



(43) International Publication Date
6 March 2014 (06.03.2014)

(10) International Publication Number
WO 2014/035523 A2

(51) International Patent Classification:
B32B 5/02 (2006.01)

(21) International Application Number:
PCT/US2013/045295

(22) International Filing Date:
12 June 2013 (12.06.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/593,813 24 August 2012 (24.08.2012) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

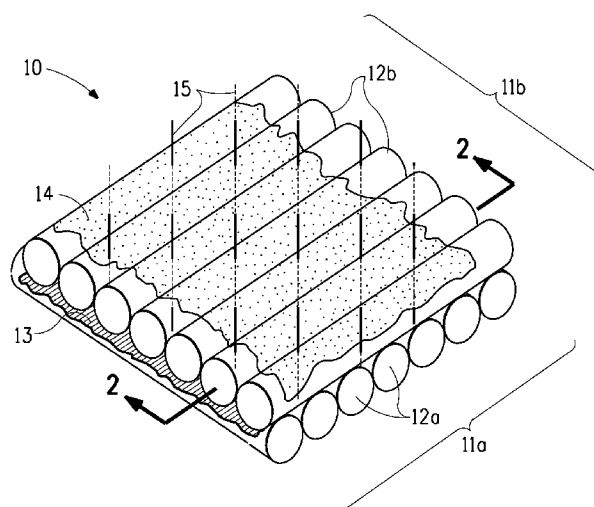
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: FIBER - RESIN COMPOSITES AND BALLISTIC RESISTANT ARMOR ARTICLES CONTAINING THE FIBER - RESIN COMPOSITES



(57) Abstract: A fiber - resin composite useful in a ballistic resistant armor article comprises a first nonwoven layer comprising a first plurality of yarns arranged parallel with each other and a second nonwoven layer comprising a second plurality of yarns arranged parallel with each other. The first plurality of yarns have an orientation in a direction that is different from the orientation of the second plurality of yarns. The composite further comprises a binding resin partially coating portions of internal surfaces of the yarns and partially filling some space between the filaments of the yarns so as to leave discrete areas of yarn surfaces that are free from binder resin coating. A viscoelastic resin coats at least portions of external surfaces of the yarns and fills in some space between the filaments of the yarns. A binding yarn is interlaced transversely within the first and second nonwoven layers.



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TITLE OF THE INVENTION

FIBER - RESIN COMPOSITES AND BALLISTIC RESISTANT ARMOR
ARTICLES CONTAINING THE FIBER - RESIN COMPOSITES

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BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to fiber - resin composites and ballistic resistant armor articles containing the fiber - resin composites. The fiber - resin composites comprise layers of yarns such as yarns of para-aramid or polyethylene filaments.

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2. Description of Related Art.

United States patent 6,990,886 to Citterio discloses an unfinished multilayer structure used to produce a finished multilayer anti-ballistic fiber - resin composite. The unfinished multilayer structure includes a first layer of threads parallel with each other, superimposed, with the interpositioning of a binding layer on at least a second layer of threads which are parallel with each other. The threads of the first layer are set in various directions with respect to the threads of the second layer. The two layers are also joined by binding threads made of a thermoplastic or thermosetting material or of a material which is water-soluble or soluble in a suitable solvent.

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There is an ongoing need to provide multilayer structures having a lower resistance to axial movement between the layers that will provide a more flexible soft body armor article with enhanced ballistic performance at a similar or lower weight.

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BRIEF SUMMARY OF THE INVENTION

This invention is directed to a fiber - resin composite useful in a ballistic resistant armor article, comprising:

(a) from 75.0 to 94.0 weight percent of

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a first nonwoven layer comprising a first plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the first plurality of yarns arranged parallel with each other,

a second nonwoven layer comprising a second plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the second plurality of yarns arranged parallel with each other,

5 wherein the first plurality of yarns of the first nonwoven layer have an orientation in a direction that is different from the orientation of the second plurality of yarns in the second nonwoven layer,

(b) from 1.0 to 10.0 weight percent of a thermoset or thermoplastic binding resin partially coating portions of internal surfaces of the first plurality and the second plurality of yarns and partially filling some space between the filaments in the first plurality and the second plurality of yarns in the region of the interface between the two nonwoven layers so as to leave discrete areas of yarn surfaces that are free from binder resin coating,

10 (c) from 0.1 to 10.0 weight percent of a viscoelastic resin coating at least portions of external surfaces of the first plurality and the second plurality of yarns and filling some space between the filaments in the first plurality and the second plurality of yarns, and

(d) a transverse binding yarn interlaced transversely within the first and second nonwoven layers.

20 wherein the weight percentages are expressed relative to the total weight of the fiber - resin composite.

The invention is further directed to a fiber - resin composite of the aforesaid character comprising four nonwoven layers wherein the yarns in any one layer have an orientation that is different from the yarns in an adjacent layer.

BRIEF SUMMARY OF THE DRAWINGS

FIG 1 shows a plan view in perspective of a fiber - resin composite used to produce a ballistic resistant armor article.

FIG 2 shows a sectional view taken at 2-2 in Figure 1.

FIG 3 shows a sectional view of another embodiment comprising four nonwoven layers.

FIGS 4A to 4D show various arrangements of the fiber - resin composite in a ballistic resistant soft armor article.

DETAILED DESCRIPTION OF THE INVENTION

5 The present invention is directed to a fiber - resin composite useful in a ballistic resistant soft armor article. The fiber - resin composite comprises a plurality of nonwoven fibrous layers, a viscoelastic resin, a thermoset or thermoplastic binding resin and binding yarns.

10 The Nonwoven Layers

 In one embodiment the fiber - resin composite comprises two layers of nonwoven fabric and in a further embodiment it comprises four layers of nonwoven fabric. A fiber - resin composite comprising a number of layers other than two or four is also possible. By "nonwoven" we mean a fabric that
15 does not have interlacing or interwoven yarns. Further a nonwoven is not a fabric comprising filaments that are oriented in random orientations within a layer.

 The first nonwoven layer comprises a first plurality of first yarns. The first plurality of first yarns are arranged parallel with each other.

20 The second nonwoven layer comprises a second plurality of second yarns. The second plurality of second yarns are arranged parallel with each other.

 The third nonwoven layer comprises a third plurality of third yarns. The third plurality of third yarns are arranged parallel with each other.

25 The fourth nonwoven layer comprises a fourth plurality of fourth yarns. The fourth plurality of fourth yarns are arranged parallel with each other.

 The orientation of yarns in one layer of the fiber - resin composite is different from the orientation of yarns in an adjacent layer.

