(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 579 032 A1**

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

(43) Date of publication:
02.07.2025 Bulletin 2025/27

(21) Application number: **23856566.7**

(22) Date of filing: **21.08.2023**

(51) International Patent Classification (IPC):
D06M 15/564 *(2006.01)* ***D06M 15/643*** *(2006.01)*
D06M 13/513 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
D06M 13/513; D06M 15/564; D06M 15/643

(86) International application number:
PCT/CN2023/113969

(87) International publication number:
WO 2024/041476 (29.02.2024 Gazette 2024/09)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **22.08.2022 CN 202211002878**

(71) Applicant: **Toray Industries, Inc.**
Tokyo 103-8666 (JP)

(72) Inventors:
- **ZHANG, Tianchi**
  Nantong, Jiangsu 226009 (CN)
- **HUANG, Yunyun**
  Nantong, Jiangsu 226009 (CN)
- **LUO, Zhourong**
  Nantong, Jiangsu 226009 (CN)

(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) WATER-REPELLENT TEXTILE

(57) The present invention discloses a water-repellent textile. The surface of a single fiber constituting the water-repellent textile is covered with a resin film with a thickness of 60 to 100 nm, and main components of the resin film are a non-fluorinated water-repellent compound and an isocyanate compound. The water-repellent textile of the present invention not only has more excellent water repellency and washing durability, but also has good hand feel and is safe and environmentally friendly.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a water-repellent textile subjected to water-repellent treatment.

BACKGROUND ART

[0002] In pursuit of a healthy, fashionable and natural life, more and more people are heading outdoors. For outdoor sportswear fabrics, people expect them to have excellent water repellency.

[0003] At present, water repellents used for water-repellent finishing are mainly divided into two categories: fluorinated water repellents and non-fluorinated water repellents. Although textiles treated with fluorinated water repellents have advantages such as high water repellency and high washing resistance, an ammonium perfluorooctanoate (hereinafter referred to as PFOA) and perfluorooctane sulfonate compound (hereinafter referred to as PFOS) contained in the fluorinated water repellents are genotoxic and reproductive toxic, and are difficult to biodegrade, which is not conducive to environmental protection. For example, Chinese patent document CN106758252A discloses a water and oil proofing agent convenient for maintenance, a preparation method thereof, and a textile, and specifically discloses a textile processed with a water and oil proofing agent containing polyurethane, wherein the polyurethane is obtained by reacting polyisocyanates, fluorosilicone polyols, silicon-containing polyols, other polyols and sealants. The textile finished with the water and oil proofing agent has better water and oil proofing effects and washing resistance. However, the water and oil proofing agent contains fluorinated compounds, and thus does not meet environmental protection requirements.

[0004] A water-repellent fabric processed with an environmentally-friendly non-fluorinated water repellent has excellent initial water repellency and durability after being washed for 10 times (or 30 times), but the water repellency decreases significantly after being washed for more times, such as 100 times. For example, Chinese patent document CN105734970A discloses a textile subjected to water-repellent treatment and a production method thereof, and specifically discloses that the surface of a single fiber of the textile is covered with a resin film, and a main component of the resin film is a non-fluorinated compound. Based upon the measurement according to the JIS L 1092 spray method criteria, this textile has a water repellency of level 3 or above after being washed for 10 times, but the problem of decreased water repellency after more washing times cannot be solved. In addition, Japanese patent document laid-open 2019-173185 discloses a water-repellent composition for fibers and a water-repellent fiber product, wherein the water-repellent composition includes a component (A), silicone resin (B) and water, the component (A) being at least one of an urethane compound (A1), acrylic resin (A2) and reactive silicone (A3). The fiber product processed with the water repellent has a water repellency of only level 3 after being washed for 5 times, and the problem of decreased water repellency after more washing times is also not solved.

SUMMARY OF THE INVENTION

[0005] An object of the present invention is to provide an environmentally-friendly textile having better water repellency and washing durability.

[0006] In order to achieve the above object, the technical solution of the present invention is as follows:
the present invention provides a water-repellent textile, wherein the surface of a single fiber constituting this textile is covered with a resin film with a thickness of 60 to 100 nm, and main components of the resin film are a non-fluorinated water-repellent compound and an isocyanate compound.

[0007] In the water-repellent textile of the present invention, the surface of its single fiber is covered with a resin film with a specific thickness, and main components of this resin film are a non-fluorinated water-repellent compound and an isocyanate compound. On the one hand, such a resin film can make it difficult for water molecules to penetrate, thereby obtaining excellent initial water repellency; on the other hand, in addition to reacting with the non-fluorinated water-repellent compound, the isocyanate compound in the resin film can also react with the fiber to make the non-fluorinated water-repellent compound firmly attached to the single fiber, thereby improving the washing durability. In addition, compared with fluorinated compounds, the non-fluorinated compound is safe and more environmentally friendly.

