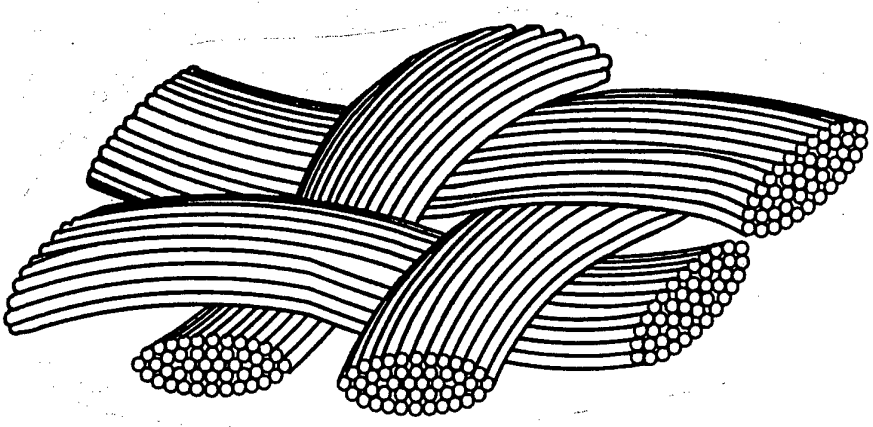




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : F41H 5/04	A1	(11) International Publication Number: WO 94/09336 (43) International Publication Date: 28 April 1994 (28.04.94)
(21) International Application Number: PCT/US93/09789 (22) International Filing Date: 13 October 1993 (13.10.93) (30) Priority data: 959,899 13 October 1992 (13.10.92) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: DUNBAR, James, Jay ; 6601 Shannon Dale Road, Mechanicsville, VA 23111 (US). TAN, Chok, Bin ; 9309 Carbe Road, Richmond, VA 23236 (US). WEE-DON, Gene, Clyde ; 4548 Shanto Court, Richmond, VA 23237 (US). TAM, Thomas, Yiu-Tai ; 3918 Harvette Drive, Richmond, VA 23234 (US). CUTRONE, Alfred, Lewis ; 1226 Gladstone Glen Place, Midlothian, VA 23113 (US). BLEDSOE, Elizabeth, Stroud ; 106 Brunswick Avenue, Blackstone, VA 23824 (US).		(74) Agent: FUCHS, Gerhard, H.; Allied-Signal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ENTANGLED HIGH STRENGTH YARN  (57) Abstract An entangled multifilament yarn made from high strength filaments having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g. The yarn is used to make ballistic resistant articles.		

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Entangled High Strength YarnBACKGROUND OF THE INVENTION

The present invention relates to entangled
5 or commingled high strength filaments and articles that
include the same, particularly ballistic resistant
articles.

Various constructions are known for
ballistic resistant articles such as vests, curtains,
10 mats, raincoats and umbrellas. These articles display
varying degrees of resistance to penetration by high
speed impact from projectiles such as BB's, bullets,
shells, shrapnel, glass fragments and the like. U.S.
Patents No. 4,820,568; 4,748,064; 4,737,402; 4,737,401;
15 4,681,792; 4,650,710; 4,623,574; 4,613,535; 4,584,347;
4,563,392; 4,543,286; 4,501,856; 4,457,985; and
4,403,012 describe ballistic resistant articles which
include high strength filaments made from materials
such as high molecular weight extended chain
20 polyethylene.

One type of common ballistic resistant
article is a woven fabric formed from yarns of high
strength filaments. For example, U.S. Patent No.
4,858,245 broadly indicates that a plain woven, basket
25 woven, rib woven or twill fabric can be made from high
molecular weight extended chain polyethylene filament.
EP-A-0 310 199 describes a ballistic resistant woven
fabric consisting of high strength, ultrahigh molecular
weight filaments in the weft or fill direction and a
30 second type of filaments in the warp direction. U.S.
Patent No. 4,737,401 describes (1) a low areal density
(0.1354 kg/m²) plain weave fabric having 70 ends/inch
in both the warp and fill directions made from
untwisted high molecular weight extended chain
35 polyethylene yarn sized with polyvinyl alcohol, (2) a 2
x 2 basket weave fabric having 34 ends/inch and a
filament areal density of 0.434 kg/m² made from twisted

(approximately 1 turn per inch ("TPI")) high molecular weight extended chain polyethylene yarn, and (3) a plain weave fabric comprised of 31 ends per inch of untwisted 1000 denier aramid yarn in both the fill and warp directions. U.S. Patent No. 4,850,050 describes fabrics made from untwisted aramid yarn having a denier per filament (dpf) of 1.68 and 1.12, respectively. A June 1990 brochure from Akzo N.V. appears to indicate that a fabric for ballistic protection purposes could be made from a 1.33 dpf aramid yarn that is described as being "tangled".

Although these documents indicate that it might be possible to construct a ballistic resistant woven fabric from untwisted or slightly twisted yarns of high strength filaments without sizing, experience has shown that a higher amount of twist is necessary in order to obtain a commercially practical weaving performance. Increasing the amount of twist, however, tends to decrease the end use performance of the fabric, presumably for a number of reasons. First, with respect to ballistic resistance, increased twisting by definition imparts higher torsion to the yarn causing each filament to absorb the energy of an impact transverse to the running direction of the filament rather than along the stronger axial direction of the filament. High strength filaments tend to be weaker in a direction transverse to the running direction of the filament because of their poor compressive strength. Second, the yarn retains a more round shape as the twist is increased, thus preventing the yarn from flattening out to provide a more compact fabric. Third, increased twist tends to increase the denier which results in a lower cover factor. Generally, the more compact the fabric the better the ballistic performance. Moreover, there is a relatively high cost associated with twisting a finer denier yarn such as those with deniers of 500 or less.

