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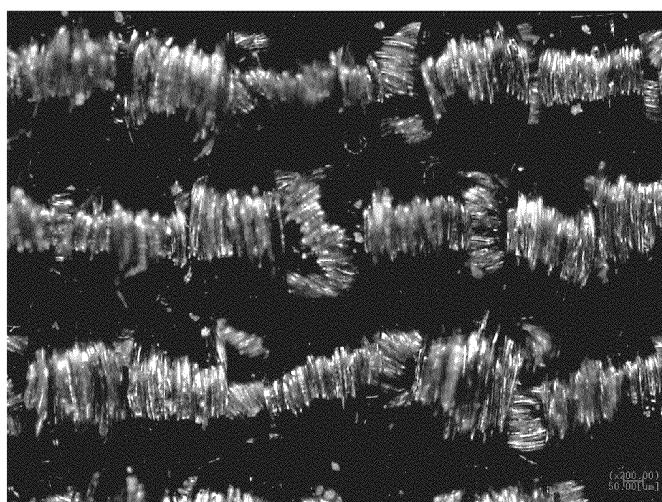
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(54) **MODIFIED FIBER AND METHOD FOR MANUFACTURING SAME**

(57) A modified fiber of the present invention has high abrasion resistance under wet conditions and high washing resistance. The modified fiber is a modified fiber in which an epoxy compound is bonded to a refined cellu-

lose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber, the epoxy compound being at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether.

FIG.1



**Description**

## TECHNICAL FIELD

**[0001]** The present invention relates to a modified fiber and a method for producing the modified fiber. More specifically, the invention relates to a modified fiber and a method for producing the modified fiber in which an epoxy compound is bonded to a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber.

## BACKGROUND ART

**[0002]** Silk fibers, which are known to have a unique gloss and a smooth texture, are in widespread use as high-grade fibers. Refined cellulose fibers and cuprammonium rayon are regenerated cellulose fibers made to imitate the silk fibers, and have a gloss and a texture similar to those of the silk fibers. Representative examples of such regenerated cellulose fibers include the refined cellulose fibers "TENCEL®" and "Lyocell®" sold from Lenzing, the cuprammonium rayon "Bemberg®" sold from Asahi Kasei Fibers Corporation, and the like.

**[0003]** While the silk fibers and the regenerated cellulose fibers are highly usable for clothing and the like, they are poor in properties such as chemical resistance, crease resistance, dimensional stability, and abrasion resistance. It is known that after repeated washing, the silk fibers and the regenerated cellulose fibers undergo fibrillation of fibers due to friction under wet conditions, which causes deterioration of the feel and texture or a whitening phenomenon (hereinafter also referred to as "white blurring").

**[0004]** Thus, various attempts have heretofore been made to improve the above-mentioned properties. Japanese Examined Patent Publication No. 47-024199 (PTD 1), for example, proposes a method for obtaining a fiber with high chemical resistance, wherein a fiber is treated in a bath containing both a neutral salt catalyst and an epoxy compound. Moreover, Hideki Shiozaki, "The present and future status of washable silk", Processing Technology, 1989, Vol. 24, No. 2, pp. 74-77 (NPD 1) proposes a method for obtaining a processed silk yarn with little fuzz, wherein a silk yarn is heat-treated in an aqueous solution containing an ethylene glycol-based epoxy compound.

## CITATION LIST

## PATENT DOCUMENT

**[0005]** PTD 1: Japanese Examined Patent Publication No. 47-024199

## NON PATENT DOCUMENT

**[0006]** NPD 1: Hideki Shiozaki, "The present and future status of washable silk", Processing Technology, 1989, Vol. 24, No. 2, pp. 74-77

## SUMMARY OF INVENTION

## TECHNICAL PROBLEM

**[0007]** In NPD 1 described above, however, no specific epoxy compound is disclosed, and the abrasion resistance of the silk fiber produced in PTD 1 is also unclear. No satisfactory technology is yet available for improving the abrasion resistance of a refined cellulose fiber, cuprammonium rayon, and a silk fiber, and the development of advanced technologies is currently ongoing.

**[0008]** The present invention was made to solve the aforementioned circumstances, and an object of the invention is to provide a modified fiber and a method for producing the modified fiber having high abrasion resistance under wet conditions and having high washing resistance.

## SOLUTION TO PROBLEM

**[0009]** The present inventors conducted extensive research to solve the aforementioned problem. Consequently, they conceived that silk fibers can be provided with high abrasion resistance by cross-linking an epoxy compound having two epoxy groups, within silk fibroin. Based on this idea, the inventors also conducted research on cellulose fibers and rayon, thus completing the present invention.

**[0010]** The present invention provides a modified fiber in which an epoxy compound is bonded to a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber. In the modified fiber, the epoxy compound is

at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether.

[0011] Preferably, the modified fiber further contains a quaternary ammonium salt.

[0012] The present invention also provides a method for producing the modified fiber. The method includes immersing a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, or rayon in a treatment solution containing an epoxy compound, and bonding the epoxy compound to the refined cellulose fiber, the natural cellulose fiber, the cuprammonium rayon, the rayon, or the silk fiber. In the method, the epoxy compound is at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether.

[0013] Preferably, the treatment solution further contains a quaternary ammonium salt.

## ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The modified fiber of the present invention has high abrasion resistance, and in particular, exhibits excellent abrasion resistance under wet conditions. The modified fiber of the present invention also has an extremely small dimensional change between dry conditions and wet conditions, and thus, has high washing resistance. Further, the production method of the present invention allows the modified fiber having the above-described properties to be produced.

[0015] In this specification, the degree of abrasion resistance represents an index indicating the unlikelihood of the fiber to have fuzz or white blurring. Silk fibers tend to have low abrasion resistance because when fibers scratch or rub against one another, they tend to break into fibrils (small fibers), and consequently, the silk fibers are likely to have fuzz or white blurring. Improving the abrasion resistance of the silk fibers makes the silk fibers unlikely to have fuzz or white blurring.

[0016] The term "bath ratio" represents an index indicating the ratio of the treatment solution (ml) relative to the weight (g) of the fiber. For example, when 5 g of the silk fiber is treated in 100 ml of the treatment solution, the bath ratio is 1:20. When 5 g of the silk fiber is treated in 200 ml of the treatment solution, the bath ratio is 1:40. That is, at a bath ratio of 1:20, the amount of the treatment solution relative to the weight of the silk fiber is smaller than that at a bath ratio of 1:40, and hence, the bath ratio of 1:20 is lower than the bath ratio of 1:40.

[0017] With regard to the weight ratio, for example, when the weight of a substance A is 5 g and the weight of a substance B is 0.5 g, the weight ratio of substance B relative to substance A is calculated according to the expression: the weight of substance B/the weight of substance A 100, and therefore, the value is 10%.

## BRIEF DESCRIPTION OF DRAWINGS

### [0018]

Fig. 1 is an image showing a surface condition of silk crepe produced in Example 1 after a friction test.

Fig. 2 is an image showing a surface condition of the silk crepe produced in Example 1 after a washing test.

Fig. 3 is an image showing a surface condition of silk crepe produced in Example 2 after a friction test.

Fig. 4 is an image showing a surface condition of the silk crepe produced in Example 2 after a washing test.

Fig. 5 is an image showing a surface condition of silk crepe produced in Comparative Example 1 after a friction test.

Fig. 6 is an image showing a surface condition of the silk crepe produced in Comparative Example 1 after a washing test.

Fig. 7 is an image showing a surface condition of 6-momme *Habutai* silk produced in Example 3 after a friction test.

Fig. 8 is an image showing a surface condition of 6-momme *Habutai* silk produced in Example 4 after a friction test.

Fig. 9 is an image showing a surface condition of 6-momme *Habutai* silk produced in Comparative Example 2 after a friction test.

Fig. 10 is an image showing a surface condition of a knit knitted with a spun silk yarn produced in Example 13 after a friction test.

Fig. 11 is an image showing a surface condition of the knit knitted with the spun silk yarn produced in Example 13 after a washing test based on the 103 method.

Fig. 12 is an image showing a surface condition of a knit knitted with a spun silk yarn produced in Comparative Example 7 after a friction test.

Fig. 13 is an image showing a surface condition of the knit knitted with the spun silk yarn produced in Comparative Example 7 after a washing test based on the 103 method.

Fig. 14 is an image showing a condition of staple of a treated refined cellulose fiber produced in Example 14 after a fibrillation resistance test.

Fig. 15 is an image showing a condition of staple of a treated refined cellulose fiber produced in Example 15 after a fibrillation resistance test.

Fig. 16 is an image showing a condition of staple of a treated refined cellulose fiber produced in Comparative

Example 8 after a fibrillation resistance test.

Fig. 17 is an image showing a condition of staple of a treated refined cellulose fiber produced in Comparative Example 9 after a fibrillation resistance test.

Fig. 18 is an image showing a condition of staple of a treated refined cellulose fiber produced in Comparative Example 10 after a fibrillation resistance test.

Fig. 19 is an image showing a condition of staple of treated cuprammonium rayon produced in Example 16 after a fibrillation resistance test.

Fig. 20 is an image showing a condition of staple of cuprammonium rayon produced in Comparative Example 11 after a fibrillation resistance test.

Fig. 21 is an image showing a condition of staple of a treated silk fiber produced in Example 17 after a fibrillation resistance test.

Fig. 22 is an image showing a condition of staple of a silk fiber produced in Comparative Example 12 after a fibrillation resistance test.

## DESCRIPTION OF EMBODIMENTS

**[0019]** The modified fiber of the present invention will be described in detail below.

<Modified Fiber>

**[0020]** The modified fiber of the present invention is a modified fiber in which an epoxy compound is bonded to a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber.

« Refined Cellulose Fiber »

**[0021]** The refined cellulose fiber used as a base material of the modified fiber of the present invention is one type of a regenerated cellulose fiber. The fiber is obtained by spinning a material obtained by dissolving wood pulp or the like in an organic solvent or the like, filtering the solution, and removing impurities. Representative examples of the refined cellulose fiber include "TENCEL®" and "Lyocell®". The refined cellulose fiber is excellent in terms of strength since it does not undergo derivatization of the raw material cellulose by chemical decomposition. Instead of the refined cellulose, a natural cellulose may be used as the base material of the modified fiber of the present invention. The natural cellulose fiber is, for example, cotton, hemp, or the like.

« Cuprammonium Rayon »

**[0022]** Cuprammonium rayon used as a base material of the modified fiber of the present invention is one type of a regenerated fiber. The fiber is obtained by spinning a material obtained by dissolving cotton extracted from cotton linters in cuprammonium solution (Schweitzer's solution), filtering the solution, and removing impurities. A representative example of cuprammonium rayon may be "Bemberg®". Rayon can also be used as a base material of the modified fiber of the present invention.

« Silk Fiber »

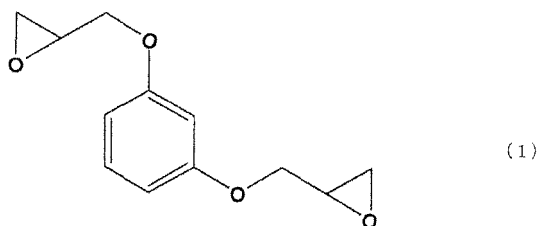
**[0023]** The silk fiber can also be used as a base material of the modified fiber of the present invention. Examples of the silk fiber include a woven silk fabric, a knitted silk fabric, a silk yarn, a spun silk yarn, silk staple, and the like. Moreover, the woven silk fabric includes a plain weave and a twill weave, as well as a fiber structure with a three-dimensional structure obtained by twisting, such as silk crepe.

**[0024]** It is noted that each of the refined cellulose fiber, the natural cellulose fiber, the cuprammonium rayon, and the rayon described above also includes a woven fabric, a knitted fabric, a long-fibered yarn, a spun yarn, staple, and the like. The fabric includes a plain weave and a twill weave, as well as a fiber structure with a three-dimensional structure obtained by twisting, such as silk crepe.

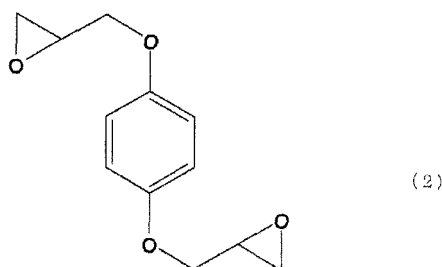
« Epoxy Compound »

**[0025]** The epoxy compound is at least any one of resorcinol diglycidyl ether (hereinafter also denoted as "RDGE") represented by chemical formula (1) below and hydroquinone diglycidyl ether (hereinafter also denoted as "HDGE") represented by the chemical formula (2) below. That is, in the modified silk fiber, either one or both of RDGE and HDGE may be bonded.

