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(54) **Titre : ARTICLE BALISTIQUE LOURD ET PROCEDE POUR FABRIQUER LEDIT ARTICLE**
(54) **Title: HARD-BALLISTIC ARTICLE AND PROCESS TO MANUFACTURE SAID ARTICLE**

(57) **Abrégé/Abstract:**

A hard-ballistic article and a method to manufacture said article are provided. The hard ballistic article comprises a hybrid panel, wherein the hybrid panel comprises a) a first package of a plurality of consolidated cross-ply, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer, wherein the first package exhibits a surface facing to the direction of a ballistic attack and a surface facing away from the direction of the ballistic attack, and b) a second package containing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer, wherein the first package is bonded with its surface facing away from the direction of the ballistic attack with the second package.

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(54) **Title:** HARD-BALLISTIC ARTICLE AND PROCESS TO MANUFACTURE SAID ARTICLE

(57) **Abstract:** A hard-ballistic article and a method to manufacture said article are provided. The hard ballistic article comprises a hybrid panel, wherein the hybrid panel comprises a) a first package of a plurality of consolidated cross-ply, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer, wherein the first package exhibits a surface facing to the direction of a ballistic attack and a surface facing away from the direction of the ballistic attack, and b) a second package containing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer, wherein the first package is bonded with its surface facing away from the direction of the ballistic attack with the second package.

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Hard-ballistic article and process to manufacture said article

5 **Description:**

The present invention pertains to a hard-ballistic article and to a process to manufacture said article.

Hard-ballistic articles are known which contain packages of woven fabric layers or packages of non-woven fabric layers. Said packages are stacked onto one
10 another to form a monolithic panel. Furthermore, hard-ballistic articles are known which contain packages of woven fabric layers and packages of non-woven fabric layers. Said packages are stacked onto one another to form a hybrid panel.

WO 2008/097362 A describes multilayer ballistic resistant articles which provide suitable protection against high energy ballistic threads, while remaining suitable
15 for flexible vest applications. Said multilayer ballistic resistant articles are formed from a combination of flexible and semi-rigid panel components. The flexible or semi-rigid panels may include woven fibrous layers, non-woven fibrous layers or both. In the examples WO 2008/0897362 A describes a ballistic shoot pack consisting of a package of woven fabric layers which consist of a plurality of
20 flexible layers of aramid fabric, followed by a semi-rigid panel consisting of a plurality of molded layers of Gold Shield[®] material and followed by another plurality of flexible layers of aramid fabric. In said example the plurality of flexible layers of aramid fabric and the plurality of molded layers of Gold Shield[®] material is varied. Gold Shield[®] material is a composite consisting of two unidirectional aligned
25 aramid fiber plies, wherein each of said fiber plies is provided with a resin, and said fiber plies are 0°/90° cross-plyed and consolidated. Aramid fabric does not contain any resin.

WO 2012/098158 A1 describes a ballistic resistant article comprising a plurality of fibrous layers, each of said layers comprising a network of fibers having a strength of at least 800 mN/tex, for example aramid fibers, and a matrix material, wherein the matrix material comprises a mixture at least one self-crosslinking acrylic resin, and/or at least one crosslinkable acrylic resin, and at least one tackifier. WO 5 2012/098158 A1 explains that the term “a network of fibers” means a plurality of fibers arranged into a predetermined configuration or a plurality of fibers grouped together to form a twisted or untwisted yarn, which yarns are arranged into a predetermined configuration, and that the fiber network can have various configurations. For example the fibers or yarns may be formed as a felt or other 10 nonwoven, knitted or woven into a network, or formed into a network by any conventional techniques.

WO 2008/060650 A2 describes ballistic resistant articles formed from a hybrid of woven and non-woven fibrous components. The hybrid structures are particularly 15 useful for the formation of soft, flexible body armor. A ballistic resistant article comprises in order: a) a first panel comprising at least one woven fibrous layer, b) a second panel comprising a plurality of non-woven fibrous layers, each of the non-woven fibrous layers being consolidated with the other non-woven fibrous layers, each of the non-woven fibrous layers comprising a unidirectional parallel 20 array of fibers, each of said fibers being coated on their surface with a polymeric composition that is resistant to dissolution by water, and resistant to dissolution by one or more organic solvents; and c) a third panel comprising at least one woven fibrous layer. A further ballistic resistant article differs from the article described above in that a panel comprising at least one woven fibrous layer is sandwiched 25 between panels each of which comprising a plurality of non-woven fibrous layers, each of the non-woven fibrous layers being consolidated with the other non-woven fibrous layers, each of the non-woven fibrous layers comprising a unidirectional parallel array of fibers, each of said fibers being coated on their surface with a polymeric composition that is resistant to dissolution by water, and resistant to

dissolution by one or more organic solvents. With regard to the woven fibrous layers WO 2008/060650 A2 explains that it is generally not necessary for the fibers to be coated with the polymeric matrix composition, because no consolidation is conducted. However, the fibers comprising the woven fibrous
5 layers may be coated with a polymeric matrix composition, preferably with a polymeric composition that is resistant to dissolution by water and resistant to dissolution by one or more organic solvents.

WO 2008/140567 A2 describes the production of a ballistic resistant article comprising: a) providing a fabric comprising a plurality of fibers, e.g. aramid fibers,
10 arranged in an array, b) heating said fabric inside a microwave oven, c) molding the heated fabric into an article, and d) allowing the molded fabric to cool.
WO 2008/140567 A2 also describes a method of forming a consolidated fiber network, said consolidated network of fibers comprising a plurality of fiber layers, said fibers having a polymeric matrix composition thereon; which consolidated
15 fiber network is consolidated under heat and pressure, wherein the heat of consolidation is generated by the application of microwave energy sufficient to thereby heat the polymeric matrix composition to a temperature of at least about the softening temperature of the polymeric matrix composition. The fabrics may comprise a hybrid combination of non-alternating woven and non-woven fibrous
20 layers. The non-woven fibrous layers comprise a plurality of layers, each layer comprising a plurality of unidirectional aligned, parallel fibers, wherein said layers are cross-plyed at an angle relative to a longitudinal fiber direction of each adjacent fiber layer; and wherein said fibers optionally have a polymeric matrix composition thereon. Prior to weaving, the individual fibers of the woven fibrous layers may or
25 may not be coated with a polymeric matrix composition in a similar fashion as the non-woven fibrous layers using the same matrix composition as the non-woven fibrous layers.

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US 2012/0174753 A1 describes soft body armor and explains that the flexible and soft body armor of the invention of this document is in contrast to rigid or hard armor and therefore, does not retain its shape when subjected to a significant amount of stress and is incapable of being free standing without collapsing. US 5 2012/0174753 A1 emphasized that this is in distinction to the characteristics of hard or rigid armor which has sufficient mechanical strength and maintains its shape when subjected to a significant amount of stress and is capable of being free-standing without collapsing. US 2012/0174753 A1 provides a flexible ballistic composite useful in soft body armor applications, the composite comprising at 10 least one woven fabric layer, at least one second fabric layer, and a first separator layer positioned between the woven fabric layer and the second fabric layer, the first separator layer comprising a lightweight, thin and flexible layer, the first separator layer not being laminated to either of the woven fabric layer or the second fabric layer such that the woven fabric layer and the second fabric layer 15 are free to move relative to each other. The woven fabric layer and the second fabric layer may be made of aramid fibers, and the second fabric layer may be formed as a unidirectional oriented fabric. And the second fabric layer is preferably coated with a matrix resin composition.

