



(11)

EP 4 053 318 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

07.09.2022 Bulletin 2022/36

(21) Application number: **20881304.8**

(22) Date of filing: **29.10.2020**

(51) International Patent Classification (IPC):

D04B 1/16 ^(2006.01) **A41D 13/00** ^(2006.01)
A41D 31/00 ^(2019.01) **A41D 31/08** ^(2019.01)
D02G 3/04 ^(2006.01) **D03D 7/00** ^(2006.01)
D03D 15/40 ^(2021.01) **D03D 15/47** ^(2021.01)
D03D 15/513 ^(2021.01) **D03D 15/533** ^(2021.01)
D03D 15/56 ^(2021.01) **D04B 1/00** ^(2006.01)
D04B 1/18 ^(2006.01)

(52) Cooperative Patent Classification (CPC):

A41D 13/00; A41D 31/00; A41D 31/08; D02G 3/04;
D03D 7/00; D03D 15/40; D03D 15/47;
D03D 15/513; D03D 15/533; D03D 15/56;
D04B 1/00; D04B 1/16; D04B 1/18

(86) International application number:

PCT/JP2020/040718

(87) International publication number:

WO 2021/085571 (06.05.2021 Gazette 2021/18)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(30) Priority: **01.11.2019 JP 2019199847**

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(54) **FLAME RETARDANT STRETCH FIBER STRUCTURE, FLAME RETARDANT STRETCH WOVEN/KNITTED FABRIC, FLAME RETARDANT STRETCH CORE SPUN YARN, AND PROTECTIVE CLOTHING USING SAME**

(57) The purpose of the present invention is to impart stretchability to a flame retardant structure composed of pilling-resistant flame retardant modacrylic fiber and blended yarn. This flame retardant stretch fiber structure is characterized in that the flame retardant modacrylic

fiber blend ratio is 44-79 weight%, the regenerated cellulose fiber blend ratio is 17-50 weight%, and the polyurethane elastic fiber blend ratio is 2-10 weight%. After-flame and afterglow according to the ISO 15025 A method both average 2.0 seconds or less.

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Description

FIELD

[0001] The present invention relates to a flame retardant stretch fiber structure, a flame retardant stretch woven/knitted fabric, a flame retardant stretch core spun yarn, and protective clothing using the same. More specifically, the invention relates to a flame retardant stretch fiber structure, flame retardant stretch woven/knitted fabric and flame retardant stretch core spun yarn comprising flame retardant modacrylic fibers, regenerated cellulose fibers and polyurethane elastic fibers in a specified mixing ratio, and to protective clothing using the same.

BACKGROUND

[0002] Clothing articles such as work clothes and uniforms are often required to exhibit flame retardance and stretchability. Flame retardance is essential at factories that handle boilers, high temperature substances such as gases, high-voltage electricity or welding, while stretchability is necessary for improved workability.

[0003] Blended yarns of cotton with flame retardant modacrylic fibers having an acrylic component (acrylonitrile) content of 35 wt% to 85 wt% are known for non-stretching flame retardant woven fabrics which do not require stretchability but exhibit adequate flame retardance.

[0004] PTL 1 discloses heat-resistant flame retardant work clothing obtained from a woven fabric with blended yarn comprising wool, flame retardant rayon and a flame retardant acrylic compound sewn in as the warp yarn and weft yarn. However, woven or knitted fabrics using these flame retardant modacrylic fibers in admixture with polyurethane elastic fibers for stretchability have poorer flame retardance, and it has therefore been difficult to produce flame retardant modacrylic fiber woven or knitted fabrics that also have stretchability.

[0005] A fabric with flame retardance and stretchability using aramid fibers instead of modacrylic fibers is disclosed in PTL 2. PTL 2 discloses technology in which a stretchable flame retardant woven fabric using aramid fibers and clothing articles employing them are provided with a different mixing ratio of aramid fiber in the warp yarn and weft yarn in order to inhibit pilling. However, aramid fibers have a hard texture and do not easily provide a comfortable feel in clothing. In addition, since the yarn is colored and therefore difficult to dye into white or other colors, there have been limitations to its use for clothing purposes.

[0006] PTL 3 discloses core spun yarn for obtaining a fabric with suitable stretchability and satisfactory texture, moisture retention and coloring properties, and with low shape distortion after washing and minimal loss of texture before and after washing, which is composed of non-stretchable fibers comprising 50 wt% or more of acrylic ultrafine fibers with a size of 0.1 to 1.3 dtex, and elastic fibers, wherein the draft ratio and twist coefficient of the elastic fibers during core spun yarn spinning, as well as their mathematical product, are in specified ranges. No restrictions are placed on other fibers other than acrylic ultrafine fibers to be included in the non-stretchable elastic fibers. However, the core spun yarn described in this publication is not itself flame retardant, and kneading in of antimony oxide for improved flame retardance is merely mentioned as a suggestion.

[CITATION LIST]

[PATENT LITERATURE]

[0007]

[PTL 1] Japanese Unexamined Patent Publication No. 2008-208509

[PTL 2] Japanese Unexamined Patent Publication No. 2014-208930

[PTL 3] Japanese Unexamined Patent Publication No. 2003-27344

SUMMARY

[TECHNICAL PROBLEM]

[0008] In light of the prior art, the problem to be solved by the invention is to provide a flame retardant stretch woven/knitted fabric having excellent texture and dyeing performance, and also exhibiting stretchability, as well as flame retardant core spun yarn and protective clothing using them.

[SOLUTION TO PROBLEM]

[0009] As a result of much diligent experimentation with the aim of solving the problem, the present inventors have completed this invention upon finding, unexpectedly, that the flame retardance of a flame retardant woven or knitted fabric employing flame retardant fibers that are blended yarn comprising flame retardant modacrylic fibers and other fibers, is remarkably improved, specifically when regenerated cellulose fibers used with mixing ratios in specified ranges are used as fibers for mix spinning with flame retardant modacrylic fibers, as determined by producing various types of woven or knitted fabrics with different polyurethane elastic fibers to impart stretchability and evaluating the flame retardance.

[0010] Specifically, the present invention provides the following.

[1] A flame retardant stretch fiber structure having a flame retardant modacrylic fiber mixing ratio of 44 wt% to 79 wt%, a regenerated cellulose fiber mixing ratio of 17 wt% to 50 wt% and a polyurethane elastic fiber mixing ratio of 2 wt% to 10 wt%.

[2] The flame retardant stretch fiber structure according to [1] above, which is a woven or knitted fabric in which the average afterflame and afterglow time are both 2.0 seconds or less according to ISO 15025 A.

[3] The flame retardant stretch fiber structure according to [1] or [2] above, wherein the flame retardant modacrylic fiber mixing ratio is 46 wt% to 75 wt%, the regenerated cellulose fiber mixing ratio is 23 wt% to 47 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 10 wt%.

