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(54) **STAINPROOF FIBER STRUCTURE**

(57) Provided is a fiber structure having high adhesion suppressibility against aqueous soil and oily soil and soil removability in washing. A soil resistant fiber structure includes a resin film on at least a part of a fiber surface, the resin film containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component, the fiber structure having a water repellency degree of 2 or less as measured by a spray test in accordance with JIS L-1092, and an oil repellency degree of 2 or more as measured in accordance with AATCC 118 method. The fluorine-based oil-repellent resin is preferably a fluorine-based oil-repellent resin containing a polyoxyalkylene group. The polyvinyl alcohol preferably has an average polymerization degree of 200 to 1500.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a fiber structure having high soil resistance.

BACKGROUND ART

10 **[0002]** Conventionally, there has been a high demand for improving the soil resistance of fiber structures of fabrics such as woven or knitted fabrics, and various methods for improving the soil resistance have been proposed. Studies have been conducted on methods for imparting soil resistance to a fiber structure, and in general, examples thereof include: a processing method in which a hydrophilic resin is added to a fiber structure to enhance affinity with a washing liquid, so that soil is easily washed out; and a processing technique in which a water-repellent and oil-repellent resin is added to a fiber structure to suppress adhesion of soil to the fiber.

15 **[0003]** However, addition of a hydrophilic resin to the fiber structure has the problem that when aqueous soil adheres, the soil is apt to expand greatly. Further, addition of a water-repellent and oil-repellent resin to a fiber structure has the problem that affinity between a washing liquid and aqueous soil is reduced due to water repellency, so that once adhering, soil is hardly washed out, and the fiber structure is easily soiled again.

20 **[0004]** In view of these problems, an attempt has been made to add to the fiber a water-repellent and oil-repellent resin containing a hydrophilic group for satisfying both resistance to adhesion of soil and ease of washing out soil.

[0005] Patent Documents 1 and 2 suggest a water-absorbing and oil-repellent soil resistance processing method in which a film of a fluorine-based water repellent having a hydrophilic component is formed.

[0006] Patent Document 3 suggests a water-repellent and oil-repellent soil resistance processing method in which a fluorine-based water repellent to a fiber fabric using a non-blocking-type water-dispersed isocyanate crosslinking agent.

25 **[0007]** Patent Document 4 suggests a water-repellent and oil-repellent soil resistance processing method in which a film of a mixture of a polymer composed of a triazine ring-containing polymerizable monomer and a fluorine-based water repellent having a hydrophilic component is formed on a surface of single fiber.

30 **[0008]** Patent Document 5 suggests Patent Documents 1 and 2 suggest a low-water-repellent and oil-repellent soil resistance processing method in which a film of a fluorine-based water repellent having a hydrophilic component, whose mass concentration ratio of oxygen atoms to fluorine atoms is adjusted, is formed.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

35 **[0009]**

Patent Document 1: Japanese Patent Laid-open Publication No. 2006-152508

Patent Document 2: Japanese Patent Laid-open Publication No. 2014-163030

40 Patent Document 3: Japanese Patent Laid-open Publication No. 2013-36136

Patent Document 4: Japanese Patent No. 5114946

Patent Document 5: International Publication No. WO 2017/006849

SUMMARY OF THE INVENTION

45 PROBLEMS TO BE SOLVED BY THE INVENTION

[0010] However, the processing methods suggested in Patent Documents 1 and 2 have the problem that because of high hydrophilicity, aqueous soil is apt to expand once the soil adheres.

50 **[0011]** The processing method suggested in Patent Document 3 has the problem that since high water repellency is exhibited, affinity between a washing liquid and aqueous soil during washing tends to be reduced, leading to deterioration of soil removability in washing, and in particular, soil removability after processing is low. The processing method suggested in Patent Document 4 has the problem that since a large amount of a polymer composed of a triazine ring-containing polymerizable monomer, fluororesin and hydrophilic components are buried, so that sufficient soil resistant cannot be exhibited.

55 **[0012]** The processing method suggested in Patent Document 5 ensures high washing durability, but has the problem that soil resistance after processing may be low.

[0013] Accordingly, in view of the above-described problems of the prior art, an object of the present invention is to

provide a fiber structure having both adhesion suppressibility against aqueous soil and oily soil and soil removability even after being repeatedly washed after processing.

SOLUTIONS TO THE PROBLEMS

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[0014] The present invention employs the following means for solving the problems described above.

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(1) A soil resistant fiber structure comprising a film on at least a part of a fiber surface, the film containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component, the soil resistant fiber structure having a water repellency degree of 2 or less as measured by a spray test in accordance with JIS L-1092, and an oil repellency degree of 2 or more as measured in accordance with AATCC 118 method.

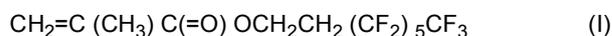
(2) The soil resistant fiber structure according to (1), wherein the fluorine-based oil-repellent resin having a hydrophilic component is a fluorine-based oil-repellent resin containing a polyoxyalkylene group.

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(3) The soil resistant fiber structure according to (1) or (2), in which the polyvinyl alcohol has an average polymerization degree of 200 to 1500.

(4) The soil resistant fiber structure according to any one of (1) to (3), wherein the fluorine-based oil-repellent resin contains a repeating unit derived from a vinyl fluoride monomer represented by a following general formula (I), and has a perfluorooctanoic acid and perfluorooctanesulfonic acid content below a detection limit.

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(5) The soil resistant fiber structure according to any one of (1) to (4), wherein the fluorine-based oil-repellent resin, polyvinyl alcohol, and a triazine ring-containing resin are added to a surface of the fiber structure.

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(6) The soil resistant fiber structure according to any one of (1) to (5), wherein a soil removability degree of the fiber structure in a soil removability test for pressed soil is 3 to 4 or more until after industrial washing is performed 50 times.