WO 2008/108882 A2 describes a ballistic resistant material comprising a first 20 panel comprising a plurality of consolidated fibrous layers, each of the fibrous layers comprising a plurality of fibers having a tenacity of about 7 g/denier or more and being coated on their surfaces with a polymeric composition, and a second panel attached to the first panel, which second panel is different than the first panel, and which second panel comprises a plurality of consolidated fibrous 25 layers, each of the fibrous layers comprising a plurality of fibers having a tenacity of about 7 g/denier or more and being coated on their surfaces with a polymeric composition, and said first panel containing a greater percentage by weight of the polymeric composition in the first panel, based on the total weight of the first panel,

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than a percentage by weight of the polymeric composition in said second panel,
based on the total weight of the second panel.

The ballistic articles described above exhibit a good ballistic performance.

5 However, there is an ongoing demand for ballistic articles which at the same areal
density have a better ballistic performance.

Therefore, the problem underlying the present invention is to provide a hard-
ballistic article which at the same areal density exhibits a better ballistic
performance.

Said problem is solved by a hard-ballistic article comprising a hybrid panel, wherein the hybrid panel comprises

- 5 a) a first package of a plurality of consolidated cross-ply, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer, wherein the first package exhibits a surface facing to the direction of a ballistic attack and a surface facing away from the direction of the ballistic attack, and
- 10 b) a second package containing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer,
- 15 and wherein the first package is bonded with its surface facing away from the direction of the ballistic attack to the second package.

Surprisingly, the hard-ballistic article according to the invention exhibits a higher v_{50} -value than a hard-ballistic article which merely contains unidirectional aligned fabric layers provided with a matrix material which is identical with the first matrix material of the first package of the hard-ballistic article according to the present invention, and which exhibits the same areal weight.

Furthermore, it is surprising that the hard-ballistic article according to the invention exhibits a higher v_{50} -value than a hard-ballistic article which merely contains woven fabric layers provided with a matrix material which is identical with the second matrix material of the second package of the hard-ballistic article according to the present invention, and which exhibits the same areal weight.

And it is surprising that the hard-ballistic article according to the invention exhibits a higher v_{50} -value than a comparative hard-ballistic article which only differs from the hard-ballistic article according to the invention in that the matrix material in the first package is identical with the matrix material in the second package. This
5 technical effect is quite the more surprising as said effect can even be reached, if the hard-ballistic article according to the invention exhibits a somewhat lower areal weight than the comparative hard-ballistic article.

In the present invention the terms "areal weight" and "areal density" have the same meaning and quantify the mass of the hard-ballistic article under consideration in
10 gram per square meter of said hard-ballistic article, [g/m²].

Within the scope of the present invention the term "hard-ballistic article" means that said article has sufficient stiffness to maintain its shape when subjected to a significant amount of stress and is capable of being free-standing without collapsing. "Sufficient stiffness" means for example, that if the hard-ballistic article
15 according to the invention is placed on a desk in a manner, wherein one half of its area lays on the desk and the other half of its area is free-hanging, no bending is observed in the free-hanging part of the hard-ballistic article.

Within the scope of the present invention the term "first matrix material" means a material that
20 - in particular bonds the unidirectional aligned aramid fibers within each of the at least two layers of unidirectional aligned aramid fibers to one another and thereby stabilizes fibers within each of the at least two layers of unidirectional aligned aramid fibers, and
- after cross-plying the at least 2 layers of unidirectional aligned aramid fibers
25 binds said at least 2 layers to one another.

Within the scope of the present invention the term “cross-ply” means an arrangement of the at least two layers of unidirectional aligned aramid fibers, wherein said at least two layers of unidirectional aligned aramid fibers are stacked to one another at an angle, preferably 90 °, with respect to the direction of the fiber-directions in said stacked layers.

Within the scope of the present invention the term “consolidated cross-ply” means that the at least two layers of unidirectional aligned aramid fibers are bonded to one another, preferably with the aid of the first matrix material.

Within the scope of the present invention the term “fibers” means an elongate body, the length dimension of which is much greater than the transverse dimensions of width and thickness. Accordingly, “fibers” includes monofilament fibers, multifilament fibers, ribbons, strips, staple fibers and yarns made from one or more of the foregoing, for example multifilament yarns or staple fiber yarns. Especially preferred “fibers” mean multifilament yarns. The cross-sections of the “fibers” to be used in the present invention may vary widely. They may be circular, flat or oblong in cross-section. They also may be of irregular or regular shape having one or more regular or irregular lobes projecting from the longitudinal axis of e.g. a filament. Preferably the “fibers” exhibit a substantially circular cross-section.

Within the scope of the present invention the term “aramid fibers” means fibers produced from an aromatic polyamide as the fiber-forming polymer. In said fiber forming polymer at least 85 % of the amide (-CO-NH-) bonds are directly bound on two aromatic rings. Especially preferred aromatic polyamides are p-aramids. Among the p-aramids poly(p-phenylene terephthalamide) is the most preferred one. Poly(p-phenylene terephthalamide) results from the mol:mol polymerization of p-phenylene diamine and terephthalic acid dichloride. Fibers consisting e.g. of

multifilament yarns made from poly(p-phenylene terephthalamide) can be obtained under the trade name Twaron[®] from Teijin Aramid (NL).

Further aramid fibers useful to form the network of fibers in the ballistic resistant article according to the present invention are those formed from an aromatic
5 copolymer as the fiber-forming polymer. In the said aromatic copolymer p-phenylene diamine and/or terephthalic acid dichloride are partly or completely substituted by other aromatic diamines and/or dicarboxylic acid chlorides.

In a preferred embodiment the hard-ballistic article according to the present invention consists of

- 10 a) a first package of a plurality of consolidated cross-plyes, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer, wherein the first package exhibits a surface facing to the direction of a
15 ballistic attack and a surface facing away from the direction of the ballistic attack, and
- b) a second package containing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix
20 material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer, and wherein the first package is bonded with its surface facing away from the direction of the ballistic attack with the second package.

25 In a further preferred embodiment of the hard-ballistic article according to the present invention a metallic or ceramic strike face is bonded to the surface of the first package facing to the direction of the ballistic attack.

The hard-ballistic article according to the present invention comprises a first package of a plurality of consolidated cross-plyes, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material.