[4] The flame retardant stretch fiber structure according to any one of [1] to [3] above, which is a woven or knitted fabric further comprising conductive fibers in a mixing ratio of 0.5 wt% to 1.5 wt%.

[5] The flame retardant stretch fiber structure according to any one of [1] to [4] above, which is a woven or knitted fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers.

[6] The flame retardant stretch fiber structure according to any one of [1] to [4] above, which is a woven or knitted fabric having flame retardant core spun yarn with 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers.

[7] The flame retardant stretch fiber structure according to [5] above, which is a knitted fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers over the entire surface, and polyurethane elastic fibers knitted or inserted over all or part of the surface.

[8] The flame retardant stretch fiber structure according to [6] above, which is a woven fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers, 20 wt% to 50 wt% regenerated cellulose fibers and conductive fibers as the warp yarn, and flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers as the weft yarn.

[9] The flame retardant stretch fiber structure according to [6] above, which is a knitted or woven fabric having flame retardant core spun yarn with 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, over the entire surface.

[10] The flame retardant stretch fiber structure according to [6] above, which is a knitted fabric having flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, and blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers, knitted alternately at 1:1.

[11] The flame retardant stretch fiber structure according to any one of [1] to [10] above, wherein the polyurethane elastic fibers are polyurethane elastic fibers selected from the group consisting of polyacrylonitrile-based polymers with a number-average molecular weight of 10,000 to 50,000, styrene-maleic anhydride-based copolymers with a number-average molecular weight of 1,500 to 5,000 and polyurethane polymers with a number-average molecular weight of 10,000 to 40,000, and containing 1 wt% to 14 wt% of a thermoplastic polymer with a hydrogen-bonding functional group concentration of 3 to 20 milliequivalent per 1 g of thermoplastic polymer when dissolved in an amide-based polar solvent.

[12] Flame retardant stretch core spun yarn according to [1] above, which comprises 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers.

[13] Flame retardant stretchable protective clothing using a woven or knitted fabric according to any one of [1] to [11] above or flame retardant core spun yarn according to claim 12.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0011] The flame retardant stretch woven or knitted fabric of the invention has excellent flame retardance demonstrated by an average afterflame and afterglow time of both 2.0 seconds or less according to ISO 15025 A, and it can therefore be suitably used as a material for flame retardant stretchable protective clothing that has excellent dye affinity, pilling properties and stretchability.

BRIEF DESCRIPTION OF DRAWINGS

[0012]

Fig. 1 is a photograph showing the results of afterflame and afterglow testing according to ISO 15025 A, for a knitted fabric with flame retardant modacryl:cotton:polyurethane elastic fiber:conductive fibers = 57.0 wt%:37.9 wt%:4.6 wt%:0.5 wt% (Comparative Example 1), knitted with a bare plain stitch by aligning blended yarn of single yarn of Protex^R flame retardant modacrylic fiber type-M:cotton = 60 wt%:40 wt% (cotton count represented as 30/1), 22 dtex polyurethane elastic fibers and 33 dtex conductive fibers. Afterglow (flame after burning out) can be confirmed 2 seconds after extinguishing the burner flame.

Fig. 2 is a photograph showing the results of afterflame and afterglow testing according to ISO 15025 A, for a knitted fabric with flame retardant modacryl:cotton:polyurethane elastic fiber:conductive fibers = 61.7 wt%:33.2 wt%:4.6 wt%:0.5 wt% (Comparative Example 2), knitted with a bare plain stitch by aligning blended yarn of Protex^R type-Q flame retardant modacrylic fiber Q type:cotton = 65 wt%:35 wt% with a cotton count of 30/1, 22 dtex polyurethane elastic fibers and 33 dtex conductive fibers. Afterflame can be confirmed 2 seconds after extinguishing the burner flame.

Fig. 3 is a photograph showing the results of afterflame and afterglow testing according to ISO 15025 A, for a knitted fabric with flame retardant modacryl:regenerated cellulose:polyurethane elastic fiber:conductive fibers = 57.0 wt%:37.9 wt%:4.6 wt%:0.5 wt% (Example 1), knitted with a bare plain stitch by aligning blended yarn of Protex^R flame retardant modacrylic fiber type-M:regenerated cellulose (Tencel^R) = 60 wt%:40 wt% with a cotton count of 30/1, 22 dtex polyurethane elastic fibers and 33 dtex conductive fibers. Afterflame and afterglow cannot be confirmed 2 seconds after extinguishing the burner flame.

DESCRIPTION OF EMBODIMENTS

[0013] The invention will now be explained in detail by embodiments.

[0014] The first embodiment of the invention is a flame retardant stretch fiber structure having a flame retardant modacrylic fiber mixing ratio of 44 wt% to 79 wt%, a regenerated cellulose fiber mixing ratio of 17 wt% to 50 wt% and a polyurethane elastic fiber mixing ratio of 2 wt% to 10 wt%.

[0015] As mentioned above, the present invention has been completed upon finding, unexpectedly, that the flame retardance of a flame retardant fiber structure employing flame retardant fibers comprising flame retardant modacrylic fibers, cellulosic fibers such as cotton or regenerated cellulose or blended yarn of cellulose-based fibers and other fibers (such as polyamide), is remarkably improved when regenerated cellulose fibers mixed in ratios in specified ranges are used as fibers for mix spinning with flame retardant modacrylic fibers, as determined by producing various types of fiber structures with different polyurethane elastic fibers to impart stretchability and evaluating the flame retardance.

[0016] While it is not fully understood why flame retardance cannot be ensured in a highly stretchable fiber structure with polyurethane elastic fibers when using flame retardant modacrylic fibers alone, or blended yarn of flame retardant modacrylic fibers and cotton, it is conjectured that this is because polyurethane elastic filaments undergo more rapid combustion propagation than other fibers and their stitched or woven gaps tend to elongate allowing air to pass through. It is conjectured that when using flame retardant modacrylic fibers, or blended yarn of flame retardant modacrylic fibers with cotton or further with synthetic fibers, which include thermoplastic synthetic fibers such as polyamide or polyester, the synthetic fibers undergo combustion while softening and melting, which results in flame fall-off or diffusion.

[0017] In a fiber structure with stretchability, if regenerated cellulose fibers are used as fibers spun in admixture with flame retardant modacrylic fibers in a mixing ratio within a specified range, the afterflame and afterglow are both improved to an average of 2.0 seconds or less according to ISO 15025 A (that is, the flame retardance is remarkably improved). While the reason for this is not entirely understood, the present inventors conjecture that since the official moisture regain of regenerated cellulose fiber (about 11.0% for cupra, lyocell and viscose rayon) is higher than that of cotton (about 8.5%), it may be due to a cooling effect by the heat of vaporization of moisture.