Accordingly, a need exists for an article, particularly a fabric, that can be made efficiently and does not suffer from the above-mentioned drawbacks relating to ballistic resistance performance.

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SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a yarn and an article made from that yarn which offers improved ballistic resistance.

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In accomplishing the foregoing object there is provided according to the invention a ballistic resistant multifilament yarn having a longitudinal axis comprising at least one type of high strength filament selected from the group consisting of extended chain polyethylene filament, extended chain polypropylene filament, polyvinyl alcohol filament, polyacrylonitrile filament, liquid crystal filament, glass filament and carbon filament, said high strength filament having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the yarn includes a plurality of sections at which the individual filaments are entangled together to form entanglements and a plurality of sections wherein the individual filaments are substantially parallel to the longitudinal axis of the yarn. Preferably, the high strength filaments comprise extended chain polyethylene filaments and the entangled yarn can have a twist of less than or equal to about 2.5 TPI.

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The invention also is an article made from the above described entangled yarn, such as a woven fabric or a composite, for protecting an object against a ballistic impact. The woven fabric typically is used in a bullet resistant vest.

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Further objects, features and advantages of the present invention will become apparent from the detailed description of preferred embodiments that

follows.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be described in more
5 detail below with reference to the drawing, wherein:

Figure 1A is a photomicrograph of a fabric
made from untwisted, entangled yarn according to the
invention;

Figure 1B is a photomicrograph of a
10 comparative fabric made from twisted, non-entangled
yarn;

Figure 2A is a perspective view of a fabric
made from entangled yarn according to the invention;

Figure 2B is perspective view of a
15 comparative fabric made from twisted, non-entangled
yarn; and

Figure 3 is a photomicrograph of a fabric
made from twisted, entangled yarn according to the
invention.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides an entangled
multifilament yarn that can be used to form improved
ballistic resistant articles, particularly "soft armor"
25 fabric. By "soft armor" is meant an article, such as a
bulletproof vest, which is sufficiently flexible to
wear as a protective garment.

As used herein, "filament" denotes a polymer
which has been formed into an elongate body, the length
30 dimension of which is much greater than the transverse
dimensions of width and thickness.

"Multifilament yarn" (also referred to
herein as "yarn bundle") denotes an elongated profile
which has a longitudinal length which is much greater
35 than its cross-section and is comprised of a plurality
or bundle of individual filament or filament strands.

The cross-sections of filaments for use in

this invention may vary widely. They may be circular, flat or oblong in cross-section. They also may be of irregular or regular multi-lobal cross-section having one or more regular or irregular lobes projecting from the linear or longitudinal axis of the filament. It is particularly preferred that the filaments be of substantially circular, flat or oblong cross-section, most preferably the former.

The multifilament yarn of the invention includes a plurality of sections wherein the individual filaments are tightly entangled together. These sections are referred to herein as "entanglements", but are also known in the art as nips, nodes or knots. The entanglements are separated by lengths of the yarn wherein the individual filaments are not entangled but are aligned substantially parallel to each other. All or only a portion of the individual filaments in a yarn bundle can be entangled together. In general, a section of the yarn wherein at least about 30% of the filaments are entangled is considered to constitute an entanglement for purposes of this invention.

Entangling is a well known method for providing cohesion between individual continuous filament filaments as they are converted into yarn. The purpose of providing this improved cohesion is to alleviate fibrillation and friction problems which occur during processing of multifilament yarn into textile products. The term "entangling" will be used herein for convenience, but other equivalent terms used in the art such as commingling or interlacing could just as easily be substituted therefor.

An important characteristic of the yarn is the distribution of entanglements, i.e., the entanglement level. A common measure of entanglement level is entanglements per meter (EPM), which measures the average number of entanglements per meter of yarn length. The yarn of the invention has an EPM ranging

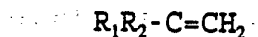
from about 5 to about 55, preferably from about 10 to about 40. If the EPM is above 55, the yarn will be damaged and if the EPM is below 5 the weaving performance will be poor.

- 5 High strength filaments for use in this invention are those having a tenacity equal to or greater than about 7 g/d, a tensile modulus equal to or greater than about 150 g/d and an energy-to-break equal to or greater than about 8 Joules/gram (J/g).
- 10 Preferred filaments are those having a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 200 g/d and an energy-to-break equal to or greater than about 20 J/g. Particularly preferred filaments are those having a
- 15 tenacity equal to or greater than about 16 g/d, a tensile modulus equal to or greater than about 400 g/d, and an energy-to-break equal to or greater than about 27 J/g. Amongst these particularly preferred
- 20 embodiments, most preferred are those embodiments in which the tenacity of the filaments is equal to or greater than about 22 g/d, the tensile modulus is equal to or greater than about 900 g/d, and the energy-to-break is equal to or greater than about 27 J/g. In the practice of this invention, filaments of choice
- 25 have a tenacity equal to or greater than about 28 g/d, the tensile modulus is equal to or greater than about 1200 g/d and the energy-to-break is equal to or greater than about 40 J/g.

- Types of filaments that meet the strength
- 30 requirements include extended chain polyolefin filament, polyvinyl alcohol filament, polyacrylonitrile filament, liquid crystalline polymer filament, glass filament, carbon filament, or mixtures thereof. Extended chain polyethylene and extended chain
- 35 polypropylene are the preferred extended chain polyolefin filaments.

