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- (71) **Applicant (for all designated States except SC):** E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 974 Centre Rd., Wilmington, Delaware, 19805 (US).
- (72) **Inventors; and**
- (71) **Applicants (for SC only):** LI, Xuedong [CN/CN]; Room 1001, No. 13, Lane 1166, Guanglan Road, Pudong New District, Shanghai, 200125 (CN). ZHANG, Liyan [CN/CN]; Room 305, No.9, Lane 18, Lianyuan Road, Pudong New District, Shanghai, 201318 (CN).
- (74) **Agent: NTD PATENT & TRADEMARK AGENCY LIMITED;** 10th Floor, Block A, Investment Plaza, 27 Jinrongdajie, Xicheng District, Beijing 100033 (CN).

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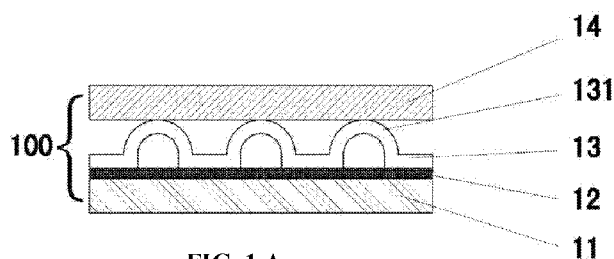


FIG. 1 A

(57) **Abstract:** A thermal protective garment, in the sequence from the exterior to the interior, comprises an outer shell (11), a moisture barrier (12), a thermal insulator (13) and a comfort liner (14). The thermal insulator (13) is a nonwoven fabric comprising 45-95 weight% of non-meltable staple fibers and 5-55 weight% of heat settable staple fibers, and the nonwoven fabric has protuberances and/or indentations formed by hot-pressing using a mold or a roller with three dimensional patterns.

IMPROVED THERMAL PROTECTIVE GARMENT

FIELD OF THE INVENTION

5 This invention relates to protective garments having improved thermally protective performance while being lightweight.

BACKGROUND OF THE INVENTION

Several occupations require the worker to be exposed to heat and flame. To avoid being injured while working in such conditions, the workers such as firefighters may wear protective garments constructed of special flame resistant materials. The protective
10 garments may be various articles of clothing, including coveralls, trousers, or jackets. For example, firefighters typically wear protective garments that are commonly referred to as turnout gears. Such protective garments typically comprise four layers of material that include, from the exterior to the interior, an outer shell, a moisture barrier, a thermal insulator, and a comfort liner. The outer shell layer is typically a woven fabric made from
15 flame resistant fibers and is provided not only to resist flame, but also to protect the wearer against abrasion. The moisture barrier, which is also flame resistant, is provided to prevent water from the firefighting environment from penetrating and saturating the protective garment. The thermal insulator is also flame resistant and offers the bulk of the thermal protection. Normally, the thermal insulator is a nonwoven layer composed of flame resistant
20 fibers. The comfort liner is a woven fabric, which typically is also composed of flame resistant fibers.

Such protective garments, which comprise four layers, are adequately thermal protective, but relatively heavy. Bulkier garment may bring the wearer fatigue and risk of heatstroke when the garment is worn in high temperature environments. Furthermore, it is
25 common for the firefighter to perspire profusely while fighting fire due to both the heat of the environment and the effort exerted by the firefighter in serving his or her duty. This perspiration is usually absorbed into the comfort liner and the thermal insulator to keep the firefighter feeling dry. If a large amount of perspiration is absorbed by the comfort liner and the thermal insulator, the weight of what is already a relatively heavy garment may be
30 significantly increased. As noted above, this added weight can contribute to heat stress and general fatigue.

Accordingly, it is desirable to provide protective garments having adequate thermal protection with the lightest possible material.

SUMMARY OF THE INVENTION

35 This invention provides a thermal protective garment, in the sequence from the exterior to the interior, comprising:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and

(d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole (PBI), acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof; and said woven fabric has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane produced from polytetrafluoroethylene (PTFE), polyurethane (PU), or a mixture thereof; and said membrane has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat settable staple fibers, and said nonwoven fabric has protuberances and/or indentations and a basis weight of about 50-200 g/m²; and

the comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole, acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

This invention also provides a method for preparing the thermal insulator (c) of the thermal protective garment described above, comprising:

i. providing an essentially flat nonwoven fabric comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat settable staple fibers;

ii. hot-pressing the nonwoven fabric of step (i) using a mold or a roller with three dimensional pattern at a temperature of above the highest glass transition temperature (T_g) of the heat settable fibers, for about 0.1-5 minutes at a pressure of about 0.1-2 MPa.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A shows a cross section view of an embodiment of the present thermal protective garment **100**, which has a layer construction of: (a) an outer shell **11**, (b) a moisture barrier **12**, (c) a thermal insulator **13**, and (d) a comfort liner **14**, wherein the thermal insulator **13** has protuberances **131** in contact with the comfort liner **14**.

FIG. 1B shows a cross section view of an embodiment of the present thermal protective garment **100**, which has a layer construction of: (a) an outer shell **11**, (b) a moisture barrier **12**, (c) a thermal insulator **13**, and (d) a comfort liner **14**, wherein the thermal insulator **13** has indentations **132** in contact with the moisture barrier **12**.

FIG. 1C shows a cross section view of an embodiment of the present thermal protective garment **100**, which has a layer construction of: (a) an outer shell **11**, (b) a

moisture barrier **12**, (c) a thermal insulator **13**, and (d) a comfort liner **14**, wherein the thermal insulator **13** has protuberances **131** in contact with the comfort liner **14** and indentations **132** in contact with the moisture barrier **12**.

FIG. 2A shows a perspective view of a thermal insulator **13** in an embodiment of the present thermal protective garment, wherein the protuberances **131** exist in arrays of spherical caps on the thermal insulator **13**.

FIG. 2B shows a perspective view of a thermal insulator **13** in an embodiment of the present thermal protective garment, wherein the protuberances **131** exist in arrays of spherical caps on the thermal insulator **13** and the indentations **132** exist in arrays of spherical caps on the thermal insulator **13**.

FIG. 3 shows a perspective view of a thermal insulator **13** in an embodiment of the present thermal protective garment, wherein the indentations **132** exist in arrays of crosses on the thermal insulator **13**.

DETAILS OF THE INVENTION

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

As used herein, the term “produced from” is synonymous to “comprising”. As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having,” “contains” or “containing,” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus.

The transitional phrase “consisting of” excludes any element, step, or ingredient not specified. If in the claim, such a phrase would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase “consisting of” appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase “consisting essentially of” is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally discussed, provided that these additional materials, steps features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term “consisting essentially of” occupies a middle ground between “comprising” and “consisting of”.

The term “comprising” is intended to include embodiments encompassed by the terms “consisting essentially of” and “consisting of”. Similarly, the term “consisting essentially of” is intended to include embodiments encompassed by the term “consisting of”.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. For example, when a range of “1 to 5” is recited, the recited range should be construed as including ranges “1 to 4”, “1 to 3”, “1-2”, “1-2 & 4-5”, “1-3 & 5”, and the like. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

When the term “about” is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

Further, unless expressly stated to the contrary, “or” refers to an inclusive “or” and not to an exclusive “or”. For example, a condition A “or” B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

“Mole%” or “mol%” refers to mole percent.

In describing and/or claiming this invention, the term “homopolymer” refers to a polymer derived from polymerization of one species of repeating unit. For example, the term “poly(*p*-phenylene terephthalamide) homopolymer” refers to a polymer consisting essentially one species of repeat unit of *p*-phenylene terephthalamide.

As used herein, the term “copolymer” refers to polymers comprising copolymerized units resulting from copolymerization of two or more comonomers.

As used herein, the term “fiber” is defined as a relatively flexible, elongate body having a high ratio of length to the width of the cross-sectional area perpendicular to that length. The fiber cross section can be any shape such as circular, flat or oblong but is typically circular. The fiber cross section can be solid or hollow, preferably, solid. Herein, the term “filament” or “continuous filament” is used interchangeably with the term “fiber.” A single fiber may be formed from just one filament or from multiple filaments. A fiber formed from just one filament is referred to herein as either a “single-filament” fiber or a “monofilament” fiber, and a fiber formed from a plurality of filaments is referred to herein as a “multifilament” fiber.