(7) A garment comprising the fiber structure according to any one of (1) to (6).

(8) A method for producing a soil resistant fiber structure, the method including treating a fiber structure with a treatment liquid containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component (hereinafter, sometimes referred to as "treatment liquid containing a soil resistant resin").

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EFFECTS OF THE INVENTION

[0015] According to the present invention, it is possible to stably provide a fiber structure having high soil resistance.

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[0016] The soil resistant fiber structure of the present invention includes on at least a part of a fiber surface a resin film containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component. Thus, oily soil difficult to wash out is inhibited from adhering to the fiber, and affinity with a washing liquid during washing is enhanced, so that the fiber structure has both adhesion suppressibility against aqueous soil and oily soil and soil removability even after being repeatedly washed after processing.

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EMBODIMENT OF THE INVENTION

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[0017] A soil resistant fiber structure of the present invention includes a film on at least a part of a fiber surface, the film containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component, the fiber structure having a water repellency degree of 2 or less as measured by a spray test in accordance with JIS L-1092, and an oil repellency degree of 2 or more as measured in accordance with AATCC 118 method.

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[0018] Since the oil repellency degree is 2 or more, sufficient oil repellency is exhibited, so that soil hardly adheres to the fiber. Further, the oil repellency degree is preferably 5 or more. Since the water repellency degree is 2 or less, sufficient hydrophilicity is exhibited, and thus affinity can be maintained between the fiber and a washing liquid, so that the washing liquid can penetrate the inside of the fiber structure without being repelled during washing, and come into contact with soil to remove the soil.

[0019] That is, the present invention provides a low-water-repellent and oil-repellent fiber structure which has reduced water repellency and has oil repellency, and is thus capable of exhibiting high soil resistance. Further, washing durability can be improved by performing control so that the water repellency degree falls within a more appropriate range of low water repellency.

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[0020] The oil repellency of the fiber structure is a value determined in accordance with AATCC 118 method (2013), and the water repellency degree of the fiber structure is a value determined by a spray method in accordance with JIS L 1092, "Testing Methods for Water Resistance of Textiles" (2009) .

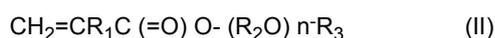
[0021] As the fluorine-based oil-repellent resin having a hydrophilic component and polyvinyl alcohol in the present

invention, a fluorine-based oil-repellent resin and polyvinyl alcohol are preferably used which ensure that the oil repellency degree is 2 or more and the water repellency degree is 2 or less when a film containing the fluorine-based oil-repellent resin and the polyvinyl alcohol is formed on a fiber surface.

[0022] The fluorine-based oil-repellent resin having a hydrophilic component is preferably a fluorine-containing copolymer having a repeating unit derived from a vinyl monomer having a perfluoroalkyl group and a vinyl monomer having a hydrophilic functional group (hydrophilic vinyl monomer).

[0023] As the vinyl monomer having a perfluoroalkyl group, a vinyl monomer having a perfluoro group having 6 or less carbon atoms is preferably used. More preferably, a vinyl monomer containing a repeating unit derived from $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{=O})\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$ is used.

[0024] Examples of the hydrophilic vinyl monomer include vinyl monomers containing a hydrophilic functional group such as a sulfonyl group, a sulfonyl base, a carboxyl group, a carboxyl base, an ammonium group, an ammonium base, an oxyalkylene group or a polyoxyalkylene group. Among them vinyl monomers represented by the following general formula (II) are preferable.



[0025] In the formula, R_1 is normally H or an alkyl group having 1 to 4 carbon atoms, preferably H or CH_3 . $-(\text{R}_2\text{O})_n-$ represents an oxyalkylene group or a polyoxyalkylene group. Normally, R_2 is preferably an alkylene group having 2 to 5 carbon atoms, more preferably CH_2CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_2$ or $\text{CH}_2(\text{CH}_3)\text{CH}_2$ from the viewpoint of ensuring that hydrophilicity can be controlled to fall within a further preferred range. R_3 normally represents H or CH_3 . n is a polymerization degree, and represents 1 to 20.

[0026] The fluorine-based oil-repellent resin that is preferably used in the present invention is preferably one having a water absorbability of 40 seconds or more as measured by a dropping method in accordance with JIS L 1907 (2010) a water repellency degree of 2 or less, and an oil repellency degree of 2 or more. Further, low water repellency corresponding to a water absorbability of 60 seconds or more is more preferable from the viewpoint of improving washing durability for soil removability against pressed soil. In addition, the oil repellency degree is more preferably 7 or less from the viewpoint of a balance between resistance to adhesion of soil and affinity with washing water.

[0027] The ratio of the vinyl monomer having a perfluoroalkyl group and the hydrophilic vinyl monomer in the fluorine-containing copolymer which is preferably used is not limited as long as the ratio satisfies the range specified in the present invention, and it is preferable that by the following method, control is performed so as to obtain low water repellency and oil repellency and water-absorption and oil repellency. The control can be performed by the following method. That is, by increasing the ratio of the vinyl monomer containing a hydrophilic functional group, water repellency can be suppressed, and for enhancing oil repellency, the ratio of the vinyl monomer having a perfluoroalkyl group may be increased.

[0028] In addition, when the ratios of both vinyl monomers are the same, the hydrophilicity of the vinyl monomer containing a hydrophilic functional group may be enhanced. As a method for reducing water repellency, the ratio of the hydrophilic functional group can be increased, or a functional group having higher hydrophilicity can be selected as the hydrophilic functional group. The hydrophilic functional group is preferably an oxyalkylene group (more preferably an oxyethylene group) or a polyoxyalkylene group (more preferably a polyoxyethylene group). When a polyoxyalkylene group is used, hydrophilicity can be enhanced as the polymerization degree thereof is increased.

[0029] It is also possible to increase oil repellency by increasing the number of carbon atoms of the perfluoroalkyl group in the vinyl monomer having a perfluoroalkyl group.