EMBODIMENTS OF THE INVENTION

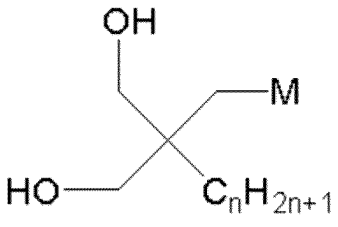
[0008] The present invention provides a water-repellent textile, wherein the surface of a single fiber constituting this water-repellent textile is covered with a resin film with a thickness of 60 to 100 nm. This is because if the thickness of the resin film is less than 60 nm, after multiple washes, especially 100 washes, the resin film will be severely damaged and the textile will not have super-high washing durability; and if the thickness of the resin film is greater than 100 nm, the effective components are already saturated and the water repellency cannot be further improved, which will affect the hand feel and

increase the cost. Preferably, the thickness of the resin film is 70 to 90 nm. This is because within this range, the textile has particularly excellent washing durability and good hand feel.

[0009] In the present invention, main components of the resin film are a non-fluorinated water-repellent compound and an isocyanate compound. The non-fluorinated water-repellent compound can form a film on the single fiber, which can give the textile good water repellency, while isocyanate groups in the isocyanate compound can not only react with the non-fluorinated water-repellent compound, but also react with the fiber to make the non-fluorinated water-repellent compound firmly attached to the single fiber, thereby significantly improving the washing durability.

[0010] Preferably, the isocyanate compound in the resin film of the present invention is a polymer formed from aromatic multifunctional isocyanates and polyols. The above-mentioned polymer has a network structure, which can lock the non-fluorinated water-repellent compound more firmly, making it less likely to fall off, and further improving the washing durability.

[0011] The polyols herein are not particularly limited and may be diols and/or triols. The polyol preferably has a structure shown in formula 1:



formula 1

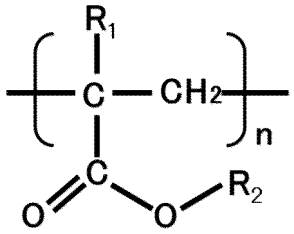
wherein, M is an H atom, alkyl, Alkoxy group, hydroxyl, Hydroxyalkyl group or carbonyl; and
$2 \leq n \leq 16$.

[0012] This is because the polyol containing the structure of Formula 1, due to its terminal groups -OH and -M, easily reacts with aromatic multifunctional isocyanate to form chemical bonds, making the formed network structure more compact, thereby locking the non-fluorinated water-repellent compound more firmly in the network structure, making it less likely to fall off, and further improving the washing durability.

[0013] Preferably, the non-fluorinated water-repellent compound is a hydrocarbon compound, a polysiloxane compound A or a copolymer thereof.

[0014] The hydrocarbon compound is not particularly limited, and may be an acrylate compound, a stearate compound, an N-hydroxymethyl compound, or the like. Examples of the acrylate compound include butyl acrylate, acrylonitrile, acrylamide, etc.; examples of the stearate compound include sodium stearate, calcium stearate, aluminum stearate, etc.; and examples of the N-hydroxymethyl compound include etherified hexamethylol melamine, N-Hydroxymethyloctadecamide, etc. The hydrocarbon compound can enhance the interaction between emulsion particles and water molecules, which is beneficial to the formation of dense cross-linked structures, and can improve the film-forming strength while being self-polymerized into a film on the surface of the single fiber.

[0015] When the hydrocarbon compound is an acrylate compound, a water-repellent film formed by this compound has better uniformity, making water molecules difficult to penetrate, and has certain stiffness to withstand the impact of external forces (washing or friction rubbing, etc.), and is thus not easy to fall off. Preferably, the hydrocarbon compound is an acrylate compound having a structural unit shown in formula 2,

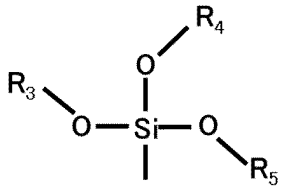


formula 2

wherein, R_1 and R_2 are alkyl or unsaturated hydrocarbon groups, respectively; and
$2 \leq n \leq 200$.

[0016] Due to its low molecular weight, the polysiloxane compound A is easy to enter the fiber, and a film formed on the surface of this compound can reduce the friction coefficient between yarns, thereby improving the hand feel. Preferably,

the polysiloxane compound A is a compound having a structure shown in formula 3,

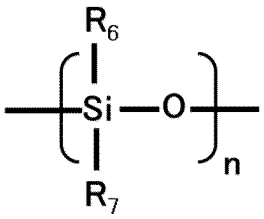


formula 3

wherein, R_3, R_4 and R_5 are alkyl or unsaturated hydrocarbon groups, respectively.

