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(54) **FIBER NETWORK LAYERS AND FLEXIBLE PENETRATION RESISTANT ARTICLES COMPRISING SAME**

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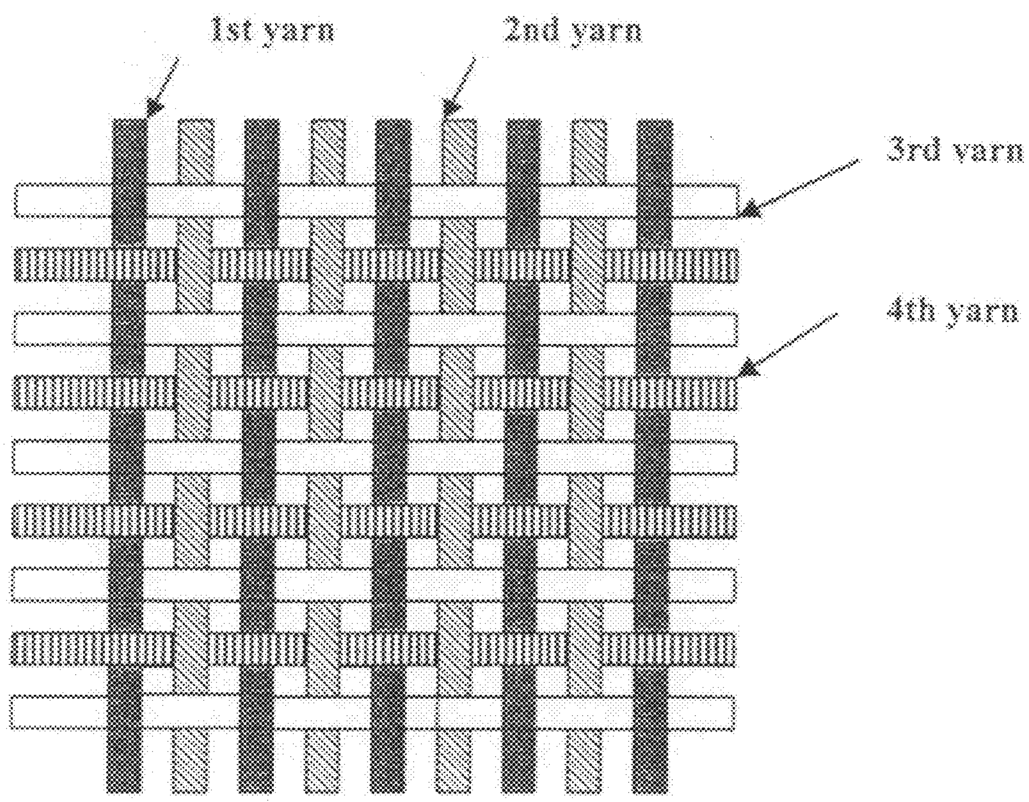
(57) **ABSTRACT**

The present invention is directed to a fiber network layer for use in penetration resistant articles having a first plurality of yarns and a second plurality of yarns, each of the first and second yarns arranged in a first direction parallel or substantially parallel to the other first and second yarns and a third plurality of yarns, each of the third yarns arranged in a second direction parallel or substantially parallel to the other third yarns; the second direction transverse to the first direction. The third yarns and either the first yarns or the second yarns are made of a first polymer. Each of the first, second and third yarns having a tenacity of at least 15 g/dtex. The layers are such that either (i) the second yarns are made of a second polymer which is different than the first polymer, or (ii) the first yarns have a different average linear density than the average linear density of the second yarns, or (iii) the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns, or (iv) combinations thereof.