- 5 Within the scope of the present invention the term “plurality of consolidated cross-plyes” means a certain number n of consolidated cross-plyes. Said number n can be chosen in a range depending on the desired ballistic protection. Said desired ballistic protection is reached for many applications of the hard-ballistic article according to the present invention, if said article – together with the plurality of
- 10 woven fabric layers as defined in b) – contains 1 to 50 consolidated cross-plyes, so that n is in the range of 1 to 50. Therefore, a hard-ballistic article, wherein the plurality of consolidated cross-plyes means a number n of consolidated cross-plyes, and n ranges from 1 to 50 constitutes a preferred embodiment of the hard-ballistic article according to the present invention. In an especially preferred embodiment
- 15 of the hard-ballistic article according to the present invention n ranges from 5 to 30, even more preferred from 10 to 20.

In the hard-ballistic article according to the present invention the cross-plyes of the first package are consolidated. Within the scope of the present invention the term

20 “consolidated” means that the at least two layers of unidirectional aligned aramid fibers contained in each consolidated cross-ply are bonded to one another. Preferably said bonding is achieved with the aid of the first matrix material.

In a preferred embodiment of the hard-ballistic article according to the present invention each of the at least two layers of unidirectional aligned aramid fibers are provided with the first matrix material.

Each consolidated cross-ply comprised by the first package of the hard-ballistic article according to the present invention contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the numbers of layers of unidirectional aligned aramid fibers are limited by practical reasons, mainly by the practical requirement that the consolidated cross-ply preferably shall be woundable for the purposes of storage and transport. In a preferred embodiment of the hard-ballistic article according to the present invention each consolidated cross-ply consists of 2 to 10 layers of said unidirectional aligned aramid fibers. In an especially preferred embodiment of the hard-ballistic article according to the present invention each consolidated cross-ply consists of 2 to 6 layers of said unidirectional aligned aramid fibers, so that in said especially preferred embodiment each consolidated cross-ply may consist of 2 or 3 or 4 layers of said unidirectional aligned aramid fibers.

The first package of the hard-ballistic article according to the present invention contains a plurality of cross-plyes each of which contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer, preferably a first organic polymer. The first, preferably organic, polymer is present on the unidirectional aramid fibers in a weight-percentage sufficient to bond the at least two layers of unidirectional aligned aramid fibers to one another. Therefore, it is not necessary that each and every space between the unidirectional aligned aramid fibers is filled with the first polymer, provided that the applied quantity of the first polymer enables a sufficient binding of the at least two layers of unidirectional aligned aramid fibers to one another. For example, the first polymer may be distributed in spots on and between the fibers.

In a preferred embodiment of the hard-ballistic article according to the present invention a concentration of the first polymer in each layer of the unidirectional aligned aramid fibers ranges from 2 to 50 wt.-% with respect to the weight of the

aramid fibers plus the weight of the first, preferably organic, polymer without moisture. From a practical point of view this means that said 2 to 50 wt.-% of the first polymer are determined after the unidirectional aligned aramid fibers bearing the first polymer have been dried to a water content of zero wt.-%.

- 5 In an especially preferred embodiment of the hard-ballistic article according to the present invention a concentration of the first polymer in each layer of the unidirectional aligned aramid fibers ranges from 5 to 30 wt.-%, even more preferred from 10 to 20 wt.-% with respect to the weight of the aramid fibers plus the weight of the first, preferably organic polymer.
- 10 In a further preferred embodiment of the hard-ballistic article according to the present invention an areal density of each layer of the unidirectional aligned aramid fibers including the first polymer, preferable the first organic polymer, ranges from 10 to 250 g/m², especially preferred from 40 to 100 g/m².
- 15 In a further preferred embodiment of the hard-ballistic article according to the present invention the first polymer is a styrene butadiene random copolymer, i.e. a copolymer, wherein the copolymerization parameters of styrene and butadiene determine a random sequence of styrene and butadiene in the copolymer chain.
- 20 In an especially preferred embodiment of the hard-ballistic article according to the present invention the styrene butadiene random copolymer is a carboxylated styrene butadiene random copolymer. Within the scope of the present invention the term "carboxylated styrene butadiene random copolymer" means a copolymer which has been synthesized by copolymerizing the monomers styrene, butadiene
25 and optionally a third monomer, wherein a low part to be quantified below of either the styrene and/or the butadiene and/or the third monomer contains at least one carboxylic group. So, the term "carboxylated styrene butadiene random

copolymer” comprises several preferred embodiments, which are described in the following.

In a first preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
5 monomers styrene and butadiene, wherein a low part of the styrene contains at least one carboxylic group.

In a second preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
10 monomers styrene and butadiene, wherein a low part of the butadiene contains at least one carboxylic group.

In a third preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
monomers styrene and butadiene, wherein a low part of both styrene and the butadiene contain at least one carboxylic group.

15 In a fourth preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the monomers styrene and butadiene and a third monomer, wherein a low part of the third monomer contains at least one carboxylic group. The third monomer is selected from the group consisting of ethylenically unsaturated carboxylic acids.
20 The selected ethylenically unsaturated carboxylic acid may be a monocarboxylic acid or a polycarboxylic acid or a mixture of such acids. Preferably the acid has 2 to 10 chain carbon atoms, i.e. C-atoms forming a C₂₋₁₀ chain, which contains the ethylenical unsaturation. The carbon atom of the carboxylic acid is not included in said 2 to 10 chain carbon atoms. Examples of preferred monocarboxylic acids are

acrylic acid, methacrylic acid and crotonic acid. Examples of polycarboxylic acids are maleic acid, fumaric acid, itaconic acid and 3-butene 1,2,3-tricarboxylic acid.

In a fifth preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
5 monomers styrene and butadiene and a third monomer, wherein a low part of both styrene and the third monomer contain at least one carboxylic group.

In a sixth preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
10 monomers styrene and butadiene and a third monomer, wherein a low part of both the butadiene and the third monomer contain at least one carboxylic group.

In a seventh preferred embodiment the carboxylated styrene butadiene random copolymer is a copolymer, which has been synthesized by copolymerizing the
15 monomers styrene and butadiene and a third monomer, wherein a low part of the styrene, the butadiene and the third monomer contain at least one carboxylic group.

In an eighth preferred embodiment the carboxylated styrene butadiene is a mixture of at least one copolymer belonging to the first, second or third embodiment and at least one copolymer belonging to the fourth, fifth, sixth and seventh embodiment.

In each of the preferred embodiments described above the term "carboxylic group"
20 means a carboxylic acid group, which is present
- either in the neutral form -COOH
- or in the anionic form which can occur as $\text{-COO}^- \text{H}^+$ or as a salt $\text{-COO}^- \text{M}^+$,
wherein M^+ is a metal cation.

As indicated before, in all embodiments of the carboxylated styrene butadiene random copolymer resin the weight percentage (wt.-%) of the monomer bearing the at least one carboxylic group with respect to the respective copolymer is generally low and for example is between 0.05 wt.-% and 10 wt.-% and may be in the range from 5 wt.-% or less down to 0.05 wt.-%. Or the weight percentage may be in the range from 1 wt.-% or less to ≥ 0.05 wt.-%.