The extended chain polyolefins can be formed

by polymerization of α,β -unsaturated monomers of the formula:



wherein:

5 R_1 and R_2 are the same or different and are hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy, alkoxy, alkoxy, cyano, hydroxy, alkyl and aryl. For greater detail of such polymers of α,β -unsaturated monomers, see U.S. Patent No. 4,916,000, hereby incorporated by reference.

15 U.S. Patent No. 4,457,985, hereby incorporated by reference, generally discusses such extended chain polyethylene and extended chain polypropylene filaments, also referred to herein as high molecular weight extended chain polyethylene and high molecular weight extended chain polypropylene. In
20 the case of polyethylene, suitable filaments are those of molecular weight of at least 150,000, preferably at least 300,000, more preferably at least one million and most preferably between two million and five million. Such extended chain polyethylene (ECPE) filaments may
25 be grown in solution as described in U.S. Patent No. 4,137,394 or U.S. Patent No. 4,356,138, or may be a filament spun from a solution to form a gel structure, as described in German Off. 3 004 699 and GB 20512667, and especially described in U.S. Patent No. 4,551,296,
30 also hereby incorporated by reference. Commonly assigned copending U.S. Patent Applications Serial No. 803,860 (filed December 9, 1991) and 803,883 (filed December 9, 1991), both hereby incorporated by reference, describe alternative processes for removing
35 the spinning solvents from solution or gel spun filaments such as the ones described previously.

According to the system described in Ser.

No. 803,860, the spinning solvent-containing filament (i.e., the gel or coagulate filament) is contacted with an extraction solvent which is a non-solvent for the polymer of the filament, but which is a solvent for the spinning solvent at a first temperature and which is a non-solvent for the spinning solvent at a second temperature. More specifically, the extraction step is carried out at a first temperature, preferably 55 to 100 °C, at which the spinning solvent is soluble in the extraction solvent. After the spinning solvent has been extracted, the extracted filament is dried if the extraction solvent is sufficiently volatile. If not, the filament is extracted with a washing solvent, preferably water, which is more volatile than the extraction solvent. The resultant waste solution of extraction solvent and spinning solvent at the first temperature is heated or cooled to where the solvents are immiscible to form a heterogeneous, two phase liquid system, which is then separated.

According to the system described in Ser. No. 803,883, the gel or coagulate filament is contacted with an extraction solvent which is a non-solvent for the polymer of the filament, but which is a solvent for the spinning solvent. After the spinning solvent has been extracted, the extracted filament is dried if the extraction solvent is sufficiently volatile. If not, the filament is extracted with a washing solvent, preferably water, which is more volatile than the extraction solvent. To recover the extraction solvent and the spinning solvent, the resultant waste solution of extraction solvent and spinning solvent is treated with a second extraction solvent to separate the solution into a first portion which predominantly comprises the first spinning solvent and a second portion which contains at least about 5% of the first extraction solvent in the waste solution.

The previously described highest values for

tenacity, tensile modulus and energy-to-break are generally obtainable only by employing these solution grown or gel filament processes. A particularly preferred high strength filament is extended chain
5 polyethylene filament known as Spectra®, which is commercially available from Allied-Signal, Inc. As used herein, the term polyethylene shall mean a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers
10 not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 weight percent of one or more polymeric additives such as alkene-1-polymers, in particular low density polyethylene, polypropylene
15 or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as antioxidants, lubricants, ultraviolet screening agents, colorants and
20 the like which are commonly incorporated by reference.

Similarly, highly oriented polypropylene of molecular weight at least 200,000, preferably at least one million and more preferably at least two million, may be used. Such high molecular weight polypropylene
25 may be formed into reasonably well-oriented filaments by techniques described in the various references referred to above, and especially by the technique of U.S. Patent Nos. 4,663,101 and 4,784,820. and U.S. Patent Application Serial No. 069 684, filed July 6,
30 1987 (see published application WO 89 00213). Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding
35 values for polyethylene. Accordingly, a suitable tenacity is at least about 10 g/d, preferably at least about 12 g/d, and more preferably at least about 15

g/d. The tensile modulus for polypropylene is at least about 200 g/d, preferably at least about 250 g/d, and more preferably at least about 300 g/d. The energy-to-break of the polypropylene is at least about 8 J/g, preferably at least about 40 J/g, and most preferably at least about 60 J/g.

High molecular weight polyvinyl alcohol filaments having high tensile modulus are described in U.S. Patent No. 4,440,711, hereby incorporated by reference. Preferred polyvinyl alcohol filaments will have a tenacity of at least about 10 g/d, a modulus of at least about 200 g/d and an energy-to-break of at least about 8 J/g, and particularly preferred polyvinyl alcohol filaments will have a tenacity of at least about 15 g/d, a modulus of at least about 300 g/d and an energy-to-break of at least about 25 J/g. Most preferred polyvinyl alcohol filaments will have a tenacity of at least about 20 g/d, a modulus of at least about 500 g/d and an energy-to-break of at least about 30 J/g. Suitable polyvinyl alcohol filament having a weight average molecular weight of at least about 200,000 can be produced, for example, by the process disclosed in U.S. Patent No. 4,599,267.

In the case of polyacrylonitrile (PAN), PAN filament for use in the present invention are of molecular weight of at least about 400,000. Particularly useful PAN filament should have a tenacity of at least about 10 g/d and an energy-to-break of at least about 8 J/g. PAN filament having a molecular weight of at least about 400,000, a tenacity of at least about 15 to about 20 g/d and an energy-to-break of at least about 25 to about 30 J/g is most useful in producing ballistic resistant articles. Such filaments are disclosed, for example, in U.S. Patent No. 4,535,027.