[0017] Preferably, the resin film of the present invention includes a flexible compound, and the flexible compound is a polyethylene compound and/or a polysiloxane compound B. This compound can make the film formed on the fiber surface have lower surface tension and smoothness, reduce the friction coefficient between fibers, and improve the hand feel.

[0018] The polysiloxane compound B is not particularly limited, but preferably has a structural unit shown in formula 4,



formula 4

wherein, R_6 and R_7 are an H atom, alkyl or unsaturated hydrocarbon groups, respectively; and $2 \leq n \leq 200$.

[0019] Preferably, the thickness of the resin film of the water-repellent textile of the present invention is 40 to 100 nm after being washed for 100 times according to the method 103 in JIS L 0217:1995 criteria or the method C4M in JIS L 1930:2014 criteria.

[0020] Preferably, the water-repellent textile of the present invention has an initial water repellency of level 4 or above according to a test using the spray method in JIS L 1092:2009 criteria.

[0021] Preferably, the water-repellent textile of the present invention has a water repellency of level 3 or above after being washed for 100 times according to the method 103 in JIS L 0217:1995 criteria or the method C4M in JIS L 1930:2014 criteria, and then tested according to the spray method in JIS L 1092:2009 criteria.

[0022] The fiber raw material of the water-repellent textile of the present invention is not particularly limited, and may be composed of cellulose fiber and/or synthetic fiber. The cellulose fibers herein include natural cellulose fibers and regenerated cellulose fibers. Wherein, examples of the natural fibers include cotton fibers, hemp fibers, etc.; examples of the regenerated cellulose fibers include viscose fibers, modal fibers, etc.; and examples of the synthetic fibers include polyester fibers (PET), polyamide fibers, polyacrylonitrile fibers, etc.

[0023] The water-repellent textile of the present invention may be a woven fabric or a knitted fabric. The weaves of the woven fabric are not particularly limited, and may include plain weave, twill weave, satin weave, etc. The weaves of the knitted fabric are not specifically limited, and may include weft plain weave, ribbing weave, double reverse weave, warp plain weave, and warp satin, etc.

[0024] A preparation method of the water-repellent textile of the present invention is not particularly limited, and may be prepared by the following method: pre-treatment of grey cloth (desizing and degreasing), intermediate shaping, dyeing (optional), and post-finishing to obtain the product of the present invention.

[0025] Wherein, the post-finishing process preferably uses a processing solution containing the following components for dipping and padding processing, which is then dried at a temperature of 80 to 150°C, and finally subjected to shaping finishing at 130 to 200°C.

[0026] The dipping and padding solution is composed of the following components:

water repellent	10 to 200 g/L
crosslinker	5 to 50 g/L
softener	0 to 40 g/L
penetrant	5 to 30 g/L

the rest being water.

[0027] The gram weight of the grey cloth here is preferably 50 to 300 g/m^2. If the gram weight of grey cloth is less than 50

g/m^2, the requirements for the weaving process are relatively high, and yarn breakage may occur, which is not conducive to production, so this grey cloth is not preferred; and if the gram weight of grey cloth is greater than 300 g/m^2, it may affect wearing comfort, so this grey cloth is not preferred.

[0028] The water repellent herein is a non-fluorinated water repellent, and its type is not particularly limited, and is preferably one or more of a hydrocarbon compound, a paraffin compound, and a polysiloxane compound A. The amount of the water repellent is preferably 40 to 100 g/L. When the amount of a water repellent is less than 40 g/L, it is difficult to form a uniform water-repellent film on the fiber surface, so this water repellent is not preferred due to poor water repellency; and when the amount of a water repellent is greater than 100 g/L, effective components covering the fiber surface are already saturated, and the water repellency cannot be further improved, which will affect the hand feel and increase the cost, so this water repellent is not preferred.

[0029] The type of the crosslinker is not particularly limited, but is preferably blocked isocyanate, and more preferably a polymer of aromatic polyfunctional isocyanate and polyol. The amount of the crosslinker is preferably 10 to 40 g/L. When the amount of a crosslinker is less than 10 g/L, reactive groups that can react with the water repellent and attach to the fiber surface are relatively few, and after multiple washes, especially after 100 washes, a large amount of isocyanate attached to the water repellent falls off, so the textile cannot have super-high washing durability, and is therefore not preferred; and when the amount of a crosslinker is greater than 40 g/L, effective components that can react with the water repellent are already saturated, and the washing durability cannot be further improved, but the hand feel will be affected, and the cost will also be increased, so this crosslinker is not preferred.