[0030] The fluorine-based oil-repellent resin having a hydrophilic component satisfying the above-described condition is preferably one that exhibits performance classified as that of a so-called water-absorbing and oil-repellent type with a water repellency degree of 2 or less (preferably 1), an oil repellency degree of 2 or more and a water absorbability of less than 40 seconds or a low-water-repellent and oil-repellent type with a water repellency degree of 2 or less, an oil repellency degree of 2 or more and a water absorbability of 40 seconds or more, particularly preferably one classified as a low-water-repellent and oil-repellent type, when the resin is added to the fiber structure. Examples of the commercially available product include "PARAZINE" KFS-100 (manufactured by KEIHIN CHEMICAL CO., LTD.) which is classified as a low-water-repellent and oil-repellent type, and "PARAZINE" KFS-150 (manufactured by KEIHIN CHEMICAL CO., LTD.) which is classified as a water-absorbing and oil-repellent type. Even a fluorine-based water-repellent resin of high-water-repellent and oil-repellent type can be used as long as it satisfies the range specified in the present invention, but caution is required because it is difficult to perform control to satisfy the range specified in the present invention when the water repellency degree and oil repellency of the resin are extremely high.

[0031] Preferably, the fluorine-based oil-repellent resin has a perfluorooctanoic acid and perfluorooctanesulfonic acid content below a detection limit. The term "below a detection limit" means that the concentration of each of perfluorooctanoic acid and perfluorooctanesulfonic acid, precursors thereof and salts thereof measured with the following high-performance liquid chromatograph-mass spectrometer (LC-MS) is each less than 5 ng/g.

[0032] Instruments: LC-MS/MS tandem mass spectrometer TSQ-7000 (Thermo Electron)
 high performance liquid chromatograph LC-10Avp (Shimadzu Corporation)
 Column: Capcellpak C8 100mm × 2mm i.d. (5 μ m)

Moving bed: A; 0.5 mmol/L ammonium acetate B; acetonitrile

Flow rate: 0.2 mL/min

Sample injection volume: 3 μ L

CP temperature: 220°C

Ionization voltage: 4.5kv

Ion multi: 1300v

Ionization method: ESI-Negative

The average polymerization degree of polyvinyl alcohol is normally 100 to 3,500, preferably 200 to 1500.

[0033] Polyvinyl alcohol may be produced by saponifying polyvinyl acetate. The saponification degree of polyvinyl alcohol is, normally, preferably 70 to 99%, more preferably 80 to 95%.

[0034] The average polymerization degree and the saponification degree are values obtained by performing measurement in accordance with JIS K 6726 (1994), paragraphs 3.7 and 3.5, respectively.

[0035] In the present invention, the fluorine-based oil-repellent resin and polyvinyl alcohol are used at a ratio such that the amount of polyvinyl alcohol is normally 5 to 60 parts by mass, preferably 10 to 40 parts by mass, based on 100 parts by mass of the solid content of the fluorine-based oil-repellent resin.

[0036] The polyvinyl alcohol used in the present invention may contain a functional group other than a hydroxyl group or acetate group. Examples of the functional group include an acetoacetyl group, a sulfonyl group, a sulfonyl base, a carboxyl group, a carboxyl base, a quaternary ammonium base, an oxyalkylene group, a polyoxyalkylene group, an alkyl group, an alkenyl group, an alkynyl group and a phenyl group.

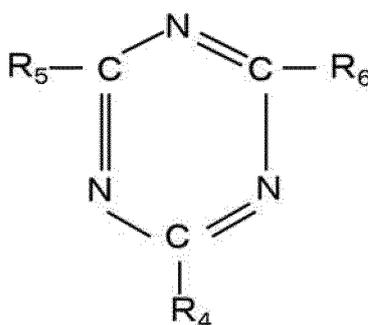
[0037] The solid content amount of the fluorine-based oil-repellent resin and polyvinyl alcohol fixed to the fiber is 0.2 to 1.0% by mass, preferably 0.4 to 0.8% by mass. It is preferable that the solid content amount is in a favorable range as described above because soil removal performance can be sufficiently exhibited, and the texture is soft.

[0038] In the present invention, in addition to the fluorine-based oil-repellent resin having a hydrophilic component and polyvinyl alcohol, other resins, and agents such as compounds can be used in combination.

[0039] It is particularly preferable to use a triazine ring-containing resin as the resin from the viewpoint of washing durability for soil resistant. Examples of the triazine ring-containing resin include melamine resins, guanamine resins and bismaleimide triazine resins, and melamine resins are particularly preferably used.

[0040] The triazine ring-containing resin means a resin including a triazine ring-containing compound as a polymerization component, and the triazine ring-containing compound is a compound containing a triazine ring and having at least two polymerizable functional groups. Examples thereof include triazine ring-containing compounds represented by the following structural formula.

[Chemical Formula 1]



where R₄ to R₆ each represent H, OH, C₆H₅, C_{n0}H_{2n0+1} (n₀ = 1 to 2), COOC_{n1}H_{2n1+1} (n₁ = 1 to 20), CONR₇R₈ or NR₇R₈; where R₇ and R₈ each represent H, OC_{n3}H_{2n3+1} (n₃ = 1 to 20), CH₂COOC_{n3}H_{2n3+1} (n₃ = 1 to 20), CH₂OH, CH₂CH₂OH, CONH₂ or CONHCH₂-O-(X-O)_{n4}-R₉ (X = C₂H₄, C₃H₆, or C₄H₈; n₄ = 1 to 1500; R₉ = H, CH₃ or C₃H₇).

[0041] In addition to the triazine ring-containing compound represented by the above general formula, ethylene urea copolymer compounds, dimethylol urea copolymer compounds, dimethylol thiourea copolymer compounds, acid colloid compounds and the like of the above-described compounds can be used.