In all embodiments of the carboxylated styrene butadiene random copolymer resin the carboxylation level, cl, which is calculated using the dry weight of carboxylic acid (COOH)-groups in the carboxylated styrene butadiene random copolymer, w_{COOH} , and the dry weight of the monomers in the carboxylated styrene butadiene random copolymer resin, w_{monomer} , by the formula

$$\text{cl} = (w_{\text{COOH}}/w_{\text{monomer}}) \cdot 100 \text{ (\%)}$$

is preferably in the range from 0.05 % to 15.0 %, more preferably in the range from 0.05 % to 10.0 % and most preferred in the range from 0.05 % to 5.0 %.

In all embodiments of the carboxylated styrene butadiene copolymer resin said copolymer is a random copolymer, i.e. a polymer wherein the sequence of the styrene, the butadiene and of the optional third monomer is a statistical sequence defined by the copolymerisation parameters of the respective bi- or ter-copolymerisation.

The at least one styrene butadiene random copolymer resin which is preferably used for the first matrix material of the ballistic resistant article of the present invention and which may be a carboxylated or a non-carboxylated styrene butadiene random copolymer resin exhibits a glass transition temperature T_g which preferably is in the range between -70 °C and 100 °C, more preferred in the range between -50 °C and 30 °C, and most preferred in the range between -30 °C and 20 °C.

In a preferred embodiment of the hard-ballistic article according to the present invention the first matrix material comprises a polymer, preferably an organic polymer, and a tackifier. Within the scope of the present invention the term “tackifier” means a chemical compound preferably present in the first matrix material of the ballistic resistant article according to the present invention and being homogeneously distributed in said first matrix material, thereby providing the first matrix material with tack. And within the scope of the present invention the term “homogeneously distributed in said first matrix material” means that the concentration of the tackifier in every volume element of the first matrix material is the same.

In a preferred embodiment of the hard-ballistic article according to the present invention the tackifier is selected from the group consisting of

- rosin resins which are derived from either tree stumps (wood resin), sap (gum rosin) or by-products of the paper making process (tall oil rosin),
- wherein the rosin resins may be
 - rosin esters obtained by the reaction between rosin acids and alcohols,
 - hydrogenated rosin esters obtained by hydrogenation of the rosin acid raw material or
 - dimerized rosin resins obtained from dimerizing rosin acids or
- terpene resins derived from terpene feedstocks either from wood sources or from citrus fruit, or
- hydrocarbon resins available from Neville Chemical Company, US under several designations, such as NP-10, NP-25 and FN-175.

In a preferred embodiment of the hard-ballistic article according to the present invention the tackifier is present in the first matrix material in a weight percentage with respect to the weight of the first matrix material resin ranging from 1 wt.-% to 20 wt.-%, more preferred from 1.5 wt.-% to 10 wt.-% and most preferred from 2 wt.-% to 6 wt.-%. If said weight percentage of the tackifier is below 1 wt.-%

handling of a single layer of unidirectional aligned aramid fibers during the manufacture of the hard-ballistic article of the present invention may become more complicated. If said weight percentage of the tackifier is above 20 wt.-%, the first package of the hard-ballistic article of the present invention may become too stiff.

5

In an especially preferred embodiment of the hard-ballistic article of the present invention the tackifier is a rosin ester which is for example contained in Aquatac[®] 6025, a waterborne dispersion containing about 58 wt.-% rosin ester, about 39 wt.-% water and less than 4 wt.-% surfactant from Arizona Chemical, US.

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The plurality of consolidated cross-plyes constitute the first package of the hard-ballistic article according to the present invention. In said first package said plurality of consolidated cross-plyes are bonded to one another. Said bonding can be achieved by an adhesive or preferably by the first matrix material.

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The hard-ballistic article according to the present invention comprises a second package of a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material.

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Within the scope of the present invention the term “plurality of woven fabric layers” means a certain number m of woven fabric layers. Said number m can be chosen in a range depending on the desired ballistic protection. Said desired ballistic protection is reached for many applications of the hard-ballistic article according to the present invention, if said article – together with the plurality of consolidated cross-plyes as defined in a) – contains 1 to 30 woven fabric layers, so that m is in the range of 1 to 30. Therefore, a hard-ballistic article, wherein the plurality of woven fabric layers means a number m of woven fabric layers, and m ranges from 1 to 30, constitutes a preferred embodiment of the hard-ballistic article according to the present invention. In an especially preferred embodiment of the hard-

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ballistic article according to the present invention m ranges from 2 to 15, even more preferred from 4 to 10.

Within the scope of the present invention the term “second matrix material” means a material that bonds adjacent woven fabric layers to one another and thereby
5 forms the second package of the hard-ballistic article according to the present invention. So, though it is possible that the plurality of woven fabric layers constituting the second package of the hard-ballistic article according to the present invention are bonded to one another by an adhesive, preferably the second matrix material serves to bind the woven fabric layers to one another.

10 The second matrix material contained in the second package of the hard-ballistic article according to the present invention is different from the first matrix material and comprises a second polymer, preferably a second organic polymer, which is different from the first polymer. In a preferred embodiment of the hard-ballistic
15 article according to the present invention the second polymer is a polychloroprene, also called neoprene.

The second, preferably organic, polymer is present on and partly in the woven fabric layers in a weight-percentage sufficient to bond neighbored woven layers to one another. Therefore, it is not necessary that each and every space in each of the woven fabric layers is filled with the second polymer, provided that the applied
20 quantity of the second polymer enables a sufficient binding of the neighbored woven layers to one another. The second polymer may exhibit a concentration gradient with its maximum on one of the surfaces of the woven layers and decreasing along the thickness of the woven layer. Or the second polymer may exhibit two concentration gradients each of which having its maximum on one of
25 the surfaces of the woven layers and decreasing along the thickness of the woven layer.

In a preferred embodiment of the hard-ballistic article according to the present invention a concentration of the second polymer in each of the woven fabric layers of aramid fibers ranges from 2 to 32 wt.-% with respect to the weight of the aramid fibers in said woven fabric layer plus the weight of the second polymer.

- 5 In an especially preferred embodiment of the hard-ballistic article according to the present invention a concentration of the second polymer in of the woven fabric layers of aramid fibers ranges from 4 to 16 wt.-% with respect to the weight of the aramid fibers plus the weight of the second polymer.

- 10 In a further preferred embodiment of the hard-ballistic article according to the present invention an areal density of each woven layer of aramid fibers including the second polymer ranges from 100 to 1000 g/m², especially preferred from 400 to 600 g/m².

- 15 In a preferred embodiment of the hard-ballistic article according to the present invention the first package is bonded with its surface facing away from the direction of the ballistic attack with the second package by a (first package / second package) - bonding layer. For example, said (first package / second package) - bonding layer may be a molten and thereafter solidified film of the first or of the second matrix material.

- 20 In an especially preferred embodiment, said (first package / second package) - bonding layer is a solidified mixed melt consisting of a solid mixture of the first matrix material with the second matrix material.

- 25 In a further preferred embodiment of the hard-ballistic article according to the present invention the first package is bonded with its surface facing the direction of the ballistic attack with the metallic or ceramic strike face by a (first package / metallic or ceramic strike face) - bonding layer. Said

(first package / metallic or ceramic strike face) - bonding layer preferably is a single layer of an adhesive material or a multilayer which for example exists of

- a primer layer P1 applied to the side of the metallic or ceramic strike face,
- a primer layer P2 applied to the surface of the first package facing the direction

5 of ballistic attack,

- an adhesive layer A1 coated on primer layer P1, and
- an adhesive layer A2 coated on primer layer P2.