FIG 1 shows generally at 10, a fiber - resin composite comprising two
30 nonwoven layers 11a and 11b of reinforcement yarns 12a and 12b. The orientation of the first plurality of yarns 12a in the first layer 11a of the fiber - resin composite is different from the orientation of the second plurality of yarns 12b in the second layer 11b. As an example, the orientation of yarns in a first layer may be at zero degrees i.e. in the machine direction while the

yarns in a second layer may be oriented at an angle of 90 degrees with respect to the orientation of yarns in the first layer. The machine direction is the long direction within the plane of the fiber - resin composite, that is, the direction in which the fiber - resin composite is produced. Examples of other
5 yarn orientation angles are + 45 degrees and - 45 degrees with respect to the machine direction. In a preferred embodiment the yarns in successive layers of the nonwoven fiber - resin composite are oriented at zero degrees and 90 degrees with respect to each other. In a four layer fiber - resin composite, the yarns may be oriented at angles of zero degrees, 90 degrees, zero degrees,
10 90 degrees respectively. FIG 2 shows a sectional view taken at 2-2 in Figure 1.

In a further embodiment the yarns in the first and second layers although being orthogonal to each other are arranged at an angle of + 45 degrees and - 45 degrees relative to the machine direction. Other
15 embodiments include other angles between the yarns in adjacent layers. In some of these embodiments the yarns in adjacent layers need not be orthogonal to each other.

Figure 3 shows generally at 30 a sectional view of a fiber - resin composite comprising four nonwoven layers of reinforcement yarns. The
20 orientation of yarns 32a and 32c in the first and third layers respectively are in the same direction. The orientation of yarns 32b and 32d in the second and fourth layers respectively are in the same direction. The orientation of the yarns in the first and third layers is orthogonal to the orientation of yarns in the second and fourth layers.

25 In some embodiments, the fiber - resin composite comprises nonwoven layers having yarns all of the same polymer. In some other embodiments of the fiber - resin composite, the yarns in different nonwoven layers may comprise different polymers. In yet some other embodiments the yarns within a nonwoven layer may comprise different polymers.

The Yarns

Each of the first yarns comprises a first plurality of first filaments. Each of the second yarns comprises a second plurality of second filaments. Each of the third yarns comprises a third plurality of third filaments. Each of the

fourth yarns comprises a fourth plurality of fourth filaments. The first, second, third and fourth filaments may be of para-aramid, polyolefin or polyazole. In a preferred embodiment, the filaments are para-aramid.

5 The first, second, third and fourth yarns preferably have a yarn tenacity of from 10 to 65 grams per dtex. In some embodiments the yarn tenacity is from 15 to 40 grams per dtex and in yet other embodiments the yarn tenacity is from 20 to 35 grams per dtex. The first, second, third and fourth yarns preferably have a yarn modulus of from 100 to 3500 grams per dtex. In some
10 embodiments the yarn modulus is from 150 to 2700 grams per dtex. The first, second, third and fourth yarns preferably have a linear density of from 50 to 4,500 dtex. In some embodiments the yarn linear density is from 100 to 3500 dtex and in yet other embodiments the linear density is from 300 to 1800 dtex. The first, second, third and fourth yarns preferably have an elongation to break of from 3.8 to 5.0 percent. In still some other embodiments, the
15 elongation to break is from 3.8 to 4.5 percent.

A finished yarn may also be made by assembling or roving together two precursor yarns of lower linear density. For example two precursor yarns each having a linear density of 850 dtex can be assembled into a finished yarn having a linear density of 1700 dtex.

20 Each nonwoven layer has a basis weight of from 30 to 800 g/m². In some preferred embodiments the basis weight of each layer is from 45 to 500 g/m². In some other embodiments the basis weight of each layer is from 55 to 300 g/m². In yet some other embodiments, the layers of the fiber - resin composite all have a similar weight.

25 Untwisted yarns are preferred because they offer higher ballistic resistance than twisted yarns and because they spread to a wider aspect ratio than twisted yarns. They enable more consistent fiber coverage across the layer.

30 The layers comprise a plurality of yarns having a plurality of continuous filaments.

In one embodiment, the yarns used in the nonwoven layers form a substantially flattened array of filaments wherein individual yarn bundles are difficult to detect. In such an embodiment, the filaments are uniformly arranged in the layer, meaning there is less than a 20 percent difference in

the thickness of the flattened array. The filaments from one yarn shift and fit next to adjacent yarns, forming a continuous array of filaments across the layer. In an alternative embodiment, the yarns can be positioned such that small gaps are present between the flattened yarn bundles, or the yarns may be positioned such that the yarn bundles butt up against other bundles, while retaining an obvious yarn structure. In other embodiments, the yarns are present in layers as substantially distinct yarns.

It is believed the use of yarns having an elongation at break of from 3.8 to 5.0 percent allows for the use of thicker layers in the fiber - resin composite without an appreciable loss in ballistic performance.

In some embodiments, the fiber - resin composite comprises at least two nonwoven layers having a ratio of the thickness of any one layer to the equivalent diameter of the filaments comprising the layer of at least 13. In some other embodiments of the fiber - resin composite, the ratio of the thickness of any layer to the equivalent diameter of the filaments comprising the layer is at least 13, more preferably at least 16 and most preferably at least 19. By "equivalent diameter" of a filament we mean the diameter of a circle having a cross-sectional area equal to the average cross-sectional area of the filaments comprising the layer. The ratio is calculated by first determining the thickness of a layer in the fiber - resin composite, typically by measuring the average thickness of the final fiber - resin composite and dividing by the number of layers, and then dividing by the equivalent diameter of a filament used in a layer. Typically, all of the layers are of the same basis weight and all of the layers have the same filaments. If resin is present between the successive yarn layers, the thickness of a layer is calculated by first determining the overall thickness of the fiber - resin composite and dividing that thickness by the number of yarn layers in the fiber - resin composite.

The yarns comprise from 75.0 to 94.0 weight percent based on the total weight of the fiber - resin composite. In some embodiments the yarn comprises 85 or 90 weight percent based on the total weight of the fiber - resin composite.

The 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 round or bean shaped. The
5 yarns may also be round, bean shaped or oval in cross section. The filaments can be any length. Preferably the filaments are continuous. Multifilament yarn spun onto a bobbin in a package contains a plurality of continuous filaments. The filaments are solid, that is they are not hollow.

The yarns of the present invention are made with filaments comprising
10 polymer of para-aramid, polyolefin or polyazole. Yarns of different polymer may be used in a nonwoven layer.