[0042] The method for forming a triazine ring-containing resin is as follows. An aqueous liquid including the triazine ring-containing compound and a catalyst are added onto the fiber, heat treatment is carried out to perform polymerization.

[0043] Examples of the catalyst to be used include acids such as acetic acid, formic acid, acrylic acid, malic acid, tartaric acid, maleic acid, phthalic acid, sulfuric acid, persulfuric acid, hydrochloric acid and phosphoric acid, and ammonium salts, sodium salts, potassium salts and magnesium salts of these acids, and one or more of these compounds can be used. Among them, ammonium persulfate and potassium persulfate are preferably used as the catalyst. The amount of the catalyst is preferably 0.1 to 20% by mass based on the amount of the monomer used.

[0044] The heat treatment for such polymerization is preferably dry heat treatment and steaming heat treatment performed at a temperature of 50 to 200°C, preferably 80 to 150°C, for 0.1 to 30 minutes. The amount of the triazine ring-containing resin deposited is preferably 10 to 100% by mass, more preferably 20 to 60% by mass, based on the total weight of the fluorine-based oil-repellent resin having a hydrophilic component and polyvinyl alcohol.

[0045] When subjected to "Soil Removability Test For Pressed Soil" conforming to method C using components of lipophilic contaminant-3 specified in JIS L 1919 (2006), "Soil Removability Test", the soil resistant fiber structure of the present invention has a soil removability degree of preferably 3 to 4 or more, more preferably 4 or more, after industrial washing is performed 50 times after processing.

[0046] Examples of the fiber raw material to be used in the soil resistant fiber structure of the present invention include synthetic fibers such as fibers composed of polyalkylene terephthalates such as polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate; aromatic polyester-based fibers obtained by copolymerizing the above-mentioned resins with a third component; aliphatic polyester-based fibers composed of aliphatic polyester such as polylactic acid typified by one containing L-lactic acid as a main component; polyamide-based fibers composed of polyamides such as nylon 6 and nylon 66; acryl-based fibers containing polyacrylonitrile as a main component; polyolefin-based fibers composed of polyolefins such as polyethylene and polypropylene; polyvinyl chloride-based fiber; semisynthetic fibers such as acetate fiber and rayon fiber; and natural fibers such as cotton fiber, silk fiber and wool fiber. In the present invention, one of these fibers can be used alone, or two or more of these fibers can also be used as a mixture. Among them, mixtures of natural fibers such as cotton fiber, silk fiber and wool fiber with fibers containing polyester-based fiber or polyamide-based fiber as a main component or fibers containing polyester-based fiber or polyamide-based fiber as a main component are preferably used. Here, the main component refers to fiber, the content of which is the highest among the contained components. Preferably, the main component is contained in an amount of 50% by mass or more.

[0047] The fibers used in the soil resistant fiber structure of the present invention may be ordinary flat yarns, or filament yarns such as false-twisted yarns, twisted yarns, Taslan processed yarns, nanofibers, slub yarns and blended yarns, and various other modes of yarns such as staple fibers, tows and spun yarns can be used. Preferably, filament yarns are used.

[0048] In addition, the single fiber cross-sectional shape of the fiber used in the soil resistant fiber structure of the present invention is not particularly limited, and fibers in various forms such as circles, triangles, flat shapes and multilobal shapes can be used. Preferably, fibers having a circular cross-sectional shape are preferably used.

[0049] The soil resistant fiber structures of the present invention include fabric-like materials such as knitted fabrics, woven fabrics and nonwoven fabrics and string-like materials which are formed using the aforementioned fibers. Preferably, knitted fabrics, woven fabrics and non-woven fabrics are used.

[0050] In addition, a general processing agent such as a fluorescent dye or a softening agent may be added to the aforementioned fabric-like material or the string-like material. Fiber internally modified with an antibacterial agent or a bacteriostatic agent may be used as a raw material for the soil resistant fiber structure. Examples of the processing agent include pyridine-based compounds such as 2-chloro-6-trichloromethylpyridine, 2-chloro-4-trichloromethyl-6-methoxy pyridine, 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine, di(4-chlorophenyl)pyridylmethanol, 2,3,5-trichloro-4-(n-propylsulfonyl)pyridine, 2-pyridylthiol-1-oxide zinc and di(2-pyridylthiol-1-oxide) can be used.

[0051] In addition, for the fabric-like material or the string-like material, fiber may be used on which a resin other than a fluorine-based oil-repellent resin having a hydrophilic component and polyvinyl alcohol, etc. (hereinafter, referred to collectively as a "soil resistant resin", and a film containing the resin is sometimes referred to as a "soil resistant resin layer") is deposited. Here, a resin layer other than the soil resistant resin layer is formed on the fiber, and the soil resistant resin layer is subsequently formed, so that two resin layers are present on the fiber. Examples of the resin other than the soil resistant resin include silicone resins, polyester resins, isocyanate compounds, epoxy resins, melamine resins, guanamine resins and bismaleimide triazine resins.

[0052] In addition, fiber modified by crosslinking may be used, and as a crosslinking agent to be used for modification by crosslinking, a compound is preferably used which is capable of forming a crosslinked structure between cellulose molecules and in cellulose molecules by reacting with hydroxyl groups in cellulose molecules forming cellulose-based fiber, particularly hydroxyl groups present in amorphous regions that cause creases, loss of shape and shrinkage. Specific examples thereof include formaldehyde, dimethylol ethylene urea, dimethyloltriazone, dimethyloluron, dimethylol glyoxal monourene, dimethylol propylene urea, fibrin reactive resins such as those obtained by methoxylating or ethoxylating some or all of methylol groups of the above-mentioned compounds, polycarboxylic acids and isocyanates.