[Chemical Formula 1]



[Chemical Formula 2]



**[0026]** The modified fiber of the present invention has high abrasion resistance. When the weight ratio of the epoxy compound relative to the fiber is not smaller than 0.7%, and more preferably, not smaller than 1.8%, the modified fiber can have sufficiently high abrasion resistance. Even if the weight ratio of the epoxy compound relative to the fiber is not greater than 5%, the modified fiber can have sufficiently high abrasion resistance. This allows prevention of deterioration of the feel and texture caused by bonding excess epoxy compound to the fiber.

**[0027]** The reason why the modified fiber of the present invention has high abrasion resistance despite the fact that the above-described weight ratio of RDGE and/or HDGE is significantly lower than that of another epoxy compound, for example, the weight ratio of the epoxy compound relative to the fiber described in PTD 1 above is not clear in detail. The inventors, however, assume the reason to be as follows.

**[0028]** When the fiber to be modified is a silk fiber, each of RDGE and HDGE, which has two epoxy groups in one molecule, can be cross-linked within silk fibroin. Therefore, even if the above-described weight ratio is low, that is, the amount of bonded epoxy compound in the modified fiber is small, silk fibroin can have a sufficiently strong structure. As a result, the modified fiber can be provided with high abrasion resistance. Moreover, because each of RDGE and HDGE has a phenyl group within their molecule, each of RDGE and HDGE can form a large number of bonds with the tyrosine group having a chemically similar structure, within silk fibroin. As a result, the structure of silk fibroin can be stabilized efficiently.

**[0029]** When the fiber to be modified is a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, or rayon, it is believed that the fiber is cross-linked with the two epoxy groups of each of RDGE and HDGE, starting from a functional group such as a hydroxy group within their molecule as the start point. The cross-linking causes fibrils within the fiber to be bound together, filling a fine gap present between fibrils. This reduces the number of start points where, upon application of friction, the fiber is torn into a plurality of fibrils. As a result, abrasion resistance can be improved.

#### «Quaternary Ammonium Salt»

**[0030]** The modified fiber of the present invention, which has a quaternary ammonium salt, can have further improved abrasion resistance. Examples of the quaternary ammonium salt include a quaternary ammonium salt with a chlorohydrin group, a quaternary ammonium salt with an epoxy group, a quaternary ammonium salt with a triazine group, polyallylamine, and polyethyleneimine. For example, 3-chloro-2-hydroxypropyltrimethylammonium chloride, 2,3-epoxypropylmethylammonium chloride, monochloroethyl-diethylamine, glycidyltrimethylammonium chloride, and the like can be used. A polyquaternary ammonium salt or the like may also be used. Among the above, 3-chloro-2-hydroxypropyltrimethylammonium chloride and 2,3-glycidyltrimethylammonium chloride are preferred.

**[0031]** The inventors found that the modified fiber of the present invention can exhibit further improved abrasion resistance when it contains the quaternary ammonium salt together with the above-described epoxy compound. While the reason why this effect can be obtained is not clear in detail, the inventors assume the reason to be as follows. The

presence of the quaternary ammonium salt promotes the cross-linking with the epoxy compound, and further strengthens the hydrogen bond and the intermolecular force between fibrils. This causes the fibrils to be bound more firmly, making it difficult for the fiber to be split into fibrils.

**[0032]** The production method of the present invention will be described in detail below.

#### <Method for Producing the Modified Fiber>

**[0033]** The production method of the present invention includes immersing the fiber in a treatment solution containing at least one of the epoxy compounds of RDGE and HDGE, and bonding the epoxy compound to the fiber.

**[0034]** Water is preferably used as the treatment solution, because of its low production cost and ease of handling. The treatment solution contains the above-described epoxy compound. In order to allow the epoxy compound to be more uniformly dispersed in the treatment solution, a dispersion in which the epoxy compound is dispersed in a dispersant such as an organic solvent, an emulsifier, or the like may be used to prepare the treatment solution. In this case, the treatment solution can be prepared, for example, by gradually adding water to a mixture of an emulsifier and the epoxy compound, so as to disperse the emulsifier and the epoxy compound in water.

**[0035]** As the dispersant, a material that does not inhibit the bonding reaction of the epoxy compound to the silk fiber is preferably used. For example, emulsifiers such as Disper VG (Meisei Chemical Works, Ltd.), Saizoru 2EX (Daiichi Kogyo Seiyaku Co., Ltd.), and BK57NM (Nikka Chemical Co, Ltd.) can be used. As the organic solvent, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or the like can be used. The treatment solution may contain other unintentional substances so long as they do not inhibit the bonding reaction of the epoxy compound to the fiber.

**[0036]** The amount of the epoxy compound added to the treatment solution is not particularly limited. The inventors, however, found that even if the concentration of the epoxy compound in the treatment solution is as low as 3% owf (the percentage of the value obtained by dividing the weight of the epoxy compound contained in the treatment solution by the weight of the fiber structure immersed in the treatment solution), the modified fiber having high abrasion resistance can be produced with good yield.

**[0037]** It is therefore preferred to prepare a treatment solution containing the epoxy compound with a weight of not smaller than 3%, based on the weight of the fiber immersed in the treatment solution. This allows the modified fiber to be efficiently produced. Further, the amount of the epoxy compound used can be appropriately restricted, thus leading to reduced production costs.

**[0038]** Advantageously, the treatment solution further contains a quaternary ammonium salt. The amount of the quaternary ammonium salt added to the treatment solution is preferably not smaller than 1 g/l and not greater than 15 g/l. The inclusion of the quaternary ammonium salt within this range promotes the cross-linking with the epoxy compound. Therefore, the amount of the epoxy compound used can be reduced, and synergistically, the abrasion resistance can be further improved. If the amount of the epoxy compound added is smaller than 1 g/l, there is a tendency that the above-described effect cannot be readily obtained, which is undesirable. In contrast, if the amount exceeds 15 g/l, the dyeing rate of the finished modified fiber will be fast, causing defects such as dyeing unevenness and the like, which is undesirable. It is noted that the method of including the quaternary ammonium salt in the treatment solution is not particularly limited. For example, the quaternary ammonium salt may be directly introduced into the above-described treatment solution containing the epoxy compound and the dispersant. Alternatively, the quaternary ammonium salt may be dispersed in advance in a solvent such as water, and then the dispersion may be introduced into the above-described treatment solution and stirred.

**[0039]** As the fiber to be immersed in the above-described treatment solution, any of a woven fabric, a knitted fabric, a long-fibered yarn, a spun yarn, and staple may be used, as stated above. For example, when a woven fabric or a knitted fabric is immersed in the above-described treatment solution to produce the modified fiber, various articles such as clothing can be efficiently manufactured with the modified fiber such as a woven fabric or a knitted fabric. Moreover, for example, when a long-fibered yarn, a spun yarn, staple, or the like is immersed to produce the modified fiber, a woven fabric or a knitted fabric can be produced with this modified fiber. The inventors found that the woven fabric or knitted fabric thus produced has not only high abrasion resistance, but also the property of being difficult to shrink.

**[0040]** The bath ratio of the fiber to be immersed in the treatment solution is not particularly limited, and may be not smaller than 1:5, for example. Particularly, when the fiber to be immersed in the treatment solution is a knitted fabric or a woven fabric, the bath ratio of the fiber is preferably not smaller than 1:15, more preferably not smaller than 1:30, and still more preferably not smaller than 1:50, in order to avoid troubles in production during the treatment. This allows prevention of scratching of the knitted fabric or the woven fabric in the treatment solution against the treatment vessel, and prevention of scratching of the knitted fabric or the woven fabric itself. Thus, the modified fiber can be produced while preventing generation of fuzz or white blurring. However, from the viewpoint of production efficiency, production costs, and the rate of the bonding reaction of the epoxy compound, it is preferred to set the bath ratio to be low, even when any of the fiber of a woven fabric, a knitted fabric, a long-fibered yarn, a spun yarn, and staple is used. As used herein, the term "not smaller than" in the context of the bath ratio means increasing the amount of the treatment solution

(ml) used relative to 1 g of the fiber.

**[0041]** Further, in the step described above, the treatment solution is preferably heated while adding, to the treatment solution in which the fiber is immersed, a catalyst for promoting bonding of the epoxy compound to the fiber. This allows the rate of the bonding reaction of the epoxy compound to be increased, and allows the epoxy compound to be bonded to the fiber with high bonding efficiency.

**[0042]** Examples of catalysts that can be used include sodium hydroxide, sodium carbonate, sodium hydrogencarbonate, tin tetrachloride, boron trifluoride, amine, and thiocyanate. Among the above, an alkaline catalyst such as sodium hydroxide, sodium hydrogencarbonate, or the like is preferably used, because of its high catalytic performance for RDGE and HDGE. The concentration of the catalyst in the treatment solution is not particularly limited, and may be adjusted as appropriate. For example, the concentration of the catalyst in the treatment solution is preferably not smaller than 5 times and not greater than 10 times higher than the concentration (mol) of the epoxy compound in the treatment solution, more preferably, not smaller than 6 times and not greater than 9 times higher, and still more preferably, 8 times higher.

**[0043]** The heating method is not particularly limited. For example, the treatment solution at room temperature (25°C) may be gradually heated to 50 to 80°C. Alternatively, the temperature of the treatment solution may be maintained at a predetermined temperature of 50 to 80°C. The heating time is not particularly limited, either, and may be not shorter than 30 minutes and not longer than 180 minutes, for example.

**[0044]** In accordance with the above-described production method, at least one of RDGE and HDGE can be bonded to silk fibroin that forms the silk fiber. The modified silk fiber in which RDGE and/or HDGE is bonded has high abrasion resistance, and has an excellent property of being resistant to fuzz and white blurring. That is, the above-described production method allows the modified silk fiber with high abrasion resistance to be produced.

**[0045]** Moreover, in accordance with the above-described production method, the modified fiber with high abrasion resistance can be produced as with the above-described silk fiber, by cross-linking a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, or rayon to the epoxy compound. Further, since the above-described treatment solution further contains a quaternary ammonium salt, abrasion resistance can be further improved.

**[0046]** As described above, in accordance with the above-described production method, since the treatment can be performed even with a high bath ratio, scratching of the fiber during the process can be effectively prevented. This allows generation of fuzz and white blurring to be prevented. Further, as described above, since the bonding efficiency of RDGE and HDGE to the fiber is high, the epoxy compound can be efficiently bonded using a small amount of the epoxy compound. As a result, production costs can be reduced.

## EXAMPLES

**[0047]** The present invention will be described below with reference to examples, which are provided for better understanding of the invention, and not for limiting the scope of the invention.

[Experiment (1): Production and Evaluation of Modified Silk Crepe]

**[0048]** First, modified silk crepe was produced, and abrasion resistance was evaluated.

(Example 1)

**[0049]** First, 0.25 g of RDGE (DENACOL EX201; manufactured by Nagase ChemteX Corporation) and 0.5 g of a dispersant (Disper VG; manufactured by Meisei Chemical Works, Ltd.) were kneaded well, and the kneaded product was accommodated in a mixing vessel. Water was then gradually added to emulsify and disperse the kneaded product, thereby preparing a treatment solution containing RDGE. The total amount of the water used was 200 ml. Next, 5 g of silk crepe (manufactured by Nagahama Chirimen Co., Ltd.) was immersed in the treatment solution prepared. The silk crepe had a basis weight of 150 g/m<sup>2</sup>. In order to achieve uniform bonding of the epoxy compound to the silk crepe, the treatment solution in which the silk crepe was immersed was stirred.

**[0050]** Then, the temperature of the treatment solution was increased from 25°C to 60°C while gradually adding a dilute sodium hydroxide aqueous solution prepared by diluting 1.25 g of 24% sodium hydroxide aqueous solution with 50 ml of water to the stirred treatment solution. Stirring of the treatment solution was then continued for another 60 minutes while maintaining the temperature of the treatment solution at 60°C.

**[0051]** The above-described treatment yielded the silk crepe in which RDGE was bonded. This silk crepe was subjected to washing treatment sequentially including washing with water, washing with 2 g/l of sodium dithionite aqueous solution (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), washing with warm water, and washing with water, and then dried to produce treated silk crepe. Here, two sheets of the treated silk crepe were produced.

(Example 2)

**[0052]** First, a product prepared by dissolving 0.25 g of HDGE (DENACOL EX203; manufactured by Nagase ChemteX Corporation) in 0.7 g of DMF and 1.7 g of a dispersant (Disper VG; manufactured by Meisei Chemical Works, Ltd.) were kneaded well, and the kneaded product was accommodated in a mixing vessel. A treatment solution was then prepared as in Example 1. Treated silk crepe was produced as in Example 1, except for the above. Here, two sheets of the treated silk crepe were produced.