In the case of liquid crystal copolyesters, suitable filaments are disclosed, for example, in U.S.

Patent Nos. 3,975,487; 4,118,372; and 4 161 470, hereby incorporated by reference. Tenacities of about 15 to 30 g/d, more preferably about 20 to 25 g/d, modulus of about 500 to 1500 g/d, preferably about 1000 to 1200 g/d, and an energy-to-break of at least about 10 J/g are particularly desirable.

Illustrative of glass filaments that can be used in this invention are those formed from quartz, magnesia aluminosilicate, non-alkaline aluminoborosilicate, soda borosilicate, soda silicate, soda lime-aluminosilicate, lead silicate, non-alkaline lead boroalumina, non-alkaline barium boroalumina, non-alkaline zinc boroalumina, non-alkaline iron aluminosilicate and cadmium borate.

The entangled yarn of the invention can include filaments of more than one type of high strength filament. Preferably, however, the entangled yarn is formed from filaments of only one type of high strength filament. The dpf of the yarn should be at least 1.75, preferably at least 2.5, and most preferably 3.0.

If high molecular weight extended chain polyethylene filament is used to form the entangled yarn, the denier of the resulting entangled yarn should range from about 100 to about 4800, preferably from about 200 to about 650. Especially preferred are 215, 375, 430 and 650 denier multifilament yarns. The number of extended chain polyethylene filaments in a single entangled yarn can range from about 30 to 480, with 60 to 120 filaments being especially preferred.

The entangled yarn of the invention can be formed by any conventional method for producing entangled yarns. Such methods are well known and are described, for example, in U.S. Patents No. 4,729,151, 4,535,516, and 4,237,187 and by Demir and Acar in their "Insight Into the Mingling Process" paper presented at the Textile World Conference, Oct. 1989, and published

by the Textile Institute in Textiles: Fashioning the Future, all hereby incorporated by reference.

As described in these documents, entangled yarn typically is formed by an apparatus referred to as an air jet. Although there are many types of jets currently utilized such as closed jets, forwarding jets and slotting jets, all air jets generally include a yarn chamber or bore extending the length of the body which accomodates various yarn and filament deniers, at least one opening for the filaments to enter the yarn chamber, at least one opening for the resulting entangled yarn to exit the yarn chamber, and at least one air orifice which is used to direct an air flow into the yarn chamber to cause the entangling of the filaments. An air jet is presumed to form an entangled yarn as follows:

Within the air jet the loose bundle of continuous multifilament yarn is subjected to a turbulent gas stream contacting the yarn at right angles to its axis. The gas stream spreads open the filaments and, within the immediate vicinity of the spread open section, forms a plurality of vortexes which cause the filaments to become entangled. The alternating entanglement nodes and non-entangled sections are formed as the yarn travels through the chamber.

The entangled yarn of the invention is obtained by adjusting the pressure of the air striking the yarn bundle, the tension of the yarn bundle as it passes through the air jet and the air jet dimensions depending upon the type of high strength filament, the number of filaments in the yarn bundle, the desired denier of the entangled yarn and the desired level of entanglement. In each instance, the above-identified processing parameters are adjusted so that the air pressure is sufficient to separate the incoming yarn bundle and generate the vortex and resonance necessary

to entangle the filaments.

There is not a limit on the number of air orifices per yarn end in the air jet, but a single, double or triple orifice air jet is preferred. The air jets also can be arranged in tandem. That is, there can be more than one air jet for each yarn end. The air jet bore can be any shape such as oval, round, rectangular, half-rectangular, triangular or half-moon. The gas stream can strike the filaments at any angle, but an approximately right angle is preferred.

One preferred double round orifice air jet has a bore which is formed by two parallel plates, the faces of which are separated equidistantly from each other by an opening which can range from about 1.5 to 3 mm. Another preferred air jet has a round orifice and an oval bore wherein the orifice diameter/bore diameter ratio is about 0.40 to 0.55, wherein the oval-shaped bore is measured at its widest diameter.

The air passing through the orifice and striking the filaments must be of sufficient pressure to achieve the degree of entanglement desired without causing any damage to the filaments. The air pressure used to produce the yarn of the invention should range from about 35 to about 55 psi.

The filaments can be transported through the air jet via any conventional method. For example, the individual filaments leaving the filament-forming apparatus such as a spinnerette could pass through draw rolls and then be collected into a yarn bundle which subsequently passes through the air jet. The entangled yarn then is sent via a guide to a winder which wraps the yarn around a bobbin or spool to form a yarn package. The winder and/or draw roll functions to control the tension of the yarn as it passes through the air jet. The preferred tension on the yarn as it passes through the air jet is about 75 to 125 g.

The entangled yarns of the present invention

can be used to make various textile articles, particularly woven or knit fabrics or nonwovens. Woven fabrics are preferred because their end use characteristics are more controllable due to woven
5 fabrics' higher dimensional stability. The weave pattern can be any conventional pattern such as plain, basket, satin, crow feet, rib and twill. Examination of fabrics woven from entangled high molecular weight extended chain polyethylene yarn has shown that
10 substantially all the entanglements remain in the yarn after it has been woven.