[0018] The flame retardant modacrylic fibers are fibers composed of a long-chain synthetic polymer comprising acrylonitrile-group repeating units in a weight ratio of 35% or greater and less than 85%. Such fibers can be suitably obtained from a copolymerized acrylonitrile copolymer comprising 35 wt% to 85 wt% acrylonitrile as the acrylic component and

15 wt% to 65 wt% of another component. The other component is not particularly restricted but may be a halogen-containing vinyl and/or halogen-containing vinylidene monomer. The content of the halogen-containing vinyl and/or halogen-containing vinylidene monomer in the acrylonitrile copolymer is more preferably 35 to 65 wt%. Examples of other components also include monomers containing sulfonic acid groups. The content of a monomer containing a sulfonic acid group in the acrylonitrile copolymer is preferably 0 wt% to 3 wt%.

[0019] The flame retardant modacrylic fibers may also contain an antimony compound. Examples of antimony compounds include any one or more of antimony trioxide, antimony tetroxide, antimony pentoxide, antimony acid and its salts, and antimony oxychloride. One or more compounds selected from the group consisting of antimony trioxide, antimony tetroxide and antimony pentoxide are most suitable for use from the standpoint of production stability in the spinning step.

[0020] Examples of flame retardant modacrylic fibers containing such antimony compounds include (high flame retardant) Protex^R type-M (high flame retardant), type-C (high flame retardant, high-strength) and type-Q (sustainable C-type) by Kaneka Corp.

[0021] In the flame retardant stretchable fiber structure of this embodiment, it is necessary that the flame retardant modacrylic fiber mixing ratio is 44 wt% to 79 wt%, the regenerated cellulose fiber mixing ratio is 17 wt% to 50 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 10 wt%, with 100 wt% as the woven or knitted fabric, from the viewpoint of exhibiting the desired flame retardance. If the regenerated cellulose fiber mixing ratio is 17 wt% to 50 wt% it will be possible to obtain the desired flame retardance even if the polyurethane elastic fibers are present in a mixing ratio of 2 wt% to 10 wt% for stretchability. Preferably, the flame retardant modacrylic fiber mixing ratio is 46 wt% to 75 wt%, the regenerated cellulose fiber mixing ratio is 23 wt% to 47 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 10 wt%, more preferably the flame retardant modacrylic fiber mixing ratio is 46 wt% to 72 wt%, the regenerated cellulose fiber mixing ratio is 24 wt% to 47 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 10 wt%, and most preferably the flame retardant modacrylic fiber mixing ratio is 49 wt% to 64 wt%, the regenerated cellulose fiber mixing ratio is 32 wt% to 44 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 8 wt%.

[0022] The flame retardant stretchable fiber structure of this embodiment may be a fabric such as a woven or knitted fabric, or a nonwoven fabric or flame retardant stretchable composite yarn, but a woven or knitted fabric and composite yarn are preferred.

[0023] The term "regenerated cellulose fibers" as used herein refers to fibers obtained by removing mainly a plant-derived cellulose component by a chemical method such as dissolution and regenerating it into fibers, and it includes viscose rayon, polynosic rayon, refined cellulose fibers, copper-ammonia rayon and high-strength rayon. The term "fibers" may refer to rayon, polynosic, lyocell, cupra or modal fibers.

[0024] Cellulose fibers such as cotton and hemp are not satisfactory in terms of afterglow. Semisynthetic fibers such as acetate fibers include deacetylated types, for example, but since these have a melting point and do not contribute to flame retardant performance, they are unsuitable for this embodiment.

[0025] The regenerated cellulose fibers may also be fibers with halogen or phosphorus compounds added by post-treatment, known as flame retardant rayon, but their effect of increasing flame retardance in the stretchable woven or knitted fabric of this embodiment is minimal while they can also impair the texture and weaving/knitting performance, and therefore the mixing ratio of halogen or phosphorus compound-added flame retardant rayon fibers is preferably 0.5 wt% or lower.

[0026] Lyocell is a type of regenerated cellulose fiber which is obtained by spinning of a solution of cellulose in a solvent without derivatization processing as is done with acetate fibers. Tencel^R is a type of lyocell that began test production by Couteau Co., England, and was followed by production of Lenzing Fibers in Austria.

[0027] There are no particular restrictions on the polyurethane elastic fibers, but they preferably have a structure with a polyurethane backbone or polyurethane-urea backbone. They may be polyurethane elastic fibers with addition of various additives and comprising a flame retardant, and are preferably polyurethane elastic fibers selected from the group consisting of polyacrylonitrile-based polymers with a number-average molecular weight of 10,000 to 50,000, styrene-maleic anhydride-based copolymers with a number-average molecular weight of 1,500 to 5,000 and polyurethane polymers with a number-average molecular weight of 10,000 to 40,000, and containing 1 to 14 wt% of a thermoplastic polymer with a hydrogen-bonding functional group concentration of 3 to 20 milliequivalent per 1 g of thermoplastic polymer when dissolved in an amide-based polar solvent, as disclosed in Japanese Unexamined Patent Publication HEI No. 7-316922.

[0028] It is not fully understood why polyurethane elastic fibers comprising these components are particularly superior for this embodiment, but it is thought that the excellent hot moldability of the fibers allow heat setting at a lower temperature than common polyurethane elastic fibers, thus reducing the high temperature load on the fabric. They are preferably polyurethane elastic fibers comprising a polyurethane polymer with a number-average molecular weight of 10,000 to 40,000 added to a polyurethane-urea polymer.

[0029] The polyurethane elastic fibers preferably contain this component together with a specific urea compound as disclosed in Japanese Patent No. 4343446. Adding both components will result in even more excellent hot moldability,

thus aiding in the effect of the invention.

[0030] Specifically, preferred polyurethane elastic fibers comprise 1 to 15 wt% of a urea compound obtained by reacting (a) a nitrogen-containing compound including a bifunctional amino group selected from among one or more primary amines and secondary amines, and a nitrogen-containing group selected from among one or more tertiary nitrogens and heterocyclic cyclic nitrogens, and (b) an organic diisocyanate, and (c) one or more compounds selected from the group consisting of mono or dialkylmonoamines, alkyl monoalcohols and organic monoisocyanates, with respect to the polyurethane-urea polymer.

[0031] In order to impart stretchability to the flame retardant woven or knitted fabric, the polyurethane elastic fiber is contained in a mixing ratio of 2 wt% to 10 wt% with respect to 100 wt% as the woven or knitted fabric.