As used herein, the term “yarn” is defined as a single strand consisting of multiple fibers. The diameter of fibers is usually characterized as a linear density termed “denier” or “dtex”; “denier” is the weight in gram of 9000 meters of fiber, and “dtex” is the weight in gram of 10,000 meters of fiber.

Embodiments of the present invention as described in the Summary of the Invention include any other embodiments described herein, can be combined in any manner, and the

descriptions of variables in the embodiments pertain not only to the composite laminate of the present invention, but also to the articles made therefrom.

The invention is described in detail herein under.

The thermal protective garment **100** of the present invention comprises in order of: (a) an outer shell **11**, (b) a moisture barrier **12**, (c) a thermal insulator **13**, and (d) a comfort liner **14**; wherein the thermal insulator **13** has protuberances **131** in contact with the comfort liner **14** and/or indentations **132** in contact with the moisture barrier **12**, as shown in FIG. 1A, FIG. 1B and FIG. 1C.

Outer shell (a)

In the present invention, the outer shell (a) is typically a woven fabric made from flame resistant fibers and is provided not only to resist flame, but also to protect the wearer against abrasion.

The woven fabric for use as the outer shell (a) may comprise fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole (PBI), acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof.

In one embodiment, the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or a mixture thereof.

In another embodiment, the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, PBI, or a mixture thereof.

In yet another embodiment, the outer shell (a) is a woven fabric comprising fibers produced from flame retardant cotton.

Poly(*p*-phenylene terephthalamide) homopolymer is resulting from mole-for-mole polymerization of *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCI). Also, poly(*p*-phenylene terephthalamide) copolymers are resulting from incorporation of as much as 10 mol% of other diamines with the *p*-phenylene diamine and of as much as 10 mol% of other diacyl chlorides with the terephthaloyl chloride, provided that the other diamines and diacyl chlorides have no reactive groups which interfere with the polymerization reaction. Examples of diamines other than *p*-phenylene diamine include but not limited to *m*-phenylene diamine, or 3,4'-diaminodiphenylether (3,4'-DAPE). Examples of diacyl chlorides other than terephthaloyl chloride include but not limited to isophthaloyl chloride, 2,6-naphthaloyl chloride, chloroterephthaloyl chloride, or dichloroterephthaloyl chloride.

As used herein, the term "*p*-aramid" refers to poly(*p*-phenylene terephthalamide) homopolymers and copolymers.

Poly(*m*-phenylene isophthalamide) homopolymer is resulting from mole-for-mole

polymerization of *m*-phenylene diamine and isophthaloyl chloride. Also, poly(*m*-phenylene isophthalamide) copolymers are resulting from incorporation of as much as 10 mol% of other diamines with the *m*-phenylene diamine and of as much as 10 mol% of other diacyl chlorides with the isophthaloyl chloride, provided only that the other diamines and diacyl chlorides have no reactive groups which interfere with the polymerization reaction. Examples of diamines other than *m*-phenylene diamine include but not limited to *p*-phenylene diamine or 3,4'-diaminodiphenylether. Examples of diacyl chlorides other than isophthaloyl chloride include but not limited to terephthaloyl chloride, 2,6-naphthaloyl chloride, chloroterephthaloyl chloride, or dichloroterephthaloyl chloride.

As used herein, the term “*m*-aramid” refers to poly(*m*-phenylene isophthalamide) homopolymers and copolymers.

Polysulfonamide homopolymers may be resulting from mole-for-mole polymerization of a diamine such as 4,4'-diaminodiphenylsulfone (*p*-DDS) or 3,3'-diaminodiphenylsulfone (*m*-DDS), and a diacyl chloride such as terephthaloyl chloride or isophthaloyl chloride.

Polysulfonamide copolymers include, for example, copolymers resulting from a diamine such as *p*-DDS and a mixture of terephthaloyl chloride and other diacyl chlorides (e.g., isophthaloyl chloride); and copolymers resulting from a diacyl chloride such as terephthaloyl chloride and a mixture of diamines such as *p*-DDS, *m*-DDS, and as much as 10 mol% of other diamine (e.g., *p*-phenylene diamine, or *m*-phenylene diamine).

Preferably, polysulfonamide copolymers are derived from *p*-DDS, *m*-DDS and terephthaloyl chloride in a mole ratio of 3:1:4.

As used herein, the term “PSA” refers to polysulfonamide homopolymers and copolymers.

Polybenzimidazole (PBI) is a polymer containing benzimidazole moiety. The most common way of PBI synthesis is to directly condense bis-*o*-diamine (i.e. a tetramine) and dicarboxylic acid or its acid derivative.

As used herein, the term “acrylonitrile copolymer” refers to “modified polyacrylintrile” that contains 35-85% by weight of acrylonitrile units; and “modified polyacrylintrile” is synonymous to “modacrylic.” Modacrylic polymer is an acrylonitrile copolymer obtained by polymerizing acrylonitrile with other materials, such as vinyl chloride, vinylidene chloride or vinyl bromide. For example, poly(acrylonitrile-*co*-vinyl chloride) is a copolymer between acrylonitrile and vinyl chloride. Although modacrylic fiber burns when directly exposed to flame, it doesn't melt or drip and is self-extinguishing when the flame is removed.

The flame retardant viscose or flame retardant cotton is obtained by incorporating flame retardants, such as nitrogen containing flame retardants or phosphorus flame retardants, into viscose or cotton fibers by blending, coating, or grafting methods. These flame retardant fibers are flame-retardant mainly due to their char-forming property which prohibits burning of materials made therefrom.

The polymers or copolymers described above can be spun into fibers via solution

spinning, using a solution of the polymer or copolymer in either the polymerization solvent or another solvent for the polymer or copolymer. Fiber spinning can be accomplished through a multi-hole spinneret by dry spinning, wet spinning, or dry-jet wet spinning (also known as air-gap spinning) to create a multi-filament fiber as is known in the art. The multi-filament fiber after spinning can then be treated to neutralize, wash, dry, or heat treat the fibers as needed using conventional technique to make stable and useful fibers. Exemplary dry, wet and dry-jet wet spinning processes are disclosed U.S. Pat. Nos. 3,063,966; 3,227,793; 3,287,324; 3,414,645; 3,869,430; 3,869,429; 3,767,756; and 5,667,743. Method of producing aromatic polyamide fibers are disclosed in U.S. Pat. Nos. 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511. Specific methods of making PSA fibers or copolymers containing sulfone amine monomers are disclosed in Chinese Patent Publication No. 1389604A. Fibers produced from flame retardant viscose or flame retardant cotton can be made by solution spinning; the flame retardant chemicals are infused before the spinning, or be treated on the surface of viscose fiber or the surface of cotton fiber.

Aromatic polyamide fibers are commercially available, for example, CONEX[®], TECHNORA[®], and TWARON[®] from Teijin (Japan), APIAIRE[®] from Unitika, NOMEX[®] and KEVLAR[®] from DuPont, TOWALON[®] from Akzo, HERACRON[®] from Kolon Industries, Inc. (Korea), SVM[™] and RUSAR[™] from Kamensk Volokno JSC of Russia, ARMOS[™] from JSC Chim Volokno of Russia, and the like. PSA fiber is commercially available as TANLON[™] from Shanghai Tanlon Fiber Co., Ltd. (China). However, the aromatic polyamide fiber is not limited to these products. PBI fibers are commercially available as Celazole[®] from PBI Performance Products Inc. Modacrylic fibers are commercially available as Kanecaron[™] from Kaneka Corporation. Flame retardant viscose fibers are commercially available as Lenzing FR[®] from Lenzing Group. Flame retardant cotton fibers are commercially available from Shenzhen Uprotec Fire Retardant Application Co. Ltd.