[0053] In the present invention, fixation of the resin to the fiber structure can be performed by treating the fiber structure

with a treatment liquid containing raw materials such as a soil resistant resin, a triazine ring-containing resin as an optional component or a polymerizable monomer for obtaining the triazine ring-containing resin, and a catalyst. Specific treatment methods include a pad-dry-cure method in which a fiber structure is immersed in a treatment liquid containing an soil resistant resin, squeezed with a certain pressure in a spread state, and then heat-treated; a pad-cure method in which a fiber structure is immersed in a treatment liquid containing an soil resistant resin, squeezed with a certain pressure in a spread state, and then heat-treated; a pad-steam method in which a fiber structure is immersed in the manner described above, and steaming heat treatment is then performed; and a bathing method in which a fiber structure is heated in a state of being immersed in a treatment liquid containing the above-described soil resistant resin. Among them, methods that are preferably used include a pad-dry-cure method in which a fiber structure is immersed in a treatment liquid containing an soil resistant resin, then squeezed with a certain pressure in a spread state, dried at a temperature of preferably 80 to 170°C, and then heat-treated at a temperature of preferably 170 to 200°C; a pad-cure method in which a fiber structure is instantaneously dried at a temperature of 170 to 200°C; a pad steam method in which steaming heat treatment is performed at a temperature of 80 to 110°C; and a bathing method in which a fiber structure is heated to a temperature of preferably 50 to 130°C in a state of being immersed in a treatment liquid containing the soil resistant resin. Further, a pad-dry-cure method is most preferably used in which a fiber structure is dried at a temperature of 120°C to 170°C, and then heat-treated at 170 to 200°C.

[0054] The soil resistant fiber structure thus obtained includes a resin film containing polyvinyl alcohol. Thus, oily soil difficult to wash out is inhibited from adhering to the fiber, and affinity with a washing liquid during washing is enhanced, so that the fiber structure has both adhesion suppressibility against aqueous soil and oily soil and soil removability even after being repeatedly washed after processing. Therefore, the soil-resistant fiber structure can be suitably used for general clothing, work uniforms, bedclothing, medical garments, interior articles, industrial material products and the like.

EXAMPLES

[0055] The soil resistant fiber structure of the present invention will now be described on the basis of examples. Various measurement and evaluation items in examples are as follows.

(Water repellency)

[0056] Evaluation was made by the spray method specified in JIS L 1092 "Testing Methods for Water Resistance of Textiles" (2009), to determine the water repellency degree. The water repellency degree was determined by making evaluation three times (n = 3). The water repellency degree ranges from 1 to 5, and a higher value shows higher water repellency. The water repellency degree is determined on the basis of assessment photographs attached to JIS L 1092.

(Oil repellency)

[0057] Measurement was made by the method specified in AATCC 118 method, to determine the oil repellency degree. The oil repellency degree ranges from 1 to 8, and a higher value shows higher oil repellency. The oil repellency degree is determined on the basis of assessment photographs attached to AATCC 118 method. The oil repellency degree was defined as an average of values obtained by making evaluation three times (n = 3).

(Industrial washing conditions in soil removal test)

[0058] Single industrial washing for washing durability and soil removability in the soil removal test was performed under the following conditions and in the following order.

1. Washing (water temperature: 60°C, bath ratio: 1:10, time: 15 minutes)
Detergent: Phosphorus-Free Dash (manufactured by Lion Corporation) 2.0g/L
Sodium metasilicate 2.0g/L
CLEWAT N (manufactured by Nagase ChemteX Corporation) 1.0g/L
2. Water removal (time: 1 minute)
3. Rinse 1 (water temperature: 50°C, bath ratio: 1:10, time: 3 minutes)
4. Water removal (time: 1 minute)
5. Rinse 2 (water temperature: 35°C, bath ratio: 1:10, time: 3 minutes)
6. Water removal (time: 1 minute)
7. Rinse 3 (normal water temperature, bath ratio: 1:10, time: 3 minutes)
8. Water removal (time: 1 minute)
9. Tumble drying

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(Soil removability test for pressed soil)

[0059] For the fiber structure after industrial washing under the above-described conditions was performed 50 times and the fiber structure before the washing, pressed soil removability performance was evaluated in accordance with JIS L 1919, "Testing Methods for Soil Resistance of Textiles" (2006), Method C. A contaminant (oil red fraction: 0.1%) was prepared using components of lipophilic contaminant-3 specified in JIS L 1919, "Testing Methods for Soil Resistance of Textiles" (2006), Method C.

1. A PET film was placed on a square-shaped filter paper, and a fabric cut to 8 cm × 8 cm was placed on the PET film. 0.1 mL of oily soil was dropped from a height of 10 cm, and the fabric was left standing for 30 seconds.

2. On a soiled fabric, a PET film cut to the same size as the that of the fabric was placed, and a load of 4 g/cm² was applied onto the PET film for 30 seconds. The load and the film were removed, a circular filter paper was then placed to absorb the soil by the filter paper under its self-weight. Further, the filter paper was displaced, so that the soil was absorbed again with an unsoiled portion of the filter paper. This operation was repeated until the filter paper no longer absorbed the soil. When the filter paper did not contact the soiled portion, the filter paper was held at both ends, so that the filter paper and the soil contacted each other to absorb the soil while the applied load was minimized. Thereafter, the fabric was left standing for 24 hours at a temperature of 20°C and a relative humidity of 65%. After the fabric was left standing, the soiled fabric was sewed to a size of about 40 cm × 40 cm, and washed. When there was not enough fabric, waste fabric was sewed up.

3. The SR degree was determined with the naked eye in accordance with JIS L 0805 (2005), "Gray Scale for Contamination Colors". The SR degree ranges from 1 to 5, and a higher value shows higher soil resistance. Table 1 shows equipment used in the above tests.

