect to durability, optional lighter weight, improved comfort and/or potential lower cost.

[0034] In accordance with the staple fiber preparation process herein, nylon polymer which is melt spun into tow-forming filaments through one or more spin pack spinnerets and quenched will have an RV value ranging from 45 to 100, including from 55 to 100, from 46 to 65; from 50 to 60; and from 65 to 100. Nylon polymer of such RV characteristics can be prepared, for example, using a melt blending of polyamide concentrate procedure such as the process disclosed in the aforementioned Kidder '652 patent. Kidder discloses certain embodiments in which the additive incorporated into the polyamide concentrate is a catalyst for the purpose of increasing the formic acid relative viscosity (RV). Higher RV nylon polymer available for melting and spinning, such as nylon having an RV of from 65 to 100, can also be provided by means of a solid phase polymerization (SPP) step wherein nylon polymer flakes or granules are conditioned to increase RV to the desired extent. Such solid phase polymerization (SPP) procedures are well-known and disclosed in greater detail in the aforementioned Schwinn/West '390, '694, '129 and '939 patents.

[0035] The nylon polymer material having the requisite RV characteristics as specified herein are fed to a spin pack, for example via a twin screw melter device. In the spin pack the nylon polymer is spun by extrusion through one or more spinnerets into a multiplicity of filaments. For purposes herein, the term "filament" is defined as a relatively flexible, macroscopically homogeneous body having a high ratio of length to width across its cross-sectional area perpendicular to its length. The filament cross section can be any shape, but is typically circular. Herein, the term "fiber" can also be used interchangeably with the term "filament".

[0036] Each individual spinneret position may contain from 100 to 1950 filaments in an area as small as 9 inches by 7 inches (22.9 cm.times.17.8 cm). Spin pack machines may contain from one to 96 positions, each of which provides bundles of filaments which eventually get combined into a single tow band for drawing/downstream processing with other tow bands.

[0037] After exiting the spinneret(s) of the spin pack, the molten filaments which have been extruded through each spinneret are typically passed through a quench zone wherein a variety of quenching conditions and configurations can be used to solidify the molten polymer filaments and render them suitable for collection together into tows. Quenching is most commonly carried

out by passing a cooling gas, e.g., air, toward, onto, with, around and through the bundles of filaments being extruded into the quenching zone from each spinneret position within the spin pack.

[0038] One suitable quenching configuration is cross-flow quenching wherein a cooling gas such as air is forced into the quenching zone in a direction which is substantially perpendicular to the direction that the extruded filaments are travelling through the quench zone. Cross-flow quenching arrangements are described, among other quenching configurations, in U.S. Pat. Nos. 3,022,539; 3,070,839; 3,336,634; 5,824,248; 6,090,485, 6,881,047 and 6,926,854, all of which patents are incorporated herein by reference.

[0039] In one embodiment of the staple fiber preparation process herein, the extruded nylon filaments used to eventually form the desired nylon staple fibers are spun, quenched and formed into tows with both positional uniformity and uniformity of quenching conditions such as described in published U.S. Patent Application Nos. 2011/0177737 and 2011/0177738, teachings of which are herein incorporated by reference in their entirety.

[0040] Quenched spun filaments can then be combined into one or more tows. Such tows formed from filaments from one or more spinnerets are then subjected to a two stage continuous operation wherein the tows are drawn and annealed in the presence of steam.

[0041] Drawing of the tows is generally carried out primarily in an initial or first drawing stage or zone wherein bands of tows are passed between a set of feed rolls and a set of draw rolls (operating at a higher speed) to increase the crystalline orientation of the filaments in the tow. The extent to which tows are drawn can be quantified by specifying a draw ratio which is the ratio of the higher peripheral speed of the draw rolls to the lower peripheral speed of the feed rolls. The effective draw ratio is calculated by multiplying the 1st draw ratio and the 2nd draw ratio.

[0042] The first drawing stage or zone may include several sets of feed and draw rolls as well as other tow guiding and tensioning rolls such as snubbing pins. Draw roll surfaces may be made of metal, e.g., chrome, or ceramic. Ceramic draw roll surfaces have been found to be particularly advantageous in permitting use of the relatively higher draw ratios specified for use in connection with the staple fiber preparation process herein. Ceramic rolls improve roll life as well as provide a surface that is less prone to wrap. An article appearing the International Fiber Journal (International Fiber Journal, 17, 1, February 2002: "Textile and Bearing Technology for

Separator Rolls", Zeitz and el.) as well as U.S. Pat. No. 4,794,680, both incorporated herein by reference, also disclose the use of ceramic rolls in to improve roll life and reduce fiber adherence to roll surface.