The woven fabrics suitable for the outer shell (a) have a plurality of warp yarns running lengthwise in the machine direction, and a plurality of fill yarns running substantially perpendicularly to the warp yarns (i.e., in the cross-machine direction), wherein each yarn, which include a plurality of fibers described above, have a preferred linear density of from about 220 dtex to about 3,300 dtex, more preferably from about 440 dtex to about 2,640 dtex, and most preferably from about 1,100 dtex to about 2,200 dtex. Any weave construction may be used, for example, such as plain weave, twill weave, satin weave, basket weave, and the like. There is not any specific requirement for tightness of the weave; however, a tight weave is preferred except to avoid extremely tight weaves to avoid damage of yarn fibers resulting from the rigors of weaving. The woven fabrics suitable for the outer shell (a) include 17 x 17 counts, 20 x 20 counts, or 34 x 34 counts per square inch.

Woven fabrics for use as outer shell (a) are commercially available, for example, NOMEX[®] IIIA from Ikena Shanghai Technical Textiles Co., Ltd., PBI Matrix[™] from PBI Performance Products Inc., and the like.

In one embodiment, the woven fabric for use as the outer shell (a) has a basis weight of about 150-250 g/m², or about 180-220 g/m².

Moisture barrier (b)

In the present invention, the moisture barrier (b) is provided to prevent water from the firefighting environment from penetrating and saturating the garment, and to permit the moisture vapor, such as water vapor of perspiration, to pass there through.

The moisture barrier (b) of the invention may be a membrane comprising or produced from polytetrafluoroethylene (PTFE), polyurethane (PU), or a mixture thereof.

The membrane for use as the moisture barrier (b) may have micro pores that permit moisture vapor to pass through, but block liquids (such as liquid water) from penetration, wherein the size of the pores ranges from about 0.01 μm to about 10 μm, or about 0.1 μm to about 8 μm; the porosity (i.e., the percentage of open space in the volume of the micro porous membrane) ranges from about 50% to about 99%, or from about 70% to about 95%.

In one embodiment, the moisture barrier (b) is a membrane comprising or produced from PTFE, and said membrane has a thickness of about 20-50 μm and a basis weight of about 20-50 g/m².

Membranes described above are commercially available, for example, DENTIK[®] from Ningbo Dentik Fluor Material Co., Ltd., GORE-TEX[®] or CROSSTECH[®] from W. L. Gore & Associates, Inc., and the like.

Thermal insulator (c)

In the present invention, the thermal insulator (c) is a nonwoven fabric comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat settable staple fibers, and said nonwoven fabric has protuberances and/or indentations.

As used herein, the term “non-melttable staple fibers” means fibers that do not melt before decomposing, and the term “heat settable staple fibers” means fibers having a melting point of from about 70°C to about 350°C, or from about 100°C to about 280°C and a glass transition temperature (T_g) of from about 40°C to about 160°C, or from about 50°C to about 110°C. T_g can be determined according to ASTM D 3418 by Differential Scanning Calorimetry (DSC).

Representative non-melttable staple fibers useful for practicing the invention include fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or a mixture thereof. Representative heat settable staple fibers useful for practicing the invention include fibers produced from polyester, e.g., polyethylene terephthalate (PET), polyamide, e.g., polyamide 66, polyphenylene sulfide (PPS), or a mixture thereof.

Non-melttable staple fibers described above are commercially available, for example, NOMEX[®] and KEVLAR[®] from DuPont; heat settable staple fibers described above are also commercially available, for example, Tairilin[®] polyester fiber from Nanya Plastics

Corporation, Dacron[®] polyester fiber from Invista Co., Torcon[®] PPS fiber from Toray Industries Inc., and polyamide 66 fiber from Invista Co.

The non-melttable staple fibers and the heat settable staple fibers used herein each independently have a linear density of from about 0.5 dtex to about 10 dtex, or a diameter
5 ranging from about 1 μm to about 50 μm , and a length of from about 5 mm to about 100 mm.

In one embodiment, the nonwoven fabrics for use as the thermal insulator (c) comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat settable staple fibers; or about 50-90 weight% of non-melttable staple fibers and about 10-50 weight% of heat settable staple fibers; or about 55-85 weight% of non-melttable staple
10 fibers and about 15-45 weight% of heat settable staple fibers.

In another embodiment, the nonwoven fabrics for use as the thermal insulator (c) comprising about 45-95 weight% of non-melttable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer and about 5-55 weight% of heat settable staple fibers produced from polyester, polyamide, PPS, or a mixture thereof.

15 In one embodiment, the nonwoven fabrics for use as the thermal insulator (c) has a basis weight of about 50-200 g/m^2 , and a thickness of from about 0.5 mm to about 20 mm.

The nonwoven fabrics for use as the thermal insulator (c) have protuberances and/or indentations on its surface. Supposed one views the inventive thermal protective garment from the side view, if the protuberances are in contact with the comfort liner (d); they are
20 recognized as "protuberances"; whereas if the protuberances are in contact with the moisture barrier (b), then they are recognized as "indentations." The number of protuberances and/or indentation ranges from about 40 to about 1000 per square meter, or from about 70 to about 700 per square meter, or from about 100 to about 400 per square meter. Each protuberance and/or indentation is separated from adjacent protuberance and/or indentation, wherein the
25 protuberances may have a height of about 1-10 mm as measured from the essentially flat surface portion of the nonwoven fabric to the highest point of the protuberance; analogously, the indentation may have a depth of about 1-10 mm as measured from the essentially flat surface portion of the nonwoven fabric to the lowest point of the indentation.

The protuberances and/or indentations of the nonwoven fabrics for use as the thermal
30 insulator (c) exist in arrays of spherical caps, parallel channels, alternating blocks, waves, crosses, stars, capsules, or flower patterns.

As used herein, the term "spherical cap" is a portion of a sphere cut off by a plane. If the plane passes through the center of the sphere, so that the height of the cap is equal to the radius of the sphere, then the spherical cap is called a hemisphere.

35 In one embodiment, the protuberances and/or indentations of the nonwoven fabrics for use as the thermal insulator (c) are spherical caps, and said each spherical cap has a height of about 1-10 mm, and an distance to the neighboring spherical cap of about 1-50 mm, as shown in FIG. 2A and FIG. 2B.

In another embodiment, the protuberances and/or indentations of the nonwoven fabrics
40 for use as the thermal insulator (c) are arrays of crosses, and each cross has a length of about

1-50 mm, a width of about 1-15 mm, and a height/depth of about 1-10 mm, as shown in FIG. 3.

In another embodiment, the protuberances and/or indentations of the nonwoven fabrics for use as the thermal insulator (c) are arrays of capsules, and each capsule has a height of about 1-10 mm, and a distance to the neighboring capsule of about 1-50 mm.

Methods for the production of nonwoven fabrics for use as the thermal insulator (c) are well known in the art. For example, firstly mixing the non-meltable staple fibers and the heat settable staple fibers, then by the method of thermal bonding, needle-punching, or water-punching the mixture of staple fibers at a suitable pressure, so as to adhering the staple fibers to each other.

The protuberances and/or indentations of the nonwoven fabrics for use as the thermal insulator (c) may be prepared by hot-pressing the essentially flat nonwoven fabrics in a mold or a roller with three dimensional patterns at a suitable pressure and a temperature of above the highest glass transition temperature (T_g) of the heat settable fibers when there are more than one kind of heat settable fibers.

In one embodiment, the nonwoven fabrics for use as the thermal insulator (c) are prepared by a method comprising:

- i. providing an essentially flat nonwoven fabric comprising about 45-95 weight% of non-meltable staple fibers and about 5-55 weight% of heat settable staple fibers;
- ii. hot-pressing the nonwoven fabric of step (i) using a mold or a roller with a three dimensional pattern at a temperature of above the highest T_g of the heat settable fibers, for about 0.1-5 minutes at a pressure of about 0.1-2 MPa, or about 0.2-1 MPa.

Comfort liner (d)

The comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole, acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

In one embodiment, the comfort liner (d) is a woven fabric, which comprises fibers produced from poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, flame retardant viscose, or a mixture thereof.