As used herein, the term para-aramid filaments means filaments made of para-aramid polymer. The term aramid means a polyamide wherein at least 85% of the amide (-CONH-) linkages are attached directly to two
15 aromatic rings. Suitable aramid fibers are described in Man-Made Fibres - Science and Technology, Volume 2, in the section titled Fibre-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers and their production are, also, disclosed in U.S. Patents 3,767,756; 4,172,938; 3,869,429; 3,869,430; 3,819,587; 3,673,143;
20 3,354,127; and 3,094,511.

The preferred para-aramid is poly (p-phenylene terephthalamide) which is called PPD-T. By PPD-T is meant the homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other
25 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
30 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. In some preferred embodiments, the yarns of

the fiber - resin composite consist solely of PPD-T filaments; in some preferred embodiments, the layers in the fiber - resin composite consist solely of PPD-T yarns; in other words, in some preferred embodiments all filaments in the fiber - resin composite are PPD-T filaments.

5 Additives can be used with the aramid and it has been found that up to as much as 10 percent or more, by weight, of other polymeric material can be blended with the aramid. Copolymers can be used having as much as 10 percent or more of other diamine substituted for the diamine of the aramid or as much as 10 percent or more of other diacid chloride substituted for the
10 diacid chloride or the aramid.

When the polymer is polyolefin, polyethylene or polypropylene is preferred. The term "polyethylene" means a predominantly linear polyethylene material of preferably more than one million molecular weight that may contain minor amounts of chain branching or comonomers not
15 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,
20 colorants and the like which are commonly incorporated. Such is commonly known as extended chain polyethylene (ECPE) or ultra high molecular weight polyethylene (UHMWPE

Yarns may also comprise polyazole filaments. In some embodiments, the polyazoles are polyarenazoles such as polybenzazoles and
25 polypyridazoles. Suitable polyazoles include homopolymers and, also, copolymers. Additives can be used with the polyazoles and up to as much as 10 percent, by weight, of other polymeric material can be blended with the polyazoles. Also copolymers can be used having as much as 10 percent or more of other monomer substituted for a monomer of the polyazoles. Suitable
30 polyazole homopolymers and copolymers can be made by known procedures.

Preferred polybenzazoles are polybenzimidazoles, polybenzothiazoles, and polybenzoxazoles and more preferably such polymers that can form fibers having yarn tenacities of 30 gpd or greater. If the polybenzazole is a polybenzothioazole, preferably it is poly(p-phenylene benzobisthiazole). If the

polybenzazole is a polybenzoxazole, preferably it is poly(p-phenylene benzobisoxazole) and more preferably poly(p-phenylene-2,6-benzobisoxazole) called PBO.

Preferred polypyridazoles are polypyridimidazoles, polypyridothiazoles, and polypyridoxazoles and more preferably such polymers that can form fibers having yarn tenacities of 30 gpd or greater. In some embodiments, the preferred polypyridazole is a polypyridobisazole. A preferred poly(pyridobisoxazole) is poly(1,4-(2,5-dihydroxy)phenylene-2,6-pyrido[2,3-d:5,6-d']bisimidazole which is called PIPD. Suitable polypyridazoles, including polypyridobisazoles, can be made by known procedures.

Other yarns based on polymers or copolymers capable of making yarns having a yarn tenacity of about 30 to about 40 grams per dtex are also suitable for use in the fiber - resin composite.

15 The Thermoset or Thermoplastic Binding Resin

The fiber - resin composite has a resin rich binding layer (binder) in the region of the interface between the respective nonwoven layers. In a two layer fiber - resin composite the binder is in the interface region between the first nonwoven layer and the second nonwoven layer. In a three layer fiber - resin composite, the binder preferably is in the interface regions between the first nonwoven layer and the second nonwoven layer and between the second nonwoven layer and the third nonwoven layer. In a four layer fiber - resin composite, the binder preferably is in the interface regions between the first nonwoven layer and the second nonwoven layer, between the second nonwoven layer and the third nonwoven layer and between the third nonwoven layer and the fourth nonwoven layer. The binder layer is shown at 13 in Figures 1 and 2 and at 33 in Figure 3. Preferably, the binding layer does not fully impregnate into the yarn bundle but penetrates into at least portions of the internal surfaces of the yarns in each layer in the interface region and fills some space between the filaments in each layer. Preferably, the binding layer is discontinuous so as to provide for discrete areas of yarn surfaces in the region of the interface between the nonwoven layers that are free from binding layer coating. Such binder free areas are shown at 25 in Figure 2 and at 35 in figure 3. In some embodiments the binding layer is a resin. The resin

may be a thermoset or thermoplastic material. A suitable binding resin comprises a blend of elastomeric block copolymers and polyethylene copolymers. In one embodiment of this resin blend, polyethylene copolymers comprise from 50 to 75 weight percent and elastomeric block copolymers
5 comprise from 25 to 50 weight percent of the blend.

In some embodiments, the binding layer is in the form of a film. Suitable materials for the binding layer include polyolefinic films, thermoplastic elastomeric films, polyester films, polyamide films, polyurethane films and mixtures thereof. Useful polyolefinic films include low density polyethylene
10 films, high density polyethylene films and linear low density polyethylene films. The films may be perforated by any suitable means to provide resin free areas. As an alternative to a binding layer, the binder may be in the form of a scrim, mesh, grid, resin or powder deposition or some other suitable form capable of providing discrete areas of yarn surfaces that are free from binder resin
15 coating. By scrim or mesh is meant a lightweight fabric characterized by open spaces between the yarns. The scrim may be woven, knit, lace, net, crochet or other suitable style. Preferably a grid comprises polymeric or elastomeric strips or yarns. The strips or yarns may be chemically or mechanically bonded.

In some other embodiments, the binding layer is in the form of a porous
20 (open) polymeric nonwoven web. Suitable polymers for the nonwoven web include polyethylene, polypropylene, polyetheretherketone (PEEK) and polyetherketoneketone (PEKK). In some embodiments, the weight of the nonwoven web is from 3 to 60 grams per square meter (gsm). In other embodiments, the weight of the nonwoven web is from 5 to 40 gsm.

25 In an alternative embodiment, the binding layer may be in the form of a low areal weight film that is attached at various contact points to the surface of the nonwoven layers so as to leave discrete areas of a nonwoven layer not attached to the film. Such a film may be continuous or discontinuous and preferably has an areal weight of less than 60 gsm. One means of forming the
30 contact points between a nonwoven layer and a film is by localized melting of the film.