Fabrics that can be formed from the entangled yarn of the present invention may include only one type of high strength filament, preferably
15 high molecular weight extended chain polyethylene. It is also contemplated that a fabric could include a second type of filament such as another high strength filament, which may or may not be entangled, or a filament that improves the feel or stretchability of
20 the fabric such as nylon (e.g., Hydrofil® available from Allied-Signal), polyester, spandex, polypropylene, cotton, silk, etc. For example, entangled extended chain polyethylene filaments can be used for the warp yarn and the second filament could be used for the fill
25 yarn, or vice versa. Regardless of what type of filament is used for the second filament, what is important to the ballistic performance of the fabric is that it includes an entangled yarn of high strength filaments in either the warp or fill direction. If the
30 fabric is formed from extended chain polyethylene exclusively, the filament used in one direction (e.g., the warp) may be of a different tenacity, modulus, filament number, filament or total denier, twist than the filament used in the other direction (e.g., the
35 fill).

The entangled yarns of the present invention also can be incorporated into composites. For example,

the entangled yarns can be arranged into a network such as woven fabric, a nonwoven or a knit and coated with, impregnated with or embedded in a resin matrix as described in U.S. Patents No. 4,403,012; 4,457,985; 5 4,501,856; 4,613,535; 4,623,574; 4,650,710; 4,737,402 and 5,124,195, all hereby incorporated by reference. Particularly preferred multi-layer composites are those wherein each layer includes entangled yarns arranged into a unidirectionally aligned network, i.e., all the 10 yarns are substantially parallel to each other, which is impregnated with a resin matrix. The layers are oriented so that the angle between the unidirectionally aligned filaments of adjacent layers is 90°.

The entangled yarn of the invention is 15 particularly effective for use in articles which are intended to protect an object from ballistic impact. Such an article could be a fabric which is used in soft armor. It is suspected that the improved ballistic resistance results from a number of unique 20 characteristics of the entangled yarn.

In the entangled yarn, except for the relatively small areas of entanglement, the individual filaments are substantially parallel to the longitudinal axis of the yarn. In other words, it is 25 estimated that on average about 50 to 95 %, preferably about 60 to 90 %, of the total length of the yarn consists of sections wherein the individual filaments are substantially parallel to the longitudinal axis of the yarn. The phrase "substantially parallel" means 30 that the angle between an individual filament along its running length and the longitudinal axis of the entangled yarn should be zero or as close to zero as possible without exceeding 5°, preferably 10°. Figure 1A shows a woven fabric made from entangled yarn 35 according to the invention wherein the individual filaments are substantially parallel to the yarn axis. The specific construction of the fabric shown in Figure

1A is described further in this document as Inventive Example 1. It should be recognized that not all the individual filaments may be substantially parallel to the longitudinal axis of the yarn, but the number of
5 filaments deviating from the yarn axis is sufficiently small so as to not adversely affect the properties of the yarn. This parallel filament characteristic of the entangled yarn leads to several advantages.

First, when the yarn is impacted by a
10 projectile, the energy of the impact is absorbed along the running direction of the filament, which is where the filament tensile strength is the greatest.

In addition, the yarn tends to assume a less round or more flat profile as depicted in Figure 2A
15 because the friction between the individual filaments is less. A more flat profile allows for tighter weaving and allows the pick or end yarns to lie in the same plane. This tighter weave and increased planarity enhances the ballistic resistance. The improved
20 coverage resulting from the flattening of the yarn also allows the utilization of lower yarn end counts in a fabric leading to a lighter fabric.

Another advantage is important in the context of composite articles which include high
25 strength yarns aligned in the previously described 0°/90° fashion. Due to the substantially parallel alignment of the filaments relative to the yarn axis, the angle between the filaments of successive layers will be maintained at the desired 90°. If the
30 individual filaments are not substantially parallel but deviate at least 10° from the yarn axis, the angle between the filaments of successive layers will also deviate.

The entangling contemplated in this
35 invention not only results in the above-described advantages but also enhances the weaving performance of the yarn. As explained previously, the entanglements

provide cohesion between the individual filaments. Accordingly, the entangled yarn without any further treatment such as twisting or sizing can be woven into a fabric. Indeed, the weaving performance of a high molecular weight extended chain polyethylene yarn (Spectra® 1000) which has been entangled according to the invention is superior to the weaving performance of such a yarn which has only been twisted (at least 3 TPI). Specifically, the twisted only yarn provides a running efficiency of approximately 30% and a yield of approximately 25%. The entangled yarn, however, provides a running efficiency of at least approximately 60% and a yield of at least approximately 85%. Running efficiency is the relative amount of time lost to weaving machine stoppage and yield measures the amount of yarn on a package that is converted into fabric. Further treatment of the entangled yarn is particularly unnecessary when the yarn is used to form a unidirectionally aligned nonwoven for utilization in a composite.

Although the entangled yarn can be woven into a fabric without any further treatment, it has been found advantageous for weaving performance if twist also is applied to the entangled yarn. As mentioned previously, prior to this invention a certain amount of twist has been imparted to high strength multifilament yarns to provide efficient weaving into a fabric as shown in Figure 1B. The fabric shown in Figure 1B has a 56 x 56 plain weave construction and is made from 215 denier extended chain polyethylene yarn having a twist of 5.0 TPI in both the fill and warp directions.

Such a relatively high amount of twist, however, significantly impairs the performance of an article woven from the twisted yarn for the reasons identified above. The disadvantages of a highly twisted yarn are particularly evident when compared to

the advantages of the entangled yarn of the invention. It is clear from a comparison of Figures 1A and 1B that twisting a yarn will impart a helical angle to the individual filaments relative to the longitudinal axis of the yarn, the consequences of which have been explained previously. In addition, comparison of Figures 2A and 2B makes it clear that twisting prevents the fabric from assuming a more compact form. Furthermore, the diameter of an entangled yarn having a certain denier is greater than the diameter of a twisted yarn having the same denier and, thus, the entangled yarn provides better coverage. The flattening out of the entangled, untwisted yarn also is apparent from Figure 3 which is a 39 x 39 plain weave fabric made according to the invention from 375 denier extended chain polyethylene yarn (Spectra® 1000 available from Allied-Signal). Both the warp yarn, which runs in the vertical direction in this photomicrograph, and the fill yarn, which runs in the horizontal direction, are entangled, but the warp yarn also has 1 TPI. It is clear that the untwisted fill yarn provides greater coverage.