In a further preferred embodiment of the present invention the hard-ballistic article

10 comprises 5 to 40 consolidated cross-plyes and 2 to 18 woven fabric layers.

In an especially preferred embodiment of the present invention the hard-ballistic article comprises 10 to 25 consolidated cross-plyes and 5 to 14 woven fabric layers.

In a further preferred embodiment of the present invention the hard-ballistic article

15 comprises a plurality of consolidated cross-plyes n and a plurality of woven fabric layers m in a ratio $n : m$, wherein $n : m$ is the range from (27 to 33) : (12 to 16), especially preferred in the range from 27 : 16 to 22 : 12.

In a further preferred embodiment of the present invention the hard ballistic article comprises a weight of consolidated cross-plyes w_1 given in wt.-% and a weight of

20 woven fabric layers w_2 given in wt.-% in a ratio $w_1 : w_2$, wherein $w_1 : w_2$ is in the range from (40 to 70) : (30 to 60), more preferred in the range from (50 to 70) : (30 to 50), even more preferred in the range from (50 to 60) : (40 to 50), and especially preferred in the range from (54 to 56) : (44 to 46).

A process to manufacture the hard-ballistic article of the present invention comprises the steps, preferably consists of the steps

- 5 i) preparing a plurality of consolidated cross-ply, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer,
- 10 ii) preparing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer,
- 15 iii) stacking the plurality of woven fabric layers prepared in step ii) resulting in a stack of said plurality of woven fabric layers,
- iv) stacking the plurality of consolidated cross-ply prepared in step i) on top of the of the stack of said plurality of woven fabric layers resulting in step iii) resulting in a stacked panel,
- 20 v) transferring the stacked panel resulting in step iv) into a press, heating the press to a constant temperature in the range from 100 to 250 °C, pressing the stacked panel at said constant temperature at a constant pressure in the range from 5 to 150 bar for a time in the range of 1 to 100 minutes,
- 25 vi) cooling down the closed press to room temperature, and then opening the press to obtain a hybrid panel, wherein the hybrid panel comprises
 - a first package containing a plurality of consolidated cross-ply, and having an outer surface, and
 - a second package containing a plurality of woven fabric layers and – optionally –
- 30 vii) binding the hybrid panel obtained in step vi) with the outer surface of the first package, i.e. with the surface of the top unidirectional layer, to a metallic or ceramic strike face.

In a preferred embodiment of step i) of the process according to the present invention aramid fibers are unidirectional aligned and provided, especially coated, with a first matrix material, wherein the first matrix material comprises a first polymer and – optionally – a tackifier. This results in a first single layer of unidirectional aligned aramid fibers which are provided with the first matrix material (first 1L-UD).

In the same manner at least one further 1L-UD is manufactured.

Said at least one further 1L-UD is cross-plyed at a cross-plying angle, preferably at 90 °, onto the first 1L-UD to yield a cross-ply containing at least two layers of unidirectional aligned aramid fibers which are provided with the first matrix material, wherein the first matrix material comprises a first polymer, and – optionally – a tackifier.

Said cross-ply is consolidated with the aid of a consolidation procedure. Preferably the consolidation procedure comprises applying a consolidation pressure p_c , a consolidation temperature T_c , and a consolidation time t_c , wherein p_c ranges from 20 bar to 120 bar, T_c ranges from 110 to 200 °C, and t_c ranges from 5 to 60 minutes. In an especially preferred embodiment of the process according to the present invention the consolidation procedure of step i) is performed with p_c ranging from 40 bar to 70 bar, T_c ranging from 130 to 170 °C, and t_c ranging from 10 to 30 minutes.

The operations described above on this page may be used to prepare a plurality of consolidated cross-plyes in step i) of the method according to the present invention.

In a preferred embodiment of step ii) of the process according to the present invention the woven fabric layers consisting of aramid fibers are provided with a second matrix material by melt-impregnating the second matrix material onto each of said woven fabric layers, wherein only one or both of the surfaces of the woven fabric layers may be treated by said melt-impregnation.

Within the process according to the present invention the stack of said plurality of woven fabric layers resulting from step iii) before step iv) may be treated by heat and/or pressure in order to pre-fix the woven fabric layers to one another.

In a preferred embodiment of step v) of the process according to the present invention the stacked panel in the press is heated to a constant temperature in the range from 110 to 200 °C, pressed at said constant temperature at a constant pressure in the range from 20 to 120 bar for a time in the range of 5 to 60 minutes.

In a preferred embodiment of step vii) of the process according to the present invention both the surface of the metallic or ceramic strike face to be bonded to the outer surface of the hybrid panel and the outer surface of the hybrid panel are first coated with a primer-layer, then coated with an adhesive-layer, and finally the metallic or ceramic strike face is bonded with the outer surface of the hybrid panel via said adhesive layers.

In the process according to the present invention the terms "first matrix material", "second matrix material", "cross-ply", "consolidated cross-ply", "fibers", "aramid fibers", "plurality of consolidated cross-ply", "tackifier", "plurality of woven fabric layers", "metallic or ceramic strike face" analogously mean the same as was already explained for the hard-ballistic article of the present invention.

The present invention is explained in more detail in the following examples and comparative examples.

Example 1: Hard-ballistic article with ceramic front plate and hybrid panel

a) Manufacture of a single unidirectional fibrous layer (1L-UD)

5 Poly(p-phenylene terephthalamide) multifilament yarns (Twaron type 1000; 3360 dtex f2000; Manufacturer: Teijin Aramid, NL) were taken from a creel and passed through a reed thus aligned substantially parallel to one another. The substantially parallel aligned yarns were coated with a pre-diluted aqueous carboxylated styrene butadiene random copolymer latex dispersion (Rovene[®] 4019, manufac-
10 tured by Mallard Creek Polymers, USA, solid content = 52.0 to 54.0 wt.-%, viscosity = 580 cps (Brookfield, spindle LV-2, 20 rpm, 25 °C); Tg = + 14°C, bound styrene = 62 %;) using a reverse roll coater. The pre-diluted latex dispersion was obtained by diluting Rovene[®] 4019 to a solid content of 25 wt.-% using tap water. The Rovene[®] 4019 coated yarns were spread on a series of spreader bars and
15 laid up on a silicone coated release paper and dried by passing over a hot-plate set at a temperature of 120 °C resulting in a single unidirectional fibrous layer (1L-UD). The resin concentration in the 1L-UD was 13 ± 1 wt.-% based on the total weight of the 1L-UD, i.e. with respect to the weight of yarn+matrix without moisture, i.e. the weight of the 1L-UD dried to a water content of well below 0.5
20 wt.%. From a practical point of view this means drying to a water content of zero wt.-%. The areal density of the poly(p-phenylene terephthalamide) multifilament yarns in the 1L-UD was 110 ± 5 g/m². The total areal density of the 1L-UD including equilibrium moisture content of the 1L-UD was 130 ± 10 g/m² depending on resin loading and equilibrium moisture content, wherein said ± 10 g/m² variation
25 results from unavoidable variations in the coating operation + variations in the humidity, wherein the 1L-UD is stored. In the 1L-UD the Rovene[®] 4019 is distributed in spots on and between the fibers.