The area of yarn surface in the region of the interface between the nonwoven layers that is free from binding material is at least 40 percent of the total surface area of the yarn surfaces in the region of the interface between

the nonwoven layers. In some embodiments the binder free area on the yarn surface is at least 65 percent or at least 90 percent or even up to 95 percent. If the amount of binding resin is too low, the yarns can move and escape from the path of the projectile leading to poor anti-ballistic performance. The

5 minimum amount of binding resin must therefore be sufficient to prevent such yarn movement. If the amount of binding resin is too high, then the flexibility of the anti-ballistic article is impaired.

The shape of the resin free areas can take any convenient form. Exemplary examples of shapes include squares, rectangles, triangles,

10 diamonds, chevrons, circles and ovals. In one embodiment, there is a distance between adjacent resin free areas of no greater than 89 mm (3.5"). In another embodiment, there is a distance between adjacent resin free areas of no greater than 38 mm (1.5"). In yet another embodiment, there is a distance between adjacent resin free areas of no greater than 15 mm (0.6").

15 It is believed that the resin free areas between the yarn layers reduce the resistance to axial movement of adjacent layers.

Preferably the binding layer is present in the fiber - resin composite in an amount from 1.0 to 10.0 or even 1.0 to 7.0 weight percent based on the total weight of the fiber - resin composite.

20 The binding layer is applied by the steps of (i) forming a first nonwoven layer comprising a first plurality of yarns comprising a first plurality of filaments, the first plurality of yarns arranged parallel with each other (ii) positioning the first surface of the resin binding layer on one surface of the first nonwoven layer (iii) forming a second nonwoven layer comprising a second plurality of

25 yarns comprising a second plurality of filaments, the second plurality of yarns arranged parallel with each other, (iv) positioning the second nonwoven layer onto the second surface of the resin binding layer such that the yarn orientation in one layer is different from the yarn orientation in an adjacent layer and (v) repeating steps (i) to (iv) as required to add additional nonwoven

30 layers to the fiber - resin composite.

The Viscoelastic Resin

The yarns of the outer surfaces of the two outer layers of the fiber - resin composite are coated with a resin solution comprising a viscoelastic

resin and a solvent. The coating also fills some space between the filaments in the yarns in the region of the outer surfaces of the two outer nonwoven layers of the fiber - resin composite. This resin is shown at 14 in Figures 1 and 2 and at 34 in Figure 3. The viscoelastic resin may be thermoplastic or
5 thermoset. Suitable materials include polymers or resins in the form of a viscous or viscoelastic liquid. Preferred materials are polyolefins, in particular polyalpha-olefins or modified polyolefins, polyvinyl alcohol derivatives, polyisoprenes, polybutadienes, polybutenes, polyisobutylenes, polyesters, polyacrylates, polyamides, polysulfones, polysulfides, polyurethanes,
10 polycarbonates, polyfluoro-carbons, silicones, glycols, liquid block copolymers, polystyrene-polybutadiene-polystyrene, ethylene co-polypropylene, polyacrylics, epoxies, phenolics and liquid rubbers. Preferred polyolefins are polyethylene and polypropylene. Preferred glycols are polypropylene glycol and polyethylene glycol. A preferred copolymer is polybutadiene-co-
15 acrylonitrile. Copolymers based on styrene may also be used. Such styrene copolymers are available under the tradename Kraton and include styrene-butadiene (SBS), styrene – isoprene (SIS), styrene-ethylene/butylene-styrene (SEBS) and styrene-ethylene/propylene-styrene (SEPS). Another suitable copolymer is based on styrene-isoprene-styrene (SIS) block copolymer and is
20 available under the tradename PRINLIN. Polyisobutylene is a suitable rubber based coating material. In a preferred embodiment, the resin coating does not fully impregnate the yarns.

Preferably the visco-elastic resin is present in the fiber - resin composite in an amount from 0.1 to 10.0 weight percent and more preferably
25 from 4.0 to 8.0 weight percent based on the total weight of the fiber - resin composite.

The solvent of the visco-elastic resin may be aliphatic, aromatic, cyclic or based on halogenated hydrocarbons. More preferably the solvent is non-polar. Suitable solvents include n-heptane and cyclohexane. Solvent-free
30 resins may also be used.

A typical process to coat or impregnate the yarns of the fiber - resin composite with visco-elastic resin comprises the steps of bringing the fiber - resin composite into contact with the resin. The resin can be in the form of a solution, emulsion, melt or film. When the resin is a solution, emulsion or melt,

the fiber - resin composite can be immersed in the resin and surplus resin removed off with a doctor blade or coating roll. The resin may also be deposited onto the surface of the fiber - resin composite as it passes beneath a resin bath in a blade over roll coating process. The next step is to

5 consolidate the resin impregnated fiber - resin composite by drying to remove the solvent or cooling to solidify the melt followed by a calendering step. The coated or impregnated fiber - resin composite is then rewound and cut for use in accordance with the present invention. When the visco-elastic resin is in the form of a film, the resin film is placed onto one or both surfaces of the fiber -

10 resin composite and consolidated onto or into the fiber - resin composite by heat and pressure in a calender. The degree of resin impregnation into the fibers is controlled by the calendering conditions. The specific values for heat and pressure need to be determined for each material combination. Typically, the temperature is in the range of from 80 to 300 degrees C, preferably from

15 100 to 200 degrees C and the pressure in the range of from 1 to 100 bar, preferably from 5 to 80 bar. The heat and pressure from this process also causes the binding layer resin to melt and flow to form the resin rich interface region between the respective layers of the fiber - resin composite. All the processes described here are well known to those skilled in the art and are

20 further detailed in chapter 2.9 of "Manufacturing Processes for Advanced Fiber - resin composites" by F.C. Campbell, Elsevier, 2004.

Transverse Binding Yarns

In some embodiments, binding threads or yarns may be present.

25 These binding yarns, shown at 15 in Figure 1, are stitched or knitted transversely through the nonwoven layers of the fiber - resin composite in a direction orthogonal to the plane of the layers. This is also known as z-directional stitching. Any suitable binding yarn may be used with polyester fiber, polyethylene fiber, polyamide fiber, aramid fiber, polyareneazole fiber,

30 polypyridazole fiber, polybenzazole fiber, and mixtures thereof being particularly suited. The spacing between rows of stitches may vary depending on design requirements. The stitches may be between yarns or through yarns. In one embodiment the rows are spaced 5 mm apart. The transverse yarns provide further mechanical support to the fiber - resin composite.