[Table 1]

	Base material used	Manufacturer	Remarks (consumption)
Contaminant	Olive oil	Wako Pure Chemical Industries, Ltd.	(61.5 g)
	Oleic acid	Sigma Aldrich Japan, Inc.	(37.0 g)
	Iron oxide (III) for ferrite	Wako Pure Chemical Industries, Ltd.	(1.0 g)
	Oil red	Sigma Aldrich Japan, Inc.	(0.1 g)
Test equipment	Square-shaped filter paper	ADVANTEC	600 × 600 mm, qualitative filter paper No. 2
	Circular filter paper	Sansho, Inc.	Diameter 11cm, Grade: 389 Whatman filter paper No.41φ110 1441-110 100 per unit
	OHP film	KOKUYO	OHP film, VF-1
	Load		5 cm × 5 cm, 100 g

(Evaluation of spread of soil after soil pressing)

[0060] In the above soil removability test for pressed soil, spread of soil after elapse of 24 hours after adhesion of soil was visually evaluated, and assessed in grades 1 to 5.

Grade 1: soil spreads over 80% or more of the area of a portion of the test fabric other than the soil-pressed portion.

Grade 2: soil spreads over about 50% of the area of a portion of the test fabric other than the soil-pressed portion.

Grade 3: soil spreads over about 30% of the area of a portion of the test fabric other than the soil-pressed portion.

Grade 4: soil slightly spreads over a portion other than the soil-pressed portion.

Grade 5: soil does not spread over a portion other than the soil-pressed portion.

(Example 1)

[0061] A single yarn with a count of 14, which includes 65% of polyethylene terephthalate and 35% of cotton, was

used as a warp yarn and a weft yarn to prepare a twill woven fabric. The obtained twill woven fabric was refined at a temperature of 95°C by a continuous refining machine in accordance with a conventional method, rinsed with hot water, and then dried at a temperature of 130°C. The twill woven fabric was then dyed fluorescent-white at a temperature of 130°C using a jet dyeing machine, washed by a conventional manner, washed with hot water, dried, heated at a temperature of 170°C to obtain a white fabric having a warp density of 86/2.54 cm and a weft density of 55/2.54 cm.

[0062] Components (A), (B), (H) and (I) as described later were then dissolved in amounts of 90 g/L, 18 g/L, 4.5 g/L and 0.75 g/L, respectively, to prepare a treatment liquid, the white fabric prepared as described above was immersed in a spread state in the treatment liquid, squeezed to a squeezing ratio of 60% with a mangle, dried at a temperature of 130°C, and then heated at a temperature of 170°C to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 in soil gray scale determination after processing, and a pressed soil removability degree of 4 in soil gray scale determination after industrial washing was performed 50 times.

(Example 2)

[0063] Except that with respect to Example 1, the amount of component (B) was 36 g/L, the same procedure as in Example 1 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 in soil gray scale determination after processing, and a pressed soil removability degree of 3 to 4 in soil gray scale determination after industrial washing was performed 50 times.

(Example 3)

[0064] Except that with respect to Example 1, component (C) was used in an amount of 18 g/L as polyvinyl alcohol, the same procedure as in Example 1 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 3 to 4 in soil gray scale determination after processing, and a pressed soil removability degree of 3 to 4 in soil gray scale determination after industrial washing was performed 50 times.

(Example 4)

[0065] Except that with respect to Example 1, component (D) was used in an amount of 18 g/L as polyvinyl alcohol, the same procedure as in Example 1 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 3 to 4 in soil gray scale determination after processing, and a pressed soil removability degree of 3 in soil gray scale determination after industrial washing was performed 50 times.

(Example 5)

[0066] A single yarn with a count of 48, which includes 65% of polyethylene terephthalate and 35% of cotton, was used as a warp yarn and a weft yarn to prepare a plain woven fabric. The obtained plain woven fabric was refined at a temperature of 95°C by a continuous refining machine in accordance with a conventional method, rinsed with hot water, and then dried at a temperature of 130°C. The plain woven fabric was then dyed fluorescent-white at a temperature of 130°C using a jet dyeing machine, washed by a conventional manner, washed with hot water, dried, heated at a temperature of 170°C to obtain a white fabric having a warp density of 138/2.54 cm and a weft density of 72/2.54 cm.

[0067] Soil resistance processing was then performed in the same manner as in Example 1 to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 in soil gray scale determination after processing, and a pressed soil removability degree of 4 to 5 in soil gray scale determination after industrial washing was performed 50 times.

(Example 6)

[0068] Except that with respect to Example 5, the amount of component (B) was 36 g/L, the same procedure as in Example 5 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 to 5 in soil gray scale determination after processing, and a pressed soil removability degree of 4 in soil gray scale determination after industrial washing was performed 50 times.

(Example 7)

[0069] A single yarn with a count of 48, which includes 55% of polyethylene terephthalate and 45% of cotton, was used as a warp yarn and a weft yarn to prepare a plain woven fabric. The obtained plain woven fabric was refined at a temperature of 95°C by a continuous refining machine in accordance with a conventional method, rinsed with hot water,

and then dried at a temperature of 130°C. The plain woven fabric was then dyed fluorescent-white at a temperature of 130°C using a jet dyeing machine, washed by a conventional manner, washed with hot water, dried, heated at a temperature of 170°C to obtain a white fabric having a warp density of 115/2.54 cm and a weft density of 72/2.54 cm.

5 [0070] Soil resistance processing was then performed in the same manner as in Example 1 to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 in soil gray scale determination after processing, and a pressed soil removability degree of 4 to 5 in soil gray scale determination after industrial washing was performed 50 times.

10 (Example 8)

[0071] Except that with respect to Example 7, the amount of component (B) was 36 g/L, the same procedure as in Example 7 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 in soil gray scale determination after processing, and a pressed soil removability degree of 4 to 5 in soil gray scale determination after industrial washing was performed 50 times.

15 (Example 9)

20 [0072] Except that with respect to Example 1, the amount of component (B) was 54 g/L, the same procedure as in Example 1 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 4 to 5 in soil gray scale determination after processing, and a pressed soil removability degree of 2 to 3 in soil gray scale determination after industrial washing was performed 50 times.