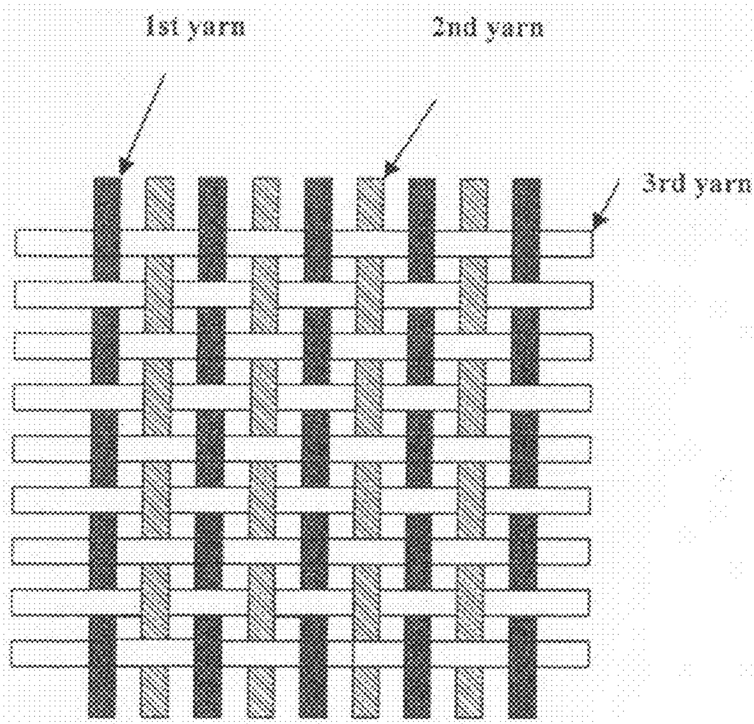


FIGURE 1

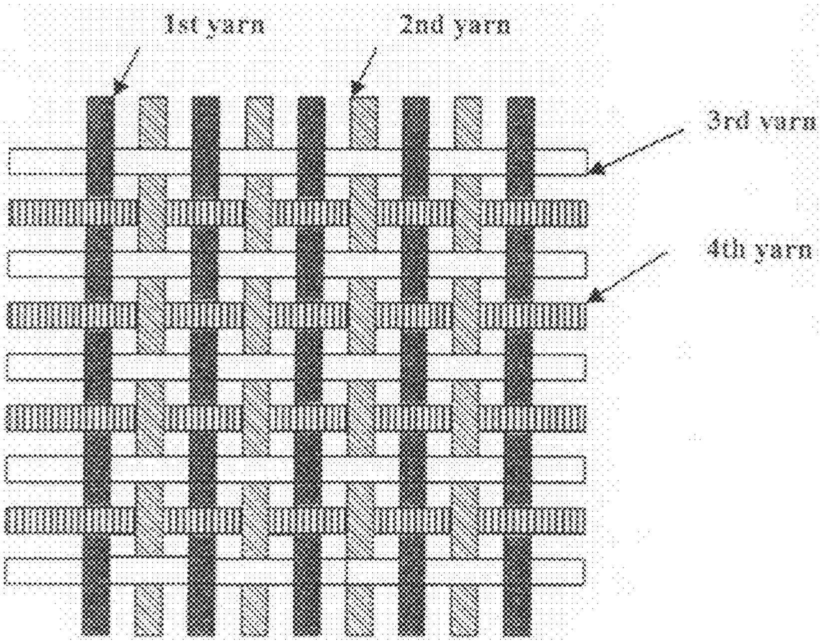


FIGURE 2

FIBER NETWORK LAYERS AND FLEXIBLE PENETRATION RESISTANT ARTICLES COMPRISING SAME

RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Application No. 60/707,200, filed Aug. 10, 2005, and U.S. Provisional Application No. 60/720,898, filed Sep. 27, 2005, the disclosures of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a fiber network layer for use in penetration resistant articles and to articles that contain one or more such layers.

BACKGROUND OF THE INVENTION

[0003] Reports indicate that antiballistic vests made of 100% poly(p-phenylene-2,6-benzobisoxazole) fabrics (PBO fabrics) can exhibit higher ballistic performance than conventional fabrics. The PBO fabrics, however, are very expensive and are of limited use for some life protection applications.

[0004] Various fabric constructions are know for anti-ballistic materials. It is know, for example, to use different layers where a first layer is constructed of fibers of a first polymer and a second layer is constructed of fibers of a different polymer.

[0005] It also known that fibers of two polymer can be used in a single layer. Canadian Patent Application CA1034842, for example, teaches multiple weave protective fabrics woven in an asymmetrical weave using warp and weft fibers of dissimilar properties. Another published application, Canadian Patent Application CA2313995, teaches a weave where two adjacent fibers in both the warp and weft are of different materials.

[0006] U.S. Pat. No. 6,155,306 teaches multifilament bulletproof fabrics that can have a warp having polyethylene fibers and a weft comprising aramid fibers. U.S. Pat. No. 6,610,619 teaches a multilayer crossplied fabrics with a first set of threads traverse to a second set of threads where the ratio of linear density of the first set of threads to the second set of threads is greater than 4.2. U.S. Pat. No. 5,180,880 teaches a soft vest having a combination of dissimilar materials where the warp yarns are aramid and the fill yarn is a thermoplastic material. European Patent Application EP 310199(A1) teaches bulletproof woven fabrics with different materials in the warp and fill directions. U.S. Pat. No. 5,187,003 discloses a woven antiballistic fabric where fibers in the fill direction have a greater elongation to break than the fibers in the warp direction.

[0007] Despite these advances, there is a need for lighter weight, higher performance life protection body armors.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a fiber network layer for use in penetration resistant articles, comprises:

[0009] a first plurality of yarns and a second plurality of yarns, each of the first and second yarns arranged in a first direction parallel or substantially parallel to the other first and second yarns; and

[0010] a third plurality of yarns, each of the third yarns arranged in a second direction parallel or substantially parallel to the other third yarns, the second direction transverse to the first direction, the third yarns and either the first yarns or the second yarns made of a first polymer;

[0011] wherein each of the first, second and third yarns having a tenacity of at least 15 g/dtex (preferably from 20 to 45 g/dtex in some embodiments), and

[0012] wherein (i) the second yarns are made of a second polymer which is different than the first polymer, or (ii) the first yarns have a different average linear density than the average linear density of the second yarns, or (iii) the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns, or (iv) combinations thereof.