In another embodiment, the comfort liner (d) is a woven fabric, which comprises fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, acrylonitrile copolymer, or a mixture thereof;

Woven fabrics for use as the comfort liner (d) are commercially available, for example, TV120 from Iben Textile Shanghai Co. China.

Preparation of the thermal protective garment

The thermal protective garment **100** of the present invention comprises in order of: (a) an outer shell **11**, (b) a moisture barrier **12**, (c) a thermal insulator **13**, and (d) a comfort liner **14**, as shown in FIG. 1(a), FIG. 1(b) and FIG. 1(c).

As used herein to describe the structure of a thermal protective garment, the “/” is used to separate each distinctive layer with the adjacent layer(s) therein. Therefore, the structure of the present thermal protective garment may be represented as a/b/c/d.

There is no special restriction on method for preparing the thermal protective garment in the present invention, and it can be any conventional known method in this field. For example, the method may comprises laying (a) an outer shell, (b) a moisture barrier, (c) a thermal insulator, and (d) a comfort liner in sequence of a/b/c/d to form an assembly, wherein the protuberances may exist on a surface of the thermal insulator (c) in contact with the moisture barrier (b), or exist on another surface of the thermal insulator (c) in contact with the comfort liner (d), or exist on both surfaces, then stitching or quilting the assembly to obtain a thermal protective garment.

As noted previously, it is desirable to provide adequate thermal protection for a firefighter with the lightest possible thermal protective garment to reduce the burden on the firefighter. The thermal protective performance (TPP) of the present thermal protective garment is evaluated by the heat transfer through thermal protective garment when exposed to flash fire conditions, according to the method published in NFPA 1971: Standard on Protective Ensemble for Structural Fire Fighting, 2000 edition, and recorded in “cal/cm²”. To exclude the basis weight factor of the thermal protective, an Fabric Failure Factor (FFF) value may be used for comparison, which is obtained by dividing the TPP value (cal/cm²) by the basis weight of the garment (in g/m²). FFF value allows for an objective comparison between thermal protective materials on an equal basis. High FFF value indicates high thermal protection per unit weight.

The goal of providing thermal protective garments having adequate thermal protection with the lightest possible weight can be achieved by providing a patterned thermal insulator (c) having surface protuberances and/or indentations that form air gaps to trap air between the thermal insulator (c) and the adjacent layers, i.e. the moisture barrier (b) and the comfort liner (d). When provided, these air gaps trap air so as to provide an increased insulation effect. Due to the absence of material in these air gaps, improved thermal protection can be provided with less material and, therefore, less weight. The thermal protective garment of the present invention exhibits a 10% or more, preferably 15% or more, more preferably 20% or more increase in the FFF value, as compared to that of a thermal protective garment having the same nonwoven fabric for use as the thermal insulator (c) without the protuberances and/or indentations. As a result, the patterned thermal insulator (c) and the thermal protective garment made therefrom as a whole, can be lighter without reducing the thermal protective performance, or alternatively can be made better in thermal protective performance without increasing its total basis weight.

Without further elaboration, it is believed that one skilled in the art using the preceding

description can utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever.

EXAMPLES

The abbreviation "E" stands for "Example" and "CE" stands for "Comparative Example" is followed by a number indicating in which example the thermal protective garment is prepared. The examples and comparative examples were all prepared and tested in a similar manner.

Materials

Outer shell (a1): a woven fabric comprising about 93 weight% *m*-aramid fibers, about 5 weight% *p*-aramid fibers and about 2 weight% anti-static fibers, provided by Iben Shanghai Technical Textiles Co., Ltd. under the trade name of NOMEX[®] IIIA, having a basis weight of about 208 g/m².

Outer shell (a2): a woven fabric comprising spun yarns composed of about 60 weight% polybenzimidazole (PBI) staple fibers and about 40 weight% *p*-aramid fibers, provided by PBI Performance Products Inc. under the trade name of PBI Matrix[™], having a basis weight of about 210 g/m².

Outer shell (a3): a woven fabric comprising flame retardant cotton fibers, provided by Shenzhen Uprotec Fire Retardant Application Co. Ltd., having a basis weight of about 180 g/m².

Moisture barrier (b1): porous PTFE membrane, provided by Ningbo Dentik Fluor Material Co., Ltd. under the trade name of DENTIK[®], having a basis weight of about 22 g/m².

Non-meltable staple fiber (f1): staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, obtained from DuPont under the trade name of KEVLAR[®]. The average length of the staple fibers is about 51 mm, the average diameter is about 12 μm, and the linear density is about 1.5 denier (1.65 dtex).

Heat settable staple fibers (f2): staple fibers produced from PET with Tg of 68°C, obtained from Nanya Plastic Co. under the trade name of Tairilin[®]. The average length of the staple fibers is about 51 mm and the linear density is about 4 denier (4.4 dtex).

Heat settable staple fibers (f3): staple fibers produced from PPS with Tg of 90°C, obtained from DuPont. The average length of the staple fibers is about 51 mm and the linear density is about 1.5 denier (1.65 dtex).

Heat settable staple fibers (f4): staple fibers produced from polyamide 66 with Tg of 90°C, obtained from Iben Textile Shanghai Co. China. The average length of the staple fibers is about 51 mm and the linear density is 1.5 denier (1.65 dtex).

Comfort liner (d1): a woven fabric comprising yarns composed of about 50 weight% *m*-aramid fibers and about 50 weight% of flame retardant viscose fibers, obtained from Iben Textile Shanghai Co. China, which has a basis weight of about 120 g/m².

Comfort liner (d2): a woven fabric comprising yarns composed of about 65 weight%

modacrylic fibers, about 25 weight% of *p*-aramid fibers and about 10 weight% *m*-aramid fibers, obtained from Iben Textile Shanghai Co. China, which has a basis weight of about 165 g/m².

Preparing the thermal protective garment assembly of E1-E13 and CE1-CE10

5 Step A. Preparing the nonwoven fabric for use as the thermal insulator (c)

The non-meltable staple fibers and the heat settable staple fibers were blended with a specified weight ratio to obtain a fiber mixture of about 2 kg, and the fiber mixture was thermal bonding or hydro entangling to obtain an essentially flat nonwoven fabric having a thickness of about 0.7-1.0 mm, and cut into a square piece of 15 cm x 15 cm.

10 In E1-E13, each nonwoven fabric was put into a steel mold (composed of two 35 cm x 35 cm x 1.5 cm stainless steel plates with a three dimensional pattern) and hot-pressing at a temperature of above the T_g of the heat settable fibers for about 0.1-5 minutes at a pressure of about 0.1-2 MPa to obtain a thermal insulator, i.e., a nonwoven fabric having protuberances and/or indentations. After hot-pressing, the mold was taken out of the hot-
15 press machine, the thermal insulator was removed from the mold, and cooled to ambient temperature. The weight ratio of non-meltable staple fiber and heat settable staple fibers, method of preparing the nonwoven fabric, hot-pressing temperature, hot-pressing pressure, shape and size of protuberances, number of protuberance per square meter, and basis weight of the nonwoven fabric for use as the thermal insulator were reported in Tables 1-6.

20 Step B. Preparing thermal protective garment assembly

For each thermal protective garment assembly, (a) an outer shell, (b) a moisture barrier, (c) a thermal insulator, and (d) a comfort liner were laid in sequence of a/b/c/d, and then stitching or quilting together to form various garment assembly samples as specified in Tables 1-6. The "thermal protective garment assembly" is abbreviated as the "TPG
25 assembly" hereunder.

Test Method

Basis weight: the basis weight of each TPG assembly sample was determined by dividing the weight of the TPG assembly by the surface area of the TPG assembly. The results were reported in Tables 1-6.

30 TPP: the TPP value of each TPG assembly sample was measured according to the method published in NFPA 1971: Standard on Protective Ensemble for Structural Fire Fighting, 2000 edition. The results were reported in Tables 1-6.

FFF: the FFF value of each TPG assembly sample was calculated by dividing the TPP value by the basis weight of the sample. The results were reported in Tables 1-6.