b) Manufacture of a laminated cross-ply (2L-UD) from two 1L-UDs

Two 1L-UDs resulting from a) were cross-plyed at a cross-plying angle of 90°. The cross-plyed 1L-UDs were laminated in a flat belt-laminator having a heating-zone followed by a pressing-zone. In the heating-zone the cross-plyed 1L-UDs were
5 heated for 15 seconds in contact with 120°C hot belts and in the pressing zone the heated cross-plyed 1L-UDs were pressed at 3.5 bar calendar roll pressure and finally cooled to room temperature by contact with cooled belts resulting in a laminated cross-ply from said two 1L-UDs, i.e. resulting in a 2L-UD. In this manner
15 2L-UD cross-plyes were manufactured.

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c) Manufacture of a rubberized woven fabric

A plain-weave fabric consisting of poly(p-phenylene terephthalamide) multifilament yarns (style T750, Twaron type 1000; 3360 dtex f2000, manufactured by Teijin Aramid, NL) was scoured in a bath containing scouring chemicals and
15 subsequently dried. The scoured and dried plain-weave fabric was impregnated at one side with 40g/m² of a Neoprene IMP361 film obtained from Impregnatex, Italy, by melting the neoprene film resulting in a one-side neoprene-impregnated woven fabric having an areal density of 500 g/m², wherein the neoprene exhibits a concentration gradient exhibiting its maximum on the surface of the woven fabric
20 layer and decreasing along the thickness of the woven fabric layer. In this manner 7 one-side neoprene-impregnated woven fabrics were manufactured.

d) Manufacture of 8 kg/m² pressed hybrid-panels

First the 7 one-side Neoprene-impregnated woven fabrics manufactured in c) were
25 stacked. Stacking was done in such a way that the rubberized side, i.e. the side on which the neoprene film has been impregnated in c), was always connected to a non-rubberized side resulting in a stack of woven fabrics the top fabric of which exhibiting a neoprene impregnation on its top side.

As a next step the 15 2L-UD cross-plyes manufactured in b) were stacked on top of
30 the stack of the woven fabrics in such a way that the neoprene side of the top

fabric is in contact with the bottom layer of the 2L-UD stack. This resulted in a stacked panel consisting of a stack of the 15 2L-UDs with Rovene[®] 4019 as the first matrix polymer on top of a stack of 7 woven fabrics with neoprene as the second matrix polymer.

- 5 The stacked panel was put into a press and pressed at 150 °C and 50 bar for 20 minutes resulting in a pressed panel. The pressed panel remained in the press under pressure until the press was cooled down. Then the press was opened and the pressed hybrid-panel was obtained. In this manner four pressed hybrid-panels were manufactured.

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e) Manufacture of a hard-ballistic article with a ceramic plate and a hybrid panel

- The top UD-layer of the hybrid-panel manufactured in d) was joined to a 7 mm thick ALOTEC[®] 96 SB ceramic front plate (500 x 500 mm) obtainable from Etec
15 Gesellschaft für Technische Keramik GmbH, DE, to produce a hard-ballistic article with a ceramic front plate and the hybrid panel. The areal density of the ceramic plate was 26.3 kg/m². For the joining operation both the ceramic front plate and the joining side of the panel, i.e. the top UD-layer, were coated with Sika[®] 209 as
20 are available from SIKA Deutschland GmbH, DE. In this manner 4 hard-ballistic articles each with a ceramic plate and a hybrid panel were manufactured.

f) Ballistic evaluation

- Four hard-ballistic articles each with a hybrid panel manufactured in d) to which a
25 ceramic front plate was joined as described in e), were evaluated for their anti-ballistic capability by measuring v_{50} , i.e. the velocity in m/s, at which 50 % of the projectiles were stopped. The projectiles used were .308 Winchester FMJ, soft core, 0° obliquity. The evaluation of v_{50} is described e.g. in MIL STD 662F. For the ballistic evaluation 4 shots were fired at a 90° angle on the ceramic front plate of
30 the respective hard-ballistic article. The result is shown in table 1.

Comparative example 1: Hard-ballistic article with a monolithic 2L-UD panel

Comparative example 1 differs from example 1 in that no neoprene-impregnated woven fabrics were used and in that instead of 15 2L-UD cross-plyies 31 2L-UD cross-plyies have been used which were manufactured as in a) and b) of example

5 1. Said 31 2L-UD cross-plyies were stacked on each other resulting in a stacked 2L-UD panel.

Said stacked 2L-UD panel was put into a press and pressed at 150 °C and 50 bar for 20 minutes resulting in a pressed 2L-UD panel. The pressed 2L-UD panel remained in the press under pressure until the press was cooled down. Then the
10 press was opened and a pressed monolithic 2L-UD panel was obtained.

The pressed monolithic 2L-UD panel was joined to a 7 mm thick ALOTEC[®] 96 SB ceramic front plate (500 x 500 mm) obtainable from Etec Gesellschaft für Technische Keramik GmbH, DE to produce a hard-ballistic article with a monolithic 2L-UD panel. The areal density of the ceramic plate was 26.3 kg/m². For the
15 joining operation both the ceramic front plate and the joining side of the panel, i.e. the top UD layer, were coated with Sika[®] 209 as primer and then both with Biresin[®] U-1305. Both Sika[®] 209 and Biresin[®] U-1305 are available from SIK A Deutschland GmbH, DE. Said hard ballistic article was evaluated for its anti-ballistic capability by measuring v_{50} as described in f) of example 1. The result is
20 shown in table 1, wherein the areal density excludes the areal density of the ceramic plate being 26.3 kg/m².

Comparative example 2: Hard-ballistic article with a monolithic woven panel

Comparative example 2 differs from example 1 in that no UD layers have been
25 used and instead of 7 neoprene-impregnated woven fabric layers, 15 neoprene-impregnated woven fabric layers have been used. The impregnation was performed as in c) of example 1, but at both sides of the woven fabrics. So, each side of a woven fabric was impregnated with 40 g/m² of a neoprene IMP361 film from Impregnatex resulting in a woven fabric with 80 g/m² neoprene, wherein the

- neoprene is distributed across the thickness of the fabric in the kind of a concentration gradient decreasing along the thickness of the woven fabric layer. and becoming zero at least in the middle of the fabric thickness. Said 15 both-side neoprene impregnated woven fabrics were stacked on one another resulting in a
- 5 stacked woven panel.
- Said stacked woven panel was put into a press and pressed at 150 °C and 50 bar for 20 minutes resulting in a pressed woven panel. The pressed woven panel remained in the press under pressure until the press was cooled down. Then the press was opened and a pressed monolithic woven panel was obtained.
- 10 The pressed monolithic woven panel was joined to a 7 mm thick ALOTEC[®] 96 SB ceramic front plate (500 x 500 mm) obtainable from Etec Gesellschaft für Technische Keramik GmbH, DE to produce a hard-ballistic article with a monolithic woven panel. The areal density of the ceramic plate was 26.3 kg/m². For the joining operation both the ceramic front plate and the joining side of the panel, i.e.
- 15 the top woven fabric, were coated with Sika[®] 209 as primer and then both with Biresin[®] U-1305. Both Sika[®] 209 and Biresin[®] U-1305 are available from SIK A Deutschland GmbH, DE. Said hard ballistic article was evaluated for its anti-ballistic capability by measuring v_{50} as described in f) of example 1. The result is shown in table 1, wherein the areal density excludes the areal density of the
- 20 ceramic plate being 26.3 kg/m².