(Comparative Example 1)

**[0053]** Silk crepe was treated as in Example 1, except that RDGE and a dispersant were not used. Specifically, in Comparative Example 1, although the silk crepe was subjected to the immersion treatment, the washing treatment, and the like as in Examples 1 and 2, the epoxy compound was not bonded to the silk crepe. Here, two sheets of the treated silk crepe were produced.

(Treatment of Dyeing in Blue)

**[0054]** The treated silk crepe sheets produced in Examples 1 and 2 and Comparative Example 1 were one by one dyed in blue, such that generation of white blurring can be readily observed in a friction test described below. Specifically, dyeing treatment was performed by immersing each treated silk crepe sheet in a dye solution A with the formulation given below, and by stirring for 60 minutes at 60°C. Each treated silk crepe sheet after the dyeing treatment was immersed in a washing solution containing 3 g/l of a nonionic surfactant (ECB-50; Dainichiseika Color & Chemicals Mfg. Co., Ltd.), and stirred and washed for 30 minutes at 60°C. Each treated silk crepe sheet after stirring and washing was then subjected to washing treatment sequentially including washing with warm water and washing with water, and then dried.

[Dye Solution A]

**[0055]**

|                                                     |          |
|-----------------------------------------------------|----------|
| Sumifix Brill Blue R (Sumika Chemtex Company, Ltd.) | : 7% owf |
| NEWBON MRW (Nicca Chemical Co, Ltd.)                | : 1% owf |
| Anhydrous sodium sulfate                            | : 40 g/l |
| Sodium carbonate                                    | : 4 g/l  |
| (Treatment of Dyeing in Black)                      |          |

**[0056]** The treated silk crepe sheets produced in Examples 1 and 2 and Comparative Example 1 were one by one dyed in black, such that generation of white blurring can be readily observed in a washing test described below. Specifically, dyeing treatment was performed by immersing each treated silk crepe sheet in a dye solution B with the formulation given below, and by stirring for 60 minutes at 70°C. Each treated silk crepe sheet after the dyeing treatment was immersed in a washing solution containing 5 g/l of a nonionic surfactant (ECB-50; Dainichiseika Color & Chemicals Mfg. Co., Ltd.), and stirred and washed for 30 minutes at 60°C. Each treated silk crepe sheet after stirring and washing was then subjected to washing treatment sequentially including washing with warm water and washing with water, and then dried.

[Dye Solution B]

**[0057]**

|                                                         |           |
|---------------------------------------------------------|-----------|
| Funder Riactive Black BG (Sumika Chemtex Company, Ltd.) | : 15% owf |
| NEWBON MRW (Nicca Chemical Co, Ltd.)                    | : 1% owf  |
| Anhydrous sodium sulfate                                | : 50 g/l  |
| Sodium carbonate                                        | : 20 g/l  |
| (Friction Experiment)                                   |           |

**[0058]** A friction test was performed on each treated silk crepe sheet dyed blue using the Gakushin-Type Rubbing Tester for Color Fastness (manufactured by Daiei Kagaku Seiki). Specifically, a friction cloth was used made of a cotton

cloth impregnated with an amount of water equal to the cloth weight, and the friction cloth was caused to slide over the treated silk crepe sheet 100 times in a reciprocating manner, under a load of 100 g. After the friction test, the presence of fuzz and white blurring on the friction surface of the treated silk crepe sheet was examined by observation with a microscope at 200x magnification.

#### (Washing Test)

**[0059]** A washing test was performed on each treated silk crepe sheet dyed black in accordance with the JIS L 0217 103 method, using a home electrical washing machine (manufactured by Toshiba Lifestyle Products & Services Corporation). Specifically, the treated silk crepe sheet was first introduced into the home electrical washing machine, and then a polyester cloth was introduced as a supply cloth. Next, water at 45°C was added to the home electrical washing machine such that the bath ratio of the treated silk crepe sheet would be 1:50. Then, 3 g/l of a polyoxyethylene alkyl ether-based neutral detergent (Acron; manufactured by Lion Corporation) was introduced. The washing test was performed for 50 minutes, and then the treated silk crepe sheet was dried flat. After the washing test, the presence of fuzz and white blurring on the surface of the treated silk crepe sheet was examined by observation with a microscope at 200x magnification.

#### (Results)

**[0060]** Fig. 1 shows a surface condition after the friction test, and Fig. 2 shows a surface condition after the washing test, of the treated silk crepe produced in Example 1. Fig. 3 shows a surface condition after the friction test, and Fig. 4 shows a surface condition after the washing test, of the treated silk crepe produced in Example 2. Fig. 5 shows a surface condition after the friction test, and Fig. 6 shows a surface condition after the washing test, of the treated silk crepe produced in Comparative Example 1. It is noted that each figure shows an image of the surface of each treated silk crepe sheet taken with a microscope and magnified by 200 times.

**[0061]** A comparison between Figs. 1 and 2 and Figs. 5 and 6 reveals that no fuzz or white blurring is observed in Figs. 1 and 2, whereas fuzz and white blurring are observed in Figs. 5 and 6. This result shows that the abrasion resistance of the silk crepe sheets was improved by bonding RDGE to the silk crepe sheets. Similarly, no fuzz or white blurring was observed in Figs. 3 and 4. This result shows that the abrasion resistance of the silk crepe sheets was improved by bonding HDGE as the epoxy compound to the silk crepe sheets.

#### [Experiment (2): Production and Evaluation of 6-Momme Modified *Habutai* Silk]

##### (Example 3)

**[0062]** A treated 6-momme *Habutai* silk sheet was produced as in Example 1, except that 5 g of 6-momme *Habutai* silk (manufactured by Konno Kigyojo Corporation (Fukushima Prefecture)) was used instead of 5 g of the silk crepe (manufactured by Nagahama Chirimen Co., Ltd.). The 6-momme *Habutai* silk sheet had a basis weight of 20 g/m<sup>2</sup>.

##### (Example 4)

**[0063]** A treated 6-momme *Habutai* silk sheet was produced as in Example 2, except that 5 g of the 6-momme *Habutai* silk described above was used instead of 5 g of the silk crepe (manufactured by Nagahama Chirimen Co., Ltd.).

##### (Comparative Example 2)

**[0064]** A treated 6-momme *Habutai* silk sheet was produced as in Comparative Example 1, except that 5 g of the 6-momme *Habutai* silk described above was used instead of 5 g of the silk crepe (manufactured by Nagahama Chirimen Co., Ltd.).

#### (Treatment of Dyeing in Blue and Friction Test)

**[0065]** A treated 6-momme *Habutai* silk sheet produced in each of Examples 3 and 4 and Comparative Example 2 was dyed blue in accordance with the method of the treatment of dyeing in blue as described above, and then the friction test was performed as described above.

(Results)

**[0066]** Fig. 7 shows a surface condition after the friction test of the treated 6-momme *Habutai* silk sheet produced in Example 3. Fig. 8 shows a surface condition after the friction test of the treated 6-momme *Habutai* silk sheet produced in Example 4. Fig. 9 shows a surface condition after the friction test of the treated 6-momme *Habutai* silk sheet produced in Comparative Example 2. It is noted that each figure shows an image of the surface of each treated 6-momme *Habutai* silk sheet taken at 200x magnification.

**[0067]** A comparison between Figs. 7 and 8 and Fig. 9 reveals that no fuzz or white blurring is observed in Figs. 7 and 8, whereas fuzz and white blurring are observed in Fig. 9. This result shows that the abrasion resistance of the 6-momme *Habutai* silk was improved by bonding RDGE thereto.

[Experiment (3): Consideration of the Epoxy Compound]

**[0068]** Experiments (1) and (2) above reveal that the abrasion resistance of the silk fiber structure is improved by bonding each of RDGE and HDGE to a silk fiber structure such as silk crepe and 6-momme *Habutai* silk. Here, the above-described effect obtained with RDGE and HDGE was compared to effects obtained by bonding other epoxy compounds.

(Example 5)

**[0069]** A treated silk crepe sheet was produced as in Example 1, except that 0.4 g of RDGE (DENACOL EX201; manufactured by Nagase ChemteX Corporation) and 0.5 g of a dispersant (Disper VG; manufactured by Meisei Chemical Works, Ltd.) were kneaded well.

(Example 6)

**[0070]** A treated silk crepe sheet was produced as in Example 2, except that 0.4 g of HDGE (DENACOL EX203; manufactured by Nagase ChemteX Corporation) was dissolved in 0.7 g of DMF.

(Comparative Example 3)

**[0071]** A treated silk crepe sheet was produced as in Example 1, except that 0.4 g of diethylene glycol diglycidyl ether (Epilight 100E; manufactured by Kyoeisha Chemical Co., Ltd.) was used instead of RDGE.

(Comparative Example 4)

**[0072]** A treated silk crepe sheet was produced as in Example 1, except that 0.4 g of glycerol polyglycidyl ether (DENACOL EX313; manufactured by Nagase ChemteX Corporation) was used instead of RDGE. The glycerol polyglycidyl ether is a mixture of glycerol diglycidyl ether and glycerol triglycidyl ether.

(Comparative Example 5)

**[0073]** A treated silk crepe sheet was produced as in Example 1, except that 0.4 g of 1,6-hexanediol diglycidyl ether (DENACOL EX212; manufactured by Nagase ChemteX Corporation) was used instead of RDGE.

(Comparative Example 6)

**[0074]** A treated silk crepe sheet was produced as in Example 1, except that 0.4 g of hydrogenated bisphenol A diglycidyl ether (Epilight 4000; manufactured by Kyoeisha Oil & Fat Chemical Co., Ltd.) was used instead of RDGE.

(Treatment of Dyeing in Blue and Friction Test)

**[0075]** The treated silk crepe sheet produced in each of Examples 5 and 6 and Comparative Examples 3 to 6 was dyed blue in accordance with the method of the treatment of dyeing in blue as described above. The friction test was then performed as described above, and the surface of the treated silk crepe sheet to which friction was applied was observed with a microscope.

## (Results)

**[0076]** No fuzz and white blurring was observed on the surface of the treated silk crepe sheet produced in each of Examples 5 and 6 after the friction test. In contrast, fuzz and white blurring were observed on the surface of the treated silk crepe sheet produced in each of Comparative Examples 3 to 6 after the friction test. This result shows that the silk crepe sheets in which RDGE or HDGE was bonded have abrasion resistance higher than the silk fibers in which the conventional epoxy compounds were bonded.

**[0077]** Further, despite the fact that the epoxy compounds used in Comparative Examples 3 to 6 are indicated to have the effect of modifying the silk fiber in PTD 1 and NPD 1, fuzz and white blurring were observed after the friction test in this consideration. One reason therefor is believed to be, for example, as follows.

**[0078]** In this consideration, the bath ratio of the silk crepe in the treatment solution is as high as 1:40 to 1:50. Moreover, the concentration of the epoxy compound in the treatment solution is as low as 8% owf, and the concentration of the epoxy compound relative to the solution is as low as 2 g/l. Under such treatment conditions, the epoxy compound used in each of Comparative Examples 3 to 6 cannot be sufficiently bonded to silk fibroin of the silk crepe, and as a result, the modified silk crepe sheet produced cannot have abrasion resistance.

## [Experiment (4): Consideration of the Amount of Epoxy Compound Added]

**[0079]** The result of the experiment (3) above reveals high bonding efficiency of each of the epoxy compounds, RDGE and HDGE, to the silk fiber. As used herein, the term "bonding efficiency" of the epoxy compound represents the percentage of the value obtained by dividing the weight of the epoxy compound bonded to the modified silk fiber, by the weight of the epoxy compound contained in the treatment solution before immersing the silk fiber therein. It was also found that bonding of RDGE or HDGE to the silk fiber leads to higher abrasion resistance than that obtained by bonding other epoxy compounds. Here, the following consideration was made.

**[0080]** Specifically, treated silk crepe sheets were produced as in Example 1, using treatment solutions each containing RDGE with a weight of 0.15 g, 0.25 g, or 0.35 g, respectively (Examples 7 to 9). Moreover, treated silk crepe sheets were produced as in Example 1, except that treatment solutions each containing RDGE with a weight of 0.5 g, 0.6 g, or 0.7 g, respectively were used, and a dilute sodium hydroxide aqueous solution prepared by diluting 5 g of 24% sodium hydroxide aqueous solution with 50 ml of water was used (Examples 10 to 12).

**[0081]** Then, the weight of each treated silk crepe sheet was measured, and a weight increase in the treated silk crepe sheet was calculated. It is noted that also in the case of treated silk crepe sheets produced as in Example 1 but without adding RDGE, the weight of the treated silk crepe sheets slightly decreased. This is because the silk crepe was not completely refined, and residual sericin in each silk crepe sheet was removed through the above-described treatment. Thus, a blank correction was made by taking the weight change in the treated silk crepe sheets treated with the treatment solution not containing RDGE as 0%, and then each weight increase was calculated.