[0013] In some preferred embodiments, the fiber network layer further comprises a fourth plurality of yarns, each of the fourth yarns arranged in the second direction parallel or substantially parallel to the third yarns wherein (i) the fourth yarns are made of the second polymer or a third polymer, or (ii) the third yarns have a different average linear density than the average linear density of the fourth yarns, or (iii) the third and fourth yarns comprise multifilament yarns with filaments and the filaments of the third yarns have an average linear density different from the filaments in the fourth yarns, or (iv) combinations thereof.

[0014] In certain embodiments, the first yarns comprise at least 35% [preferably 40 to 60% in some embodiments] of the total number of yarns in the first direction, and

[0015] the second yarns comprise at least 35% [preferably 40 to 60% in some embodiments] of the total number of yarns in the first direction.

[0016] In some embodiments, all fibers in the second direction are of the third plurality of yarns.

[0017] In some fiber networks, the fiber network layer has an areal density of no more than 10 kg/m^2. In some embodiments, the areal density is preferably 2 to 8 kg/m^2.

[0018] In certain aspects of the invention, each of the first, second, and third yarns have an elongation at break of at least 2% (preferably from 2.5% to 10% in some embodiments) and a modulus of elasticity of at least 150 grams per dtex (preferably from 250 to 2000 in some embodiments).

[0019] Certain layers are such that each of the first, second, and third yarns yearns have a tenacity of at least 15 grams per denier (preferably at least 20 grams per denier in some embodiments). In other embodiments, the fiber network layer has at least one of the first, second, and third yarns have a tenacity of at least 30 grams per denier. In some embodiments, the tenacity is preferably at least 35 grams per denier.

[0020] Some layers have at least one of the first, second, and third yarns yearns have a tenacity of least 30 grams per denier and density of at least 1.6 grams per cubic centimeter.

[0021] In some embodiments, the second yarns are made of a second polymer which is different than the first polymer.

[0022] In certain embodiments, the first yarns have a different average linear density than the average linear density of the second yarns. In some embodiments, the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns.

[0023] In some aspects, the invention concerns a fiber network layer where the first and third yarns are made of the first polymer and have substantially the same average linear density, and the filaments of the first and third yarns have substantially the same average linear density.

[0024] In some layers, each of the first, second, and third yarns have a linear density of 100 to 5000 decitex. In some embodiments, the linear density is preferably 220 to 3300 decitex. In certain layers, the first, second, and third yarns have a linear density of 0.1 to 10 decitex. In certain embodiments, the yarns are preferably 0.2 to 5.5 decitex.

[0025] Some layers of the invention comprise filaments of the first, second and third yarns are continuous filaments, staple fibers, or mixtures of both.

[0026] In some embodiments, the first and second yarns arranged in an alternating sequence.

[0027] The first and second polymers, in some embodiments, are selected from the group consisting of polyamide, polyolefin, polybenzoxazole, polybenzothiazole, poly{2,6-diimidazo[4,5-b4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene}, polyareneazoles, polypyridazoles, polypyridobisimidazoles and mixtures thereof. In certain embodiments, the first polymer is poly (p-phenylene terephtahlamide).

[0028] Some layer of the invention are such that the first yarns, the second yarns, and the third yarns are woven, non-woven, or a unidirectional array stacked othogonally on a unidirectional array.

[0029] The invention also relates to a flexible penetration resistant article comprising a plurality of fiber network layers as described herein. Some flexible penetration resistant articles have an areal density of 2 to 12 kg/m^2. Certain articles have at least one layer of fabric layers being impregnated with a polymeric matrix comprising a thermoset resin, a thermoplastic resin, or mixtures thereof.

[0030] In some embodiments, the invention also concerns a method of weaving fiber networks. In one embodiments, A method of making a fiber network layer comprising:

[0031] weaving a first plurality of yarns and a second plurality of yarns, each of the first and second yarns in a first direction parallel or substantially parallel to the other first and second yarns;

[0032] with a third plurality of yarns, each of the third yarns arranged in a second direction parallel or substantially parallel to the other third yarns, the second direction transverse to the first direction, the third yarns and either the first yarns or the second yarns made of a first polymer;

wherein:

- [0033] each of the first, second and third yarns having a tenacity of at least 15 g/dtex, and
- [0034] (i) the second yarns are made of a second polymer which is different than the first polymer, or (ii) the first yarns have a different average linear density than the average linear density of the second yarns, or (iii) the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns, or (iv) combinations thereof.