35 Improvement of FFF (ΔF): the improvement of FFF in percentage was calculated by the equation shown below:

$$\Delta F \% = [(FFF_n - FFF_0) / FFF_0] \times 100$$

where FFF_0 is the FFF value of a reference example; and

FFF_n is the FFF value of a comparing example.

Table 1

Sample ID	CE1 ^{*a}	CE2	CE3 ^{#a}	E1
TPG assembly construction in order of: a/b/c/d	a1/b1/c1/d1	a1/b1/c2/d1	a1/b1/c3/d1	a1/b1/c4/d1
Thermal insulator (c)	c1	c2	c3	c4
Non-meltable staple fiber (weight%)	f1:100	f1:100	f1:90	f1:90
Heat settable staple fibers (weight%)	0	0	f2:10	f2:10
Method of preparing the nonwoven fabric	hydro entangling	hydro entangling	hydro entangling	hydro entangling
Hot-pressing temperature (°C)	-	-	-	200
Hot-pressing pressure (MPa)	-	-	-	0.2
Shape and size of protuberance	-	-	-	spherical cap; H ^b : 3 mm; D ^b : 7 mm
Number of protuberance/m ²	-	-	-	138
Protuberance contacting layer	-	-	(d)	(d)
Basis weight of thermal insulator (c) (g/m ²)	90	140	60	59
Basis weight of TPG assembly (g/m ²)	468	536	420	419
TPP (cal/cm ²)	21.5	27.5	18.1	26.4
FFF (cal/g)	459	513	431	630
Improvement of FFF (%)	-	11.8	-	46.2

^a “*” indicates the comparative example is the reference example used for the FFF improvement calculation of CE2, “#” indicates the comparative example is the reference example used for the FFF improvement calculation of E1.

^b “H” indicates the height of the spherical cap protuberance; “D” indicates the diameter of the spherical cap protuberance.

From the results of Table 1, the followings are evident.

Comparison between the TPP and FFF data of CE2 and CE1, the TPG assembly of CE2 having a heavier thermal insulator (14.5% heavier than that of thermal insulator CE1) provided an increase of 27.9% in TPP and 11.8% in FFF than that of the TPG assembly of CE1. The results confirmed that a commonly known trend that incorporation of a thicker thermal insulator (thus heavier insulation) might provide significant increase in TPP, however, factoring the increased basis weight, it only provided some FFF improvement (about 12%).

Comparison between the TPP and FFF data of CE3 and E1, the TPG assembly of E1 having a thermal insulator (c) with the protuberances on the nonwoven fabric provided an increase of 45.9% in TPP and 46.2% in FFF than that of the garment assembly of CE3 having the same nonwoven fabric without the protuberances on the surface for use as the thermal insulator (c). The significant TPP and FFF improvements provided by the inventive thermal protective garment assembly of E1 clearly can be attributed to protuberances existing on the surface of the thermal insulator.

Table 2

Sample ID	CE4 ^a	E2	E3	E4
TPG assembly construction in order of: a/b/c/d	a1/b1/c5/d1	a1/b1/c6/d1	a1/b1/c7/d1	a1/b1/c8/d1
Thermal insulator (c)	c5	c6	c7	c8
Non-meltable staple fiber: content (weight%)	f1:78	f1:78	f1:78	f1:78
Heat settable staple fibers: content (weight%)	f2:22	f2:22	f2:22	f2:22
Method of manufacturing the nonwoven fabric	hydro entangling	hydro entangling	hydro entangling	hydro entangling
Hot-pressing temperature (°C)	-	190	190	190
Hot-pressing pressure (MPa)	-	0.2	0.2	0.2
Shape and size of protuberance	-	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm	cross; L ^c : 27 mm; W ^c : 7 mm; H ^c : 5 mm
Number of protuberance/m ²	-	324	138	77
Protuberance contacting layer	-	(d)	(d)	(d)
Basis weight of thermal insulator (g/m ²)	96	101	111	87
Basis weight of garment assembly (g/m ²)	456	461	471	447
TPP (cal/cm ²)	21.3	31.4	30.5	28.9
FFF (cal/g)	467	681	648	647
Improvement of FFF (%)	-	45.8	38.8	38.5

^a “*” indicates CE4 is the reference example used for the FFF improvement calculation of E2-E4.

^b “H” indicates the height of the spherical cap protuberance, “D” indicates the diameter of the spherical cap protuberance.

^c “L” indicates the length of one cross protuberance, “W” indicates the width of one cross protuberance, and “H” indicates the height of one cross protuberance.

From the results of Table 2, the followings are evident.

Comparison between the FFF data of CE4 and E2-E4, surprisingly, the TPG assembly of E2-E4 having a thermal insulator (c) with the protuberances on the nonwoven fabric provided significant increase of 38.5%-45.8% in FFF value than that of garment assembly of CE4. Comparison between the FFF data of E2 versus E3, the TPG assembly of E2 having a thermal insulator (c) with more protuberances in the same shape and size of spherical caps on the nonwoven fabric provided a higher FFF value than that of TPG assembly of E3.

Table 3

Sample ID	CE5 ^a	E5	E6
TPG assembly construction in order of: a/b/c/d	a1/b1/c9/d1	a1/b1/c10/d1	a1/b1/c11/d1
Thermal insulator (c)	c9	c10	c11
Non-meltable staple fiber: content (weight%)	f1:70	f1:70	f1:70
Heat settable staple fibers: content (weight%)	f2:30	f2:30	f2:30
Method of manufacturing the nonwoven fabric	thermal bonding	thermal bonding	thermal bonding
Hot-pressing temperature (°C)	-	260	224
Hot-pressing pressure (MPa)	-	0.1	0.2
Shape and size of protuberance	-	capsule; H ^b : 6 mm; D ^b : 7.5 mm	spherical cap; H ^b : 3 mm; D ^b : 7.5 mm
Number of protuberance/m ²	-	160	160
Protuberance contacting layer	-	(d)	(b) and (d)
Basis weight of thermal insulator (g/m ²)	106	121	115
Basis weight of garment assembly (g/m ²)	466	481	475
TPP (cal/cm ²)	26.2	34.8	31.4
FFF (cal/g)	562	723	661
Improvement of FFF (%)	-	28.6	17.6

^a “*” indicates CE5 is the reference example used for the FFF improvement calculation.

^b “H” indicates the height of the spherical cap protuberance; “D” indicates the diameter of the spherical cap protuberance.

5 From the results of Table 3, the followings are evident.

Comparison between the FFF data of CE5 and E5-E6, surprisingly, the TPG assembly of E5 having a thermal insulator (c) with the protuberances on the nonwoven fabric, and E6 having the protuberances and indentations on the nonwoven fabric provided respectively, obvious increase of 28.6% and 17.6% in FFF value than that of the TPG assembly of CE5.

10 In one embodiment of the present invention, the thermal protective garment, in the sequence from the exterior to the interior, comprises:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and
- 15 (d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or a mixture thereof, and has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane comprising or produced from PTFE, and has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 65-95 weight% of

non-melttable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, and about 5-35 weight% of heat settable staple fibers produced from PET; and said nonwoven fabric has about 50-350 protuberances and/or indentations in arrays of spherical caps, crosses or capsules and a basis weight of about 50-150 g/m²; and

- 5 The comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, flame retardant viscose, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

Table 4

Sample ID	CE6 ^{*a}	E7	E8	CE7 ^{#a}	E9	E10
TPG construction in order of: a/b/c/d	a1/b1/c12/d1	a1/b1/c13/d1	a1/b1/c14/d1	a1/b1/c15/d1	a1/b1/c16/d1	a1/b1/c17/d1
Thermal insulator (c)	c12	c13	c14	c15	c16	c17
Non-melttable staple fiber: content (weight%)	f1:78	f1:78	f1:78	f1:50	f1:50	f1:50
Heat settable staple fibers: content (weight%)	f3:22	f3:22	f3:22	f3:50	f3:50	f3:50
Method of manufacturing the nonwoven fabric	hydro entangling	hydro entangling	hydro entangling	hydro entangling	hydro entangling	hydro entangling
Hot-pressing temperature (°C)	-	200	200	-	230	230
Hot-pressing pressure (MPa)	-	0.2	0.2	-	0.2	0.2
Shape and size of protuberance	-	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm	-	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm	spherical cap; H ^b : 4 mm; D ^b : 7.0 mm
Number of protuberance/m ²	-	138	324	-	138	324
Protuberance contacting layer	-	(d)	(d)	-	(d)	(d)
Basis weight of thermal insulator (g/m ²)	74	70	66	113	111	109
Basis weight of garment assembly (g/m ²)	434	430	426	473	471	469
TPP (cal/cm ²)	21.5	26.5	25.9	21.8	29.8	29.5
FFF (cal/g)	495	616	608	461	633	629
Improvement of FFF (%)	-	24.4	22.8	-	37.3	36.4

- 10 ^a “*” indicates CE6 is the reference example used for the FFF improvement calculation of E7-E8, “#” indicates CE7 is the reference example used for the FFF improvement calculation of E9-E10.