[0043] While the greatest extent of drawing of the tows of filaments herein takes place in the initial or first drawing stage or zone, some additional drawing of the tows will generally also take place in a second or annealing and drawing stage or zone hereinafter described. The total amount of draw to which the filament tows herein are subjected can be quantified by specifying a total effective draw ratio which takes into account drawing that occurs in both a first initial drawing stage or zone and in a second zone or stage where annealing and some additional drawing are conducted simultaneously.

[0044] In the process of some embodiments, the tows of nylon filaments are subjected to a total effective draw ratio of from 2.3 to 5.0, including from 3.0 to 4.0. In one embodiment wherein the denier per filament of the tows is generally smaller, a total effective draw ratio can range from 3.12 to 3.40. In another embodiment, wherein the denier per filament of the tows is generally larger, the total effective draw ratio can range from 3.5 to 4.0.

[0045] In the process herein, most of the drawing of the tows, as noted hereinbefore, occurs in the first or initial drawing stage or zone. In particular, from 85% to 97.5%, including from 92% to 97%, of the total amount of draw imparted to the tows will take place in the first or initial drawing stage or zone. The drawing operation in the first or initial stage will generally be carried out at whatever temperature the filaments have when passed from the quench zone of the melt spinning operation. Frequently, this first stage drawing temperature will range from 80°C to 125°C.

[0046] In the present invention, steam is introduced between feeding and drawing to maximize draw of the nylon. In one embodiment, a steam chamber located between the feed and draw modules is used to allow higher draw ratios versus normal draw ratios such as described herein.

[0047] From the first or initial drawing stage or zone, the partially drawn tows are passed to a second annealing and drawing stage or zone wherein the tows are simultaneously heated and further drawn. Heating of the tows to effect annealing serves to increase crystallinity of the nylon polymer of the filaments. In this second annealing and drawing stage or zone, the filaments of the tows are subjected to an annealing temperature of from 145°C to 205°C, such as from 165°C to 205°C. In one embodiment, the temperature of the tow in this annealing and drawing stage

may be achieved by contacting the tow with a steam-heated metal plate that is positioned between the first stage draw and the second stage drawing and annealing operation. In the present invention, annealing/oven drying under tension helps remove excess moisture gained during steam draw.

[0048] After the annealing and drawing stage of the process herein, the drawn and annealed tows are cooled to a temperature of less than 80°C, such as less than 75°C. Throughout the drawing, annealing and cooling operations described herein, the tows are maintained under controlled tension and accordingly are not permitted to relax.

[0049] After drawing in the presence of steam and annealing/oven drying under tension, the multifilament tows are converted into staple fiber in conventional manner, for example using a staple cutter. Staple fiber formed from the tows will frequently range in length from 2 to 13 cm (0.79 to 5.12 inches). For example, staple fibers may range from 2 to 12 cm (0.79 to 4.72 inches), from 2 to 12.7 cm (0.79 to 5.0 inches), or from 5 to 10 cm can be formed. The staple fiber herein can optionally be crimped.

[0050] The high tenacity nylon staple fibers formed in accordance with the process herein will generally be provided as a collection of fibers, e.g., as bales of fibers, having a denier per fiber of from 1.0 to 3.0. When staple fibers having a denier per fiber of from 1.6 to 1.8, are to be prepared, a total effective draw ratio of from 3.12 to 3.40, such as from 3.15 to 3.30, can be used in the process herein to provide staple fibers of the requisite load-bearing capacity. When staple fibers having a denier per fiber of from 2.5 to 3.0 or 2.3 to 2.7 are to be prepared, a total effective draw ratio of from 3.5 to 4.0, or from 3.74 to 3.90, should be used in the process herein to provide staple fibers of the requisite load-bearing capacity.

[0051] Using this process and then annealing the fiber at 180°C using standard annealing rolls produced a significantly higher tenacity fiber with a tenacity greater than 7.5 g/den.

[0052] In one nonlimiting embodiment of the current invention a nylon staple fiber is disclosed with tenacity at break greater than 7.5 g/den. In another nonlimiting embodiment of the current invention nylon staple fiber is disclosed with tenacity at break greater than 7.8 g/den. In another nonlimiting embodiment of the current invention a nylon staple fiber is disclosed with tenacity at break of at least 8.0 g/den.