[0030] The type of the softener is not particularly limited, but is preferably a polyethylene compound and/or a polysiloxane compound B. The amount of the softener is preferably 10 to 30 g/L. When the amount of a softener is less than 10 g/L, it is difficult to form a uniform soft film on the fiber surface, and to improve the hand feel, so this softener is not preferred; and when the amount of a softener is greater than 30 g/L, the effect of improving the hand feel is not obvious, and the water repellency of the textile possibly decreases, so this softener is not preferred.

[0031] The type of the penetrant here is not particularly limited, but is preferably isopropanol and/or aliphatic ethoxylated alcohol. The amount of the penetrant is preferably 10 to 20 g/L. When the amount of a penetrant is less than 10 g/L, It is difficult for a agent to penetrate into the fibers, and it is difficult to form a uniform water-repellent film between the fibers, which makes it possible for water molecules to enter and affect the water repellency, so this penetrant is not preferred; and when the amount of a penetrant is greater than 20g/L, active components are already saturated, and the cost will be increased, so this penetrant is not preferred.

[0032] The above-mentioned agents may be commercially available or synthesized according to the known techniques in the art.

[0033] This is because the water repellent can form a film at a drying temperature of $\geq 80°C$ to produce a water-repellent effect; and the crosslinker undergoes a chemical reaction at a setting temperature of more than 130°C and firmly adheres to the textile, making the textile both water-repellent and wash-resistant.

[0034] A method for preparing a processing solution is not particularly limited and may be carried out as follows: a water repellent and a crosslinker are added in sequence, further added with a softener if the hand feel needs to be improved, added with water for blending, and stirred continuously, but the stirring speed should not be too fast to avoid demulsification. A processing agent used in actual processing and its amount need to be adjusted according to different textiles to be processed. At the same time, local adjustments should be made to the processing method in a timely manner to ensure that the processing solution can fully play its role and improve the properties of the textiles.

[0035] The present invention will be further described below with reference to the examples and comparative examples.

[0036] Various physical property parameters involved in the present invention are tested according to the following method.

(1) Confirmation of water repellency of textiles and content of fluorine in resin film

[0037]

1) A piece of 5 cm × 2 cm sample cloth was taken, and fixed on a sample cloth holder according to DB44/T 1872-2016 Test Criteria for wetting performance of textile surfaces (contact angle method); the sample cloth holder was placed on a laboratory table of a contact angle meter; and the surface of the sample cloth was adjusted to a height of 10 mm away from a needle tip of an injection needle. 5 μL droplets were dropped on the surface of the sample cloth. After a contact time of 60 seconds, the sample cloth and the droplets on the sample cloth were photographed. If a contact angle $\theta > 0°$, it can be preliminarily determined that the sample cloth was a textile containing a water-repellent compound.

2) Another piece of sample cloth with a size of 1 cm × 1 cm was then taken, the surface of the sample cloth was scanned with an element analyzer, and the fluorine content was measured. If the measured fluorine content was 0, it can be determined that the resin film contained a non-fluorinated compound.

(2) Thickness of resin film

A. Sampling and measurement

[0038] A piece of sample cloth having a size of 1 cm × 1 cm was taken, and cut along a position perpendicular to a warp or weft direction of the textile to obtain a cross section, and then the following equipment was used to observe the thickness of the resin film deposited on the surface of the textile on the cross section to be tested. One of the equipment was selected as needed for measurement.

Equipment 1:

[0039]

Equipment Model: Hitachi Regulus-8100 Field Emission Scanning Electron Microscope
Test conditions: No gold spraying, 1kV voltage deceleration mode
The operating method referred to JY/T 010-1996 "General Rules for Analytical Scanning Electron Microscopy Methods".

Equipment 2:

[0040]

Equipment Model: JEOL JEM-2200FS 200kV Energy Filtered Field Emission Transmission Electron Microscope
Test conditions: RuO_4 stained ultrathin sections, accelerating voltage: 200 kV
The operation method referred to KS D 8544-2006 "Metallic Coatings. Coating Thickness Measurement. Transmission Electron Microscopy Method".

B. Calculation

[0041]

1) The diameter d of the single fiber to be tested was calculated by the following formula:

$$d = \sqrt{\frac{4 \times 10^2}{9\pi} \times \frac{N_{dt}}{\gamma}}$$

d: Single fiber diameter (cm)
γ: Fiber density (g/cm^3)
N_{dt}: Fiber linear density (dtex)

2) Point A at any position on the cross section of the single fiber was taken;
3) a circle was drawn with A as the center and 0.1 times the diameter of the single fiber d as the radius, and intersected with the cross section of the single fiber at point B;
4) tangent lines were drawn with A and B as tangent points along the cross section surface and intersected at point O, and an internal angle of intersection was measured as θ;
5) when $90° \leq \theta < 178°$, taking O as an endpoint, a ray was drawn at an angle of $\theta°/2$ and the internal angle $\angle$AOB, and intersected with the cross section at point E, and the film thickness at this point was measured; and
6) steps 1) to 5) were repeated for a total of five measurements, that is, five times at different positions on the same sample cloth, to obtain five groups of data, which were then averaged as the thickness of the resin film of the present invention.