[0032] The conductive fibers are not particularly restricted and may be Beltron[®] by KB Seiren Co., Ltd., for example. Beltron[®] is a melt spun fiber of two components, a conductive layer comprising carbon black or a white metal compound as conductive particles at high concentration, and an ordinary polymer layer (nylon or polyester) protecting it. Conductive fibers are usually contained in a mixing ratio of 0.5 wt% to 1.5 wt% with respect to 100 wt% as the woven or knitted fabric to impart an antistatic property for protective clothing, without affecting the flame retardance of the flame retardant stretch woven/knitted fabric of this embodiment.

[0033] For this embodiment, fibers other than the fiber types mentioned above may also be used in admixture in order to impart texture and other functionality, examples of which include synthetic fibers such as polyester, polyamide and aramid fibers, cellulose fibers such as hemp and silk, and animal hair fibers such as wool. To avoid lowering the flame retardance, however, the mixing ratio of such fibers is preferably less than 10 wt%, more preferably 2 wt% or lower and especially 0.1 wt% or lower. When aramid fibers are included as mixed fibers, the heat resistance and flame retardance are satisfactory but the texture and dyeing performance of obtained fiber structures and especially woven or knitted fabrics is impaired, and therefore the mixing ratio for aramid fibers is preferably 2 wt% or lower and more preferably 0.1 wt% or lower, and most preferably no aramid fibers are present.

[0034] As the flame retardance of the flame retardant stretch woven/knitted fabric of this embodiment, the afterflame and afterglow are both an average of 2.0 seconds or less according to ISO 15025 A.

[0035] ISO 11612:2015(E) specifies the requirements for protective clothing, one of which is 6.3 Limited Flame Spread which requires passing a test according to ISO 15025 A. The method of ISO 15025 A, an example of which is shown in Figs. 1 to 3, is a method of applying a flame on the surface of a monolayer fabric sample of clothing for 10 seconds with a flame with a length of 25 mm in the horizontal direction, using propane gas or butane gas, and after extinction of the flame, confirming that the flame does not spread to the top edge or both ends of the sample, that the flame or molten drops do not fall, and that the afterflame time (the time the test fabric continues to burn with a flame after completion of heating) is 2 seconds or less and the afterglow time (the time period of flameless combustion after completion of heating) is 2 seconds or less (see ISO 15025 First edition 2000-05-01 and ISO 11612 Third edition 2015-0701 6.3.2.1. Table 1).

[0036] In the flame retardant stretch woven/knitted fabric of this embodiment, the afterflame and afterglow are both 2 seconds or less, preferably 1 second or less and more preferably 0.5 seconds or less, and most preferably both are 0 seconds.

[0037] The flame retardant stretch woven/knitted fabric of this embodiment may be either a knitted fabric or a woven fabric. There are no restrictions on the texture of a knitted fabric. The texture of a woven fabric is also not particularly restricted and may be a plain weave, twill weave or satin weave.

[0038] The flame retardant modacrylic fibers and regenerated cellulose fibers may be distributed in the woven or knitted fabric of the embodiment in the form of spun yarn obtained by mix spinning. The proportion of both in the blended yarn is preferably in a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers, more preferably 52 wt% to 73 wt% flame retardant modacrylic fibers and 27 wt% to 48 wt% regenerated cellulose fibers, and most preferably 55 wt% to 65 wt% flame retardant modacrylic fibers and 35 wt% to 45 wt% regenerated cellulose fibers.

[0039] When such blended yarn is used as the warp yarn of a woven fabric the spun yarn may be either single yarn or doubled yarn. Doubled yarn is yarn comprising two different single yarns twisted together. Using doubled yarn can provide strength against destruction of the woven fabric due to tearing, rupture or pulling, while also offsetting thickness spots of single yarn and contributing to a cleaner appearance.

[0040] Twisting may also be applied to single yarn.

[0041] The size of blended yarn of flame retardant modacrylic fibers and lyocell is not particularly restricted, and it may have a yarn count of 30 to 20 (197 to 295 dtex). The basis weight of the woven or knitted fabric may be 150 g/m² to 380 g/m².

[0042] The stretchability of the flame retardant stretch woven/knitted fabric of this embodiment, in the case of a woven fabric, is preferably 15% or greater and more preferably 20% or greater as the weft elongation percentage in a test according to JIS L 1096 8.16.1 B. For a knitted fabric, it is preferably 60% or greater and more preferably 80% or greater as the warp or weft elongation percentage with a load of 14.7 N, in a test according to the cut strip method of JIS L 1096 8.16.1 D.

[0043] The pilling resistance of the flame retardant stretch woven/knitted fabric of the embodiment is preferably grade 3 or higher for 30 hours and more preferably 3 to 4 grade or higher for 30 hours, in a test according to JIS L 1076 A (ICI cork).

[0044] Another embodiment of the invention is flame retardant core spun yarn of flame retardant modacrylic fibers, regenerated cellulose combined filament yarn and polyurethane elastic fibers (45 wt% to 78 wt% mixing ratio of flame retardant modacrylic fibers, 18 wt% to 50 wt% mixing ratio of regenerated cellulose and 2 wt% to 10 wt% mixing ratio of polyurethane elastic fiber).

[0045] Since the materials in the composition of the flame retardant core spun yarn are the same as the composition in the flame retardant stretch woven/knitted fabric of the embodiment, it can exhibit the same level of flame retardance. The proportions of the three components are preferably a 47 wt% to 71 wt% mixing ratio of flame retardant modacrylic fibers, a 25 wt% to 48 wt% mixing ratio of regenerated cellulose and a 2 wt% to 10 wt% mixing ratio of polyurethane elastic fibers, and more preferably a 50 wt% to 63 wt% mixing ratio of flame retardant modacrylic fibers, a 33 wt% to 45 wt% mixing ratio of regenerated cellulose and a 2 wt% to 8 wt% mixing ratio of polyurethane elastic fibers.

[0046] The flame retardant core spun yarn of the embodiment can be produced using a common core yarn spinning machine. Specifically, crude yarn comprising fibers other than polyurethane elastic fibers are supplied to the back roller of a spinning machine and fleeced between it and the front roller at a low rate of draft, with the core polyurethane elastic fibers being supplied with tension applied at the center of the fleece to a predetermined draft ratio just before the front roller, and then after passing through the front roller, both are wound up as twisted spun tube yarn.

[0047] The flame retardant stretch woven/knitted fabric of the embodiment preferably comprises this blended yarn and/or flame retardant core spun yarn. The following are specific examples of yarn patterns.

(I) A knitted fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers over the entire surface, and polyurethane elastic fibers knitted or inserted over all or part of the surface.

(II) A woven fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers, 20 wt% to 50 wt% regenerated cellulose fibers and conductive fibers as the warp yarn, and flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers as the weft yarn.

(III) A knitted or woven fabric having flame retardant core spun yarn with 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, over the entire surface.

(IV) A knitted fabric having flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, and blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers, knitted alternately at 1:1.