**[0082]** The results are shown in Table 1. In Table 1, the weight (g) of RDGE contained in the prepared treatment solution, the concentration (% owt) of RDGE contained in the prepared treatment solution relative to the silk crepe, the weight increase (%) in the silk crepe, and the bonding efficiency (%) of RDGE are shown in order from the left. Here, the weight increase in the silk crepe was determined by making a blank correction to the percentage of the value obtained by dividing the weight of the treated silk crepe by the weight of the silk crepe used in the treatment

[Table 1]

|        | Weight of RDGE (g) | Concentration of RDGE Relative to Silk Crepe (% owf) | Weight Increase in Silk Crepe (%) | Bonding Efficiency of RDGE (%) |
|--------|--------------------|------------------------------------------------------|-----------------------------------|--------------------------------|
| Ex. 7  | 0.15               | 3                                                    | 0.77                              | 26                             |
| Ex. 8  | 0.25               | 5                                                    | 1.81                              | 36                             |
| Ex. 9  | 0.35               | 7                                                    | 2.51                              | 36                             |
| Ex. 10 | 0.5                | 10                                                   | 3.7                               | 37                             |
| Ex. 11 | 0.6                | 12                                                   | 4.3                               | 36                             |
| Ex. 12 | 0.7                | 14                                                   | 4.9                               | 35                             |

**[0083]** Moreover, Table 2 shows, as Reference Examples 1 to 5, the weight increase (%) in the silk fiber and the bonding efficiency (%) of the epoxy compound calculated based on the results of each of Examples 1 to 5 described in PTD 1.

[Table 2]

|            | Concentration of Epoxy Compound Relative to Silk Fiber (% owf) | Weight Increase in Silk Crepe (%) | Bonding Efficiency of RDGE (%) |
|------------|----------------------------------------------------------------|-----------------------------------|--------------------------------|
| Ref Ex. 1  | 160                                                            | 14.2                              | 8.9                            |
| Ref. Ex. 2 | 160                                                            | 15.8                              | 9.9                            |
| Ref. Ex. 3 | 160                                                            | 8.3                               | 5.2                            |
| Ref. Ex. 4 | 160                                                            | 11.3                              | 7.1                            |
| Ref. Ex. 5 | 160                                                            | 15.8                              | 9.9                            |

**[0084]** With reference to Table 1, it is found that even when the concentration of RDGE in the treatment solution is as low as 3% owf, RDGE is bonded to the silk crepe with a bonding efficiency as high as 26%. It is also found that when the concentration of RDGE in the treatment solution is not lower than 5% owf, the bonding efficiency of RDGE to the silk crepe is further improved. On the other hand, with reference to Table 2, it is understood that although each silk fiber is treated using an epoxy compound at a concentration as high as 160% owf, the bonding efficiency of the epoxy compound to the treated silk fiber is lower than 10%. This reveals that modifying the silk fiber with each of RDGE and HDGE allows efficient utilization of the epoxy compound, leading to improved production efficiency and reduced production costs.

**[0085]** Moreover, with reference to Table 1, the silk crepe sheets obtained by the treatment using RDGE as the epoxy compound have high abrasion resistance, despite having weight increases of not greater than 5%, which are relatively low. On the other hand, with reference to Table 2, the silk fibers obtained by the treatment using other epoxy compounds had low abrasion resistance, despite having weight increases of not smaller than 8.3%, which are relatively high. It is therefore understood that the use of RDGE as the epoxy compound can provide high abrasion resistance, even though the amount of bonded RDGE is smaller than the amounts of the other epoxy compounds bonded. Consequently, it is found that in the modified silk fiber in which RDGE was bonded, deterioration of the feel and texture caused by bonding excess epoxy compound can be prevented.

**[0086]** It is also found that RDGE is bonded to the silk crepe with high bonding efficiency, even when the amount of the catalyst (sodium hydroxide) relative to the treatment solution is as small as 5 g/l or 20 g/l. The use of RDGE as the epoxy compound, therefore, leads to reduced production costs. Further, because the amount of the catalyst used is small, the amount of the catalyst incorporated in the resulting modified silk fiber decreases, and/or the amount of the catalyst attached to the resulting modified silk fiber decreases. Thus, deterioration of the feel and texture caused by the catalyst being attached to the silk fiber can be prevented.

[Experiment (5): Production and Evaluation of Modified Spun Silk Yarns]

**[0087]** In Experiments (1) to (4) above, woven silk fabrics were used in the consideration. On the other hand, in Experiment (5), spun silk yarns were used in the consideration. Here, the spun silk yarns were those obtained by spinning silk staple.

(Example 13)

**[0088]** First, 25 g of RDGE (DENACOL EX201; manufactured by Nagase ChemteX Corporation) and 50 g of a dispersant (Disper VG; manufactured by Meisei Chemical Works, Ltd.) were kneaded well, and water was gradually added to emulsify and disperse the kneaded product, thereby preparing a treatment solution containing RDGE. The total amount of the water used was 500 ml. Next, 500 g of a spun silk yarn of yarn number MC2/60 (SPCC; manufactured by Siyang Silk Spinning Factory) was wound around a dyeing tube, and set in a cheese dyeing machine. Next, the above-prepared

treatment solution was gradually added to the cheese dyeing machine while circulating 4000 ml of water.

**[0089]** Then, the temperature of the treatment solution was increased from 25°C to 60°C while gradually adding a dilute sodium hydroxide aqueous solution prepared by diluting 25 g of 24% sodium hydroxide aqueous solution with 500 ml of water to the cheese dyeing machine. The treatment solution was circulated for another 60 minutes while maintaining the temperature of the treatment solution at 60°C.

**[0090]** The above-described treatment yielded a spun silk yarn in which RDGE was bonded. This spun silk yarn was subjected to washing treatment sequentially including washing with water, washing with 2 g/l of sodium dithionite aqueous solution ( $\text{Na}_2\text{S}_2\text{O}_4$ ), washing with warm water, and washing with water, and then dried to produce a treated spun silk yarn.

(Comparative Example 7)

**[0091]** A treated spun silk yarn was produced as in Example 13, except that RDGE and the dispersant were not used, and the amount of water circulated in the cheese dyeing machine and the amount of 24% sodium hydroxide aqueous solution used were changed. Specifically, in Comparative Example 7, 5 g of 24% sodium hydroxide aqueous solution was directly and gradually added to the cheese dyeing machine, while circulating 5000 ml of water in the cheese dyeing machine.

(Treatment of Dyeing in Black, Friction Test and Washing Test)

**[0092]** Next, the treated spun silk yarns produced in Example 13 and Comparative Example 7 above were subjected to the treatment of dyeing in black, using the cheese dyeing machine. Dye solution B described above was used in the treatment of dyeing in black. After the dyeing treatment, a cylinder weaving machine (180 needles; manufactured by Maruzen Sangyo Co., Ltd.) was used to produce knits having a width of 10 cm and a length of 30 cm. The friction test was then performed as described above, and the surface of each of the knits was observed with a microscope. Further, each knit was washed 30 times as described above in accordance with the JIS L 0217 103 method, and the surface of each knit after washing was observed with a microscope.

(Results)

**[0093]** Figs. 10 and 11 show a surface condition after the friction test and a surface condition after the washing test, respectively, of the knit knitted with the treated spun silk yarn produced in Example 13. Figs. 12 and 13 show a surface condition after the friction test and a surface condition after the washing test, respectively, of the knit knitted with the treated spun silk yarn produced in Comparative Example 7. It is noted that each figure shows an image of the surface of the knit knitted with each treated spun silk yarn taken at 200x magnification.

**[0094]** A comparison between Figs. 10 and 11 and Figs. 12 and 13 reveals that no fuzz or white blurring is observed in Figs. 10 and 11, whereas fuzz and white blurring are observed in Figs. 12 and 13. This result shows that the abrasion resistance was improved for the knit produced using the spun silk yarn in which RDGE was bonded.

**[0095]** Further, each of the knits produced in Example 13 and Comparative Example 7 was subjected to the following experiment. A friction cloth was used made of a cotton cloth impregnated with an amount of water equal to the cloth weight, and the friction cloth was caused to slide over the knit 200 times in a reciprocating manner, under a load of 100 g. The surface of the knit was then observed. In this case also, as in the case of sliding 100 times in a reciprocating manner, no fuzz or white blurring was observed in the knit produced in Example 13, whereas fuzz and white blurring were observed in the knit produced in Comparative Example 7.

(Dimensional Stability Test (1))

**[0096]** Next, a knit was prepared in accordance with the preparation conditions shown below, using the treated spun yarn prepared in Example 13 after the treatment of dyeing in black.

|                    |                                                                             |
|--------------------|-----------------------------------------------------------------------------|
| Knitting machine   | : a flat knitting machine, gauge 14 (manufactured by Shima Seiki MGF, Ltd.) |
| Knitting structure | : T-cloth                                                                   |
| Knit size          | : 25 cm x 50 cm (length x width)                                            |

**[0097]** The knit was then washed 10 times in accordance with the JIS L 0217 103 method, and dimensional changes in the knit after washing were measured. The dimensional changes were observed as follows. Marking sets were formed by sewing a white thread on opposite ends of a width of 40 cm related to the width direction and opposite ends of a width of 20 cm related to the longitudinal direction of the knit before washing, and lengths between the positions of the

respective marking sets were measured after washing. Table 3 shows dimensions of the knit before and after washing.

[Table 3]

|          | Before Washing (cm) | After Washing (cm) |
|----------|---------------------|--------------------|
| Width 1  | 19.7                | 19.8               |
| Width 2  | 20.1                | 20.0               |
| Length 1 | 37.3                | 38.0               |
| Length 2 | 39.8                | 39.8               |

**[0098]** With reference to Table 3, it is found that the knit of Example 13 is stable without a significant dimensional change before and after the washing treatment. Consequently, it is found that the use of a knit produced using the treated spun yarn can provide articles having high abrasion resistance and having high dimensional stability.

[Experiment (6): Production and Evaluation of Modified Cellulose Fibers and Modified Rayon]

**[0099]** Fibers modified by the production method of the invention using refined cellulose fibers and cuprammonium rayon were produced, and fibrillation resistance and dimensional stability were evaluated.

(Example 14)

**[0100]** First, "TENCEL®" (titer: 1.4 dtex, fiber length: 38 mm) sold from Lenzing was prepared as a refined cellulose fiber.

**[0101]** Next, 5 g (5.0 owf%) of RDGE (DENACOL EX201; manufactured by Nagase ChemteX Corporation) and 5 g (5.0 owf%) of a dispersant (Disper VG; manufactured by Meisei Chemical Works, Ltd.) were kneaded well, and the kneaded product was accommodated in the mixing vessel of a liquid circulating-type dyeing machine (Obermaier dyeing machine). Water was then gradually added to emulsify and disperse the kneaded product, thereby preparing a treatment solution containing RDGE. The total amount of water used was 1000 ml. To the treatment solution, 10 g (10 g/l) of a quaternary ammonium salt (Cationon KCN; a quaternary ammonium salt containing as main components 3-chloro-2-hydroxypropyltrimethylammonium chloride and 2,3-glycidyltrimethylammonium chloride; manufactured by Ipposha Oil Industries, Co., Ltd.) was further added and uniformly dispersed by stirring. Then, 100 g of the refined cellulose fiber was immersed in the treatment solution.

**[0102]** A dilute sodium hydroxide aqueous solution prepared by diluting 8 g (8 g/l) of 24% sodium hydroxide aqueous solution with 50 ml of water was then added in three divided portions to the stirred treatment solution, and the temperature of the treatment solution was increased from 25°C to 80°C. Stirring of the treatment solution was then continued for another 45 minutes while maintaining the temperature of the treatment solution at 80°C.

**[0103]** The above-described treatment yielded a refined cellulose fiber in which RDGE was bonded. This fiber was washed with water, and then washed with 4 g/l of sodium dithionite aqueous solution ( $\text{Na}_2\text{S}_2\text{O}_4$ ) at 60°C for 10 minutes. The fiber was further washed with 2 g/l of acetic acid aqueous solution at 60°C for 10 minutes, and finally washed with water, dehydrated and dried to produce a treated refined cellulose fiber.

(Example 15)

**[0104]** A treated refined cellulose fiber was produced as in Example 14, except that a quaternary ammonium salt (Cationon KCN) was not added to the treatment solution.

(Comparative Example 8)

**[0105]** As Comparative Example 8, "TENCEL®" (titer: 1.4 dtex, fiber length: 38 mm) sold from Lenzing was used as it was.

(Comparative Example 9)

**[0106]** A treated refined cellulose fiber was produced as in Example 14, except that RDGE (DENACOL EX201) and a dispersant (Disper VG) were not added to the treatment solution.

(Comparative Example 10)

**[0107]** A treated refined cellulose fiber was produced as in Comparative Example 9, except that the amount of a quaternary ammonium salt (Cationon KCN) added to the treatment solution was 50 g/L.