Uses of the Fiber - resin composite

A ballistic resistant soft armor article can be produced by combining a plurality of fiber - resin composites as described in the above embodiments.

- 5 Examples of soft armor include protective apparel such as vests or jackets that protect body parts from projectiles. It is preferable that the fiber - resin composites are positioned in the article in such a way as to maintain the offset yarn alignment throughout the finished assembly. For example, in an article comprising two fiber - resin composites, the second fiber - resin composite of
- 10 the article is placed on top of the first fiber - resin composite in such a way that the orientation of the yarns comprising the bottom layer of the second fiber - resin composite is offset with respect to the orientation of the yarns comprising the adjacent top layer of the first fiber - resin composite.

- The actual number of fiber - resin composites used will vary according
- 15 to the design needs of each article being made. An armor article may comprise only the fiber - resin composites of this invention or the fiber - resin composites may be combined with other fabric structures. In Figures 4A to 4D, a plurality of fiber - resin composites of this invention is indicated by 42 and a plurality of fabric structures different from this invention (other fabric
- 20 structures) is indicated by 43. Examples of other fabric structures are woven fabrics, multiaxial fabrics or nonwoven fabrics comprising no resin or binder components. Figure 4A shows a plurality of fiber - resin composites 42 facing the projectile (strike direction) 41 and a plurality of other fabric structures 43 facing the body or non-strike direction.

- 25 Another embodiment covers, as in Figure 4B, an arrangement of alternating assemblies of pluralities of fiber - resin composites 42 and other fabric structures 43. A plurality of fiber - resin composites is facing the strike direction 41.

- A further embodiment is one of a plurality of fiber - resin composites 42
- 30 located on either side of a core of other structures 43. One of the plurality of fiber - resin composites is facing the strike direction 41. This is depicted in Figure 4C.

In yet another embodiment, a plurality of other fabric structures is located on either side of a core of a plurality of fiber - resin composites. One

of the plurality of other fabric structures is facing the strike direction 41. This is shown in Figure 4D.

Combinations of materials other than those described in the drawings 4A to 4D are also useful.

- 5 An assembly comprising a fiber - resin composite and other fabric structures for an antiballistic vest pack typically has a total areal density of between 3.5 to 7.0 kg / m². Thus the number of fiber - resin composites will be selected to meet this weight target with the number typically being from 5 to 25. Other components such as foam or a felt may also be incorporated into
10 the armor article.

TEST METHODS

The following test methods were used in the following Examples.

- Linear Density: The linear density of a yarn or fiber was determined by
15 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. Denier (d) is 9/10 times the decitex (dtex).

- Yarn Mechanical Properties: The yarns to be tested were conditioned
20 and then tensile tested based on the procedures described in ASTM D885-98. Tenacity (breaking tenacity), modulus of elasticity and elongation to break were determined by breaking yarns on an Instron® universal test machine.

- Areal Density: The areal density of a nonwoven layer was determined by measuring the weight of a 10 cm x 10 cm sample of the layer. The areal
25 density of the final article was the weight of a 10 cm x 10 cm sample of the article.

- Ballistic Performance: Ballistic tests of the multi-sheet panels were conducted in accordance with standard procedures such as those described in procurement document FQ/PD 07-05B (Body Armor, Multiple Threat /
30 Interceptor Improved Outer Tactical Vest) and MIL STD-662F (V50 Ballistic Test for Armor). Four targets were tested for most examples and between six to nine shots, at zero degree obliquity, fired at each dry target. The reported V50 values are average values for the number of shots fired for each example.

Ballistic resistance values are reported as V50 which is a statistical measure that identifies the average velocity at which a bullet or a fragment penetrates the armor equipment in 50% of the shots, versus non penetration of the other 50%. The parameter measured is V50 at zero degrees where the degree angle refers to the obliquity of the projectile to the target. The reported values are average values for the number of shots fired for each example. Projectiles used were 16 grain, 17 grain and 64 grain.

Layer Thickness and Equivalent Filament Diameter can be determined by standard electron microscopy techniques.

EXAMPLES

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. In all the Examples and Comparative Examples the nonwoven fiber - resin composite comprised first and second layers of para-aramid yarns aligned unidirectionally in an orthogonal configuration relative to each other and at $+45^{\circ}/-45^{\circ}$ relative to the machine direction. The first yarn layer comprised a first plurality of yarns and the second yarn layer comprised a second plurality of yarns. A thermoplastic binding layer coated at least portions of the internal surfaces of the first plurality and the second plurality of yarns and filled some space between the filaments in the first plurality and the second plurality of yarns in the center region of the fiber - resin composite. Polyester 140 denier threads were used for z-direction stitching through the plane of the first and second layers. The nonwoven fiber - resin composite further comprised a viscoelastic resin coating at least portions of external surfaces of the first plurality and the second plurality of yarns and filling some space between the filaments in the first plurality and the second plurality of yarns. The viscoelastic resin coated the first and second layers in regions remote from the interface of the two layers of the fiber - resin composite. The nonwoven fiber - resin composite had a nominal weight of 300 g/m^2 .

Comparative Example A

Ten 380×380 mm sheets of nonwoven fiber - resin composite were held together by stitches located at the four corners of the sheets (corner

stitch. The yarn used in the nonwoven fabric construction was 440 dtex Kevlar® 129, available from E. I. du Pont de Nemours and Company, Wilmington, DE. The yarn had a nominal tenacity of 24.5 g/dtex, a modulus of 565 grams/dtex and an elongation at break of 3.85 percent. The binding layer material was a 0.025 mm thick layer of polyurethane that coated the entire surface of yarns in the region of the interface between the two nonwoven layers. The viscoelastic coating resin was polyisobutene. The corner stitching thread was Tex 70 spun Kevlar® available from Saunders Thread Company, Gastonia, NC. No other fabric structures were built into the article. The total weight of fiber - resin composite was 5.0 kg/m². Ballistic testing was conducted using 16, 17 and 64 grain projectiles. Results of the ballistic tests over two rounds of shots are summarized in Table 1. The test results from flexural evaluation of the fabric are in Table 2.