[0048] For (I) above, for example, the blended yarn and polyurethane elastic yarn may be made into a bare plain stitch knitted fabric by knitting in a single jersey texture, in combination with conductive fibers if necessary. The polyurethane elastic yarn may be distributed over the entire stitch or in only parts of the stitch. For (II) above, for example, the blended yarn and if necessary conductive fibers may be used in a predetermined proportion as warp yarn, and the flame retardant core spun yarn may be used as weft yarn to obtain a woven fabric. This type of construction can provide satisfactory flame retardant stretch performance according to the invention.

[0049] Another embodiment of the invention is flame retardant stretchable protective clothing using the woven or knitted fabric or flame retardant core spun yarn. The woven or knitted fabric may be used to produce various types of clothing that require flame retardance and stretchability, such as working clothes or uniforms.

EXAMPLES

[0050] The invention will now be described in concrete detail by Examples and Comparative Examples. The flame retardance test method used for the Examples and Comparative Examples of the invention was the method of ISO 15025 A described above. In the test method of ISO 15025 A, the evaluations of "average afterflame time of 2.0 seconds or less", "average afterglow time of 2.0 seconds or less", "no hole burning or flame drops" and "no combustion to edge of fabric" were the averages for 3 samples in the weft direction and 3 samples in the warp direction of the fabric, for a total of 6 samples.

[0051] The stretchability for woven fabrics was considered acceptable if the elongation percentage was 15% or greater in either the warp or weft direction of the fabric in a test according to JIS L 1096 8.16.1 B, or for knitted fabrics it was considered acceptable if the elongation percentage was 60% or greater in either the warp or weft direction of the fabric under a load of 14.7 N in a test by the cut strip method according to JIS L 1096 8.16.1 D, while the pilling resistance (snag resistance) was considered acceptable if the result was grade 3 or higher for 30 hours in a test according to JIS

L 1076 A (ICI cork).

[Example 1]

[Preparation of Protex^R type-M:Tencel^R = 60 wt%:40 wt%, 30/1 count blended yarn]

[0052] Protex^R type-M (high flame retardance) by Kaneka Corp. as flame retardant modacrylic fibers (2.2 dtex single fiber size, 51 mm fiber length) at 60 wt% and Tencel^R (single fiber size: 1.3 dtex, 38 mm fiber length) at 40 wt% were spun together to obtain blended yarn with a count of 30/1. The number of twists of the blended yarn was 16.5/inch (2.54 cm).

[Knitting of bare plain stitch knitted fabric]

[0053] Using a single knit circular knitting machine (Model 3FA by Fukuhara Works, Ltd.) with an aperture of 30-inch, 28 gauge, a needle count of 2640 and a hole count of 90, Protex^R type-M:Tencel^R = 60%:40% blended yarn with a yarn count of 30/1, 22 dtex polyurethane elastic fibers and 33 dtex Beltron^R were combined to produce a knitted fabric with a bare plain stitch pattern. The polyurethane elastic fibers were distributed over the entire surface (all stitches) of the knitted fabric. The obtained greige was preset at 180°C, the Tencel was dyed with a reactive dye at 60°C, and then the modacryl was dyed with a cation dye at 98°C, after which it was dried and further treated by final setting at 130°C to obtain a black bare plain stitch knitted fabric having a basis weight of 349 g/m².

[0054] The polyurethane elastic fibers used were fibers made of a polyurethane-urea polymer comprising 3.0 wt% of a polyurethane polymer and 4.0 wt% of a urea compound, as described in Example 7 of Japanese Patent No. 4343446. The pattern of the polyurethane polymer and urea compound for this example was the following:

Polyurethane polymer: thermoplastic polymer with a number-average molecular weight of 30,000 obtained by polymerizing 1,4-butanediol, polytetramethylene glycol with a number-average molecular weight of 650 and methylene-bis(4-phenylisocyanate) in a molar ratio of 0.99:0.11:1.0, dissolved in an amide-based polar solvent and with a hydrogen-bonding urethane group concentration of 4.8 milliequivalent per 1 g of thermoplastic polymer,

[0055] Urea compound: urea compound with an average urea bond unit count of 4, obtained by reacting N,N'-bis(3-aminopropyl)piperazine, isophorone diisocyanate and phenyl isocyanate in a molar ratio of 2:1:2.

[0056] The material mixing ratio of the bare plain stitch knitted fabric was Protex^R type-M:Tencel^R:polyurethane elastic fiber:Beltron^R = 57.0 wt%:37.9 wt%:4.6 wt%:0.5 wt%.

[Example 2]

[0057] A bare plain stitch knitted fabric having a basis weight of 352 g/m² was obtained in the same manner as Example 1, except for using Protex^R type-Q:Tencel^R = 65 wt%:35 wt% blended yarn with a yarn count of 30/1 as the blended yarn.

[0058] The material mixing ratio of the bare plain stitch knitted fabric was Protex^R type-Q:Tencel^R:polyurethane elastic fiber:Beltron^R = 61.7 wt%:33.2 wt%:4.6 wt%:0.5 wt%.

[Example 3]

[0059] A bare plain stitch knitted fabric having a basis weight of 371 g/m² was obtained in the same manner as Example 2, except for using 33 dtex polyurethane elastic fibers.

[0060] The material mixing ratio of the bare plain stitch knitted fabric was Protex^R type-Q:Tencel^R:polyurethane elastic fiber:Beltron^R = 60.2 wt%:32.4 wt%:6.9 wt%:0.5 wt%.

[Example 4]

[Preparation of blended yarn of Protex^R type-Q:Tencel^R = 65 wt%:35 wt%, 20 count blended single yarn (20/1)]

[0061] Protex^R type-Q (high flame retardance) by Kaneka Corp. as flame retardant modacrylic fibers (1.7 dtex single fiber size, 51 mm fiber length) at 65 wt% and Tencel^R (single fiber size: 1.3 dtex, 38 mm fiber length) at 35 wt% were spun together to obtain blended yarn with a count of 20/1. The number of twists of the blended yarn was 19/inch (2.54 cm).

[Preparation of flame retardant core spun yarn of flame retardant modacrylic fibers, Tencel^R and polyurethane elastic fibers (flame retardant modacrylic fiber mixing ratio: 61.2 wt%, Tencel^R mixing ratio:33.9 wt%, polyurethane elastic fiber mixing ratio: 4.9 wt%)]

[0062] Flame retardant core spun yarn having 19 twists/inch (2.54 cm) and a yarn count of 20/1 was produced using

61.2 wt% Protex^R type-Q (high flame retardant) (single fiber size: 1.7 dtex, fiber length: 51 mm) by Kaneka Corp. and 33.9 wt% Tencel^R (single fiber size: 1.3 dtex, fiber length: 38 mm) as flame retardant modacrylic fibers, inserting 44 dtex polyurethane elastic fiber (4.9 wt% weight ratio) during spinning in the same pattern as Example 1, as core thread at a draft ratio of 3.0.