[0035] in certain embodiments, the method further comprises weaving a fourth plurality of yarns, each of the fourth yarns arranged in the second direction parallel or substantially parallel to the third yarns,

[0036] wherein (i) the fourth yarns are made of the second polymer or a third polymer, or (ii) the third yarns have a different average linear density than the average linear density of the fourth yarns, or (iii) the third and fourth yarns comprise multifilament yarns with filaments and the filaments of the third yarns have an average linear density different from the filaments in the fourth yarns, or (iv) combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0037] FIG. **1** shows a weave having a first and a second yarn in a first direction and a third yarn in a second direction.

[0038] FIG. **2** shows a weave having a first and a second yarn in a first direction and a third and fourth yarn in a second direction.

DETAILED DESCRIPTION

[0039] The present invention may be understood more readily by reference to the following detailed description of illustrative and preferred embodiments that form a part of this disclosure. It is to be understood that the scope of the claims is not limited to the specific devices, methods, conditions or parameters described and/or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of the claimed invention. Also, as used in the specification including the appended claims, the singular forms "a," "an," and "the" include the plural, and reference to a particular numerical value includes at least that particular value, unless the context clearly dictates otherwise. When a range of values is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment. All ranges are inclusive and combinable.

[0040] Penetration resistant composites and articles of the present invention preferably include a plurality of fibrous layers that are made from polymer fibers.

[0041] For purposes herein, the term "fiber" 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 fiber cross section can be any shape, but is typically round. The fibers can be present in uncoated, or coated, or otherwise pretreated (for example, pre-stretched or heat-treated) form. Herein, the term "filament" is used interchangeably with the term "fiber."

[0042] As herein defined, "yarn" refers to a continuous length of two or more fibers, wherein fiber is as defined herein.

[0043] For purposes herein, "fabric" refers to any woven, knitted, or non-woven structure. By "woven" is meant any fabric weave, such as, plain weave, crowfoot weave, basket weave, satin weave, twill weave, and the like. By "knitted" is meant a structure produced by interlooping or intermeshing one or more ends, fibers or multifilament yarns. By "non-woven" is meant a network of fibers, including unidirectional fibers, felt, and the like.

[0044] The fibrous layers can take on numerous configurations, including, but not limited to, knitted or woven fabrics or non-woven structures. By non-woven is meant a network of fibers, including unidirectional (if contained within a matrix resin), felt, and the like. By woven is meant any fabric weave, such as, plain weave, crowfoot weave, basket weave, satin weave, twill weave, and the like. Plain weave is believed to be the most common weave used in the trade.

[0045] In some preferred embodiments, the fabric is a made by weaving a plurality of yarns.

[0046] The areal density of the fabric layer is determined by measuring the weight of each single layer of selected size, e.g., 10 cm×10 cm. The areal density of the composite structure is determined by the sum of the areal densities of the individual layers.

[0047] Denier is determined according to ASTM D 1577 and is the linear density of a fiber as expressed as weight in grams of 9000 meters of fiber.

[0048] Tenacity is determined according to ASTM D 885 and is the maximum or breaking stress of a fiber as expressed as grams per denier.

[0049] A wide variety of suitable thermoset and thermoplastic resins and mixtures thereof are well known in the prior art and can be used as the matrix material. For example, thermoplastic resins can comprise one or more polyurethane, polyimide, polyethylene, polyester, polyether etherketone, polyamide, polycarbonate, and the like. Thermoset resins can be one or more epoxy-based resin, polyester-based resin, phenolic-based resin, and the like, preferably a polyvinylbutyral phenolic resin. Mixtures can be any combination of the thermoplastic resins and the thermoset resins.

[0050] A representative list of fibers suitable for this invention include polyamide fibers, polyolefin fibers, polybenzoxazole fibers, polybenzothiazole fibers, poly{2,6-diimidazo[4,5-b4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD) fiber, or mixtures thereof. Preferably, the fibers are made of poly{2,6-diimidazo[4,5-b4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD) fiber.

[0051] When the polymer is polyamide, aramid is preferred. By "aramid" is meant a polyamide wherein at least 85% of the amide (—CO—NH—) linkages are attached directly to two aromatic rings. Suitable aramid fibers are described in *Man-Made Fibers—Science and Technology*, Volume 2, Section titled Fiber-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers are, also, disclosed in U.S. Pat. Nos. 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511. Additives can be used with the aramid and it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the aramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted for the diacid chloride or the aramid.

[0052] The preferred aramid is a para-aramid and poly(p-phenylene terephthalamide) (PPD-T) is the preferred para-aramid. By PPD-T is meant the homopolymer resulting from approximately mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other diamines with the p-phenylene diamine and of small amounts of other diacid chlorides with the terephthaloyl chloride. As a general rule, other diamines and other diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction. PPD-T, also, means copolymers resulting from incorporation of other aromatic diamines and other aromatic diacid chlorides such as, for example, 2,6-naphthaloyl chloride or chloro- or dichloroterephthaloyl chloride or 3,4'-diaminodiphenylether.