(3) Qualitative analysis of compounds in resin film

1) Sampling and testing

[0042] Two pieces of 10 cm x 10 cm sample cloth were taken. Qualitative analysis was performed using a Fourier

transform attenuated total reflection infrared spectrometer, and the operating method referred to GB/T 6040-2002 "General Rules for Infrared Spectroscopy Analysis Methods". Wherein, the parameters in the test conditions were selected as follows: ATR crystal: Ge, incident angle: 45°, measurement range: 4000 to 680 cm^{-1}. One piece of sample cloth was taken and placed directly on a reflection surface of the Ge crystal of the Fourier transform attenuated total reflection infrared spectrometer for testing, to obtain a spectrum X with an absorption peak in a wavelength range of 4000 to 680 cm^{-1}. The remaining piece of sample cloth was taken, and the sample cloth was wiped with a cotton ball dipped in a carbon tetrachloride reagent, and then applied on a potassium bromide crystal for testing to obtain a spectrum Y.

2) Data analysis

[0043] According to the spectrum X, there were characteristic absorption peaks at 1725 cm^{-1}, 1250 cm^{-1}, 1200-1150 cm^{-1} and 1125-1100 cm^{-1}, and strong absorption peaks between 1725 cm^{-1} and 1200-1150 cm^{-1}, indicating the presence of an acrylic compound; there were characteristic absorption peaks near 2953.1 cm^{-1}, 2921.0 cm^{-1}, 2853.3 cm^{-1}, 1456.9 cm^{-1}, 1376.9 cm^{-1}, and 722.7 cm^{-1}, among which there were strong absorption peaks near 2953.1 cm^{-1} and 2921.0 cm^{-1}, indicating the presence of a paraffin compound; there were a weak absorption band near 1420 cm^{-1}, a sharp strong absorption peak near 1265-1270 cm^{-1}, as well as strong wide absorption bands near 1087 cm^{-1} and 1020 cm^{-1}, indicating the presence of a polysiloxane compound B; and there were characteristic absorption peaks near 1563 cm^{-1} and 816 cm^{-1}, indicating the presence of an isocyanate compound.

[0044] According to the spectrum Y, there were a weak absorption peak near 1458 cm^{-1}, and sharp strong absorption peaks near 827 cm^{-1}, 1091 cm^{-1}, 1193 cm^{-1}, 2840 cm^{-1}, and 2941 cm^{-1}, indicating the presence of a polysiloxane compound A. There were a weak absorption peak in a range of 1200-700 cm^{-1}, a strong absorption peak at 2960-2850 cm^{-1}, and an absorption peak in a range of 1275-1020 cm^{-1}, indicating the presence of polyols.

(4) Qualitative analysis of polyol having a structure of formula 1

1) Sampling

[0045] A 10 g piece of sample cloth was cut into pieces and put into a reactor, wherein treatment conditions were as follows: the temperature was 250-340°C and the pressure was 50-150 KPa; and under the catalysis of an alkali metal hydroxide (such as sodium hydroxide), a mixture containing a polyol was obtained. The mixture containing the polyol was extracted and separated with an organic solvent, N,N-dimethylformamide, and dried to obtain polyol crystals.

2) Testing

[0046] The polyol crystals separated and extracted above were analyzed by element analysis using an EDS spectrometer (model: OXFORD INSTRUMENTS Xplore); an infrared spectrum was obtained using the Fourier transform attenuated total reflection infrared spectrometer, and a carbon spectrum (^{13}C NMR) and a hydrogen spectrum (^{1}H NMR) were obtained using a nuclear magnetic resonance spectrometer (model: Bruker AVANCE 600), to determine whether a polyol containing the structure of Formula 1 was present.

(5) Water repellency

[0047] According to the spray method in JIS L 1092:2009 criteria.

(6) Washing

[0048] Washing for 100 times according to the method 103 of JIS L 0217:1995 criteria or the method C4M of JIS L 1930:2014 criteria.

(7) Hand feel

[0049] The stiffness of the textile was tested according to JIS L 1096 2010: Method A (cantilever method). The lower the stiffness value is, the softer the textile is.