It has been discovered that these unique characteristics of entangled yarn of the invention compensate for the problems caused by twisting and, thus, permit the use of high strength yarn that includes a limited amount of twist. In particular, the entangled yarn of the invention can have a twist of up to about 2.5 TPI, preferably 2.0 TPI, and most preferably 0.5 TPI. This twisted entangled yarn can be used to make a fabric which has good weaving performance as well as significantly improved ballistic performance. If the fabric is woven, the fill and/or the warp yarns can be twisted and entangled, although twisting in the warp direction only is preferred. Particularly advantageous is a fabric having as the warp yarn an entangled high molecular weight extended

chain polyethylene multifilament yarn which has a twist of 1.7 TPI or 0.25 TPI and as the fill yarn an untwisted, entangled high molecular weight extended chain polyethylene multifilament yarn.

- 5 The needle pattern used for the woven fabrics made from the entangled yarn can be any conventional pattern, but a 56 x 56 plain weave pattern (56 yarns ends/inch in the warp direction; 56 yarn ends/inch in the fill direction) is preferred,
10 particularly if the entangled yarn is also twisted. If the entangled yarn is not twisted, a 45 x 45, 34 x 34, or 28 x 56 plain weave pattern is preferred.

- The advantages of the entangled yarn will become more apparent from the following exemplified
15 embodiments. Ballistic testing of the examples was performed in accordance with NIJ standard 0101.03. According to this method, samples are prepared, placed on a clay backing, and shot 16 times with a .357 Magnum or a 9 mm. The protective power of the sample is
20 expressed by citing the impacting velocity at which 50% of the projectiles are stopped which is designated the V_{50} value and the impacting velocity at which 95% of the projectiles are stopped which is designated V_5 .

25 Comparative Example 1

- A 640 filament, 840 denier Kevlar® 129 yarn, an aramid yarn available from E.I. duPont, was woven into a fabric using a 31 x 31 plain weave pattern wherein both the warp and fill yarns had a twist of 3
30 TPI but no entanglement. The fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/wt².

 Comparative Example 2

- A 60 filament, 215 denier Spectra® 1000
35 yarn, a high molecular weight extended chain polyethylene yarn available from Allied-Signal, was woven into a fabric using a 56 x 56 plain weave pattern

wherein both the warp and fill yarns had a twist of 5 TPI but no entanglement. The fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/ft².

5 Inventive Example 1

 A 60 filament, 215 denier Spectra® 1000
untwisted yarn was woven into a fabric using a 56 x 56
plain weave pattern wherein both the warp and fill
yarns had an entanglement level of 18 EPM. The
10 Spectra® 1000 yarn used in this example had a tensile
strength of about 26 g/d prior to entangling while the
Spectra® 1000 yarn used in the other examples,
including Comparative Example 2, had a tensile strength
of about 36 g/d prior to entangling. The weaving
15 performance was good. The fabric was cut into 18 in²
squares which were stacked to form a sample having an
areal weight of 0.75 lb/ft².

 Inventive Example 2

 A 60 filament, 215 denier Spectra® 1000
20 untwisted yarn was woven into a fabric using a 56 x 56
plain weave pattern wherein both the warp and fill
yarns had an entanglement level of 35 EPM. The weaving
performance was adequate, but not as good as that for
Inventive Example 1. The fabric was cut into 18 in²
25 squares which were stacked to form a sample having an
areal weight of 0.75 lb/ft².

 Inventive Example 3

 A 60 filament, 215 denier Spectra® 1000
untwisted yarn was woven into a fabric using a 56 x 56
30 plain weave pattern wherein both the warp and fill
yarns had an entanglement level of 25 EPM. The weaving
performance was adequate, but not as good as that in
Inventive Example 1. The fabric was cut into 18 in²
squares which were stacked to form a sample having an
35 areal weight of 0.75 lb/ft².

 Inventive Example 4

 A 60 filament, 215 denier Spectra® 1000 yarn

was woven into a fabric using a 56 x 56 plain weave pattern wherein both the warp and fill yarns had an entanglement level of 25 EPM. In addition, the warp yarn had a twist of 1.7 TPI. The fill yarn was
5 untwisted. The weaving performance was better than that in Inventive Example 1. The fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/ft².

Inventive Example 5

10 A 60 filament, 215 denier Spectra® 1000 untwisted yarn was woven into a fabric using a 45 x 45 plain weave pattern wherein both the warp and fill yarns had an entanglement level of 25 EPM. It was possible to weave this fabric, but the weaving
15 performance was poor compared to the other inventive examples. The fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/ft².

Inventive Example 6

20 A 60 filament, 215 denier Spectra® 1000 untwisted yarn was woven into a fabric using a 28 x 56 plain weave pattern wherein both the warp and fill yarns had an entanglement level of 22 EPM. The weaving performance was better than that in Inventive Examples
25 1, 2, 3 and 5. The fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/ft².

Inventive Example 7

A 60 filament, 215 denier Spectra® 1000 yarn
30 was woven into a fabric using a 56 x 56 plain weave pattern wherein both the warp and fill yarns had an entanglement level of 22 EPM. In addition, the warp yarn had a twist of 0.25 TPI. The fill yarn was untwisted. The weaving performance was adequate. The
35 fabric was cut into 18 in² squares which were stacked to form a sample having an areal weight of 0.75 lb/in².