(Example 16)

**[0108]** Treated cuprammonium rayon was produced as in Example 14, except that "Bemberg®" (titer: 1.4 dtex, fiber length: 38 mm) sold from Asahi Kasei Fibers Corporation was prepared as cuprammonium rayon and used instead of the refined cellulose fiber.

(Comparative Example 11)

**[0109]** As Comparative Example 11, "Bemberg®" (titer: 1.4 dtex, fiber length: 38 mm) sold from Asahi Kasei Fibers Corporation was used as it was.

(Example 17)

**[0110]** A treated silk fiber was produced as in Example 14, except that Silk Sliver A1 (brand name "Maple Tree"; manufactured by Tongxiang Heshan Weiye Textile Co., Ltd., Zhejiang Province) was prepared and used instead of the refined cellulose fiber.

(Comparative Example 12)

**[0111]** As comparative example 12, Silk Sliver A1 (brand name "Maple Tree"; manufactured by Tongxiang Heshan Weiye Textile Co., Ltd., Zhejiang Province) was used as it was.

(Fibrillation Resistance Test)

**[0112]** The following test was performed in order to evaluate the fibrillation resistance of each of the fibers of Examples 14 to 17 and Comparative Examples 8 to 12 produced as above.

**[0113]** First, the fiber of Example 14 was cut into a plurality of staple fibers with a length of not greater than 3.0 mm. Next, 3.3 g of the plurality of staple fibers was weighed into a home mixer (the Pure Black TM Series; manufactured by Tescom) together with 500 ml of water. These components were then stirred in the home mixer for 2 minutes, and then allowed to stand for 10 minutes. The same operation of stirring and allowing to stand was repeated a total of 12 times.

**[0114]** Then, 500 ml of water was added into the mixer, and the staple and water in the mixer were transferred into a plastic container. Next, the pour spout of the plastic container was fixed by being completely covered with a nylon mesh sheet (mesh width: 80  $\mu$ m), and then the plastic container was inverted. In this way, the amount of water that flowed out of the inside of the plastic container in a period of 50 seconds was measured.

**[0115]** Here, the amount of water that flowed out in a period of 50 seconds represents an index of the fibrillation resistance of the staple stirred in the mixer. If fibrillation occurs due to friction under wet conditions, the resulting staple does not pass through the mesh to cause clogging. This causes the amount of water that flowed out in a certain period to decrease. In the above-described test, therefore, the more the amount of water that flowed out, the higher the fibrillation resistance is.

**[0116]** The above-described test was performed for Examples 15 to 17, as well as for Comparative Examples 8 to 12. The results are shown in Table 4.

[Table 4]

|        | Fiber    | Modifying Treatment                             |                                                                | Fibrillation Resistance Test         |
|--------|----------|-------------------------------------------------|----------------------------------------------------------------|--------------------------------------|
|        |          | Concentration of RDGE Relative to Fiber (% owf) | Amount of Quaternary Ammonium Salt in Treatment Solution (g/l) | Amount of Water That Flowed Out (ml) |
| Ex. 14 | TENCEL®  | 5                                               | 10                                                             | 880                                  |
| Ex. 15 | TENCEL®  | 5                                               | 0                                                              | 320                                  |
| Ex. 16 | Bembere® | 5                                               | 10                                                             | 900                                  |

(continued)

|              | Fiber          | Modifying Treatment                             |                                                                | Fibrillation Resistance Test         |
|--------------|----------------|-------------------------------------------------|----------------------------------------------------------------|--------------------------------------|
|              |                | Concentration of RDGE Relative to Fiber (% owf) | Amount of Quaternary Ammonium Salt in Treatment Solution (g/l) | Amount of Water That Flowed Out (ml) |
| Ex. 17       | Silk Sliver A1 | 5                                               | 10                                                             | 860                                  |
| Comp. Ex. 8  | TENCEL®        | 0                                               | 0                                                              | 160                                  |
| Comp. Ex. 9  | TENCEL®        | 0                                               | 10                                                             | 180                                  |
| Comp. Ex. 10 | TENCEL®        | 0                                               | 50                                                             | 620                                  |
| Comp. Ex. 11 | Bemberg®       | 0                                               | 0                                                              | 550                                  |
| Comp. Ex. 12 | Silk Sliver A1 | 0                                               | 0                                                              | 550                                  |

[0117] As is clear from Table 4, the modified fibers of the Examples obtained by the production method of the present invention have excellent fibrillation resistance, as compared to the modified fibers of the Comparative Examples.

[0118] The results of Comparative Examples 8 to 10 reveal that although increasing the amount of the quaternary ammonium salt added improves the fibrillation resistance of the refined cellulose fibers, the obtained fibrillation resistance does not surpass that of the treated refined cellulose fiber obtained in Example 14 in which the epoxy compound was bonded. The results of Examples 14 and 15 also reveal that the use of the quaternary ammonium salt with the epoxy compound further improves the fibrillation resistance of the refined cellulose fiber. It is noted that although the treated refined cellulose fiber of Comparative Example 10 has improved fibrillation resistance, it shows a substantial deterioration in dye affinity, and thus, is poor in practicability.

[0119] Similarly, the results of Example 16 and Comparative Example 11 and the results of Example 17 and Comparative Example 12 reveal that the fibrillation resistance can be significantly improved by modifying cuprammonium rayon and the silk fiber in accordance with the production method of the invention.

[0120] Each of Figs. 14 to 22 shows an image of staple dried after the fibrillation resistance test described above, taken with a microscope at 800x magnification.

[0121] As is clear from Figs. 14 to 22, the modified fibers of the Examples show very little formation of fibrils (small fibers). In contrast, the fibers of the Comparative Examples show the formation of fibrils. Moreover, a comparison between Figs. 14 and 15 reveals that the use of the quaternary ammonium salt with the epoxy compound can further prevent the formation of fibrils.

#### (Dimensional Stability Test (2))

[0122] Next, the following test was performed in order to evaluate the dimensional stability of each of the fibers of Examples 14, 16 and 17 and Comparative Examples 8, 11 and 12.

[0123] First, the elongation under dry conditions Sd (%) of the fiber of Example 1 was measured in accordance with JIS L 1013: 2010 "Chemical Fiber Staple Testing Method" (8.7.1 "Test under Normal Conditions"). The measurement was performed in an environment at 20°C and a relative humidity of 60%.

[0124] Next, the elongation under wet conditions Sh (%) of the fiber of Example 14 was measured in accordance with JIS L 1013: 2010 "Chemical Fiber Staple Testing Method" (8.7.2 "Test under Wet Conditions"). The temperature of water during the measurement was 20°C.

[0125] Then, ΔS was calculated in accordance with the expression:  $\Delta S (\%) = Sh (\%) - Sd (\%)$ , where ΔS represents an index of dimensional stability (i.e., washing resistance) after repeated washing. The smaller ΔS is, the smaller the change in elongation between dry conditions and wet conditions, which indicates that the dimensions are stable even after repeated washing and drying.

[0126] The above-described test was performed for Examples 16 and 17, as well as for Comparative Examples 8, 11 and 12. The results are shown in Table 5.

[Table 5]

|              | Fiber          | Modifying Treatment                             |                                                                | Dimensional Stability Test (2)      |                                     |                |
|--------------|----------------|-------------------------------------------------|----------------------------------------------------------------|-------------------------------------|-------------------------------------|----------------|
|              |                | Concentration of RDGE Relative to Fiber (% owf) | Amount of Quaternary Ammonium Salt in Treatment Solution (g/l) | Elongation in Dry Conditions Sd (%) | Elongation in Wet Conditions Sh (%) | $\Delta S$ (%) |
| Ex. 14       | TENCEL®        | 5                                               | 10                                                             | 9.3                                 | 10.5                                | 1.2            |
| Ex. 16       | Bemberg®       | 5                                               | 10                                                             | 10.6                                | 17.2                                | 6.6            |
| Ex. 17       | Silk Sliver A1 | 5                                               | 10                                                             | 14.5                                | 14.7                                | 0.2            |
| Comp. Ex. 8  | TENCEL®        | 0                                               | 0                                                              | 11.0                                | 14.7                                | 3.7            |
| Comp. Ex. 11 | Bemberg®       | 0                                               | 0                                                              | 15.7                                | 32.0                                | 16.3           |
| Comp. Ex. 12 | Silk Sliver A1 | 0                                               | 0                                                              | 15.0                                | 25.1                                | 10.1           |

[0127] As is clear from Table 5, the fibers of the Examples in which the epoxy compound was bonded have an extremely small  $\Delta S$ , and thus, exhibit excellent dimensional stability, as compared to the fibers of the Comparative Examples. That is, the fibers of the Examples have high washing resistance.

[0128] The foregoing confirmed that the modified fiber of the invention in which the epoxy compound is bonded to the refined cellulose fiber or cuprammonium rayon, wherein the epoxy compound is at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether, exhibits both high abrasion resistance and high washing resistance. The foregoing also confirmed that abrasion resistance and washing resistance are further improved by bonding the quaternary ammonium salt to the modified fiber. This fact reveals that similar effects are obtained in either case where a natural cellulose fiber or rayon is used as the base material of the modified fiber.

[0129] While the embodiments and examples of the present invention have been described above, it is originally envisaged to combine features of various embodiments and examples as appropriate.

[0130] It should be understood that the embodiments and examples disclosed herein are illustrative and non-restrictive in every respect. It is intended that the scope of the present invention is defined by the terms of the claims rather than by the foregoing embodiments and examples, and includes all modifications within the scope and meaning equivalent to the claims.

#### INDUSTRIAL APPLICABILITY

[0131] The present invention can be widely used for improving the abrasion resistance and the washing resistance of textile articles.

#### Claims

1. A modified fiber in which an epoxy compound is bonded to a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber, said epoxy compound being at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether.
2. The modified fiber according to claim 1, further containing a quaternary ammonium salt.
3. A method for producing a modified fiber comprising:
 

immersing a refined cellulose fiber, a natural cellulose fiber, cuprammonium rayon, rayon, or a silk fiber in a treatment solution containing an epoxy compound, and bonding said epoxy compound to said refined cellulose fiber, said natural cellulose fiber, said cuprammonium rayon, or said rayon, said epoxy compound being at least any one of resorcinol diglycidyl ether and hydroquinone diglycidyl ether.

4. The method for producing a modified fiber according to claim 3, wherein said treatment solution contains a quaternary ammonium salt.