^b “H” indicates the height of the spherical cap protuberance; “D” indicates the diameter of the spherical mold for making the spherical cap protuberance.

From the results of Table 4, the followings are evident.

- 15 Comparison between the FFF data of CE6 and E7-E8, surprisingly, the TPG assembly

of E7-E8 having a thermal insulator (c) with the protuberances on the nonwoven fabric provided significant increase of 22.8%-24.4% in FFF than that of the TPG assembly of CE6.

Comparison between the FFF data of CE7 and E9-E10, surprisingly, the TPG assembly of E9-E10 having a thermal insulator (c) with the protuberances on the nonwoven fabric provided significant increase of 36.4%-37.3% than that of the garment assembly of CE7.

In one embodiment of the present invention, the thermal protective garment, in the sequence from the exterior to the interior, comprises:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and
- (d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or a mixture thereof, and has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane comprising or produced from PTFE, and has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 45-85 weight% of non-melttable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, and about 15-55 weight% of heat setttable staple fibers produced from PPS, and said nonwoven fabric has at least about 50, or 70, or 100 protuberances and/or indentations per square meter in arrays of spherical caps and a basis weight of about 50-150 g/m²; and

The comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, flame retardant viscose, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

Table 5

Sample ID	CE8 ^a	E11
TPG assembly construction in order of: a/b/c/d	a1/b1/c18/d1	a1/b1/c19/d1
Thermal insulator (c)	c18	c19
Non-meltable staple fiber: content (weight%)	f1:78	f1:78
Heat settable staple fibers: content (weight%)	f4:22	f4:22
Method of manufacturing the nonwoven fabric	hydro entangling	hydro entangling
Hot-pressing temperature (°C)	-	200
Hot-pressing pressure (MPa)	-	0.2
Shape and size of protuberance	-	spherical cap; H ^b : 3 mm; D ^b : 8.5 mm
Number of protuberance/m ²	-	138
Protuberance contacting layer	-	(d)
Basis weight of thermal insulator (g/m ²)	73	64
Basis weight of garment assembly (g/m ²)	433	424
TPP (cal/cm ²)	18.1	27
FFF (cal/g)	418	637
Improvement of FFF (%)	-	52.4

^a “*” indicates CE8 is the reference example used for the FFF improvement calculation for E11.

^b “H” indicates the height of the spherical cap protuberance; “D” indicates the diameter of the spherical mold for making the spherical cap protuberance.

5 From the results of Table 5, the followings are evident.

Comparison between the FFF data of CE8 and E11, the TPG assembly of E11 having a thermal insulator (c) with the protuberances on the nonwoven fabric provided significant increase of 52.4% in FFF than that of the garment assembly of CE8.

10 In one embodiment of the present invention, the thermal protective garment, in the sequence from the exterior to the interior, comprises:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and
- (d) a comfort liner;

15 wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or a mixture thereof, and has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane comprising or produced from PTFE, and has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 65-95 weight% of non-meltable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, and about 5-35 weight% of heat settable staple fibers produced from polyamide 66, and said

nonwoven fabric has at least about 50, or 70, or 100 protuberances and/or indentations per square meter in arrays of spherical caps and a basis weight of about 50-150 g/m²; and

the comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, flame retardant viscose, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

Table 6

Sample ID	CE9 ^a	E12	CE10 ^{#a}	E13
TPG assembly construction in order of: a/b/c/d	a2/b1/c20/d1	a2/b1/c21/d1	a3/b1/c22/d2	a3/b1/c23/d2
Thermal insulator (c)	c20	c21	c22	c23
Non-meltable staple fiber: content (weight%)	f1:78	f1:78	f1:78	f1:78
Heat settable staple fibers: content (weight%)	f2:22	f2:22	f2:22	f2:22
Method of manufacturing the nonwoven fabric	hydro entangling	hydro entangling	hydro entangling	hydro entangling
Hot-pressing temperature (°C)	-	190	-	190
Hot-pressing pressure (MPa)	-	0.3	-	0.3
Shape and size of protuberance	-	cross; L ^b : 27 mm; W ^b : 7 mm; H ^b : 5 mm	-	cross; L ^b : 27 mm; W ^b : 7 mm; H ^b : 5 mm
Number of protuberance/m ²	-	138	-	138
Protuberance contacting layer	-	(b)	-	(b)
Basis weight of thermal insulator (g/m ²)	96	105	90	103
Basis weight of assembly (g/m ²)	456	465	450	463
TPP (cal/cm ²)	16.6	24.1	14	18.8
FFF (cal/g)	364	518	311	406
Improvement of FFF (%)	-	42.3	-	30.5

^a “#” indicates CE9 is the reference example used for the FFF improvement calculation of E12, “#” indicates CE10 is the reference example used for the FFF improvement calculation of E13.

^b “L” indicates the length of one cross protuberance, “W” indicates the width of one cross protuberance, “H” indicates the height of one cross protuberance.

From the results of Table 6, the followings are evident.

Comparison between the FFF data of CE9 and E12, the TPG assembly of E12 having a thermal insulator (c) with protuberances in contact with the moisture barrier (b), i.e. indentations, provided a significant increase of 42.3% in FFF than that of the garment assembly of CE9. Comparison between the FFF data of CE10 and E13, the TPG assembly of E13 having a thermal insulator (c) with protuberances in contact with the moisture barrier (b), i.e. indentations, provided a significant increase of 30.5% in FFF than that of the TPG assembly of CE10.

In one embodiment of the present invention, the thermal protective garment, in the

sequence from the exterior to the interior, comprises:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and
- 5 (d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, polybenzimidazole, or a mixture thereof, and has a basis weight of about 150-
10 250 g/m²;

the moisture barrier (b) is a membrane comprising or produced from PTFE, and has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 65-95 weight% of non-melttable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, and about 5-35 weight% of heat settable staple fibers produced from PET, and said
15 nonwoven fabric has at least about 50, or 70, or 100 protuberances and/or indentations in arrays of crosses and a basis weight of about 50-150 g/m²; and

the comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, flame retardant viscose, or a mixture thereof; and
20 said comfort liner has a combined basis weight of about 100-200 g/m².

In another embodiment of the present invention, the thermal protective garment, in the sequence from the exterior to the interior, comprises:

- (a) an outer shell;
- 25 (b) a moisture barrier;
- (c) a thermal insulator; and
- (d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from flame retardant
30 cotton, and has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane comprising or produced from PTFE, and has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 65-95 weight% of non-melttable staple fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, and about 5-35 weight% of heat settable staple fibers produced from PET, and said
35 nonwoven fabric has at least about 50, or 70, or 100 protuberances and/or indentations in arrays of crosses and a basis weight of about 50-200 g/m²; and

the comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer,
40

poly(*m*-phenylene isophthalamide) copolymer, acrylonitrile copolymer, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

5 While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions are possible without departing from the spirit of the present invention. As such, modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.