[Preparation of 2/1 left twill weave fabric]

[0063] A 2/1 left twill weave greige was woven using 5206 Protex^R type-Q:Tencel^R = 65%: 35% blended yarns with a yarn count of 20/1, and 93 Beltron^R yarns with a size of 22 dtex, as the warp yarn, and Protex^R type-Q (high flame retardant) :Tencel^R:polyurethane elastic fiber = 61.2 wt%:33.9 wt%:4.9 wt% flame retardant core spun yarn with a yarn count of 20/1 as the weft yarn. The obtained greige was preset at 160°C, the Tencel was dyed with a reactive dye at 60°C, and then the modacryl was dyed with a cation dye at 98°C, after which it was dried and further treated by final setting at 130°C to obtain a royal blue 2/1 left twill weave fabric having a basis weight of 280 g/m².

[0064] The material mixing ratio of the obtained 2/1 left twill weave fabric was Protex^R type-Q:Tencel^R:polyurethane elastic fiber:Beltron^R = 62.5 wt%:34.0 wt%:2.3 wt%:1.2 wt%.

[Example 5]

[0065] A navy blue 2/1 left twill weave woven fabric having a basis weight of 281 g/m² was obtained by the same method as Example 4, except that Protex^R type-M:Tencel^R = 60 wt%:40 wt% blended yarn with a yarn count of 20/1 was used as the warp yarn, and flame retardant core spun yarn with a blending ratio of Protex^R type-M:Tencel^R = 60 wt% 40 wt% was used as the weft yarn, and the dyeing color was changed.

[0066] The material mixing ratio of the obtained 2/1 left twill weave fabric was Protex^R type-M:Tencel^R:polyurethane elastic fiber:Beltron^R = 57.7 wt%:38.9 wt%:2.3 wt%:1.2 wt%.

[Comparative Example 1]

[0067] A bare plain stitch knitted fabric was obtained in the same manner as Example 1, except for using cotton instead of Tencel^R.

[Comparative Example 2]

[0068] A bare plain stitch knitted fabric was obtained in the same manner as Example 2, except for using cotton instead of Tencel^R.

[Comparative Example 3]

[0069] A 2/1 left twill weave woven fabric was obtained in the same manner as Example 4, except for using cotton instead of Tencel^R for both the warp yarn and weft yarn.

[0070] The results for Examples 1 to 5 and Comparative Examples 1 to 3 are shown in Table 1.

[Table 1]

		Average afterflame time	Average afterglow time	Hole burning or flame drops	Combustion to edge of fabric	Snagging	Stretchability
Example 1	Bare plain stitch knit	0 sec	0 sec	None	None	Acceptable	Acceptable
Example 2	Bare plain stitch knit	0 sec	0 sec	None	None	Acceptable	Acceptable

(continued)

		Average afterflame time	Average afterglow time	Hole burning or flame drops	Combustion to edge of fabric	Snagging	Stretchability
Example 3	Bare plain stitch knit	0 sec	0 sec	None	None	Acceptable	Acceptable
Example 4	2/1 Left twill weave	0 sec	0 sec	None	None	Acceptable	Acceptable
Example 5	2/1 Left twill weave	0 sec	0 sec	None	None	Acceptable	Acceptable
Comp. Ex. 1	Bare plain stitch knit	0 sec	12.1 sec	None	None	Acceptable	Acceptable
Comp. Ex. 2	Bare plain stitch knit	34.5 sec	Unconfirmable due to afterflame	None	None	Acceptable	Acceptable
Comp. Ex. 3	2/1 Left twill weave	33.4 sec	Unconfirmable due to afterflame	None	None	Acceptable	Acceptable

INDUSTRIAL APPLICABILITY

[0071] The flame retardant stretch woven/knitted fabric of the invention has an average for both the afterflame and afterglow time of 2.0 seconds or less according to ISO 15025 A, and it can therefore be suitably used as a material for flame retardant stretchable protective clothing, work clothing, firefighting clothes, police dispatch uniforms, general uniforms and school uniforms with excellent dye affinity, high pilling resistance and stretchability.

Claims

1. A flame retardant stretch fiber structure having a flame retardant modacrylic fiber mixing ratio of 44 wt% to 79 wt%, a regenerated cellulose fiber mixing ratio of 17 wt% to 50 wt% and a polyurethane elastic fiber mixing ratio of 2 wt% to 10 wt%.
2. The flame retardant stretch fiber structure according to claim 1, which is a woven or knitted fabric in which the average afterflame and afterglow time are both 2.0 seconds or less according to ISO 15025 A.
3. The flame retardant stretch fiber structure according to claim 1 or 2, wherein the flame retardant modacrylic fiber mixing ratio is 46 wt% to 75 wt%, the regenerated cellulose fiber mixing ratio is 23 wt% to 47 wt% and the polyurethane elastic fiber mixing ratio is 2 wt% to 10 wt%.
4. The flame retardant stretch fiber structure according to any one of claims 1 to 3, which is a woven or knitted fabric further comprising conductive fibers in a mixing ratio of 0.5 wt% to 1.5 wt%.
5. The flame retardant stretch fiber structure according to any one of claims 1 to 4, which is a woven or knitted fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers.

6. The flame retardant stretch fiber structure according to any one of claims 1 to 4, which is a woven or knitted fabric having flame retardant core spun yarn with 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers.
- 5 7. The flame retardant stretch fiber structure according to claim 5, which is a knitted fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers over the entire surface, and polyurethane elastic fibers knitted or inserted over all or part of the surface.
- 10 8. The flame retardant stretch fiber structure according to claim 6, which is a woven fabric having blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers, 20 wt% to 50 wt% regenerated cellulose fibers and conductive fibers as the warp yarn, and flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers as the weft yarn.
- 15 9. The flame retardant stretch fiber structure according to claim 6, which is a knitted or woven fabric having flame retardant core spun yarn with 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, over the entire surface.
- 20 10. The flame retardant stretch fiber structure according to claim 6, which is a knitted fabric having flame retardant core spun yarn comprising 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers, and blended yarn with a spinning ratio of 50 wt% to 80 wt% flame retardant modacrylic fibers and 20 wt% to 50 wt% regenerated cellulose fibers, knitted alternately at 1:1.
- 25 11. The flame retardant stretch fiber structure according to any one of claims 1 to 10, wherein the polyurethane elastic fibers are polyurethane elastic fibers selected from the group consisting of polyacrylonitrile-based polymers with a number-average molecular weight of 10,000 to 50,000, styrene-maleic anhydride-based copolymers with a number-average molecular weight of 1,500 to 5,000 and polyurethane polymers with a number-average molecular weight of 10,000 to 40,000, and containing 1 wt% to 14 wt% of a thermoplastic polymer with a hydrogen-bonding functional group concentration of 3 to 20 milliequivalent per 1 g of thermoplastic polymer when dissolved in an amide-based polar solvent.
- 30 12. Flame retardant stretch core spun yarn according to claim 1, which comprises 45 wt% to 78 wt% flame retardant modacrylic fibers, 18 wt% to 50 wt% regenerated cellulose fibers and 2 wt% to 10 wt% polyurethane elastic fibers.
- 35 13. Flame retardant stretchable protective clothing using a woven or knitted fabric according to any one of claims 1 to 11 or flame retardant core spun yarn according to claim 12.