Comparative example 1a): Hard-ballistic article with ceramic front plate and a hybrid panel exhibiting the same matrix material in the UD-package and in the woven package

- 25 Comparative example 1a) differs from example 1 in that impregnation of the woven fabrics with the neoprene IPM361 was replaced by impregnation of the woven fabric with Rovene[®] 4019 so that the woven fabrics contained 16 wt.-% based on the total weight of the woven fabrics and exhibited an areal weight of 74 g/m² per woven fabric layer. The UD-layers contained 13 wt.-% Rovene[®] 4019
- 30 based on the total weight of the UD-layers. The obtained hard ballistic article was

evaluated for its anti-ballistic capability by measuring v_{50} as described in f) of example 1. The result is shown in table 1, wherein the areal density excludes the areal density of the ceramic plate being 26.3 kg/m².

5 **Table 1**

	2L-UDs	Woven fabric layers		v_{50} [m/s]	Areal weight without the ceramic plate [kg/m ²]
	Number of 2L-UDs	Number of woven layers	Neoprene per woven fabric layer		
Example 1	15	7	1 x 40 g/m ²	942	7.4
Comparative example 1	31	-	-	908	8.1
Comparative example 2	-	15	2 x 40 g/m ²	838	8.1
Comparative example 1a)	15	7	-	847	7.6

Comparison of ballistic performance of the hard-ballistic articles resulting from example 1 and comparative examples 1 and 2

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As can be seen from table 1 the hard-ballistic article with a ceramic front plate and a hybrid panel from example 1 exhibits a higher v_{50} -value than both the hard ballistic articles of comparative examples 1 and 2 each with a ceramic front plate but with a monolithic panel, even though the ballistic article of example 1 has a

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lower areal weight.

The hard-ballistic article of example 1 with a ceramic front plate and a hybrid panel exhibits a v_{50} -value which is 3.7 % higher than the v_{50} -value of the hard ballistic article of comparative example 1 with a monolithic UD panel, even though the areal density of the hard-ballistic article of example 1 is 8.6 % lower.

5

The hard-ballistic article of example 1 with a ceramic front plate and a hybrid panel exhibits a v_{50} -value which is 12.4 % higher than the v_{50} -value of the hard ballistic article of comparative example 2 with a monolithic woven fabric panel, even though the areal density of the hard-ballistic article of example 1 is 8.6 % lower.

10

The results of table 1 indicate that the ballistic superiority of a hard-ballistic article with a ceramic front plate and a hybrid panel like that of example 1 but having some more 2L-UDs and/or some more woven fabrics so that its areal density without the ceramic front plate is 8.1 kg/m² is even more pronounced if compared with a hard-ballistic article with a monolithic panel of the same areal density.

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Comparison of ballistic performance of the hard-ballistic articles resulting from example 1 and comparative example 1a)

As can be seen from table 1 the hard-ballistic article with a ceramic front plate and a hybrid panel from example 1 with different matrix materials in the package of consolidated cross-ply and in the package of woven fabric layers exhibits an 11.2 % higher v_{50} -value than the hard ballistic article of comparative example 1a) with a ceramic front plate and with a hybrid panel but with the same matrix material in the package of consolidated cross-ply and in the package of woven fabric layers, even though the ballistic article of example 1 has a 2.6 % lower areal weight than the ballistic article of comparative example 1a).

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Example 2: Hard-ballistic article only with hybrid panel

Example 2 differs from example 1 only in that

- instead of 15 2L-UD cross-plyes 16 2L-UD cross plies were used,
- instead of 7 one-side Neoprene-impregnated woven fabrics
- 5 8 one-side Neoprene-impregnated woven fabrics were used, and
- no ceramic front plate was joined to the hybrid panels.

Comparative example 3

Comparative example 3 differs from example 2 in that no neoprene-impregnated
10 woven fabric has been used and instead of 16 2L-UD cross-plyes 32 2L-UD cross-
plyes have been used which were manufactured as in a) and b) of example 1. Said
32 2L-UD cross-plyes were stacked on each other resulting in a stacked 2L-UD
panel.

Said stacked 2L-UD panel was put into a press and pressed at 150 °C and 50 bar
15 for 20 minutes resulting in a pressed 2L-UD panel. The pressed 2L-UD panel
remained in the press under pressure until the press was cooled down. Then the
press was opened and a pressed monolithic 2L-UD panel was obtained.

Comparative example 4

20 This example differs from example 2 in that in that no UD layers have been used
and instead of 8 neoprene-impregnated woven fabric layers, 15 neoprene-
impregnated woven fabric layers have been used. The impregnation was
performed as in c) of example 1, but at both sides of the woven fabrics. So, each
side of a woven fabric was impregnated with 40 g/m² of a neoprene IMP361 film
25 from Impregnatex resulting in a woven fabric with 80 g/m² neoprene. Said 15 both-
side neoprene impregnated woven fabrics were stacked on one another resulting
in a stacked woven panel.

Said stacked woven panel was put into a press and pressed at 150 °C and 50 bar for 20 minutes resulting in a pressed woven panel. The pressed woven panel remained in the press under pressure until the press was cooled down. Then the press was opened and a pressed monolithic woven panel was obtained.

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Comparison of ballistic performance of the hard-ballistic articles resulting from example 2 and comparative examples 3 and 4

The panels resulting from example 2 and comparative examples 3 and 4 were evaluated for their anti-ballistic capability by measuring v_{50} , i.e. the velocity in m/s, at which 50 % of the projectiles were stopped. The projectiles used were FSP according to STANAG 2920 with a weight of 1.102 g, 0° obliquity. The evaluation of v_{50} is described e.g. in STANAG 2920. For this test 1 panel from each example was used with at least 6 shots fired at an 90° angle on the ceramic front plate of the respective hard-ballistic article. The hybrid panel of example 2 was directed with its UD-panel to the ballistic attack. The results are shown in table 2.

As can be seen from table 2 the hard-ballistic article with a hybrid panel from example 1 exhibits a higher v_{50} -value than both the hard ballistic articles of comparative examples 1 and 2 each with a monolithic panel, even though the ballistic article of example 1 has a lower areal weight than the hard-ballistic article of comparative example 3.