(Example 10)

25 [0073] Except that with respect to Example 1, component (E) was used in an amount of 90 g/L as a fluorine-based oil-repellent resin, the same procedure as in Example 1 was carried out to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 3 to 4 in soil gray scale determination after processing, and a pressed soil removability degree of 2 to 3 in soil gray scale determination after industrial washing was performed 50 times.

30 (Comparative Example 1)

35 [0074] Except that with respect to Example 1, component (B) was not used, the same procedure as in Example 1 was carried out to obtain a low-water-repellent and oil-repellent soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 2 to 3 in soil gray scale determination after processing, and a pressed soil removability degree of 3 to 4 in soil gray scale determination after industrial washing was performed 50 times.

(Comparative Example 2)

40 [0075] Except that with respect to Example 1, component (A) was not used, the same procedure as in Example 1 was carried out to obtain a fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 1 to 2 in soil gray scale determination after processing, and a pressed soil removability degree of 2 in soil gray scale determination after industrial washing was performed 50 times.

45 (Comparative Example 3)

50 [0076] Except that with respect to Comparative Example 1, component (E) was used in an amount of 90 g/L as a fluorine-based oil-repellent resin, the same procedure as in Comparative Example 1 was carried out to obtain a water-absorbing soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 3 to 4 in soil gray scale determination after processing, and a pressed soil removability degree of 2 to 3 in soil gray scale determination after industrial washing was performed 50 times. Pressed soil spread over a larger area as compared to Example 8.

(Comparative Example 4)

55 [0077] The white fabric obtained in Example 1 was immersed in a treatment liquid prepared by dissolving components (F), (H) and (J) in amounts of 45 g/L, 15 g/L and 3.0 g/L, respectively, and the white fabric was squeezed to a squeezing ratio of 60% using a mangle, and treated in a saturated water vapor atmosphere at 105°C for 5 minutes. The white fabric

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was then washed in an aqueous solution containing sodium carbonate at 1 g/L at 60°C for 1 minute, rinsed with water, dried at a temperature of 130°C, and then heated at a temperature of 170°C to obtain a soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 3 in soil gray scale determination after processing, and a pressed soil removability degree of 3 in soil gray scale determination after industrial washing was performed 50 times.

(Comparative Example 5)

[0078] Except that with respect to Comparative Example 1, component (G) was used in an amount of 90 g/L instead of fluorine-based oil-repellent resin (A), the same procedure as in Comparative Example 1 was carried out to obtain a water-absorbing and oil-absorbing soil resistant fiber structure. The obtained soil resistant fiber structure had a pressed soil removability degree of 2 to 3 in soil gray scale determination after processing, and a pressed soil removability degree of 2 to 3 in soil gray scale determination after industrial washing was performed 50 times.

(A) "PARAZINE" KFS-100 (manufactured by KEIHIN CHEMICAL CO., LTD., fluorine-based oil-repellent resin of low-water-repellent and oil-repellent type, solid content: 10%, containing a polyoxyethylene group, water repellency degree: 2, oil repellency degree: 6, water absorbability: 60 seconds or more)

(B) Polyvinyl alcohol (solid content: 10%, average polymerization degree: 500, saponification degree: 90%)

(C) Polyvinyl alcohol (solid content: 10%, average polymerization degree: 1500, saponification degree: 90%)

(D) Polyvinyl alcohol (solid content: 10%, average polymerization degree: 2000, saponification degree: 90%)

(E) "PARAZINE" KFS-150 (manufactured by KEIHIN CHEMICAL CO., LTD., fluorine-based resin of water-absorbing and oil-repellent type, solid content: 10%, containing a polyoxyethylene group, water repellency degree: 1, oil repellency degree: 6, water absorbability: 30 seconds)

(F) "AsahiGuard" AG-1100 (manufactured by Asahi Glass Co., Ltd., fluorine-based resin of high-water-repellent and oil-repellent type, solid content: 20%, containing a polyoxyethylene group, water repellency degree: 3, oil repellency degree: 6, water absorbability: 60 seconds or more)

(G) "BRIAN" SR2100 (manufactured by Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 10%, hydrophilic polyester resin, water repellency degree: 1, oil repellency degree: 0, water absorbability: 1 second or less)

(H) "AMIDIR" M-3 (triazine ring-containing compound manufactured by DIC Corporation, solid content: 80%)

(I) "CATALYST" ACX (catalyst manufactured by DIC Corporation, solid content: 35%)

(J) Ammonium persulfate

[0079] Table 2 shows the compositions of the treatment liquids (A) to (J) and the results of performance etc. of obtained fiber structures in Examples 1 to 8 and Comparative Examples 1 to 5.

[Table 2-1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	
With soil resistance	A	90	90	90	90	90	90	90	90		
	B	18	36			18	18	36	54	18	
	C			18							
	D				18						
	E									90	
	F										
	G										
	H	5	5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
	I	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
	J										
Water repellency degree (grade)	Before washing	2	2	2	2	2	2	2	2	1	
	After washing	1	1	1	1	1	1	1	1	1	
Oil repellency degree (grade)	Before washing	6	6	6	6	6	6	6	4-5	6	
	After washing	2	2	2	2	2	2	2	1	1	
Soil removability against pressed soil (grade)	Before washing	4	4	3-4	3-4	4	4	4	4-5	3-4	
	After washing	4	3-4	3-4	3	4-5	4	4-5	2-3	2-3	
Evaluation of spread of soil after soil pressing (grade)	Before washing	5	5	5	5	5	5	5	5	4	
	After washing	4	4	4	3	4	4	4	3	2	

[Table 2-2]