[0053] In one nonlimiting embodiment of the current invention a nylon staple fiber is disclosed a tenacity at 10% elongation of at least 4.0g/den.

[0054] Fiber with properties above can be used at lower blend ratios or spun into yarns using alternative spinning systems that significantly reduce fabric manufacturing costs and still meet existing fabrics specifications. A fiber that has very high tenacity (both break and tenacity at 7% or 10% elongation) and possibly stronger, lower cost or lighter weight fabrics that can be made from this fiber. This said fiber can be used to significantly reduce yarn spinning and finished fabric costs by allowing the use of lower nylon blend levels and/or alternative spinning system while maintaining fabric properties. This offers value to the down-stream customer versus competition. To achieve these properties in the fiber, a steam chamber is used help maximize draw of the nylon. The fiber tenacity obtained is higher than any produced on normal staple equipment.

[0055] Having the ability to produce a significantly higher strength fiber versus completion is extremely advantageous. The higher strength nylon fiber allows yarns spinners and fabric weavers to reduce costs while still meeting strength requirements in the finished fabric/garment. This higher strength would put the competitive offering at a large disadvantage in terms of cost. This cost difference potential could be from \$0.34 to over \$1.00/lb. Example of lower cost yarns /fabrics include lower usage of nylon content in the spun yarn while still meeting yarn and fabric strength requirements and use of lower cost yarn spinning system (Vortex or OES) while still meeting fabric strength requirements. These lower cost alternatives could save over \$1.00/fabric yard if successfully implemented. Having the ability to produce this higher strength fiber gives significant advantages that the competition cannot meet. Another possible advantage is allowing the production of lower weight fabrics/garments while still meeting existing fabric specifications. Adoption of the new fiber in any new fabric specification such as lighter weight fabrics would prevent competitive fibers manufacturers from entering market.

[0056] The nylon staple fibers provided herein are especially useful for blending with other fibers for various types of textile applications. Blends can be made, for example, with the nylon staple fibers of some embodiments in combination with other synthetic fibers such as rayon or polyester. Examples of blends of the nylon staple fibers herein include those made with natural cellulosic fibers such as cotton, flax, hemp, jute and/or ramie. Suitable methods for intimately blending these fibers may include: bulk, mechanical blending of the staple fibers prior to carding; bulk mechanical blending of the staple fibers prior to and during carding; or at least two

passes of draw frame blending of the staple fibers subsequent to carding and prior to yarn spinning.

[0057] In accordance with one embodiment, the high load-bearing capacity nylon staple fibers herein may be blended with cotton staple fibers and spun into textile yarn. Such yarns may be spun in conventional manner using commonly known short and long staple spinning methods including ring spinning, air jet or vortex spinning, open end spinning, or friction spinning. When the yarn blend includes cotton, the resulting textile yarn will generally have a cotton fiber to nylon fiber weight ratio of from 20:80 to 80:20, including from 40:60 to 60:40, and frequently a cotton:nylon weight ratio of 50:50. It is well-known in the art that nominal variation of the fiber content, e.g., 52:48 is also considered to be a 50:50 blend. Textile yarns made with the high load-bearing capacity nylon staple fibers herein will frequently exhibit LEA product values of at least 2800, such as at least 3000 at 50:50 NYCO content. Alternatively, such yarns may have a breaking tenacity of at least 17.5 or 18 cN/tex, including at least 19 cN/tex, at 50:50 NYCO content.

[0058] In one embodiment, the textile yarns herein will be made from nylon staple fibers having a denier per filament of from 1.6 to 1.8. In another embodiment, the textile yarns herein will be made from nylon staple fibers having a denier per filament of from 2.5 to 3.0, including from 2.3 to 2.7.

[0059] The nylon/cotton (NYCO) yarns of some embodiments can be used in conventional manner to prepare NYCO woven fabrics of especially desirable properties for use in military or other rugged use apparel. Thus such yarns may be woven into 2x1 or 3x1 twill NYCO fabrics. Spun NYCO yarns and 3x1 twill woven fabrics comprising such yarns are in general described and exemplified in U.S. Pat. No. 4,920,000 to Green. This '000 patent is incorporated herein by reference.