CLAIMS

What is claimed is:

1. A thermal protective garment, in the sequence from the exterior to the interior, comprising:

- (a) an outer shell;
- (b) a moisture barrier;
- (c) a thermal insulator; and
- (d) a comfort liner;

wherein

the outer shell (a) is a woven fabric comprising fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole, acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof; and said woven fabric has a basis weight of about 150-250 g/m²;

the moisture barrier (b) is a membrane produced from polytetrafluoroethylene, polyurethane, or a mixture thereof; and said membrane has a thickness of about 10-100 μm and a basis weight of about 20-50 g/m²;

the thermal insulator (c) is a nonwoven fabric comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat setttable staple fibers, and said nonwoven fabric has protuberances and/or indentations and a basis weight of about 50-200 g/m²; and

the comfort liner (d) is at least one layer of a woven fabric or a knit fabric, which comprises fibers produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, polysulfonamide homopolymer, polysulfonamide copolymer, polybenzimidazole, acrylonitrile copolymer, flame retardant viscose, flame retardant cotton, or a mixture thereof; and said comfort liner has a combined basis weight of about 100-200 g/m².

2. The thermal protective garment of claim 1, wherein the thermal insulator (c) is prepared by a method comprising:

i. providing an essentially flat nonwoven fabric comprising about 45-95 weight% of non-melttable staple fibers and about 5-55 weight% of heat setttable staple fibers;

ii. hot-pressing the nonwoven fabric of step (i) using a mold or a roller with three dimensional pattern at a temperature of above the highest glass transition temperature of the heat setttable fibers for about 0.1-5 minutes at a pressure of about 0.1-2 MPa.

3. The thermal protective garment of claim 1 or 2, wherein the non-melttable staple fibers composed of the thermal insulator (c) are produced from poly(*p*-phenylene terephthalamide) homopolymer, poly(*p*-phenylene terephthalamide) copolymer, poly(*m*-phenylene isophthalamide) homopolymer, poly(*m*-phenylene isophthalamide) copolymer, or
5 a mixture thereof.

4. The thermal protective garment of claim 1 or 2, wherein the heat settable staple fibers composed of the thermal insulator (c) are produced from polyester, polyamide, polyphenylene sulfide, or a mixture thereof.

10 5. The thermal protective garment of claim 2, wherein the essentially flat nonwoven fabric is manufactured by thermal bonding, needle punching, or hydro entangling.

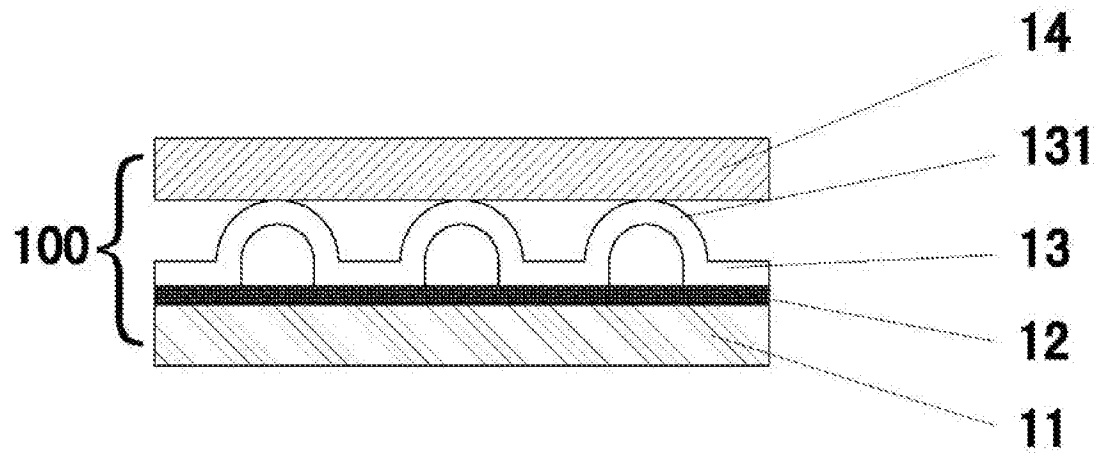
6. The thermal protective garment of claim 1, wherein the thermal insulator (c) has
15 a thickness of about 0.5-20 mm, and the number of protuberances and/or indentations of about 40-1000 per square meter, and the protuberances and/or indentations have an height and/or depth of about 1-10 mm as measured from the essentially flat surface portion of the nonwoven fabric.

20 7. The thermal protective garment of claim 6, wherein the protuberances and/or indentations of the thermal insulator (c) exist in arrays of spherical caps, parallel channels, alternating blocks, waves, crosses, stars, capsules, or flower patterns.

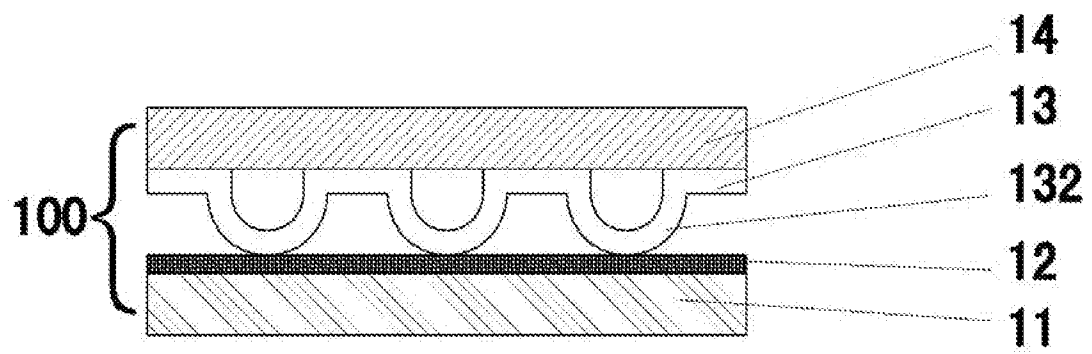
8. The thermal protective garment of claim 7, wherein the protuberances and/or
25 indentations are arrays of spherical caps, and each spherical cap has a height and/or depth of about 1-10 mm, and a distance to the neighboring spherical cap of about 1-50 mm.

9. The thermal protective garment of claim 7, wherein the protuberances and/or
30 indentations are arrays of crosses, and each cross has a length of about 1-50 mm, a width of about 1-15 mm, and a height and/or depth of about 1-10 mm.

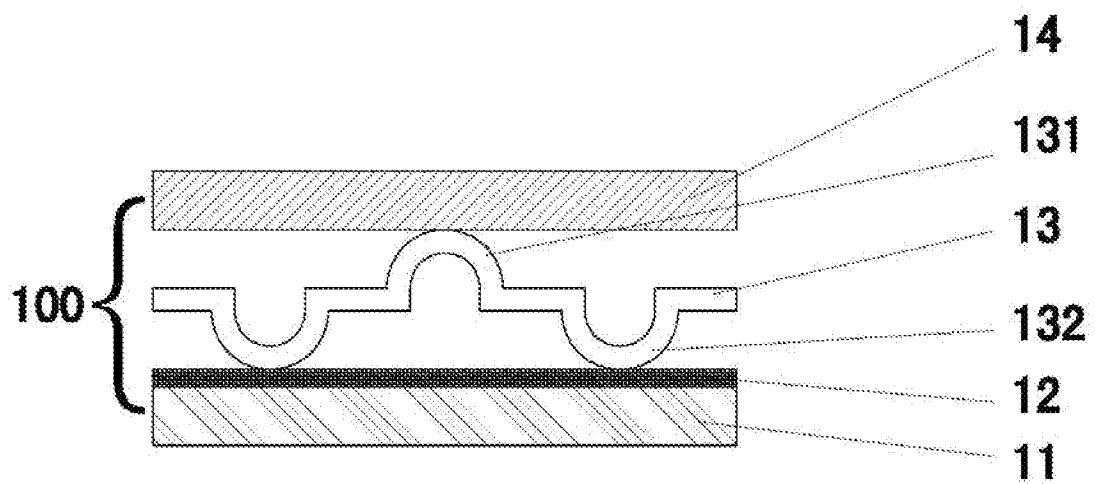
10. The thermal protective garment of claim 1, which has a 10% or more increase in the fabric failure factor, as compared to that of a thermal protective garment having the thermal insulator (c) without the protuberances and/or indentations on the nonwoven fabric,
35 wherein the fabric failure factor is determined by dividing the thermal protective performance by the basis weight of fabric, and the thermal protective performance is measured according to the method of NFPA 1971.