15 Comparative Example B

Seventeen 380 x 380 mm sheets of nonwoven fiber - resin composite made of Kevlar® were held together by stitches located at the four corners of the sheets (corner stitch). The yarn used in the nonwoven fabric construction was 440 dtex Kevlar® 129, available from E. I. du Pont de Nemours and Company, Wilmington, DE. The yarn had a nominal tenacity of 24.5 g/dtex, a modulus of 565 grams/dtex and an elongation at break of 3.85 percent. The binding layer material was a 0.0125 mm thick layer of polyurethane that coated the entire surface of yarns in the region of the interface between the two nonwoven layers. The viscoelastic coating resin was polyisobutene. The corner stitching thread was Tex 70 spun Kevlar® available from Saunders Thread Company, Gastonia, NC. No other fabric structures were built into the article. The total weight of fiber - resin composite was 5.1 kg/m². Ballistic testing was conducted using 16, 17 and 64 grain projectiles against targets supported on a Roma Plastina number 1 clay backing medium. Results of the ballistic tests over two rounds of shots are summarized in Table 1. The test results from flexural evaluation of the fabric are in Table 2.

Example 1

Twenty one 380 x 380 mm sheets of nonwoven were held together by stitches located at the four corners of the sheets (corner stitch). The yarn used in the nonwoven fabric construction was 666 dtex (600 denier) KM2 Kevlar®, available from E. I. du Pont de Nemours and Company, Wilmington, DE. The yarn had a nominal tenacity of 25.5 g/dtex, a modulus of 622 grams/dtex and an elongation at break of 3.9 percent. The binding layer material was a 0.0125 mm thick perforated film layer of a blend of elastomeric block copolymers and polyethylene copolymers available from Scott Materials Group Inc., Sioux Falls, SD that partially coated the surface of yarns in the region of the interface between the two nonwoven layers. The binding layer had resin free areas in the region the interface between the two nonwoven layers of about 50 percent. The viscoelastic coating resin was styrene-isoprene-styrene block copolymer. The corner stitching thread was Tex 70 spun Kevlar® available from Saunders Thread Company, Gastonia, NC. No other fabric structures were built into the article. The total weight of fiber - resin composite was 4.9 kg/m². Ballistic testing was conducted using 16, 17 and 64 grain projectiles. Results of the ballistic tests over two rounds of shots are summarized in Table 1. The test results from flexural evaluation of the fabric are in Table 2.

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Table 1

Reference	Areal Density (kg/m ²)	Bullet Type	V50 (m/s)	Bullet Type	V50 (m/s)	Bullet Type	V50 (m/s)
Comparative Example A	5.1	16 grain	583	17 grain	522	64 grain	408
Comparative Example B	5.0	16 grain	609	17 grain	569	64 grain	461
	5.2	16 grain	620	17 grain	573	64 grain	501
Example 1	4.9	16 grain	627	17 grain	590	64 grain	512
	5.2	16 grain	666	17 grain	604	64 grain	544

Comparison of the above results shows that examples comprising a binding layer having discrete areas of yarn surfaces that are free from binder resin coating in the region of the interface between the nonwoven layers had a significantly better V50 performance when compared with examples of

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similar areal weight comprising a binding layer in the region of the interface between the two nonwoven layers that was continuous in nature so as to have no discrete areas of yarn surfaces that were free from binder resin coating.

- The flexural testing of the fabrics also demonstrates that fabrics of the
- 5 invention have improved flexibility, and hence enhanced wearer comfort, when compared with the comparative examples.

CLAIMS

What is claimed is:

- 5 1. A fiber - resin fiber - resin composite useful in a ballistic resistant soft armor article, comprising:

(a) from 75.0 to 94.0 weight percent of

a first nonwoven layer comprising a first plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100
10 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the first plurality of yarns arranged parallel with each other,

a second nonwoven layer comprising a second plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the
15 second plurality of yarns arranged parallel with each other,

wherein the first plurality of yarns of the first nonwoven layer have an orientation in a direction that is different from the orientation of the second plurality of yarns in the second nonwoven layer,

(b) from 1.0 to 10.0 weight percent of a thermoset or thermoplastic
20 binding resin partially coating portions of internal surfaces of the first plurality and the second plurality of yarns and partially filling some space between the filaments in the first plurality and the second plurality of yarns in the region of the interface between the two nonwoven layers so as to leave discrete areas of yarn surfaces that are free from binder resin coating,

25 (c) from 0.1 to 10.0 weight percent of a viscoelastic resin coating at least portions of external surfaces of the first plurality and the second plurality of yarns and filling some space between the filaments in the first plurality and the second plurality of yarns, and

(d) a transverse binding yarn interlaced transversely within the first and
30 second nonwoven layers.

wherein the weight percentages are expressed relative to the total weight of the fiber - resin composite.

2. The fiber - resin composite of Claim 1, wherein the yarns of the first and second pluralities of yarns have a yarn linear density of 50 to 4500 dtex and a yarn modulus of 100 to 3500 g/dtex.
- 5 3. The fiber - resin composite of Claim 1, wherein the yarns of the first and second pluralities of yarns have a yarn tenacity of 20 to 35 grams per dtex.
- 10 4. The fiber - resin composite of Claim 1, wherein the yarns of the first and second pluralities of yarns have an yarn elongation at break of 3.8 to 4.5 percent.
- 15 5. The fiber - resin composite of claim 1, wherein the second plurality of yarns in the second nonwoven layer are oriented orthogonally to the first plurality of yarns in the first nonwoven layer.
- 20 6. The fiber - resin composite of claim 1, wherein the first and the second pluralities of yarns are present in the first and the second nonwoven layers as substantially distinct yarns.
7. The fiber - resin composite of claim 1, wherein the first and second nonwoven layers comprise yarns comprising filaments of para-aramid, polyolefin, polyazole or blends thereof.
- 25 8. The fiber - resin composite of claim 1, wherein the viscoelastic resin is polyolefin, polyvinyl alcohol, polyisoprene, polybutadiene, polybutene, polyisobutylene, polyester, polyacrylate, polyamide, polysulfone, polysulfide; polyurethane, polycarbonate, polyfluorocarbon, silicone, glycol, liquid block copolymer, polyacrylic, epoxy, phenolic, liquid rubber, styrene copolymer or
- 30 mixtures thereof.
9. The fiber - resin composite of claim 1, wherein the thermoplastic binding resin is polyurethane, polyethylene or a blend of elastomeric block copolymer and polyethylene copolymer.

10. The fiber - resin composite of claim 1 wherein the area of yarn surface in the region of the interface between the nonwoven layers that is free from binding resin is from 40 to 95 percent of the total surface area of the yarn surfaces in the region of the interface between the nonwoven layers.

11. The fiber - resin composite of claim 1, wherein the transverse yarn comprises a plurality of filaments wherein the filaments are polyester filaments, polyethylene filaments, polyamide filaments, aramid filaments, polyareneazole filaments, polypyridazole filaments, polybenzazole filaments, or mixtures thereof.