[0060] NYCO woven fabrics, of course, comprise both warp and weft (fill) yarns. The woven fabrics of some embodiments are those which have the NYCO textile yarns herein woven in at least one, and optionally both, of these directions. In one embodiment, fabrics herein of especially desirable durability and comfort will have yarns woven in the weft (fill) direction comprising nylon staple fibers herein which have a denier per filament of from 1.6 to 1.8 and will have yarns woven in the warp direction comprising nylon staple fibers herein which have a

denier per filament of from 2.3 to 3.0, including from 2.5 to 3.0, and from 2.3 to 2.7 denier per filament.

[0061] The woven fabrics of some embodiments made using yarns which comprise the high load bearing nylon staple fibers herein can use less of the nylon staple fibers than conventional NYCO fabrics while retaining many of the desirable properties of such conventional NYCO fabrics. Thus, such fabrics can be made to be relatively lightweight and low cost while still desirably durable. Alternatively, such fabrics can be made using equal or even greater amounts of the nylon staple fibers herein in comparison with nylon fiber content of conventional NYCO fabrics with such fabrics herein providing superior durability properties.

[0062] Lightweight fabrics such as NYCO fabrics of some embodiments may have a fabric weight of less than 220 grams/m² (6.5 oz/yd²), including less than 200 grams/m² (6.0 oz/yd²), and less than 175 grams/m² (5.25 oz/yd²). Suitable durable NYCO fabrics of the some embodiments will have a grab strength of 190 lbs or greater in the warp direction and 80 lbs or greater in the weft (fill) direction. Other durable fabrics have a Tear Strength in "as received" fabric in warp direction of 11.0 lbf (poundfoot) or greater and fill direction of 9.0 lbf or greater.

[0063] The present invention also relates to non-woven fabric composites comprising high tenacity fiber and cellulosic or recycled synthetic or natural fiber. The inventors herein have found that inclusion of high tenacity fiber imparts additional tensile, tear, abrasion, wash durability and longevity to non woven substrates, inclusive of, but not limited to, spunlace, airlaid, needlepunch and other carded non woven technologies. In one embodiment, the high tenacity fiber used in the non-woven fabric composite comprises load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0g/den. As will be understood by the skilled artisan upon reading this disclosure, however, alternative high tenacity fibers such as, but not limited to, those described in published U.S. Patent Application Nos. 2011/0177737 and 2011/0177738 can also be used. Additional nonlimiting examples of nylon staple fiber having a relatively high load-bearing tenacity which can be used in these non-woven composites are disclosed in U.S. Pat. Nos. 3,044,250; 3,188,790; 3,321,448; 3,459,845; 5,093,195 and 5,011,645. The high tenacity fiber can be combined with various cellulosic or recycled synthetic or natural fiber technologies including, but not limited to, recycled denim. End uses for the non-woven fabric composites include, but are not limited to, industrial (felts/backings/filtration/insulation), apparel (inclusive of liner fabrics), footwear,

bag/pack hard gear, durable and semi-durable (disposable or semi disposable) clothing or PPE, including FR (chemically treated or in combination with inherent FR fiber technologies), bio chemical, or other specialty protective wear.

Test Methods

[0064] When the various parameters, properties and characteristics for the polymers, fibers, yarns and fabrics herein are specified, it is understood that such parameters, properties and characteristics can be determined using the following types of testing procedures and equipment:

Nylon Polymer Relative Viscosity

[0065] The formic acid RV of nylon materials used herein refers to the ratio of solution and solvent viscosities measured in a capillary viscometer at 25°C. The solvent is formic acid containing 10% by weight of water. The solution is 8.4% by weight nylon polymer dissolved in the solvent. This test is based on ASTM Standard Test Method D 789. The formic acid RVs are determined on spun filaments, prior to or after drawing, and can be referred to as spun fiber formic acid RVs.

Instron Measurements on Staple Fibers

[0066] All Instron measurements of staple fibers herein are made on single staple fibers, taking appropriate care with the clamping of the short fiber, and making an average of measurements on at least 10 fibers. Generally, at least 3 sets of measurements (each for 10 fibers) are averaged together to provide values for the parameters determined.

Filament Denier

[0067] Denier is the linear density of a filament expressed as weight in grams of 9000 meters of filament. Denier can be measured on a Vibroscope from Textechno of Munich, Germany. Denier times (10/9) is equal to decitex (dtex). Denier per filament can be determined gravimetrically in accordance with ASTM Standard Test Method D 1577. A Favimat machine having a vibration based linear density measurement such as used in a Vibroscope can also be used to determine DPF or denier per filament of the individual fiber and is comparable to ASTM D1577.