[0050] The resins used in the following examples and comparative examples were as follows:

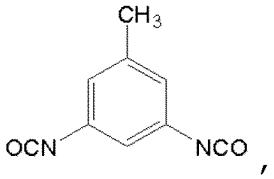
(1) Water repellent A: A copolymer of a hydrocarbon compound and a polysiloxane compound, with the trade name of RUCO-DRY DHT and the manufacturer of Rudolf Chemical.
(2) Water repellent B: Polysiloxane, with the trade name of NEOSEED NR-8800, and the manufacturer of NICCA

Chemical (China) Co., Ltd.

(3) Water repellent C: pyridine quaternary ammonium salt, with the trade name of PF, and the manufacturer of Changsha Jianglong Chemical Technology Co., Ltd.

(4) Crosslinker A: a self-made polymer formed from an aromatic isocyanate compound and a polyol, wherein:

a structural formula of the aromatic isocyanate compound was:



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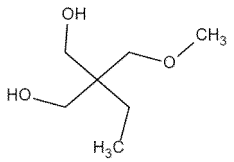
a structural formula of the polyol was:



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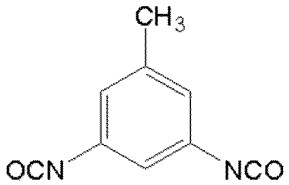
(5) Crosslinker B: aliphatic isocyanate, with the trade name of FB-12, and the manufacturer of Shanghai Siwo Polymer Materials Co., Ltd.

(6) Crosslinker C: aromatic isocyanate (excluding polyols), with the trade name of XDI, and the manufacturer of Mitsui Chemicals Inc.

(7) Crosslinker D: melamine, with the trade name of M-3, and the manufacturer of DIC Corporation.

(8) Crosslinker E: a self-made polymer formed from an aromatic isocyanate compound and a polyol, wherein:

a structural formula of the aromatic isocyanate compound was:



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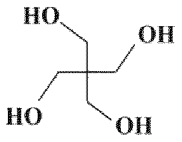
a structural formula of the polyol was:



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(9) Softener A: polysiloxane, with the trade name of S-1723, and the manufacturer of Nantong Dongrou Industry and Trade Co., Ltd.

(10) Softener B: polyethylene, with the trade name of RUCO-LUB KSA, and the manufacturer of Rudolf Chemical Co., Ltd.

(11) Penetrant: isopropanol, with the trade name of TEXPORT BG-2, and the manufacturer of Zhejiang NICCA Chemical Co., Ltd.

EMBODIMENT 1

[0051] A piece of 100% plain woven grey cloth containing polyester fibers with a density of 200 × 170 fibers/inch was selected, and then subjected to conventional pretreatment (desizing and degreasing), dyeing (disperse dye at 130°C × 45

min), intermediate setting (170°C × 1min), and post-finishing to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

[0052] Wherein, the specific conditions of the post-finishing process were as follows: one dipping and one padding were adopted, wherein the pickup rate was about 80%, then heat treatment was performed at a temperature of 130°C for 2 min, and finally shaping and finishing were performed at 170°C for 1 min. A dipping and padding processing solution was composed of the following components:

water repellent A	70 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 2

[0053] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent A	100 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 3

[0054] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent A	70 g/L
crosslinker B	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 4

[0055] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent A	70 g/L
crosslinker A	30 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 5

[0056] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent B	70 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 6

[0057] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent C	70 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 7

[0058] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1

water repellent A	70 g/L
crosslinker A	30 g/L
softener B	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 8

[0059] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 1.

water repellent A	150 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 9

[0060] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	30 g/L
crosslinker A	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 10

[0061] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker A	10 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 11

[0062] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker A	50 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 12

[0063] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker A	30 g/L
softener A	30 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 13

[0064] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker C	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

EMBODIMENT 14

[0065] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain the water-repellent textile of the present invention. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker E	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

COMPARATIVE EXAMPLE 1

[0066] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain a water-repellent textile. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

COMPARATIVE EXAMPLE 2

[0067] A dipping and padding solution was composed of the following components, with the rest being the same as in Example 1, to obtain a water-repellent textile. The test results of various properties were shown in Table 2.

water repellent A	70 g/L
crosslinker D	30 g/L
softener A	10 g/L
penetrant	10 g/L

the rest being water.