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	
With soil resistance	90					
Composition of treatment liquid (g/L)	A					
	B	18				
	C					
	D					
	E		90			
	F			45		
	G				90	
	H	4.5	4.5	4.5	15	4.5
	I	0.75	0.75	0.75		0.75
	J				3.0	
Water repellency degree (grade)	Before washing	1	1	1	1	
	After washing	1	1	1	1	
Oil repellency degree (grade)	Before washing	0	6	6	0	
	After washing	0	1	2	0	
Soil removability against pressed soil (grade)	Before washing	1-2	3-4	3	2-3	
	After washing	2	2-3	3	2-3	
Evaluation of spread of soil after soil pressing (grade)	Before washing	1	3	5	1	
	After washing	1	1	4	1	

[0080] Table 2 reveals that in each of Examples 1 to 10 as the fiber structures of the present invention, pressed soil was easily repelled, an area over which soil spread was small, and soil hardly adhered. In addition, excellent soil removability against pressed soil was exhibited. On the other hand, in Comparison Examples 1 to 5 as soil resistant fiber structures different from those of the present invention, soil removability against pressed soil was lower as compared to examples. It was possible to improve washing durability for soil resistance in Example 9 where a larger amount of polyvinyl alcohol was added, or by optimizing the amount of polyvinyl alcohol added. By improving washing durability, the functionality can be maintained even after repeated washing, and the life of clothing can be extended.

INDUSTRIAL APPLICABILITY

[0081] The soil resistant fiber structure of the present invention has both high adhesion suppressibility against aqueous soil and oily soil and soil removability in washing, and is therefore suitably used for general clothing, work uniforms, bedclothing, medical garments, interior articles, industrial material products and the like. In particular, the soil resistant fiber structure is suitably used as a work uniform which is apt to suffer adhesion of oily soil difficult to wash out, and thus needs to have soil resistance performance.

Claims

1. A soil resistant fiber structure comprising a resin film on at least a part of a fiber surface, the resin film containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component, the soil resistant fiber structure having a water repellency degree of 2 or less as measured by a spray test in accordance with JIS L-1092, and an oil repellency degree of 2 or more as measured in accordance with AATCC 118 method.
 2. The soil resistant fiber structure according to claim 1, wherein the fluorine-based oil-repellent resin is a fluorine-based oil-repellent resin containing a polyoxyalkylene group.
 3. The soil resistant fiber structure according to claim 1 or 2, wherein the polyvinyl alcohol has an average polymerization degree of 200 to 1500.
 4. The soil resistant fiber structure according to any one of claims 1 to 3, wherein the fluorine-based oil-repellent resin contains a repeating unit derived from a vinyl fluoride monomer represented by a following general formula (I), and has a perfluorooctanoic acid and perfluorooctanesulfonic acid content below a detection limit.
- $$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(=\text{O})\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3 \quad (\text{I})$$
5. The soil resistant fiber structure according to any one of claims 1 to 4, wherein the fluorine-based oil-repellent resin, polyvinyl alcohol, and a triazine ring-containing resin are added to a surface of the fiber structure.
 6. The soil resistant fiber structure according to any one of claims 1 to 5, wherein a soil removability degree of the fiber structure in a soil removability test for pressed soil is 3 to 4 or more until after industrial washing is performed 50 times.
 7. A garment comprising the fiber structure according to any one of claims 1 to 6.
 8. A method for producing a soil resistant fiber structure, the method comprising treating a fiber structure with a treatment liquid containing polyvinyl alcohol and a fluorine-based oil-repellent resin having a hydrophilic component.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/037209

5 A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D06M15/277 (2006.01) i, A41D31/00 (2006.01) i,
D06M15/333 (2006.01) i, D06M15/423 (2006.01) i
According to International Patent Classification (IPC) or to both national classification and IPC

10 B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. D06M15/277 (2006.01) i, A41D31/00 (2006.01) i,
D06M15/333 (2006.01) i, D06M15/423 (2006.01) i

15 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 1971-2018
Registered utility model specifications of Japan 1996-2018
Published registered utility model applications of Japan 1994-2018

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.
20 X Y	JP 50-94293 A (TOYOBO BOSEKI KABUSHIKI KAISHA) 26 July 1975, claims, page 2, upper left column, line 6 to upper right column, line 4, page 2, upper right column, line 14 to lower right column, line 1, page 3, upper right column, lines 1-5, examples 2, 3 (Family: none)	1-3, 7-8 4-6
25 Y	WO 2017/006849 A1 (TORAY INDUSTRIES, INC.) 12 January 2017, paragraph [0036] & US 2018/0179699 A1, paragraph [0042] & EP 3321418 A1 & CN 107735525 A & KR 10-2018-0022647 A	4
30 Y	JP 2008-163475 A (TORAY INDUSTRIES, INC.) 17 July 2008, claim 1, paragraph [0010] (Family: none)	5-6

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

* Special categories of cited documents:
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 "P" document published prior to the international filing date but later than the priority date claimed
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 "&" document member of the same patent family

50 Date of the actual completion of the international search 12 December 2018 (12.12.2018)
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55 Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/037209

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-330354 A (OHARA PARAGIUM CHEMICAL CO., LTD.) 02 December 2005, claims 1, 5, 6, paragraph [0029] (Family: none)	1-8
A	JP 2001-525010 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 04 December 2001, claims 1-7, 11, examples & WO 1998/051727 A1, claims 1-7, 11, examples & US 6383633 B1 & EP 981567 A1 & DE 69801002 T & AU 7796298 A & BR 9808776 A & CN 1255932 A	1-8

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2006152508 A [0009]
- JP 2014163030 A [0009]
- JP 2013036136 A [0009]
- JP 5114946 B [0009]
- WO 2017006849 A [0009]

Non-patent literature cited in the description

- Testing Methods for Water Resistance of Textiles. *JIS L 1092*, 2009 [0056]
- Testing Methods for Soil Resistance of Textiles. *JIS L 1919*, 2006 [0059]
- Gray Scale for Contamination Colors. *JIS L 0805*, 2005 [0059]