Tenacity at Break

[0068] Tenacity at break (T) is the maximum or breaking force of a filament expressed as force per unit cross-sectional area. The tenacity can be measured on an Instron model 1130 available from Instron of Canton, Mass. and is reported as grams per denier (grams per dtex). Filament tenacity at break (and elongation at break) can be measured according to ASTM D 885.

Filament Tenacity at 7% and 10% Elongation

[0069] Filament tenacity at 7% elongation (T_7) is the force applied to a filament to achieve 7% elongation divided by filament denier. T_7 can be determined according to ASTM D 3822.

Tenacity at 10% elongation can be run on a Favimat, which is comparable to ASTM D3822.

[0070]

Yarn Strength

[0071] Strength of the spun nylon/cotton yarns herein can be quantified via a Lea Product value or yarn breaking tenacity. Lea Product and skein breaking tenacity are conventional measures of the average strength of a textile yarn and can be determined in accordance with ASTM D 1578. Lea Product values are reported in units of pounds force. Breaking tenacity is reported in units of cN/tex.

Fabric Weight

[0072] Fabric weight or basis weight of the woven fabrics herein can be determined by weighing fabric samples of known area and calculating weight or basis weight in terms of grams/m² or oz/yd² in accordance with the procedures of the standard test method of ASTM D 3776.

Fabric Grab Strength

[0073] Fabric grab strength can be measured in accordance with ASTM D 5034. Grab strength measurements are reported in pounds-force in both warp and fill directions.

Fabric Tear Strength--Elmendorf

[0074] Fabric tear strength can be measured in accordance with ASTM D 1424 titled Standard Test Method for Tearing Strength of Fabrics by Falling-Pendulum Type (Elmendorf) Apparatus. Grab strength measurements are reported in pounds-force in both warp and fill directions.

Fabric Abrasion Resistance--Taber

[0075] Fabric abrasion resistance can be determined as Taber abrasion resistance measured by ASTM D3884-01 titled Abrasion Resistance Using Rotary Platform Double Head Abrader. Results are reported in terms of cycles to failure.

Fabric Abrasion Resistance--Flex

[0076] Fabric abrasion resistance can be determined as Flex abrasion resistance measured by ASTM D3885 titled Standard Test Method for Abrasion Resistance of Textile Fabrics (Flexing and Abrasion Method). Results are reported in terms of cycles to failure.

[0077] The following section provides further illustration of the synthetic fiber and its characteristics as compared to fiber prepared by standard processes without steam draw assist. These working examples are illustrative only and are not intended to limit the scope of the invention in any way.

EXAMPLES

[0078] Example 1: Comparison of Standard T420 versus High Strength T420

[0079] Properties of fiber produced in accordance with the steam draw assist process of the present invention were compared with fiber prepared by a standard process on a Favimat instrument after cutting and bailing. Results are shown in Table 1.

Table 1

Comparison of Standard T420 versus High Strength T420 (Oerlikon Analysis)						
Process	DPF	Elongation (%)	Tenacity (g/den)	Tenacity @ 10% Elongation (g/den)	Feed - Draw Ratio	Total Draw Ratio
Standard T420 Fiber	1.69	48	7.1	2.9	3.12	3.15
High Strength T420 Fiber	1.55	34	7.82	4.1	3.69	3.75
High Strength T420 Fiber	1.59	35.7	8	4.54	3.97	4.05

What is claimed is:

1. A nylon staple fiber comprising a nylon polymer, said fiber having a break tenacity greater than 7.5 g/den.
2. The nylon staple fiber of claim 1 wherein the nylon polymer is nylon 6,6.
3. The nylon staple fiber of claim 1 wherein the tenacity at 10% elongation of greater than 4.0 g/den.
4. A yarn spun from the nylon staple fiber of any of claims 1-4.
5. The yarn of claim 5 further comprising at least one companion staple fiber.
6. The yarn of claim 6 wherein the companion staple fiber is selected from the group consisting of cellulosics, modified cellulosics, animal fibers, fire resistant polyester, fire resistant nylon, fire resistant rayon, fire resistant treated cellulose, m-aramid, p-aramid, modacrylic, novoloid, melamine, polyvinyl chloride, antistatic fiber, PBO (1,4-benzenedicarboxylic acid, polymer with 4,6-diamino-1,3-benzenediol dihydrochloride) and PBI (polybenzimidazole), and combinations thereof.
7. A fabric comprising nylon staple fiber of any of claims 1 through 4 or yarn of any of claims 5 through 7.
8. The fabric of claim 8 with a weight of less than 6.0 oz./yd².
9. The fabric of claim 8 which meets or exceeds military fabrics strength and tear specifications established for fabrics that weigh less than 6.0 oz./yd².