The results of ballistic resistance esting

performed on the above-described examples are listed in Table 1.

Table 1 - Ballistic Resistance

5		V_i	V_{50}
		(ft/sec)	(ft/sec)
	Comp. Ex.1	1269 (9mm);	1412 (9mm);
		1339 (.357)	1442 (.357)
10	Comp. Ex.2	1207 (9mm);	1383 (9mm);
		1404 (.357)	1479 (.357)
	Inv. Ex.1	1334 (.357)	1428 (.357)
	Inv. Ex.2	1416 (.357)	1524 (.357)
	Inv. Ex.3	1330 (9mm);	1486 (9mm);
		1398 (.357)	1542 (.357)
15	Inv. Ex.4	1336 (9mm)	1482 (9mm)
	Inv. Ex.5	1366 (9mm)	1562 (9mm)
	Inv. Ex.6	1328 (9mm)	1531 (9mm)
	Inv. Ex.7	1291 (9mm)	1470 (9mm)

20

It is clear from Table 1 that fabrics made from the entangled yarn of the invention exhibit significant improvement over the fabrics of the comparative examples with respect to ballistic resistance to deformable projectiles such as most bullets. Moreover, it is apparent from a comparison of Comparative Example 2 and Inventive Examples 1-3 and 5 that fabrics made from entangled yarn, untwisted yarn exhibit improved ballistic resistance to deformable projectiles relative to fabric made from non-entangled, twisted yarn.

This improvement in ballistic resistance is even more surprising when the physical properties of a non-entangled, untwisted 60 filament, 215 denier Spectra® 1000 control yarn and an entangled(25 EPM), untwisted yarn made from the control yarn are compared. The control yarn had a breaking strength of 18.43 lb.,

a tensile strength of 37.8 g/d and a modulus of 2457 g/d while the entangled yarn had a breaking strength of 17.2 lb, a tensile strength of 36.1 g/d and a modulus of 2,291 g/d. The entangling actually decreased the
5 physical properties of the yarn, yet a superior ballistic performance was achieved.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without
10 departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

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CLAIMS

We claim:

1. A ballistic resistant multifilament yarn having a longitudinal axis comprising at least one type of high strength filament selected from the group consisting of extended chain polyethylene filament, extended chain polypropylene filament, polyvinyl alcohol filament, polyacrylonitrile filament, liquid crystal filament, glass filament and carbon filament, said high strength filament having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the yarn includes a plurality of sections at which the individual filaments are entangled together to form entanglements and a plurality of sections wherein the individual filaments are substantially parallel to the longitudinal axis of the yarn.
2. A ballistic resistant yarn according to claim 1, wherein the high strength filament comprises extended chain polyethylene.
3. A ballistic resistant yarn according to claim 1, wherein the sections of substantially parallel filaments form about 50 to 95 % of the total length of the yarn.
4. A ballistic resistant yarn according to claim 1, wherein the average number of entanglements per meter of yarn length is about 5 to 55.
5. A ballistic yarn according to claim 1, wherein the yarn includes a twist of less than or equal to about 2.5 turns per inch.
6. A ballistic resistant yarn according to claim 5, wherein the yarn includes a twist of less than or equal to about 2.0 turns per inch.

7. An article for protecting an object against a ballistic impact, including at least one multifilament yarn having a longitudinal axis, the yarn comprising at least one type of high strength filament selected from the group consisting of extended chain polyethylene filament, extended chain polypropylene filament, polyvinyl alcohol filament, polyacrylonitrile filament, liquid crystal filament, glass filament and carbon filament, said high strength filament having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the yarn includes a plurality of sections at which the individual filaments are entangled together to form entanglements and a plurality of sections wherein the individual filaments are substantially parallel to the longitudinal axis of the yarn.

8. An article according to claim 7, wherein the article comprises a woven fabric having a fill yarn and a warp yarn and at least one of the fill and warp yarns is the entangled multifilament high strength yarn.

9. An article according to claim 7, wherein the high strength filament comprises extended chain polyethylene.

10. An article according to claim 8, wherein the fill and warp yarns are both entangled multifilament high strength yarn comprised of extended chain polyethylene filaments and the warp yarn has a twist of less than or equal to about 2.0 turns per inch and the fill yarn has a twist of less than or equal to about 0.50 turns per inch.