[0053] When the polymer is polyolefin, polyethylene or polypropylene are preferred. By polyethylene is meant a predominantly linear polyethylene material of preferably more than one million molecular weight that may contain minor amounts of chain branching or comonomers 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, propylene, and the like, or low molecular weight additives such as anti-oxidants, lubricants, ultra-violet screening agents, colorants and the like which are commonly incorporated. Such is commonly known as extended chain polyethylene (ECPE). Similarly, polypropylene is a predominantly linear polypropylene material of preferably more than one million molecular weight. High molecular weight linear polyolefin fibers are commercially available. Preparation of polyolefin fibers is discussed in U.S. Pat. No. 4,457,985.

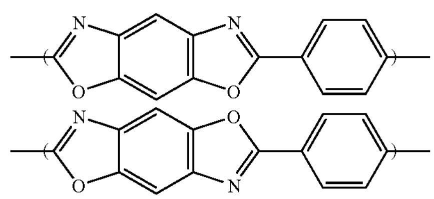
[0054] Polyareneazole polymer may be made by reacting a mix of dry ingredients with a polyphosphoric acid (PPA) solution. The dry ingredients may comprise azole-forming monomers and metal powders. Accurately weighed batches of these dry ingredients can be obtained through employment of at least some of the preferred embodiments of the present invention.

[0055] Exemplary azole-forming monomers include 2,5-dimercapto-p-phenylene diamine, terephthalic acid, bis-(4-benzoic acid), oxy-bis-(4-benzoic acid), 2,5-dihydroxyterephthalic acid, isophthalic acid, 2,5-pyridodicarboxylic acid, 2,6-napthalenedicarboxylic acid, 2,6-quinolinedicarboxylic acid, 2,6-bis(4-carboxyphenyl)pyridobisimidazole, 2,3,5,6-tetraminopyridine, 4,6-diaminoresorcinol, 2,5-diaminohydroquinone, 1,4-diamino-2,5-dithiobenzene, or any combination thereof. Preferably, the azole forming monomers include 2,3,5,6-tetraminopyridine and 2,5-dihydroxyterephthalic acid. In certain embodiments, it is preferred that that the azole-forming monomers are phosphorylated. Preferably, phosphorylated azole-forming monomers are polymerized in the presence of polyphosphoric acid and a metal catalyst.

[0056] Metal powders can be employed to help build the molecular weight of the final polymer. The metal powders typically include iron powder, tin powder, vanadium powder, chromium powder, and any combination thereof.

[0057] The azole-forming monomers and metal powders are mixed and then the mixture is reacted with polyphosphoric acid to form a polyareneazole polymer solution. Additional polyphosphoric acid can be added to the polymer solution if desired. The polymer solution is typically extruded or spun through a die or spinneret to prepare or spin the filament.

[0058] Polybenzoxazole (PBO) and polybenzothiazole (PBZ) two suitable polymers. These polymers are described in PCT Application No. WO 93/20400. Polybenzoxazole and polybenzothiazole are preferably made up of repetitive units of the following structures:



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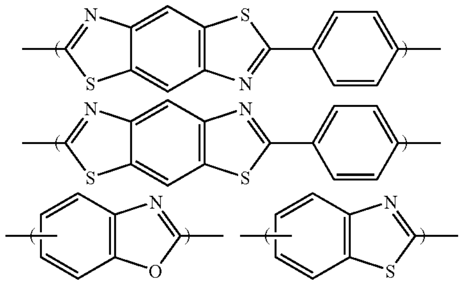

[0059] While the aromatic groups shown joined to the nitrogen atoms may be heterocyclic, they are preferably carbocyclic; and while they may be fused or unfused polycyclic systems, they are preferably single six-membered rings. While the group shown in the main chain of the bis-azoles is the preferred para-phenylene group, that group may be replaced by any divalent organic group which doesn't interfere with preparation of the polymer, or no group at all. For example, that group may be aliphatic up to twelve carbon atoms, tolylene, biphenylene, bis-phenylene ether, and the like.

[0060] The polybenzoxazole and polybenzothiazole used to make fibers of this invention should have at least 25 and preferably at least 100 repetitive units. Preparation of the polymers and spinning of those polymers is disclosed in the aforementioned PCT application WO 93/20400.

[0061] M5 fiber is suitable for use in the instant invention. This fiber is based on poly [diimidazo pyridinylene (dihydroxy)phenylene]. M5 fibers are known to have an average modulus of about 310 GPa and an average tenacities of up to about 5.8 GPa. M5 fibers have been described by Brew, et al., *Composites Science and Technology* 1999, 59, 1109; Van der Jagt and Beukers, *Polymer* 1999, 40, 1035; Sikkema, *Polymer* 1998, 39, 5981; Klop and Lammers, *Polymer,* 1998, 39, 5987; Hageman, et al., *Polymer* 1999, 40, 1313.