The hard-ballistic article of example 2 consisting of a hybrid panel exhibits a v_{50} -value which is 3.8 % higher than the v_{50} -value of the hard ballistic article of comparative example 3 with a monolithic UD panel, even though the areal density of the hard-ballistic article of example 2 is 2.4 % lower.

The hard-ballistic article of example 2 consisting of a hybrid panel exhibits a v_{50} -value which is 10.0 % higher than the v_{50} -value of the hard ballistic article of

comparative example 4 with a monolithic woven fabric panel, even though the areal density of the hard-ballistic article of example 2 is only 2.6 % higher.

Table 2

	2L-UDs	Woven fabric layers		V ₅₀ [m/s]	Areal weight of the hybrid panel [kg/m ²]
	Number of 2L-UDs	Number of woven layers	Neoprene per woven fabric layer		
Example 2	16	8	1 x 40 g/m ²	606	8.0
Comparative example 3	32	-	-	584	8.2
Comparative example 4	-	15	2 x 40 g/m ²	551	7.8

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Claims:

1. A hard-ballistic article comprising a hybrid panel, wherein
the hybrid panel comprises
 - a) a first package of a plurality of consolidated cross-ply, wherein each
5 consolidated cross-ply contains at least two layers of unidirectional aligned
aramid fibers, wherein the aramid fibers are provided with a first matrix
material, wherein the first matrix material comprises a first polymer,
wherein the first package exhibits a surface facing to the direction of a
ballistic attack and a surface facing away from the direction of the ballistic
10 attack, and
 - b) a second package containing a plurality of woven fabric layers, wherein
the woven fabric layers consist of aramid fibers provided with a second matrix
material, wherein the second matrix material is different from the first matrix
material, wherein the second matrix material comprises a second polymer,
15 wherein the second polymer is different from the first polymer,
and wherein the first package is bonded with its surface facing away from the
direction of the ballistic attack with the second package.
2. The hard-ballistic article according to claim 1, wherein a metallic or ceramic
20 strike face is bonded to the surface of the first package facing to the direction of
the ballistic attack.
3. The hard-ballistic article according to claim 1 or 2, wherein the plurality of
consolidated cross-ply means a number n of consolidated cross-ply, and
25 n ranges from 2 to 50.
4. The hard-ballistic article according to claim 1 or 3, wherein
each consolidated cross-ply consists of 2 to 10 layers of unidirectional aligned
aramid fibers.

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5. The hard-ballistic article according to any one of claims 1 to 4, wherein a concentration of the first polymer in each layer of the unidirectional aligned aramid fibers ranges from 2 to 50 wt.-% with respect to the weight of the aramid fibers plus the weight of the first polymer without moisture.
- 5
6. The hard-ballistic article according to any one of claims 1 to 5, wherein an areal density of each layer of the unidirectional aligned aramid fibers including the first polymer ranges from 10 to 250 g/m².
- 10
7. The hard-ballistic article according to any one of claims 1 to 6, wherein the first polymer is a styrene butadiene random copolymer.
8. The hard-ballistic article according to claim 7, wherein the styrene butadiene random copolymer is a carboxylated styrene butadiene random copolymer.
- 15
9. The hard-ballistic article according to any one of claims 1 to 8, wherein the first matrix material comprises a first polymer and a tackifier.
10. The hard-ballistic article according to any one of claims 1 to 9, wherein the plurality of the woven fabric layers means a number m of woven fabric layers, and m ranges from 2 to 30.
- 20
11. The hard-ballistic article according to any one of claims 1 to 10, wherein the second polymer is a polychloroprene.
- 25
12. The hard-ballistic article according to any one of claims 1 to 11, wherein a concentration of the second polymer in each of the woven fabric layers of aramid fibers ranges from 2 to 32 wt.-% with respect to the weight of the aramid fibers in said woven fabric layer plus the weight of the second polymer.
- 30

13. The hard-ballistic article according to any one of claims 1 to 12, wherein an areal density of each woven fabric layer of aramid fibers including the second first polymer ranges from 100 to 1000 g/m².
- 5 14. The hard-ballistic article according to any one of claims 1 to 13, wherein the first package is bonded with its surface facing away from the direction of the ballistic attack with the second package by a (first package / second package) - bonding layer.
- 10 15. The hard-ballistic article according to claim 14, wherein the (first package / second package) - bonding layer is a solidified mixed melt consisting of a solid mixture of the first matrix material with the second matrix material.
- 15 16. The hard-ballistic article according to any one of claims 1 to 15, wherein the first package is bonded with its surface facing the direction of the ballistic attack with the metallic or ceramic strike face by a (first package / metallic or ceramic strike face) - bonding layer.
- 20 17. The hard-ballistic article according to claim 16, wherein the (first package / metallic or ceramic strike face) - bonding layer is a single layer of an adhesive material or a multilayer.
18. The hard-ballistic article according to any one of claims 1 to 17, wherein
25 the hard-ballistic article comprises 5 to 40 consolidated cross-ply and 2 to 18 woven fabric layers.
19. The hard-ballistic article according to any one of claims 1 to 18, wherein
30 the hard ballistic article comprises a plurality of consolidated cross-ply n and a plurality of woven fabric layers m in a ratio n : m, wherein n : m is in the range from (27 to 33) : (12 to 16).

20. The hard-ballistic article according to any one of claims 1 to 19, wherein the hard ballistic article comprises a weight of consolidated cross-ply w_1 given in wt.-% and a weight of woven fabric layers w_2 given in wt.-% in a ratio $w_1 : w_2$, wherein $w_1 : w_2$ is in the range from (40 to 70) : (30 to 60).

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21. Process to manufacture the hard-ballistic article of any one of claims 1 to 20 comprising the steps

- 10 i) preparing a plurality of consolidated cross-ply, wherein each consolidated cross-ply contains at least two layers of unidirectional aligned aramid fibers, wherein the aramid fibers are provided with a first matrix material, wherein the first matrix material comprises a first polymer,
- 15 ii) preparing a plurality of woven fabric layers, wherein the woven fabric layers consist of aramid fibers provided with a second matrix material, wherein the second matrix material is different from the first matrix material, wherein the second matrix material comprises a second polymer, wherein the second polymer is different from the first polymer,
- 20 iii) stacking the plurality of woven fabric layers prepared in step ii) resulting in a stack of said plurality of woven fabric layers,
- 25 iv) stacking the plurality of consolidated cross-ply prepared in step i) on top of the of the stack of said plurality of woven fabric layers resulting in step iii) resulting in a stacked panel,
- 30 v) transferring the stacked panel resulting in step iv) into a press, heating the press to a constant temperature in the range from 100 to 250 °C, pressing the stacked panel at said constant temperature at a constant pressure in the range from 5 to 150 bar for a time in the range of 1 to 100 minutes,
- vi) cooling down the closed press to room temperature, and then opening the press to obtain a hybrid panel, wherein the hybrid panel comprises
 - a first package containing a plurality of consolidated cross-ply, and having an outer surface, and
 - a second package containing a plurality of woven fabric layersand – optionally –

- vii) binding the hybrid panel obtained in step vi) with the outer surface of the first package to a metallic or ceramic strike face.