[Table 1]

			Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4	Embodiment 5	Embodiment 6	Embodiment 7	Embodiment 8
Base cloth	Fiber type		Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester
Treatment solution	Water repellent	Type	A	A	A	A	B	C	A	A
		Amount (g/L)	70	100	70	70	70	70	70	150
	Crosslinker	Type	A	A	B	A	A	A	A	A
		Amount (g/L)	30	30	30	30	30	30	30	30
	Softener	Type	A	A	A	-	A	A	B	A
		Amount (g/L)	10	10	10		10	10	10	10
Textile	Thickness of resin film (nm)	Not washed	80	90	80	80	70	75	60	95
		Washed for100 times	50	80	40	50	50	45	50	65
	Water repellency (level)	Not washed	5	5	5	5	5	5	5	5
		Washed for100 times	4	4	3	4	3	3	4	4
	Hand feel	Stiffness (mm)	49	58	48	56	46	48	48	60

[Table 2]

			Embodiment 9	Embodiment 10	Embodiment 11	Embodiment 12	Embodiment 13	Embodiment 14	Comparative example 1	Comparative example 2
Base cloth	Fiber type		Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester
Treatment solution	Water repel-lent	Type	A	A	A	A	A	A	A	A
		Amount (g/L)	30	70	70	70	70	70	70	70
	Crosslinker	Type	A	A	A	A	C	E	-	D
		Amount (g/L)	30	10	50	30	30	30		30
	Softener	Type	A	A	A	A	A	A	A	A
		Amount (g/L)	10	10	10	30	10	10	10	10
Textile	Thickness of resin film (nm)	Not washed	60	80	80	80	80	70	60	80
		Washed for100 times	40	40	55	50	50	45	20	30
	Water repel-lency (level)	Not washed	5	5	5	4	5	5	5	5
		Washed for100 times	3	3	4	3	3	2	2	2
	Hand feel	Stiffness (mm)	43	40	52	46	45	50	38	48

[0068] According to Table 1 and Table 2,

(1) it can be seen from Embodiment 1 and Embodiment 3 that, under the same conditions, the water-repellent textile processed with the crosslinker generated by the reaction of a polyol and aromatic isocyanate was compared with the water-repellent textile processed with an aliphatic isocyanate crosslinker, both of which had comparable water repellency and hand feel before being washed, but the water repellency of the former after being washed for 100 times was better than that of the latter.

(2) It can be seen from Embodiment 1 and Embodiment 4 that, under the same conditions, the water-repellent textile processed with the softener was compared with the water-repellent textile processed without the softener, both of which had comparable water repellency before and after being washed, but the former had better hand feel than that of the latter.

(3) It can be seen from Embodiment 1 and Embodiment 5 that, under the same conditions, the water-repellent textile processed with the water repellent formed from a copolymer of the hydrocarbon compound and the polysiloxane compound was compared with the water-repellent textile processed with a polysiloxane water repellent, both of which had comparable water repellency before being washed, but the water repellency of the former after being washed for 100 times was better than that of the latter although the hand feel of the former was slightly worse than that of the latter.

(4) It can be seen from Embodiment 1 and Embodiment 6 that, under the same conditions, the water-repellent textile processed with the water repellent formed from a copolymer of the hydrocarbon compound and the polysiloxane compound was compared with the water-repellent textile processed with the pyridine quaternary ammonium salt water repellent, both of which had comparable water repellency and hand feel before being washed, but the water repellency of the former after being washed for 100 times was better than that of the latter.

(5) It can be seen from Embodiment 1 and Embodiment 14 that, under the same conditions, the water-repellent textile processed with the crosslinker A (containing a polyol having a structure of formula 1) was compared with the water-repellent textile processed with the crosslinker E (not containing a polyol having a structure of formula 1), both of which had comparable water repellency and hand feel before being washed, but the water repellency of the former after being washed for 100 times was far better than that of the latter.

(6) It can be seen from Comparative Example 1 and Example 13 that, under the same conditions, the textile processed without a crosslinker was compared with the textile processed with an aromatic isocyanate crosslinker (not containing a polyol), wherein the former had better water repellency and hand feel before being washed, but only had the water repellency of level 2 after being washed for 100 times.

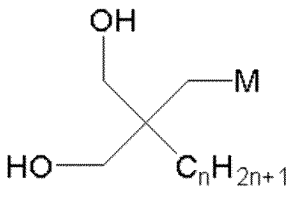
(7) It can be seen from Comparative Example 2 and Embodiment 13 that, under the same conditions, the textile processed with a melamine crosslinker was compared with the textile processed with the aromatic isocyanate crosslinker (not containing a polyol), wherein the former had better water repellency before being washed, but only had the water repellency of level 2 after being washed for 100 times.

Claims

1. A water-repellent textile, wherein the surface of a single fiber constituting the textile is covered with a resin film with a thickness of 60 to 100 nm, and main components of the resin film are a non-fluorinated water-repellent compound and an isocyanate compound.

2. The water-repellent textile according to claim 1, wherein the isocyanate compound is a polymer formed from aromatic multifunctional isocyanate and a polyol.