[0062] A laminated layer is defined as a network of fibers impregnated with a polymeric matrix comprising a thermoset or thermoplastic resin, or mixtures thereof. Each layer adds to the thickness and weight of the composite structure, thereby reducing its flexibility, wearability and comfort. Therefore, the numbers of layers have been selected such that the total composite structure is designed and used to protect against a specific threat.

[0063] The layers can be held together or joined in any manner, such as, by being sewn together or they can be stacked together and held, for example, in a fabric envelope or carrier. The layers which form the sections can be separately stacked and joined, or all of the plurality of layers can be stacked and joined as a single unit.

[0064] The layers can also be held together by the polymeric matrix comprising a thermoset or thermoplastic resin, or mixtures thereof. A wide variety of suitable thermoset and thermoplastic resins and mixtures thereof are well known in the prior art and can be used as the matrix material. For example, thermoplastic resins can comprise one or more polyurethane, polyimide, polyethylene, polyester, polyether etherketone, polyamide, polycarbonate, and the like. Thermoset resins can be one or more epoxy-based resin, polyester-based resin, phenolic-based resin, and the like, preferably a polyvinlybutyral phenolic resin. Mixtures can be any combination of the thermoplastic resins and the thermoset resins. The proportion of the matrix material in each layer is from about 10% to about 80% by weight of the layer preferably 20% to 60% by weight of the layer.

[0065] Various amounts of ultraviolet absorbers or sabilizers can be added to the fiber or laminated layers to absorb harmful ultraviolet radiation and dissipate it as thermal energy. UV absorbers act by shielding the fiber or laminated layers from the UV light, while the UV stabilizers act by scavenging the radical intermediates formed in the photo-oxidation process to enhance the service life of fiber or laminated layers when exposed to UV light. Examples of UV absorbers include benzophenone or the benzotriazole of Ciba Specialty Chemicals.

[0066] In FIG. **1**, a weave having a first and a second yarn in a first direction and a third yarn in a second direction is depicted. In this illustration, the first and second yarns are substantially parallel and traverse to the direction of the third yarn.

Test Methods

[0067] The following test methods were used in the following Examples.

[0068] Linear Density. The linear density of a yarn or fiber is determined by weighing a known length of the yarn or fiber based on the procedures described in ASTM D1907-97 and D885-98. Decitex or "dtex" is defined as the weight, in grams, of 10,000 meters of the yarn or fiber.

[0069] Areal Density. The areal density of the fabric layer is determined by measuring the weight of each single layer of selected size, e.g., 10 cm×10 cm. The areal density of the composite structure is determined by the sum of the areal densities of the individual layers.

[0070] Ballistic Resistance Penetration. The V50 Ballistic tests of the multi-layer panels were conducted in accordance with NIJ Standard—0101.04 "Ballistic Resistance of Personal Body Armor", issued in September 2000. this test only discloses use of 9 mm but we used same test with 9 mm and also 0.357 bullets

EXAMPLES

[0071] This invention will now be illustrated by the following specific examples. All parts and percentages are by weight unless otherwise indicated. Examples prepared according to the process or processes of the current invention are indicated by numerical values. Control or Comparative Examples are indicated by letters.

Preparation and Testing of Examples

[0072] In the following examples, a plurality layers of woven fabric with various combinations of aramid and polybenzoxazole (PBO) yarns in both warp and fill directions were prepared. The aramid yarn was sold by E.I. du Pont de Nemours and Company under the trademark KEVLAR®. The aramid was poly(p-phenylene terephthalamide). The polybenzoxazole (PBO) yarn was sold by Toyobo Co., Ltd., under the trademark ZYLON®. Composites of a plurality of fabric layers were tested for ballistic resistance penetration. Ballistic panels of 16 in^2 (40.6 cm^2) were constructed for each test, wherein all of the fabric layers were sewn around the edges and were additionally sewn diagonally with cross-stitches. Several different fabrics made from yarns of various materials and different linear density of yarns were tested at various areal densities between 3.7 and 6.0 kg/m^2.

Example 1

[0073] In Example 1, forty-four layers of fabric were woven from 440 dtex KEVLAR® 129 and 550 dtex ZYLON® yarns arranged in an alternate sequence, i.e., a KEVLAR® yarn/a ZYLON® yarn/a KEVLAR® yarn/a ZYLON® yarn, in both the warp and fill directions in a plain weave at 10.2 ends per centimeter and an areal density of about 4.7 kg/m2.

Comparative Example A

[0074] In Comparative Example A, forty-four layers of fabric were made with 550 dtex ZYLON® yarn in the warp direction at 9.8 ends per centimeter and 440 dtex KEVLAR® 129 yarn in the fill direction at 11.0 ends per centimeter in a plain weave, and an areal density of about 4.7 kg/m^2.