12. The fiber - resin composite of claim 8, wherein the viscoelastic resin is polybutene or polyisobutylene.

13. A fiber - resin fiber - resin composite useful in a ballistic resistant soft armor article, comprising:

(a) from 75.0 to 94.0 weight percent of

a first nonwoven layer comprising a first plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the first plurality of yarns arranged parallel with each other,

a second nonwoven layer comprising a second plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the second plurality of yarns arranged parallel with each other,

a third nonwoven layer comprising a third plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the third plurality of yarns arranged parallel with each other,

a fourth nonwoven layer comprising a fourth plurality of yarns having a yarn tenacity of from 10 to 65 grams per dtex, a modulus of from 100 to 3500 grams per dtex and an elongation at break of 3.8 to 5.0 percent, the fourth plurality of yarns arranged parallel with each other,

wherein the second plurality of yarns of the second nonwoven layer have an orientation in a direction that is different from the orientation of the first plurality of yarns in the first nonwoven layer and the third plurality of yarns in the third nonwoven layer, and

5 the fourth plurality of yarns of the fourth nonwoven layer have an orientation in a direction that is different from the orientation of the third plurality of yarns in the third nonwoven layer,

 (b) from 1.0 to 10.0 weight percent of a thermoset or thermoplastic binding resin partially coating portions of internal surfaces of the first, second,
10 third and fourth pluralities of yarns and partially filling some space between the filaments of the first, second, third and fourth pluralities of yarns in the region of the interfaces between the nonwoven yarn layers so as to leave discrete areas of yarn surfaces that are free from binder resin coating, and

 (c) from 0.1 to 10.0 weight percent of a viscoelastic resin coating at
15 least portions of external surfaces of the first plurality and the fourth plurality of yarns and filling some space between the filaments in the first plurality and the fourth plurality of yarns, and

 (d)) a transverse binding yarn interlaced transversely within the first and fourth nonwoven layers.

20 wherein the weight percentages are expressed relative to the total weight of the fiber - resin composite.

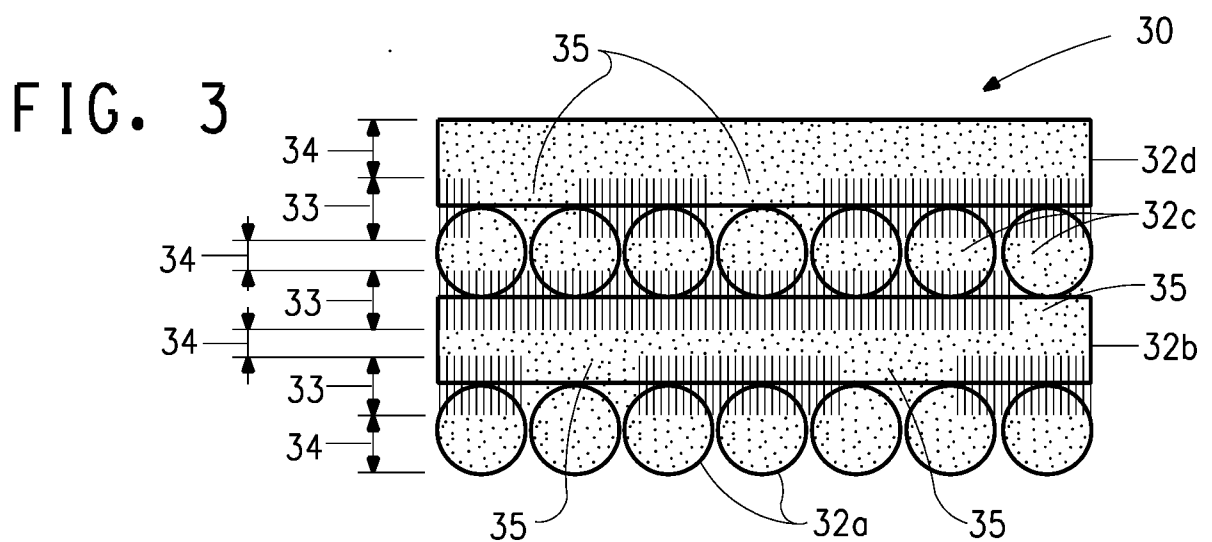
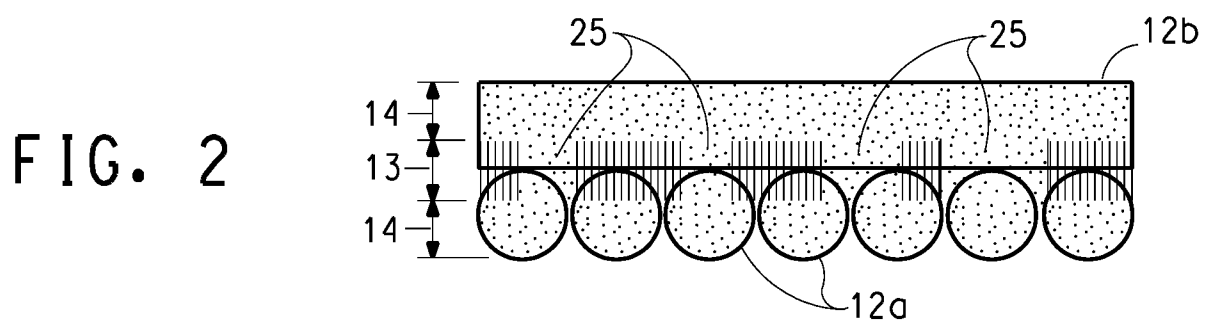
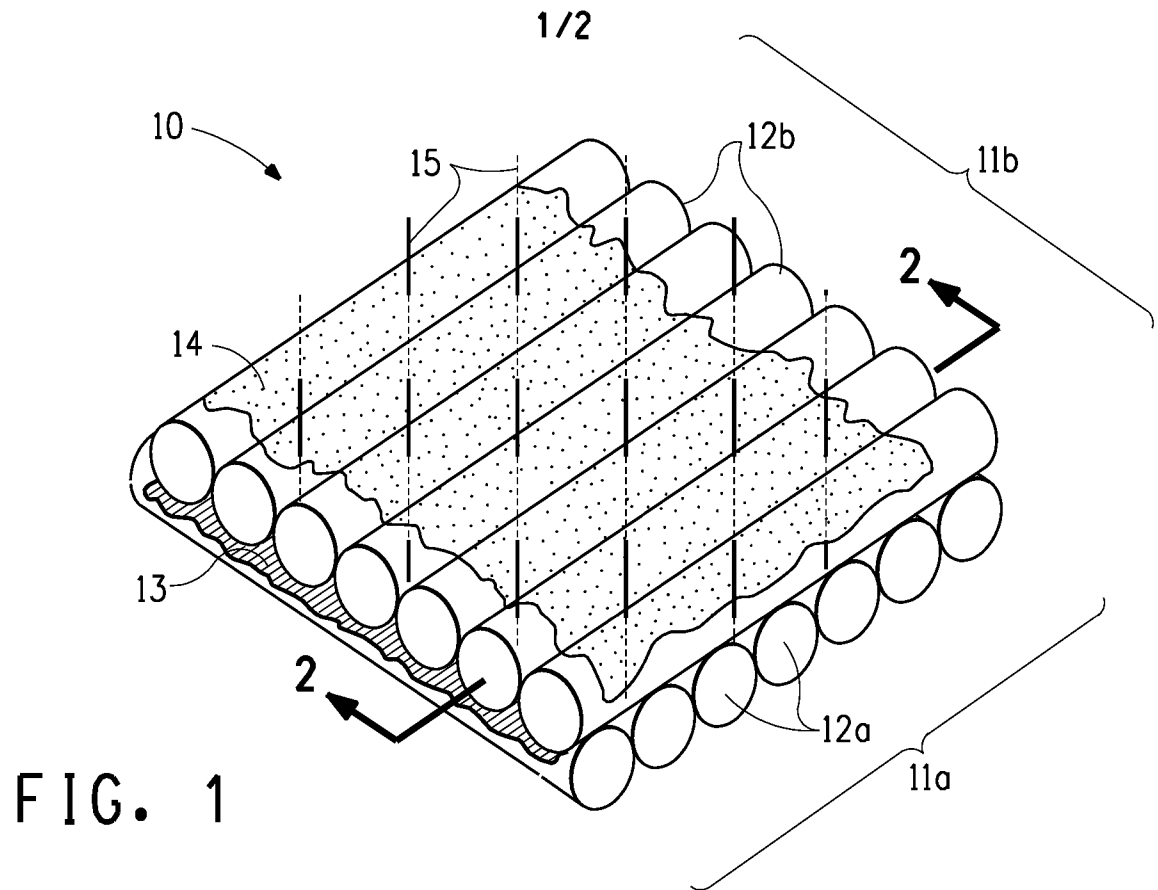
14. A ballistic resistant armor article comprising a plurality of the fiber – resin fiber - resin composites of claim 1.