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FIG.1

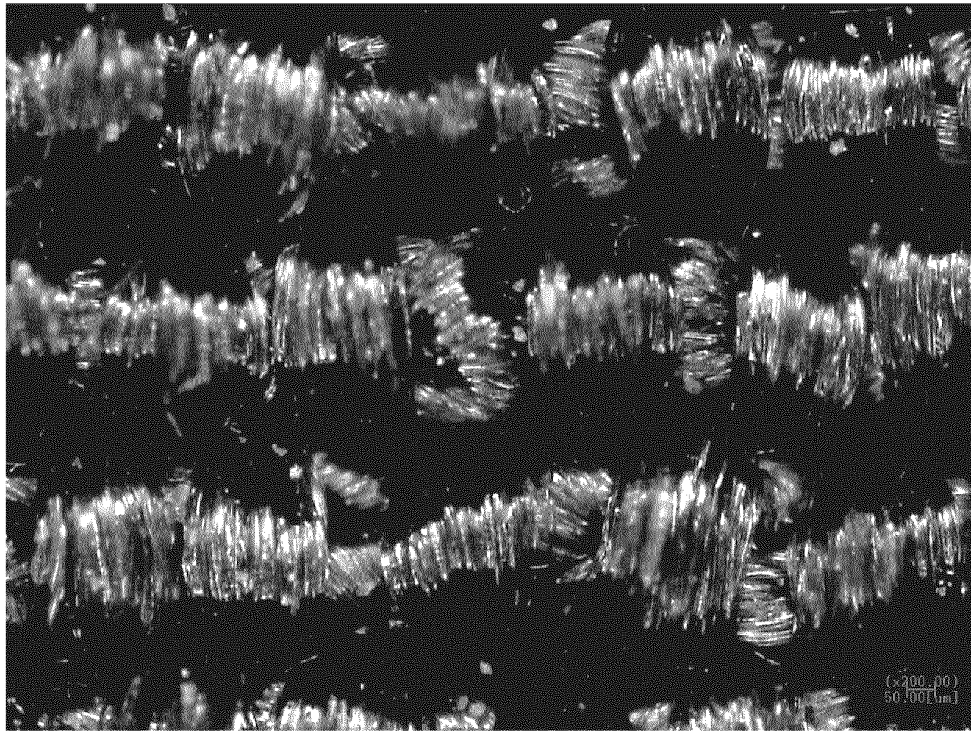


FIG.2

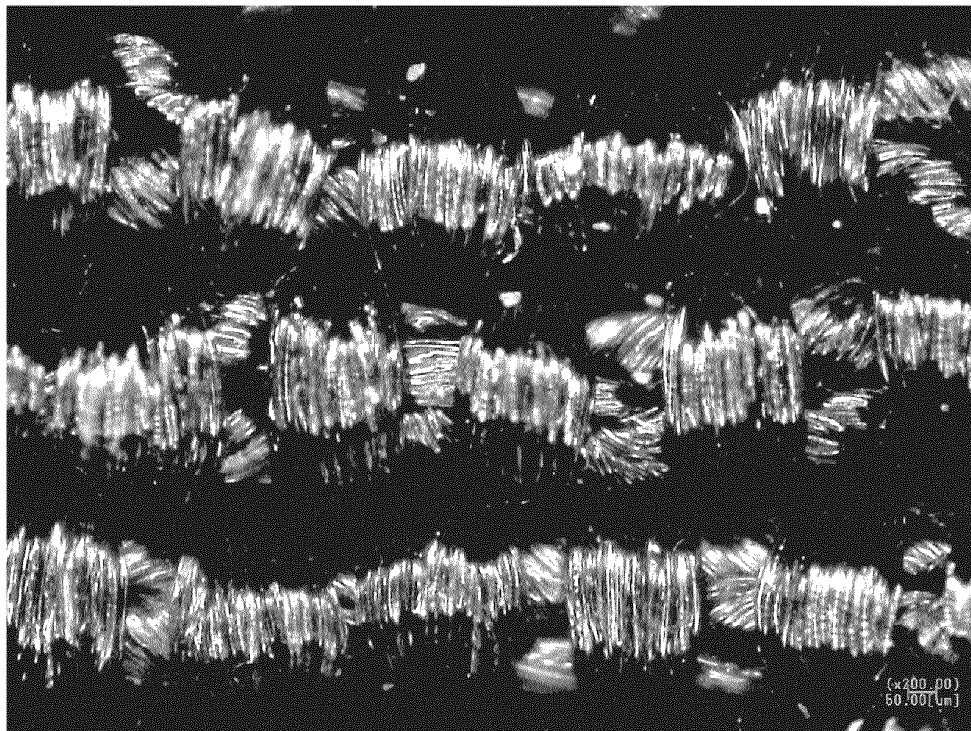


FIG.3

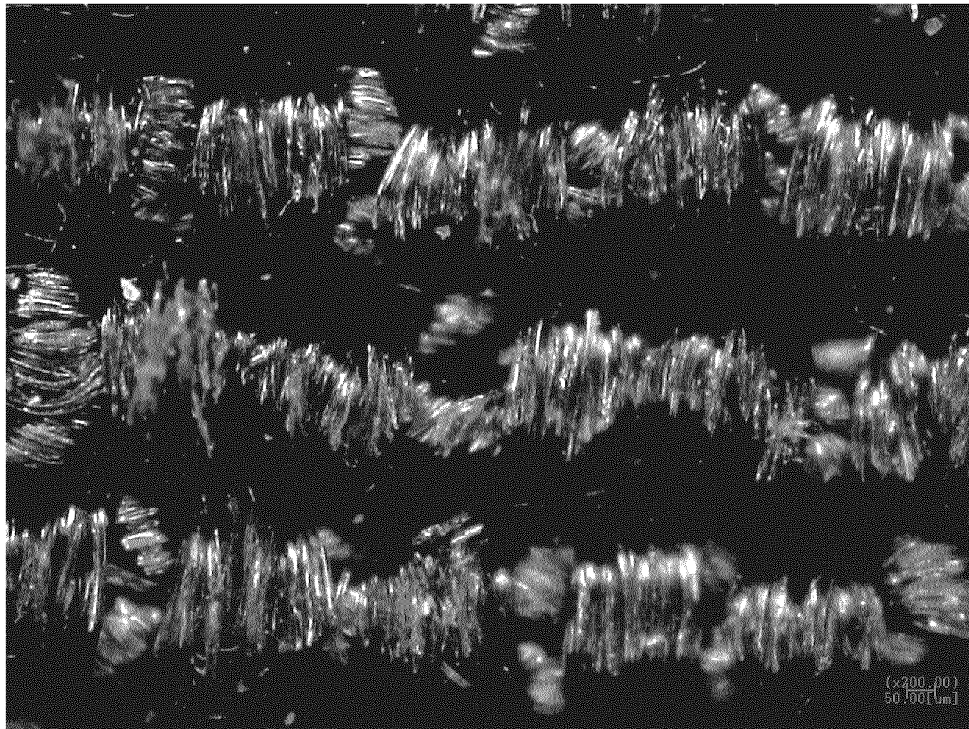


FIG.4

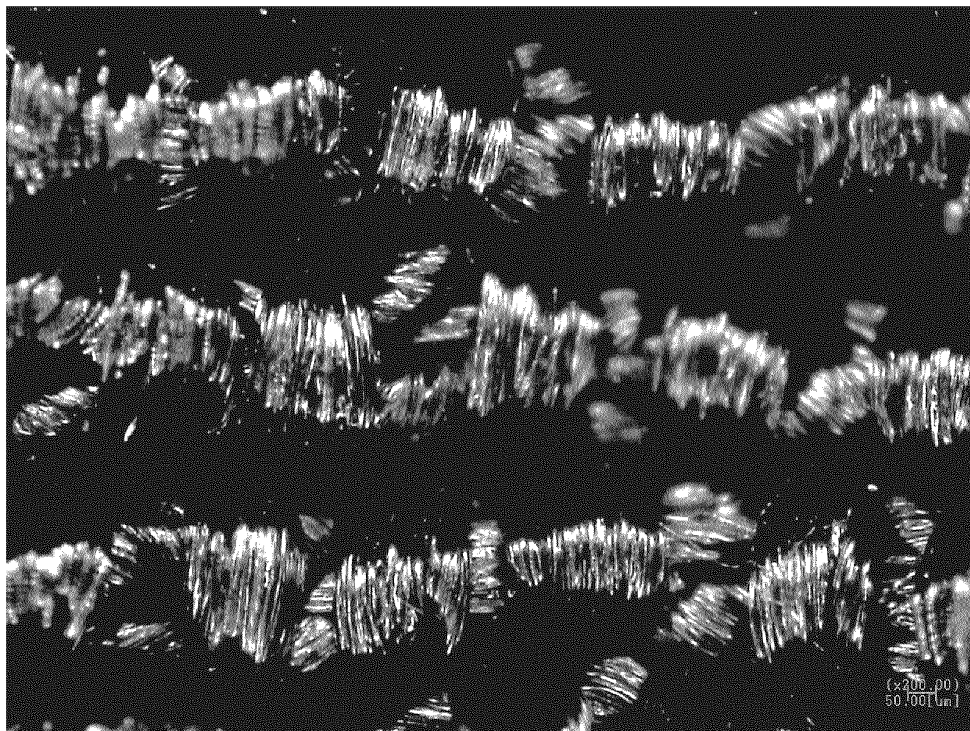


FIG.5

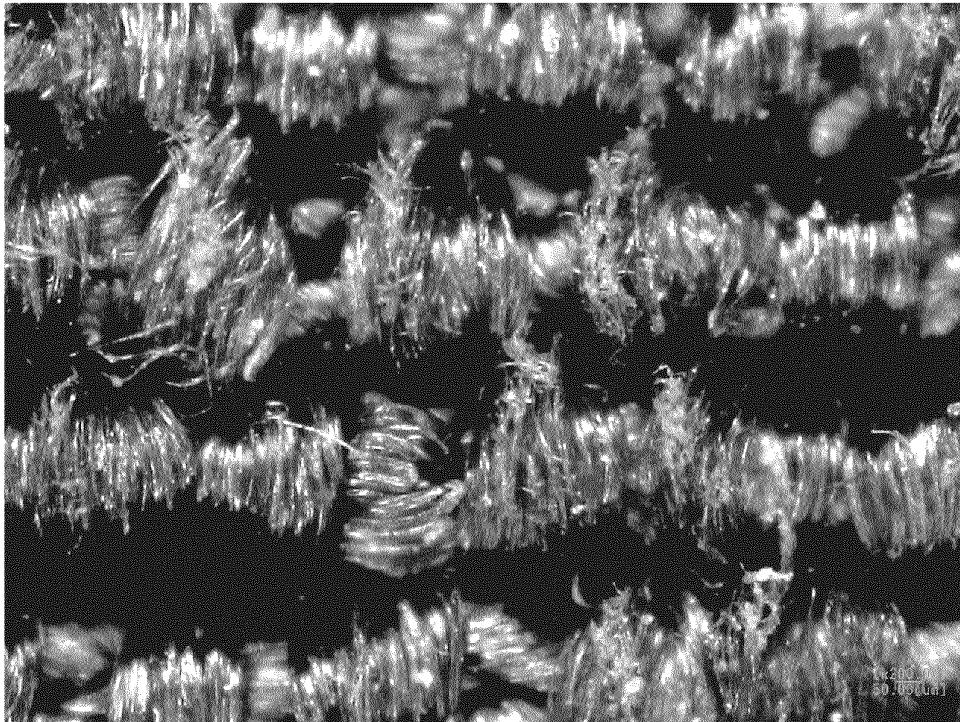


FIG.6

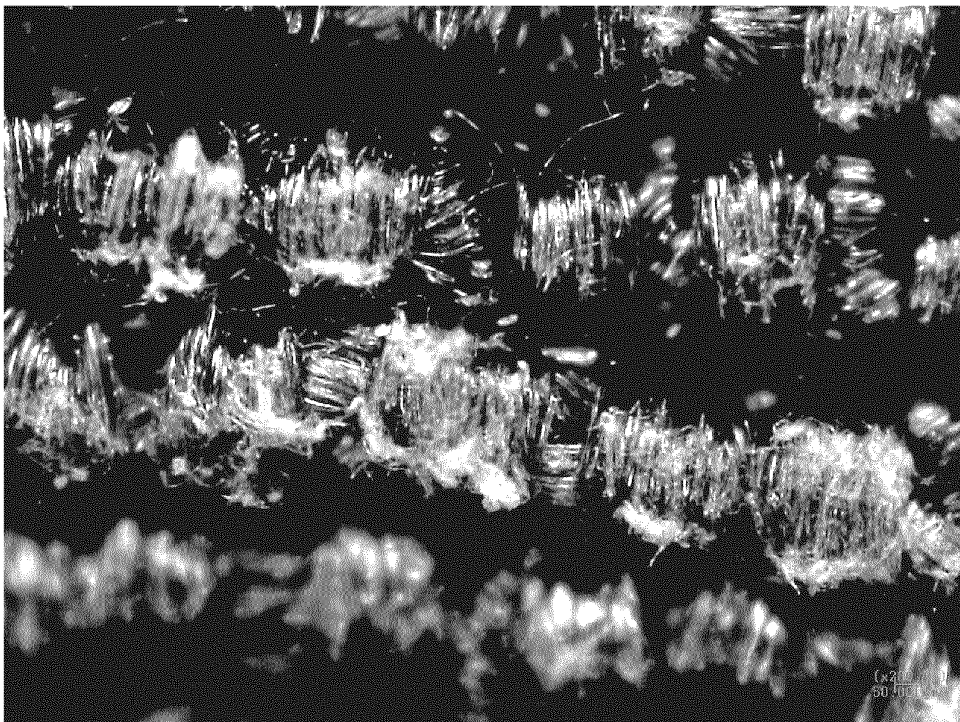


FIG.7

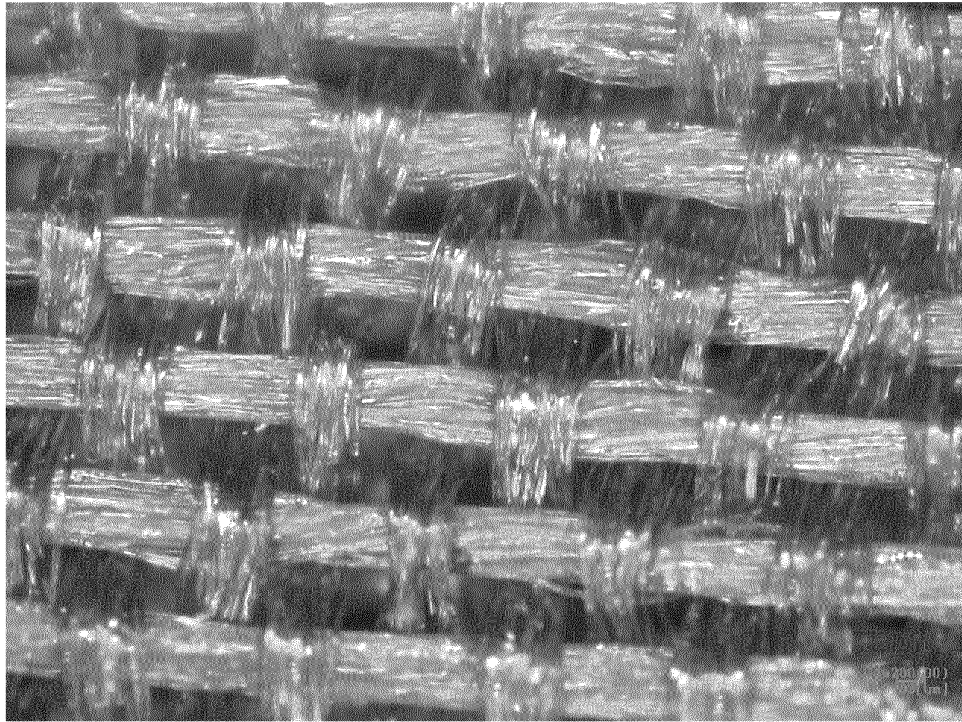


FIG.8

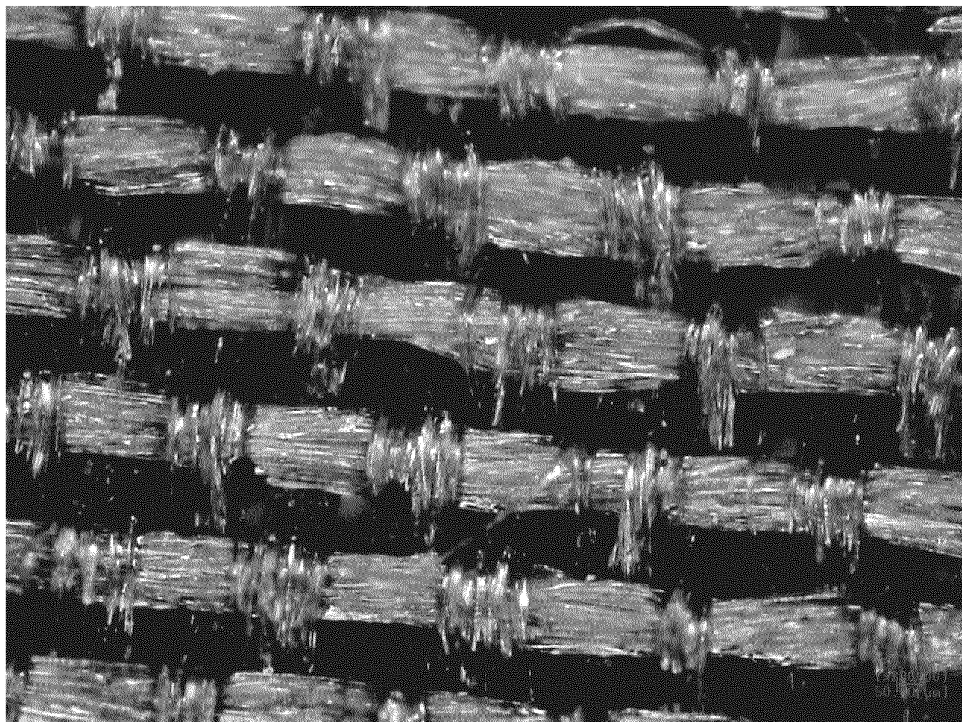


FIG.9

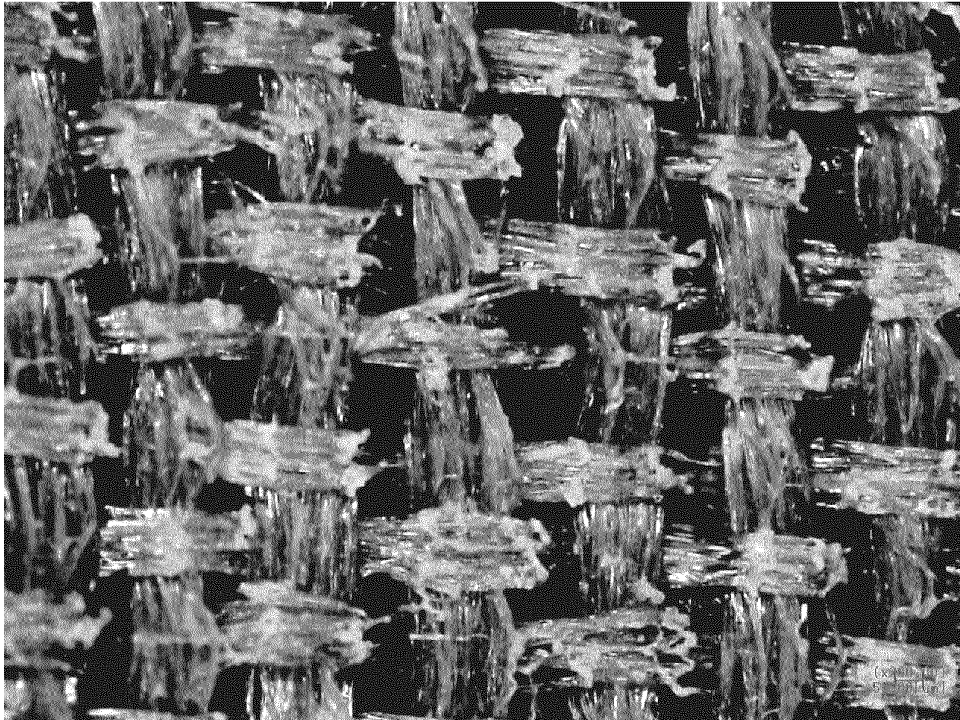


FIG.10

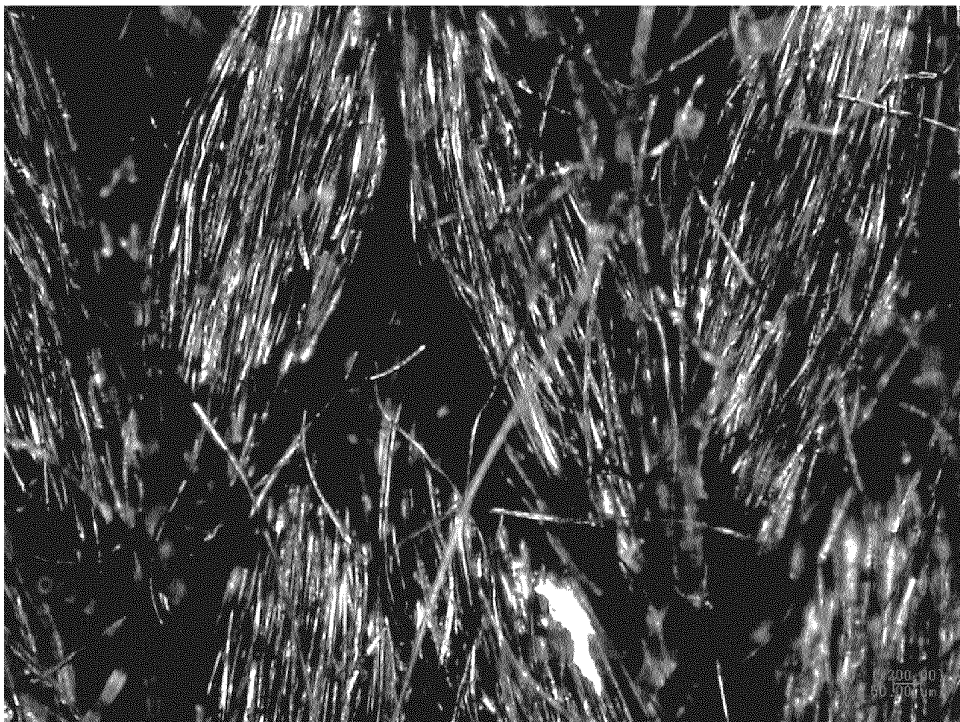


FIG.11

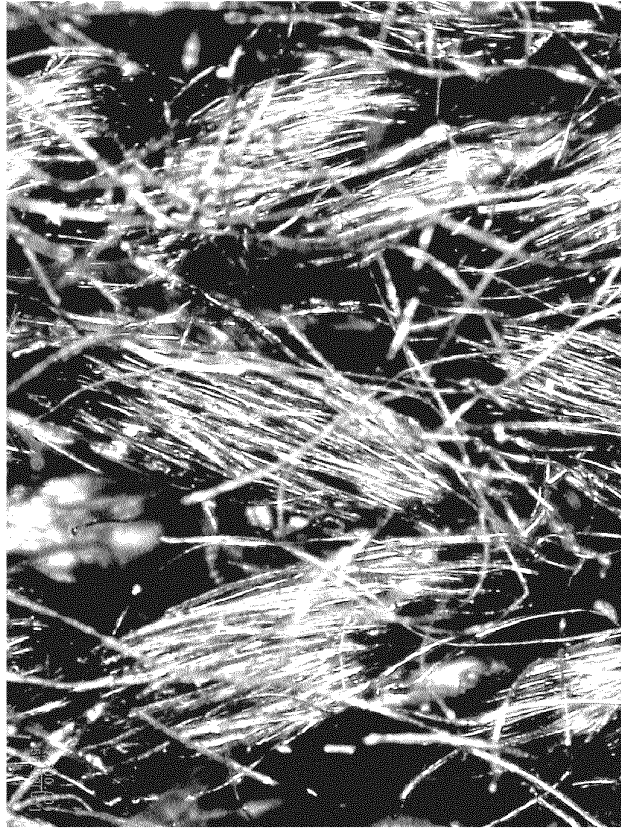


FIG.12

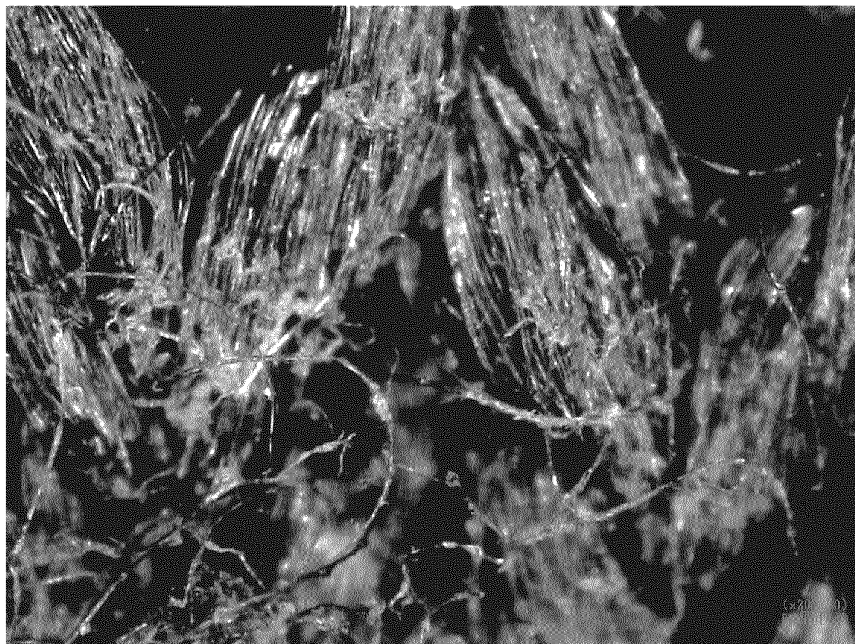


FIG.13



FIG.14

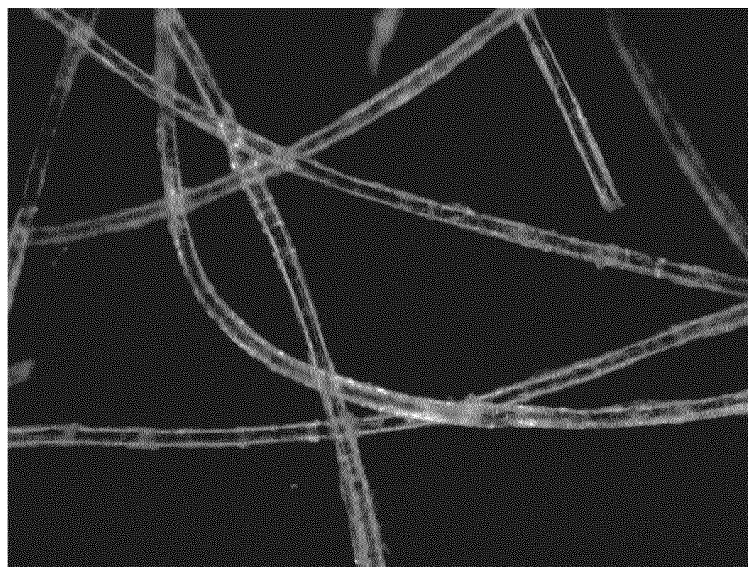


FIG.15

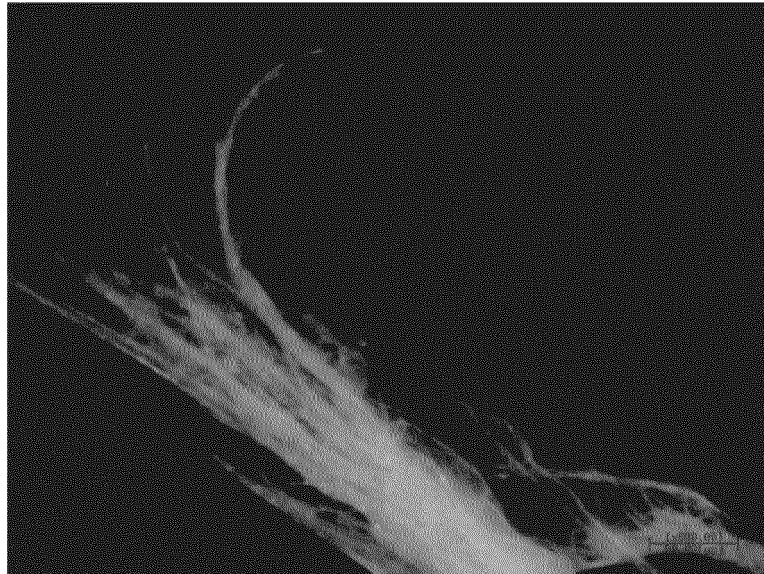


FIG.16



FIG.17

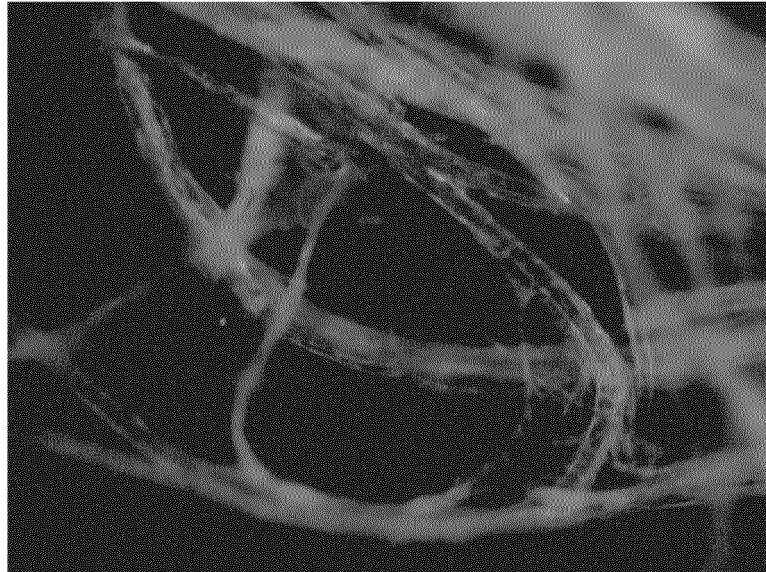


FIG.18

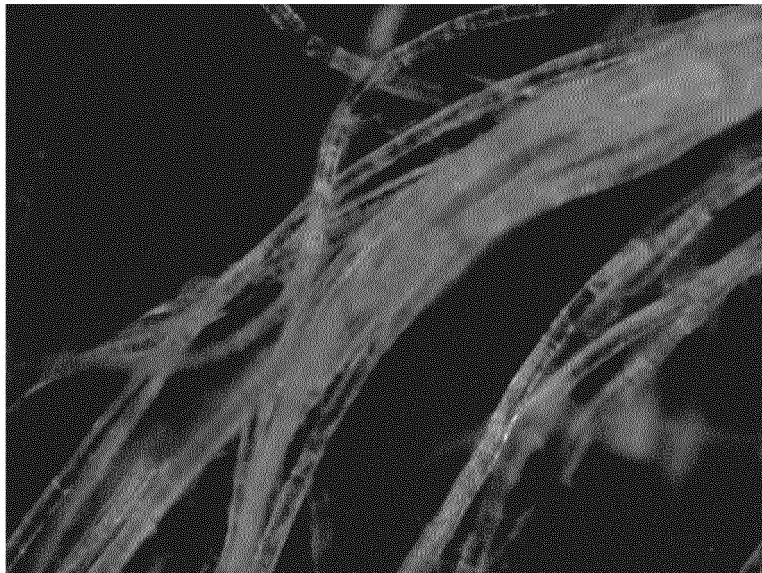


FIG.19

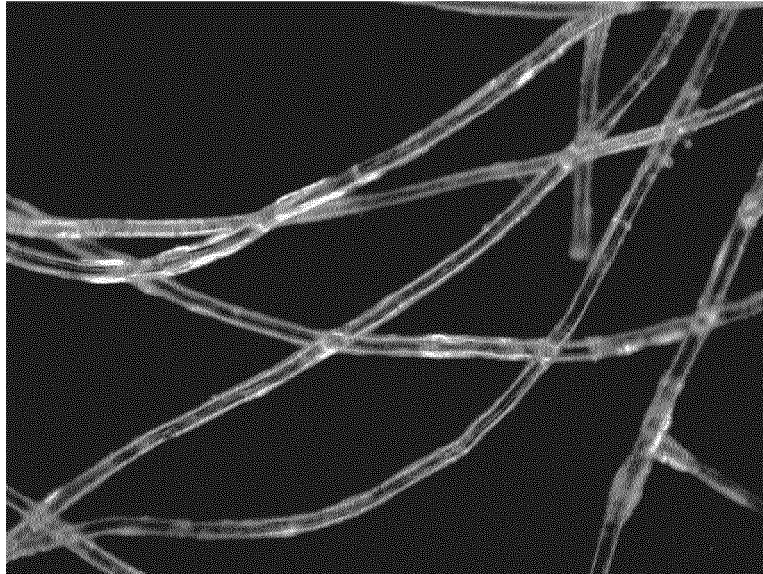


FIG.20

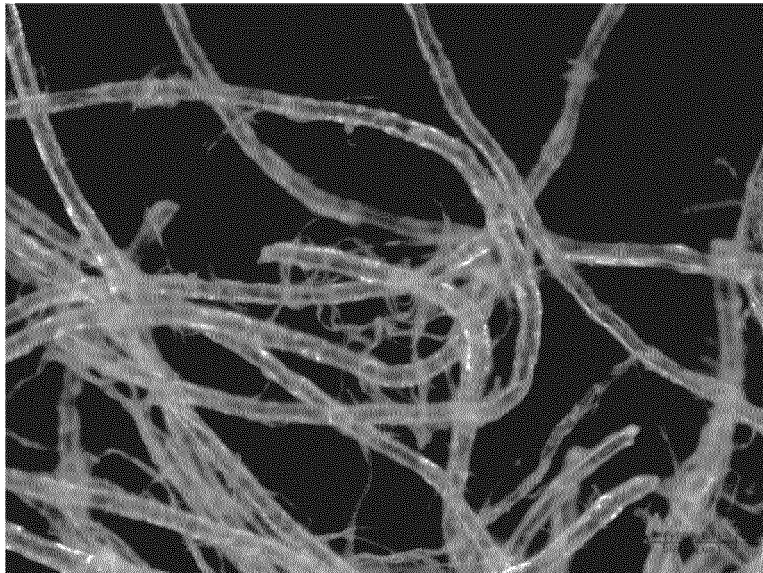


FIG.21

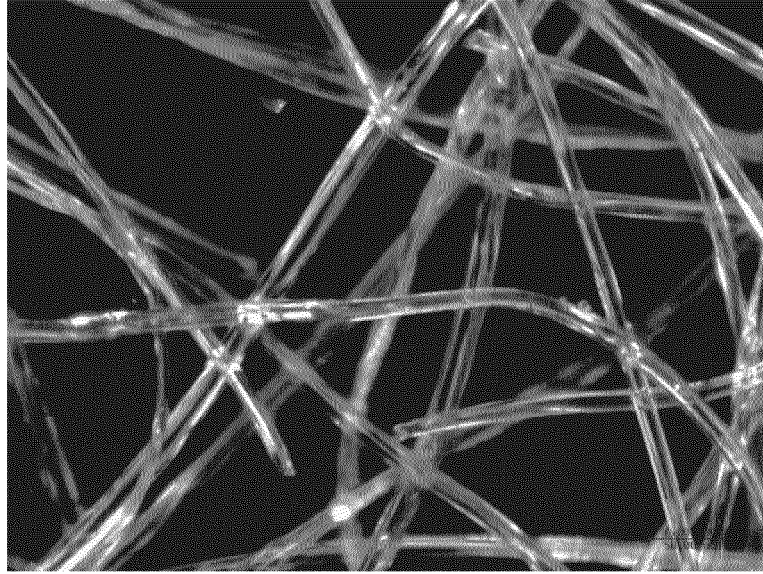
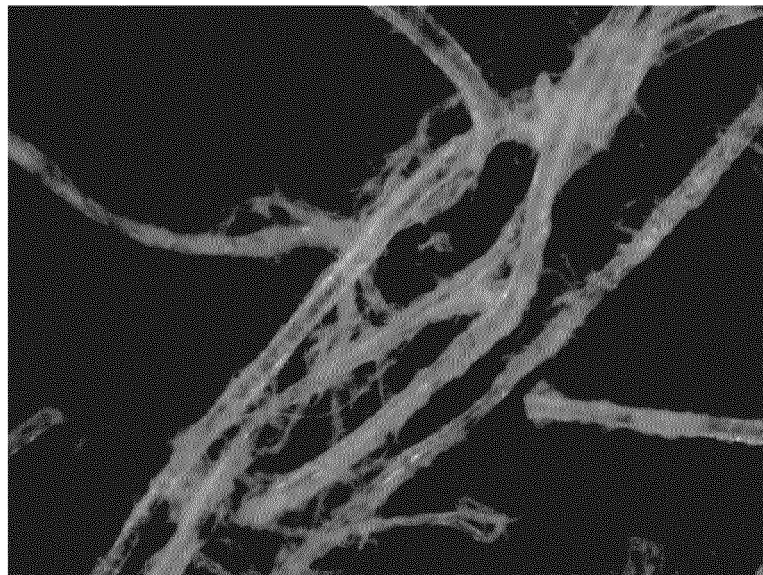


FIG.22



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/077755

## A. CLASSIFICATION OF SUBJECT MATTER

D06M15/55(2006.01)i, D06M13/46(2006.01)i, D06M101/04(2006.01)n,  
D06M101/12(2006.01)n

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)

D06M15/55, D06M13/46, D06M101/04, D06M101/12

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