Comparative Example B

[0075] In Comparative Example B, forty-four layers of fabric were made with 440 dtex KEVLAR® 129 yarn in the warp direction at 11.0 ends per centimeter and 550 dtex ZYLON® yarn in the fill direction at 9.8 ends per centimeter in a plain weave, and an areal density of about 4.7 kg/m^2.

[0076] The layers of fabrics in Example 1 and Comparative Examples A and B were tested for ballistic V50 against 9 mm and 0.357 mag bullets. The ballistic test results, shown in Table 1, indicate the V50 results for the articles of this invention as shown in Example 1 were significantly greater than the V50 of the article of Comparative Examples A and B. In summary, the articles of the invention showed an improvement in ballistic V50 of from about 3% to 8% compared to the article of Comparative Examples A and B.

TABLE 1

Example	V50 (9 mm) (m/sec)	improvement of Ex 1	V50 (.357 mag) (m/sec)	improvement of Ex 1
1	540		536	
A	522	3.5%	495	8.3%
B	525	2.9%	516	3.9%

Example 2

[0077] In Example 2, thirty-five layers of fabric were woven from 440 dtex KEVLAR® 129 and 550 dtex ZYLON® yarns arranged in an alternate sequence in both the warp and fill directions in a plain weave at 10.2 ends per centimeter and an areal density of about 3.7 kg/m^2.

Comparative Example C

[0078] In Comparative Example C, thirty-five layers of fabric were made with 550 dtex ZYLON® yarn in the warp direction at 9.8 ends per centimeter and 440 dtex KEVLAR® 129 yarn in the fill direction at 11.0 ends per centimeter in a plain weave, and an areal density of about 3.7 kg/m^2.

Comparative Example D

[0079] In Comparative Example D, thirty-five layers of fabric were made with 440 dtex KEVLAR® 129 yarn in the warp direction at 11.0 ends per centimeter and 550 dtex ZYLON® yarn in the fill direction at 9.8 ends per centimeter in a plain weave, and an areal density of about 3.7 kg/m^2.

[0080] The layers of fabrics in Example 2 and Comparative Examples C and D were tested for ballistic V50 against 9 mm and 0.357 mag bullets. The ballistic test results, shown in Table 2, indicate the V50 results for the articles of this invention as shown in Examples 2 were significantly greater than the V50 of the article of Comparative Examples C and D.

TABLE 2

Example	V50 (9 mm) (m/sec)	Improvement of Ex 2	V50 (.357 mag) (m/sec)	Improvement of Ex 2
2	500		508	
C	496	0.1%	472	7.6%
D	469	6.6%	470	8.1%

Example 3

[0081] In Example 3, thirty-six layers of fabric were woven from 1110 dtex KEVLAR® 129 and 1110 dtex ZYLON® yarns arranged in an alternate sequence in both the warp and fill directions in a plain weave at 7.5 ends per centimeter and an areal density of about 6.0 kg/m^2.

Comparative Example E

[0082] In Comparative Example E, thirty-six layers of fabric were made with 1110 dtex ZYLON® yarn in the warp direction at 7.5 ends per centimeter and 1110 dtex KEVLAR® 129 yarn in the fill direction at 7.5 ends per centimeter in a plain weave, and an areal density of about 6.0 kg/m^2.

[0083] The layers of fabrics in Example 3 and Comparative Example E were tested for ballistic V50 against 9 mm and 0.357 mag bullets. The ballistic test results, shown in Table 3, indicate the V50 results for the articles of this invention, as shown in Example 3, were significantly greater than the V50 of the article of Comparative Example E.

TABLE 3

Example	V50 (9 mm) (m/sec)	Improvement of Ex 3	V50 (.357 mag) (m/sec)	Improvement of Ex 3
3	594		564	
E	564	5.3%	558	1.1%

Example 4

[0084] In Example 4, the structures of examples 1-3 may be replicated with a fiber selected from polyareneazoles, polypyridazoles, polypyridobisimidazoles or any combination thereof in place of the KEVLAR® fiber.

Example 5

[0085] In Example 5, the structures of Examples 1-3 may be replicated with a fiber selected from polyareneazoles, polypyridazoles, polypyridobisimidazoles or any combination thereof in place of the ZYLON® fiber.

[0086] While the present invention has been described in connection with the preferred embodiments of the figures, it is to be understood that other similar embodiments may be used or modifications and additions may be made to the described embodiment for performing the same function of the present invention without deviating therefrom. Therefore, the present invention should not be limited to any single embodiment, but rather construed in breadth and scope in accordance with the recitation of the appended claims.

[0087] All patents and publications disclosed herein are incorporated by reference in their entirety.