1/3

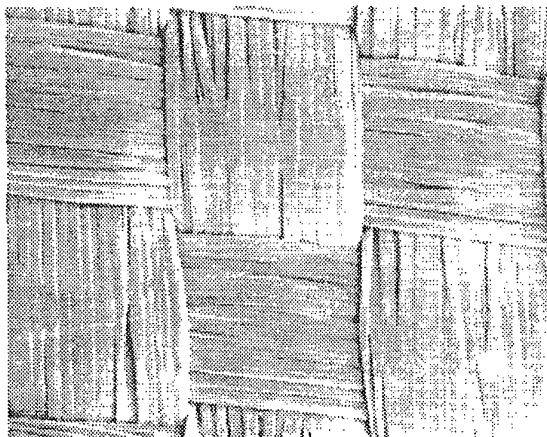


FIGURE 1A

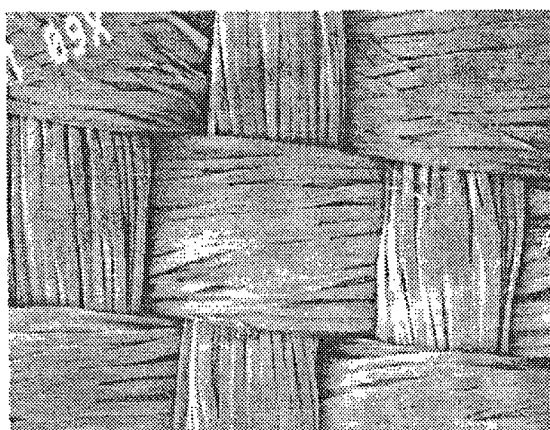


FIGURE 1B

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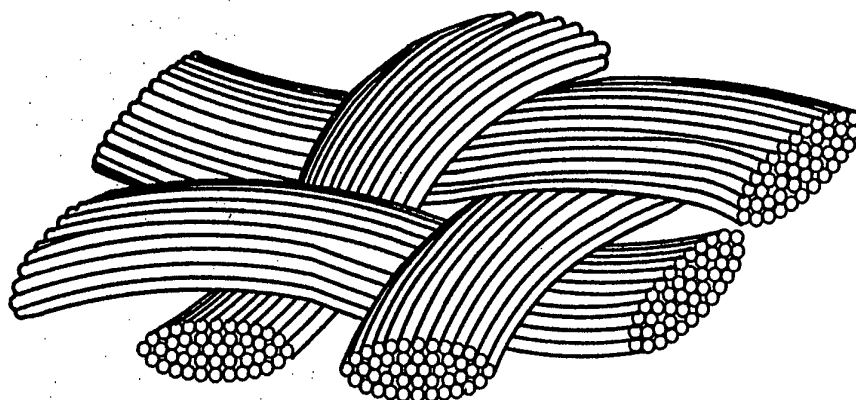


FIGURE 2A

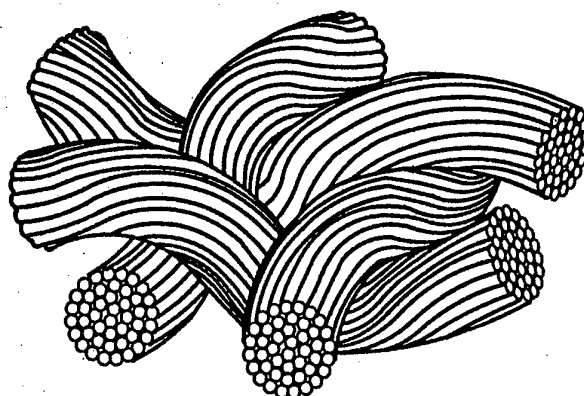


FIGURE 2B

SUBSTITUTE SHEET

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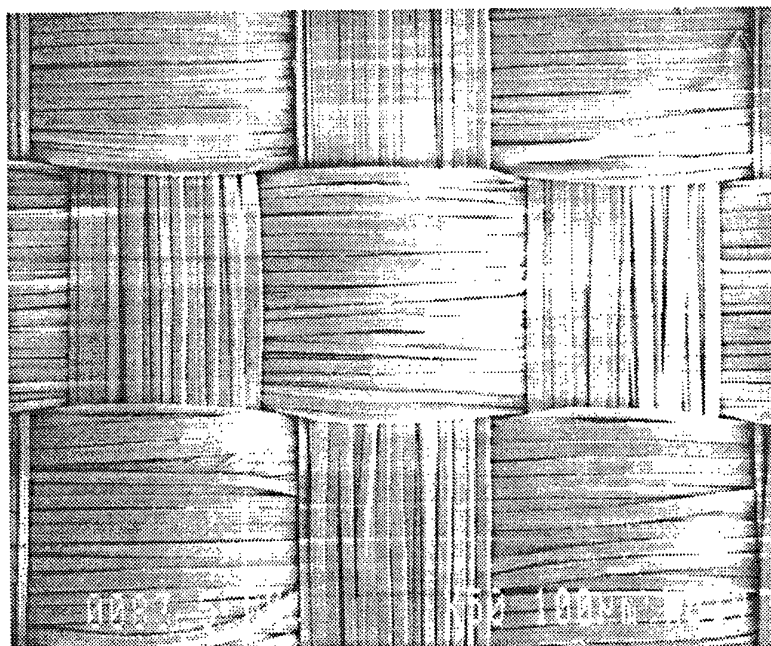


FIGURE 3

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 93/09789

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 F41H5/04

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)
IPC 5 F41H

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 04855 (JAMES RIVER CORPORATION) 18 April 1991 see page 1, line 5 - page 2, line 28 see page 6, line 7 - line 25; claims	1-4,7-9
Y	---	5,6,10
Y	EP,A,0 199 019 (ALLIED CORPORATION) 29 October 1986 see page 13, line 20 - page 14, line 14 ---	5,6,10
X	WO,A,92 14608 (CUSTOM PAPERS GROUP INC) 3 September 1992 see page 11, line 21 - page 12, line 16 see page 14, line 24 - page 15, line 26; claims 1-17,47 --- -/--	1-4,7-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

14 January 1994

Date of mailing of the international search report

28. 01. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 cpo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

DOUSKAS, K

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 93/09789

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 168 298 (FITZGERALD) 18 September 1979 see claims -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/09789

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9104855	18-04-91	AU-A- 6899191 EP-A- 0494269	28-04-91 15-07-92
EP-A-0199019	29-10-86	US-A- 4650710 CA-A- 1244300 DE-A- 3684807 JP-A- 63092448	17-03-87 08-11-88 21-05-92 22-04-88
WO-A-9214608	03-09-92	AU-A- 1797992	15-09-92
US-A-4168298	18-09-79	US-A- 4064214	20-12-77