FIG. 1

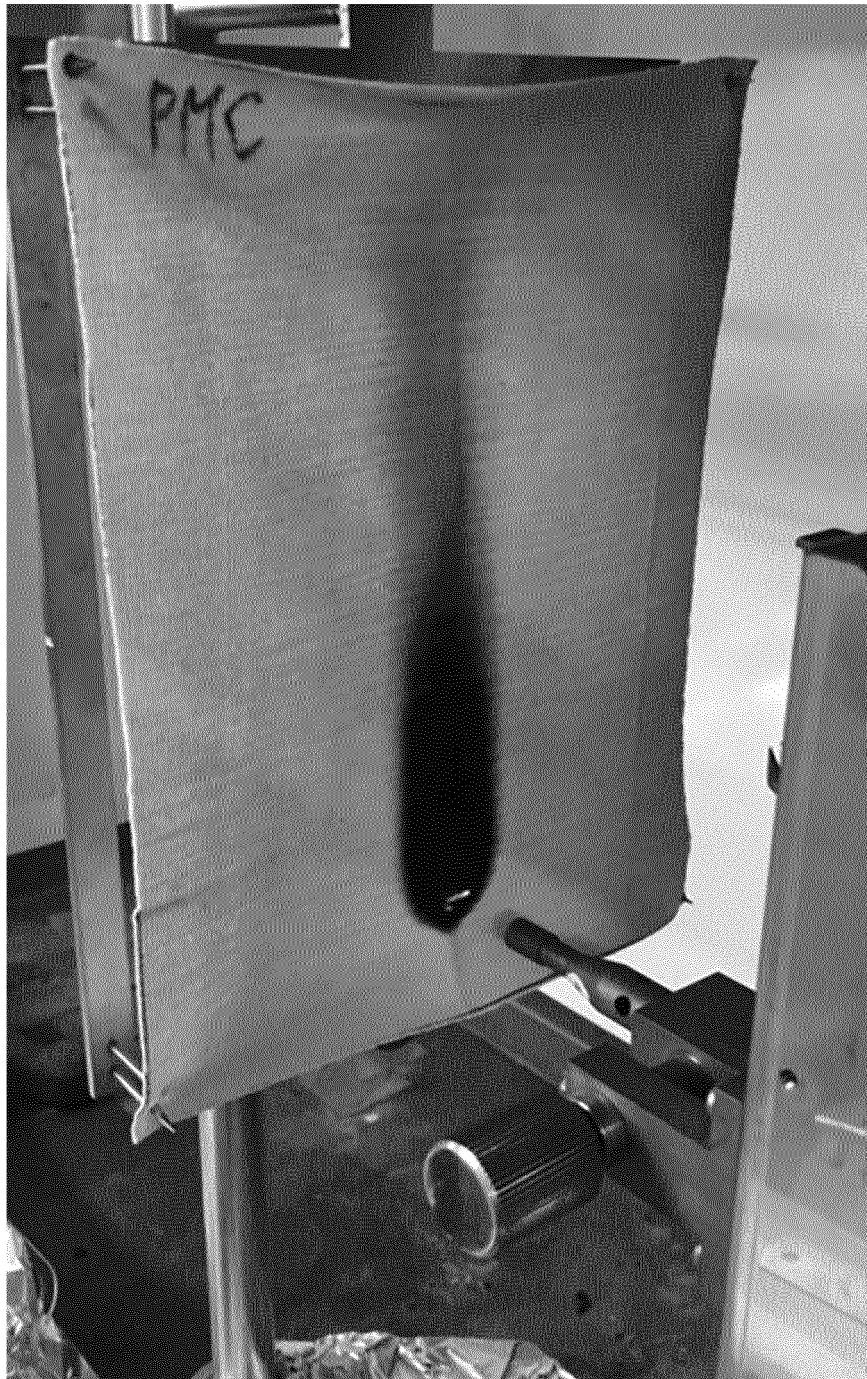
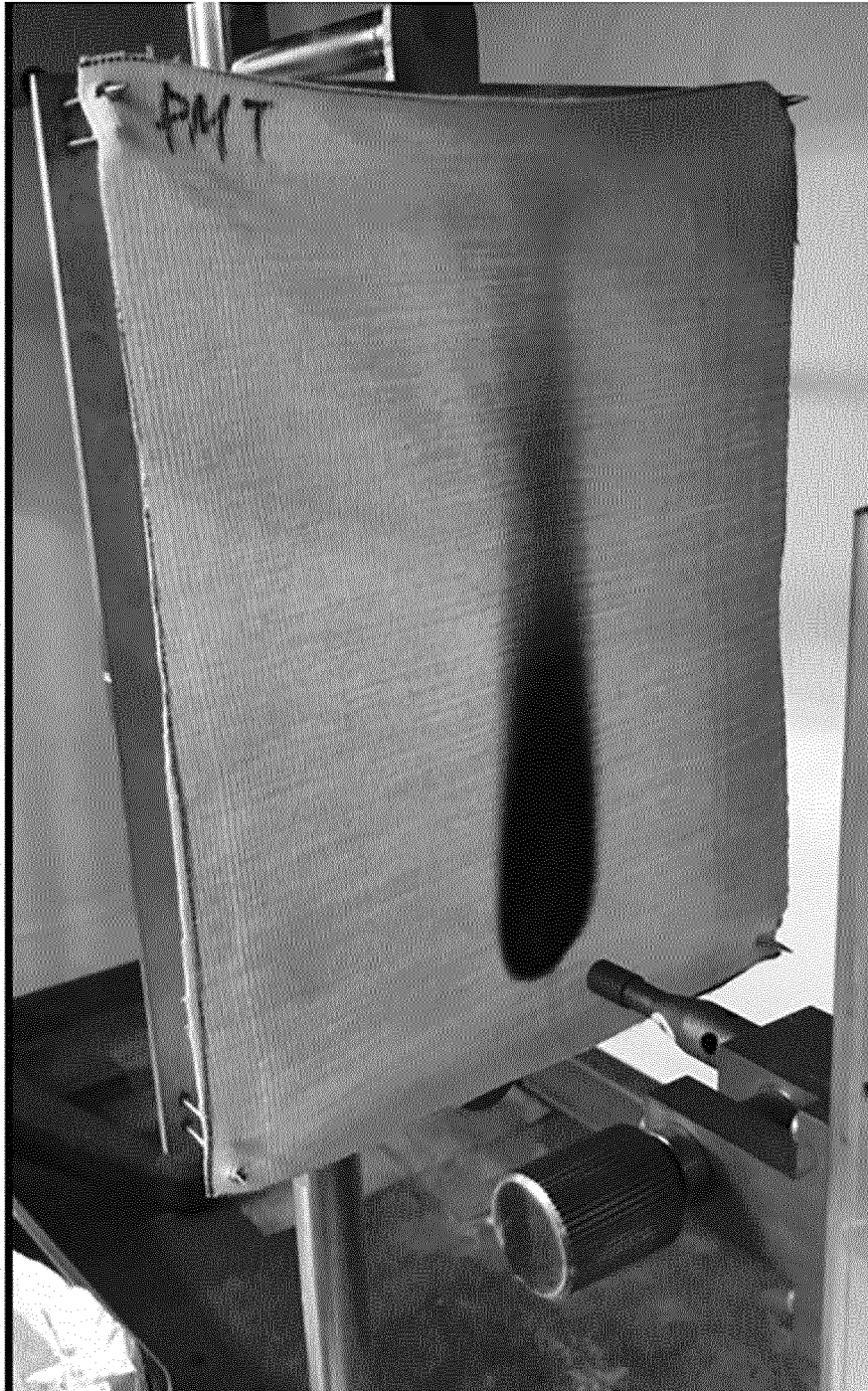