What is claimed:

1. A fiber network layer for use in penetration resistant articles, comprising:

a first plurality of yarns and a second plurality of yarns, each of the first and second yarns arranged in a first direction parallel or substantially parallel to the other first and second yarns;

a third plurality of yarns, each of the third yarns arranged in a second direction parallel or substantially parallel to the other third yarns, the second direction transverse to the first direction, the third yarns and either the first yarns or the second yarns made of a first polymer; and

each of the first, second and third yarns having a tenacity of at least 15 g/dtex;

wherein (i) the second yarns are made of a second polymer which is different than the first polymer, or (ii) the first yarns have a different average linear density than the average linear density of the second yarns, or (iii) the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns, or (iv) combinations thereof.

2. The fiber network layer of claim 1, further comprising:

a fourth plurality of yarns, each of the fourth yarns arranged in the second direction parallel or substantially parallel to the third yarns,

wherein (i) the fourth yarns are made of the second polymer or a third polymer, or (ii) the third yarns have a different average linear density than the average linear density of the fourth yarns, or (iii) the third and fourth yarns comprise multifilament yarns with filaments and the filaments of the third yarns have an average linear density different from the filaments in the fourth yarns, or (iv) combinations thereof.

3. The fiber network layer of claim 1, wherein:

the first yarns comprise at least 35% of the total number of yarns in the first direction, and

the second yarns comprise at least 35% of the total number of yarns in the first direction.

4. The fiber network layer of claim 2, wherein:

the third yarns comprise at least 25% of the total number of yarns in the second direction, and

the fourth yarns comprise at least 25% of the total number of yarns in the second direction.

5. The fiber network layer of claim 1, wherein the fiber network layer has an areal density of no more than 10 kg/m^2.

6. The fiber network layer of claim 2, wherein each of the first, second, third and fourth yarns have an elongation at break of at least 2% and a modulus of elasticity of at least 150 grams per dtex.

7. The fiber network layer of claim 1, wherein the second yarns are made of a second polymer which is different than the first polymer.

8. The fiber network layer of claim 1, wherein the first yarns have a different average linear density than the average linear density of the second yarns.

9. The fiber network layer of claim 1, wherein the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns.

10. The fiber network layer of claim 1, wherein:

the first and third yarns are made of the first polymer, have the same average linear density, and the filaments of the first and third yarns have the same average linear density, and

the second and fourth yarns are made of the second polymer, have the same average linear density, and the filaments of the second and fourth yarns have the same average linear density.

11. The fiber network layers of claim 2, wherein the filaments of the first, second, third and fourth yarns have a linear density of 0.1 to 10 decitex.

12. The fiber network layer of claim 1, wherein the first and second yarns arranged in an alternating sequence.

13. The fiber network layer of claim 2, wherein the third and fourth yarns arranged in an alternating sequence.

14. The fiber network layer of claim 1, wherein the first and second polymers are selected from the group consisting of polyamide, polyolefin, polybenzoxazole, polybenzothiazole, poly{2,6-diimidazo[4,5-b4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene}, polyareneazoles, polypyridazoles, polypyridobisimidazoles and mixtures thereof.

15. A flexible penetration resistant article comprising a plurality of fiber network layers of claim 1.

16. The flexible penetration resistant article of claim 15, wherein the article has an areal density of 2 to 12 kg/m^2.

17. A flexible ballistic resistant article, comprising a plurality of layers of fabric having two different types of yarns arranged in an alternating sequence in both warp and fill directions of the fabric.

18. The flexible ballistic resistant article of claim 17 wherein at least one layer of said fabric layers being impregnated with a polymeric matrix comprising a thermoset resin, a thermoplastic resin, or mixtures thereof.

19. A method of forming a fiber network comprising:

weaving a first plurality of yarns and a second plurality of yarns, each of the first and second yarns arranged in a first direction parallel or substantially parallel to the other first and second yarns; with

a third plurality of yarns, each of the third yarns arranged in a second direction parallel or substantially parallel to the other third yarns, the second direction transverse to the first direction, the third yarns and either the first yarns or the second yarns made of a first polymer; and

each of the first, second and third yarns having a tenacity of at least 15 g/dtex;

wherein (i) the second yarns are made of a second polymer which is different than the first polymer, or (ii) the first yarns have a different average linear density than the average linear density of the second yarns, or (iii) the first and second yarns comprise multifilament yarns with filaments and the filaments of the first yarns have an average linear density different from the filaments in the second yarns, or (iv) combinations thereof.

20. The method of claim 19 further comprising:

weaving a fourth plurality of yarns, each of the fourth yarns arranged in the second direction parallel or substantially parallel to the third yarns,

wherein (i) the fourth yarns are made of the second polymer or a third polymer, or (ii) the third yarns have a different average linear density than the average linear density of the fourth yarns, or (iii) the third and fourth yarns comprise multifilament yarns with filaments and the filaments of the third yarns have an average linear density different from the filaments in the fourth yarns, or (iv) combinations thereof.

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