A

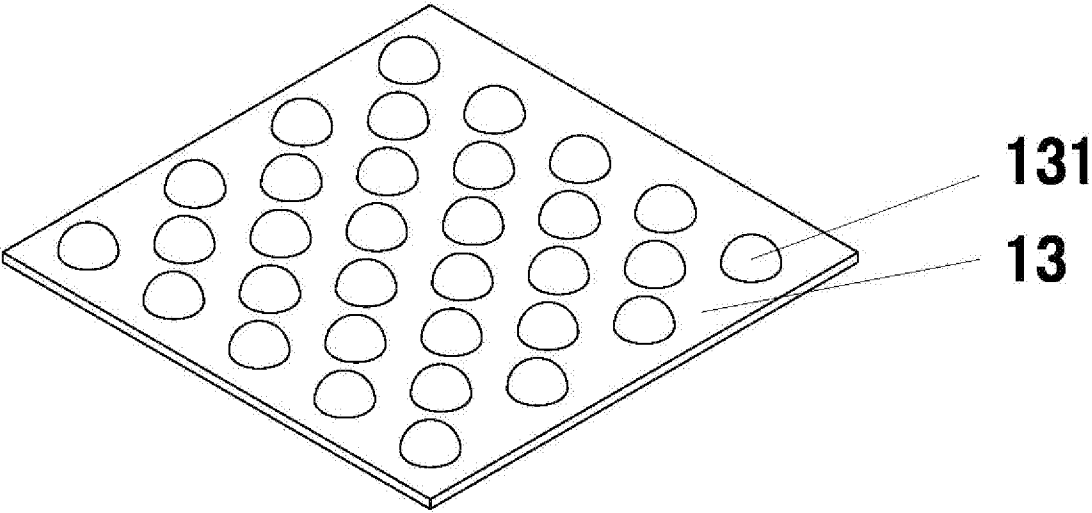


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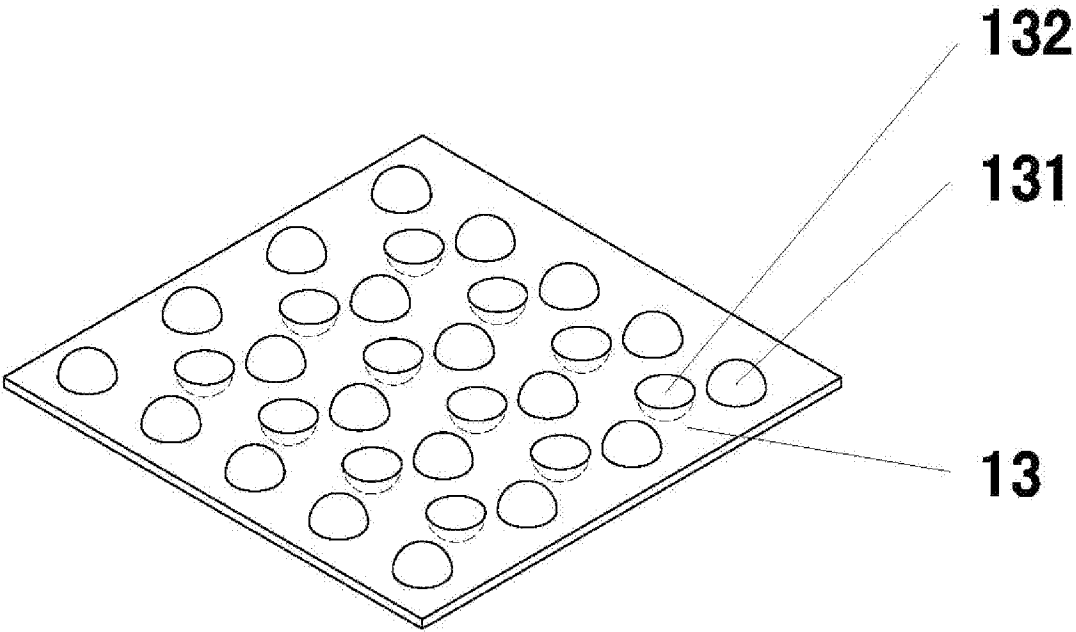


C

FIG.1



A



B

FIG.2

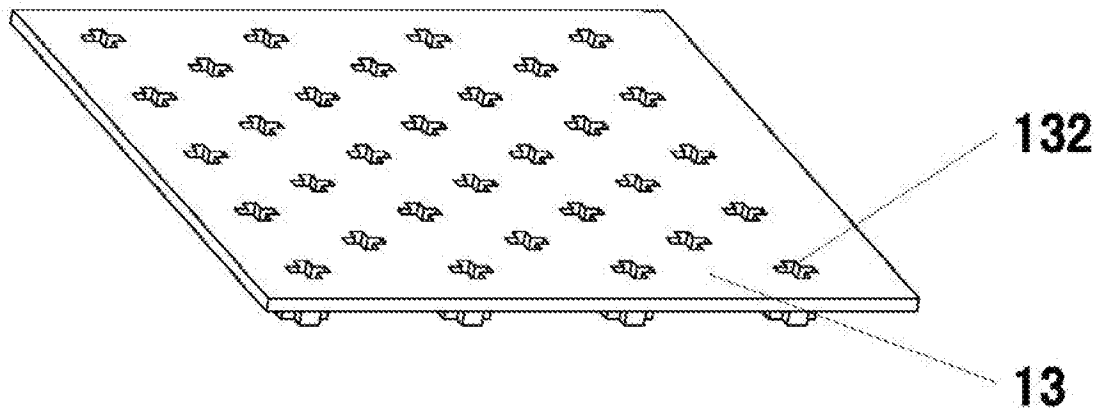


FIG.3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/070808

A. CLASSIFICATION OF SUBJECT MATTER

A41D 13/00(2006.01)i; A41D 31/02(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A41D13,A41D31,B32B5,B32B27,D04H

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

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

CNABS;CNTXT;CNKI;VEN:thermal insulator, moisture barrier, waterproof,aramid,ppta,pbi,flame retardant,ptfe, polyurethane,project,protrude,protuberance,indentation,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014087129 A1 (PBI PERFORMANCE PRODUCTS INC) 27 March 2014 (2014-03-27) description paragraphs 0021-0029 and figures 1-2	1-10
Y	CN 203913518 U (CHANGSHU BAOFENG SPECIAL FIBER CO LTD) 05 November 2014 (2014-11-05) description paragraph 0015 and figure 1	1-10
Y	CN 103562613 A (MITSUBISHI ELECTRIC CORP) 05 February 2014 (2014-02-05) description paragraphs 0058-0069 and figure 4	1-10
Y	CN 202319169 U (BEIJING YINGTELAI SCI&TECH CO LTD) 11 July 2012 (2012-07-11) description paragraphs 0008-0021 and figures 1-2	1-10
Y	CN 202342719 U (BEIJING YINGTELAI SCI&TECH CO LTD) 25 July 2012 (2012-07-25) description paragraphs 0007-0020 and figure 1	1-10
A	CN 1714187 A (DU PONT DE NEMOURS & CO E I) 28 December 2005 (2005-12-28) the whole document	1-10

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

22 September 2016

Date of mailing of the international search report

19 October 2016

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Authorized officer

TAN,Yuan

Facsimile No. (86-10)62019451

Telephone No. (86-10)62085489

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/070808**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CN 101036536 A (UNIV DONGHUA) 19 September 2007 (2007-09-19) the whole document	1-10
A	US 7013496 B2 (SOUTHERN MILLS INC) 21 March 2006 (2006-03-21) the whole document	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/070808

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				US	2016227858	A1	11 August 2016
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				WO	2004046441	A3	08 July 2004
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CN	104228239	A	24 December 2014	CN	104228239	B	25 May 2016
CN	101036536	A	19 September 2007	None			
US	7013496	B2	21 March 2006	US	2005050619	A1	10 March 2005
				US	7676855	B2	16 March 2010
				US	2006143809	A1	06 July 2006