FIG. 2



FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/040718

A. CLASSIFICATION OF SUBJECT MATTER

D04B 1/16 (2006.01)i; A41D 13/00 (2006.01)i; A41D 31/00 (2019.01)i; A41D 31/08 (2019.01)i; D02G 3/04 (2006.01)i; D03D 7/00 (2006.01)i; D03D 15/40 (2021.01)i; D03D 15/47 (2021.01)i; D03D 15/513 (2021.01)i; D03D 15/533 (2021.01)i; D03D 15/56 (2021.01)i; D04B 1/00 (2006.01)i; D04B 1/18 (2006.01)i

FI: D04B1/16; A41D13/00 102; A41D31/00 502A; A41D31/00 503J; A41D31/00 503K; A41D31/08; D02G3/04; D03D7/00; D03D15/00 C; D03D15/00 D; D03DL5/00 101; D03D15/08; D03DL5/12 Z; D04B1/00 C; D04B1/18

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)

D04B1/00-1/28, 21/00-21/20; D03D1/00-27/18; D02G1/00-3/48; D02J1/00-13/00; A41D13/00-13/12; A41D31/00-31/32

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013-511628 A (OUTLAST TECHNOLOGIES LLC) 04	1-3, 13
Y	April 2013 (2013-04-04) claims 1, 4, 6, paragraphs [0002]-[0004], [0108]-[0111], example 2	4, 11, 13
A		5-10, 12
Y	JP 2010-502849 A (SOUTHERN MILLS, INC.) 28 January 2010 (2010-01-28) claims 1, 2, 8, 10, 14, 16, 26, paragraphs [0001], [0012], [0023], [0024], [0029]-[0032]	1-5, 7, 11, 13
A		6, 8-10, 12
Y	JP 2009-275296 A (TEIJIN FIBERS LTD.) 26 November 2009 (2009-11-26) claims 6, 8, paragraph [0017]	1-5, 7, 11, 13



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search
11 December 2020 (11.12.2020)

Date of mailing of the international search report
28 December 2020 (28.12.2020)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/040718

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-303326 A (KANEGAFUCHI CHEM IND CO., LTD.) 31 October 2000 (2000-10-31) claim 1, paragraph [0001]	1-5, 7, 11, 13
Y	US 2016/0249685 A1 (SILVERSKIN ITALIA S.R.L.) 01 September 2016 (2016-09-01) claims 1, 2, fig. 1, 2, paragraphs [0004]-[0006]	1-4, 6, 9, 11-13
A		5, 7, 8, 10
Y	WO 2003/080909 A1 (KANEGAFUCHI CHEM IND CO., LTD.) 02 October 2003 (2003-10-02) examples 4-6, comparative example 1	1-4, 6, 9, 11-13
Y	JP 2015-530485 A (E.I. DU PONT DE NEMOURS AND COMPANY) 15 October 2015 (2015-10-15) paragraphs [0001] [0048]	4-7, 9, 11, 13
Y	JP 7-316922 A (ASAHI KASEI INDUSTRY CO., LTD.) 05 December 1995 (1995-12-05) claim 2, paragraph [0005]	11, 13
A	CN 108851257 A (ZHEJIANC HONCSHANC INTELLECENT TECHNOLOGY CO., LTD.) 23 November 2018 (2018-11-23) claim 1, examples	1-13
A	JP 2014-529690 A (E.I. DU PONT DE NEMOURS AND COMPANY) 13 November 2014 (2014-11-13) claims 1, 7, paragraph [0020]	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2020/040718

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
JP 2013-511628 A	04 Apr. 2013	US 2011/0117353 A1 claims 1, 4, 6, paragraphs [0002]- [0004], [0126], [0127], example 2 WO 2011/062938 A2 EP 2501846 A2	
JP 2010-502849 A	28 Jan. 2010	US 2008/0057807 A1 claims 1, 2, 8, 10, 14, 16, 26, [0001], [0012], [0023], [0024], [0029]-[0032] WO 2008/027454 A1 EP 2079332 A1	
JP 2009-275296 A	26 Nov. 2009	(Family: none)	
JP 2000-303326 A	31 Oct. 2000	(Family: none)	
US 2016/0249685 A1	01 Sep. 2016	WO 2016/135562 A1	
WO 2003/080909 A1	02 Oct. 2003	US 2005/0130535 A1 examples 4-6, comparative example 1 EP 1498523 A1 CN 1653220 A	
JP 2015-530485 A	15 Oct. 2015	US 2014/0026303 A1 paragraphs [0002], [0050] WO 2014/018697 A1 EP 2877620 A1 KR 10-2015-0036204 A CN 104685118 A	
JP 7-316922 A	05 Dec. 1995	(Family: none)	
CN 108851257 A	23 Nov. 2018	(Family: none)	
JP 2014-529690	13 Nov. 2014	US 2013/0055491 A1 claims 1, 7, paragraph [0022] WO 2013/032562 A1 EP 2751318 A1 CN 103857837 A KR 10-2014-0059265 A	

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2008208509 A [0007]
- JP 2014208930 A [0007]
- JP 2003027344 A [0007]
- JP 7316922 A [0027]
- JP 4343446 B [0029] [0054]