CAPLUS/REGISTRY (STN)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                             | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 4-185765 A (Goshi Kaisha Ishikawa Kigyo),<br>02 July 1992 (02.07.1992),<br>claims; page 2, lower right column, lines 2 to<br>7; page 3, example 2<br>(Family: none)                                                                         | 1, 3                  |
| X         | JP 62-250275 A (Director General, Agency of<br>Industrial Science and Technology, Ban Senko<br>Kabushiki Kaisha),<br>31 October 1987 (31.10.1987),<br>claims; page 3, lower right column, lines 2 to<br>8; page 9, example 2<br>(Family: none) | 1, 3                  |

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

\* Special categories of cited documents:

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

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

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

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

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

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

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Date of the actual completion of the international search

07 January, 2014 (07.01.14)

Date of mailing of the international search report

14 January, 2014 (14.01.14)

Name and mailing address of the ISA/  
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Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/077755

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                            | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 62-231079 A (Director General, Agency of Industrial Science and Technology),<br>09 October 1987 (09.10.1987),<br>claims; page 4, lower left column, line 6 to lower right column, line 1; page 6, example 2 (Family: none) | 1-3                   |
| X         | JP 6-299469 A (Masumi Kabushiki Kaisha),<br>25 October 1994 (25.10.1994),<br>claims; paragraphs [0012], [0017], [0027], [0028] (Family: none)                                                                                 | 1-4                   |
| X         | WO 2012/014762 A1 (Matsumoto Yushi-Seiyaku Co., Ltd.),<br>02 February 2012 (02.02.2012),<br>claims 1, 2; paragraphs [0038], [0040], [0047], [0049] & CN 103025951 A                                                           | 1-4                   |
| P,X       | JP 2012-197538 A (Nihon Sanmo Dyeing Co., Ltd.),<br>18 October 2012 (18.10.2012),<br>claims (Family: none)                                                                                                                    | 1, 3                  |
| A         | JP 11-350358 A (Asahi Chemical Industry Co., Ltd.),<br>21 December 1999 (21.12.1999),<br>claims; paragraph [0029] (Family: none)                                                                                              | 1-4                   |
| A         | JP 2007-154395 A (Nihon Sanmo Dyeing Co., Ltd.),<br>21 June 2007 (21.06.2007),<br>claims; paragraphs [0009] to [0014] (Family: none)                                                                                          | 2, 4                  |

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 47024199 A [0004] [0005]

**Non-patent literature cited in the description**

- **HIDEKI SHIOZAKI.** The present and future status of washable silk. *Processing Technology*, 1989, vol. 24 (2), 74-77 [0004] [0006]