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15. A ballistic resistant armor article comprising a plurality of the fiber – resin fiber - resin composites of claim 13.

16. A ballistic resistant armor article of claim 14 comprising a plurality of
30 the fiber – resin fiber - resin composites of claim 1 as a strike face.

17. A ballistic resistant armor article of claim 15, comprising a plurality of the fiber – resin fiber - resin composites of claim 13 as a strike face.



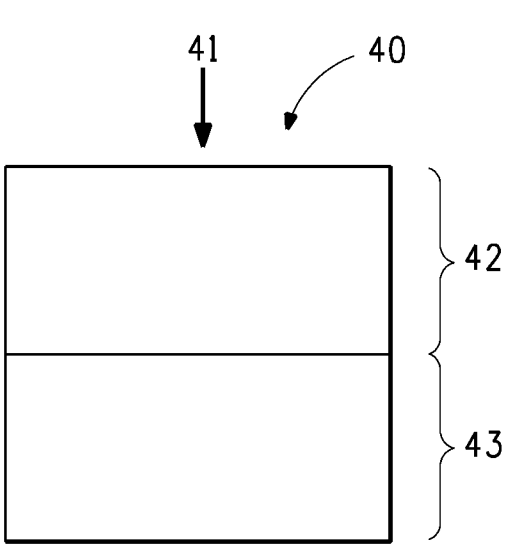


FIG. 4A

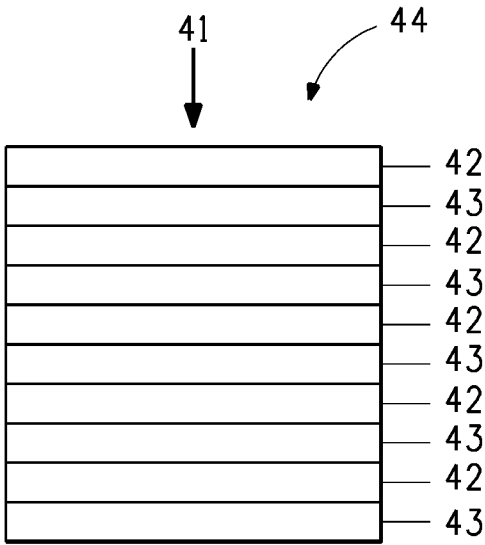


FIG. 4B

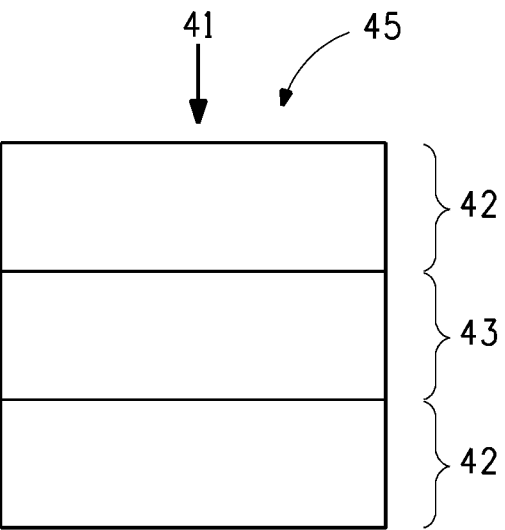


FIG. 4C

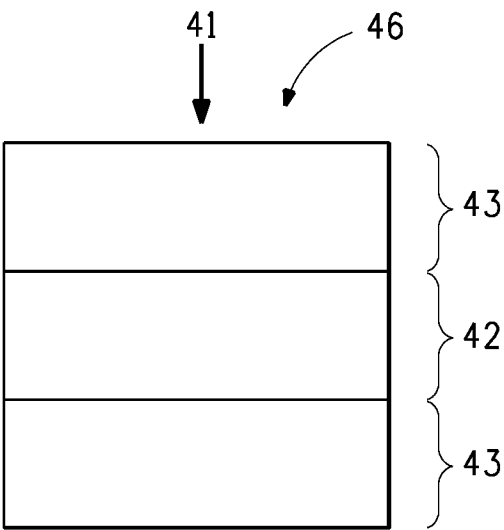


FIG. 4D