3. The water-repellent textile according to claim 2, wherein the polyol has a structure shown in formula 1,

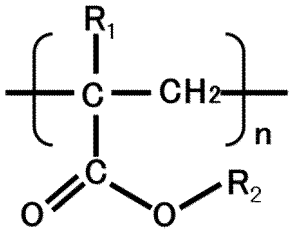


formula 1

wherein M is an H atom, alkyl, Alkoxy group, hydroxyl, Hydroxyalkyl group or carbonyl; and $2 \leq n \leq 16$.

4. The water-repellent textile according to claim 1, wherein the non-fluorinated water-repellent compound is a hydrocarbon compound, a polysiloxane compound A or a copolymer thereof.

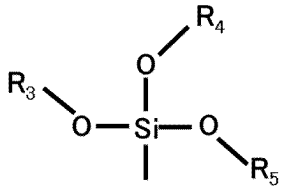
5. The water-repellent textile according to claim 4, wherein the hydrocarbon compound is an acrylate compound having a structural unit shown in formula 2,



formula 2

wherein R_1 and R_2 are alkyl or unsaturated hydrocarbon groups, respectively; and
$2 \leq n \leq 200$.

6. The water-repellent textile according to claim 4, wherein the polysiloxane compound A is a compound having a structure shown in formula 3,



formula 3

wherein R_3, R_4, and R_5 are alkyl or unsaturated hydrocarbon groups, respectively.

7. The water-repellent textile according to claim 1, wherein the resin film comprises a flexible compound, and the flexible compound is a polyethylene compound and/or a polysiloxane compound B.

8. The water-repellent textile according to any one of claims 1 to 7, wherein the resin film has a thickness of 40 to 100 nm after being washed for 100 times according to the method 103 in JIS L 0217:1995 criteria or the method C4M in JIS L 1930:2014 criteria.

9. The water-repellent textile according to any one of claims 1 to 7, wherein the initial water repellency of the textile is level 4 or above according to a test using the spray method in JIS L 1092:2009 criteria.

10. The water-repellent textile according to any one of claims 1 to 7, wherein the textile has a water repellency of level 3 or above after being washed for 100 times according to the method 103 in JIS L 0217:1995 criteria or the method C4M in JIS L 1930:2014 criteria, and then tested according to the spray method in JIS L 1092:2009 criteria.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/113969

A. CLASSIFICATION OF SUBJECT MATTER

D06M15/564(2006.01)i; D06M15/643(2006.01)i; D06M13/513(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)

IPC:D06M15/-; D06M13/-

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)

CJFD, CNTXT, ENTXTC, VCN: 纺织品, 织物, 丙烯酸酯, 多元醇, 异氰酸酯, 芳香族, 防水, 拒水, 憎水, 共聚, 硅烷, 硅氧烷, 厚度, 纳米, 三羟甲基??烷, 三羟甲基丙烷, Textile, fabric, fiber, thickness, water, resist+, reject+, repell+, proof+, isocyanate, polyatomic, alcohol, polybasic, isocyanate, trimethylolpropane, aromatic, acrylic, ester, polyorganosiloxane, polysiloxane, nano+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2019065443 A (DAIWABO HOLDINGS CO., LTD. et al.) 25 April 2019 (2019-04-25) description, paragraphs 9-51	1-10
Y	CN 103174025 A (TORAY FIBERS & TEXTILES RESEARCH LABORATORIES (CHINA) CO., LTD.(TFRC)) 26 June 2013 (2013-06-26) description, embodiment 2	1-10
Y	JP 2015165056 A (TEIJIN FRONTIER CO., LTD.) 17 September 2015 (2015-09-17) description, paragraphs 3-4 and 9-11	4
A	CN 107447523 A (TORAY FIBERS & TEXTILES RESEARCH LABORATORIES (CHINA) CO., LTD.(TFRC)) 08 December 2017 (2017-12-08) entire document	1-10
A	JP 2006328624 A (NICCA CHEMICAL CO., LTD.) 07 December 2006 (2006-12-07) entire document	1-10
A	JP 2020200456 A (NICCA CHEMICAL CO., LTD.) 17 December 2020 (2020-12-17) entire document	1-10

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

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"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	Date of mailing of the international search report
26 October 2023	**03 November 2023**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/113969

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2022011640 A (SHOWA DENKO MATERIALS CO., LTD.) 17 January 2022 (2022-01-17) entire document	1-10

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/113969

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CN 107447523 A	08 December 2017	None	
JP 2006328624 A	07 December 2006	JP 4996875 B2	08 August 2012
JP 2020200456 A	17 December 2020	None	
JP 2022011640 A	17 January 2022	None	

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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- GB T60402002 A **[0042]**