10. An article of manufacture at least a portion of which comprises nylon staple fiber of claim 1.
11. A non-woven fabric composite comprising high tenacity fiber and cellulosic or recycled synthetic or natural fiber.
12. The non-woven composite of claim 12 wherein the high tenacity fiber comprises load bearing nylon fiber with break tenacity greater than 7.5 g/den and/or a tenacity at 10% elongation of greater than 4.0/den.
13. The non-woven composite of claims 12 or 13 wherein the cellulosic or recycled synthetic or natural fiber comprises recycled denim.
14. A method for producing high strength or load bearing nylon fiber, said method comprising melt-spinning nylon polymer into filaments, uniformly quenching the filaments and forming a tow from a multiplicity of these quenched filaments, subjecting the tow to drawing in the presence of steam, annealing, and converting the resulting drawn and annealed tow into staple fibers.
15. The method of claim 15 wherein annealing is performed under tension.
16. The method of claims 15 or 16 wherein the nylon fiber has a break tenacity greater than 7.5 g/den.
17. The method of claim 15 or 16 wherein the nylon fiber has a tenacity at 10% elongation of greater than 4.0g/den.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/055333**A. CLASSIFICATION OF SUBJECT MATTER****D04H 1/4334(2012.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D04H 1/4334; D01G 1/02; D03D 15/00; D01F 6/60; D03D 1/00; B32B 27/02; D02G 3/00; D02G 3/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: nylon staple fiber, break tenacity, tenacity at 10% elongation, fabric, yarn, article, non-woven fabric, cellulosic fiber, recycled synthetic fiber, natural fiber, steam, drawing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010-042929 A2 (INVISTA TECHNOLOGIES S.A. R.L.) 15 April 2010 See abstract; paragraphs [0009], [0011]-[0012], [0020], [0032], [0058]; claims 1-2, 10, 12, 18.	1-2, 4-6, 10
Y		3, 12, 14-17
A		11, 13
Y	CA 1107022 A (FIRESTONE TIRE & RUBBER COMPANY) 18 August 1981 See abstract; claims 1, 4.	3, 14-17
X	US 2013-0115837 A1 (KITCHEN, DALE S. et al.) 09 May 2013 See abstract; paragraphs [0042]-[0043]; claims 1, 6-7.	11, 13
Y		12
A	US 2010-0330351 A1 (CRNOJA-COSIC, MARINA et al.) 30 December 2010 See abstract; claims 1-2, 7, 9-10.	1-6, 10-17
A	US 5093195 A (THOMPSON, JR., ALFRED H.) 03 March 1992 See abstract; claims 1-2.	1-6, 10-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 January 2016 (15.01.2016)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

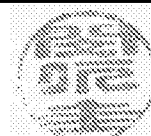
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International application No.
PCT/US2015/055333

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 8-9
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 8 is too unclear to make a meaningful opinion because claim 8 is referring to itself, thereby rendering the definition of the subject matter of said claim unclear. Since claim 9 refers to unsearchable claim 8, it is not possible to make a meaningful opinion to claim 9.
3. ☒ Claims Nos.: 7
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/055333

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010-042929 A2	15/04/2010	CN 102245818 A CN 102245818 B CN 102245819 A CN 102245819 B EP 2334855 A2 EP 2347042 A2 KR 10-2011-0069152 A KR 10-2011-0069153 A US 2011-0177737 A1 US 2011-0177738 A1 WO 2010-042928 A2 WO 2010-042929 A3	16/11/2011 29/10/2014 16/11/2011 31/12/2014 22/06/2011 27/07/2011 22/06/2011 22/06/2011 21/07/2011 21/07/2011 15/04/2010 26/08/2010
CA 1107022 A	18/08/1981	None	
US 2013-0115837 A1	09/05/2013	None	
US 2010-0330351 A1	30/12/2010	EP 2222909 A2 EP 2222909 B1 JP 05732653 B2 JP 2011-509353 A KR 10-2010-0099305 A WO 2009-079674 A2	01/09/2010 04/09/2013 10/06/2015 24/03/2011 10/09/2010 02/07/2009
US 5093195 A	03/03/1992	EP 0399262 A3 EP 0399262 B1 JP 03-206115 A JP 2992566 B2 US 5011645 A	20/03/1991 08/03/1995 09/09/1991 20/12/1999 30/04/1991