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(54) **Natural cellulosic fibers treated with inorganic metal compounds and polycarboxylic acids**

Natürliche Zellulosefasern behandelt mit anorganischen Metallverbindungen und Polycarbonsäuren

Fibres cellulosiques naturelles traitées avec des composés inorganiques de métaux et des acides polycarboxyliques

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**Description**

The present invention relates to natural cellulose fibers having an inorganic metal compound therein, and a process for producing such fibers.

5 It is known for long to deodorize ammonia, hydrogen sulfide, mercaptan, trimethylamine or like substance having an offensive odor by reacting the substance with zinc, aluminum, copper or like metal compound and thereby converting the substance to another substance.

10 On the other hand, copper compounds have antibacterial activity and fungicidal activity, oxides of zirconium, cerium and the like have ability to absorb ultraviolet rays, and zirconium oxide and carbide have the nature of releasing heat by absorbing light. Methods have been provided of imparting various functions to fibers by utilizing these known properties of such metal compounds.

15 Attempts have been made to knead the metal compound with a material such as nylon or polyester and make the mixture into synthetic fibers having such a function. With this method, the metal compound is admixed with the material for preparing the synthetic fibers, so that the fibers can be given the desired function to a satisfactory extent, whereas the kneading method is in no way applicable to natural fibers such as natural cellulose fibers.

20 Accordingly, heretofore proposed for treating natural cellulose fibers is a method of coating the surface of cellulose fibers with polyurethane or like resin containing a metal compound to cause the fibers to support the metal compound thereon (Examined Japanese Patent Publication HEI 2-10274, etc.), a method of causing cellulose fibers to support thereon the reaction product of a transition metal and tannic acid (Unexamined Japanese Patent Publications HEI 1-292169 and HEI 1-266275, etc.) and the like. However, these methods are unable to prepare natural cellulose fibers capable of retaining the imparted function for a prolonged period of time. When the former method is practiced using, for example, a zinc compound as the metal compound to obtain deodorant fibers, the finished fibers are hard, have a poor hand and are low in washing fastness such that the deodorant properties become halved or lower when the fibers are washed repeatedly about 10 times. With the latter method wherein the tannic acid is used to attach the transition metal to the cellulose fibers, the transition metal becomes inevitably released from the fibers, for example, owing to hydrolysis when the fibers are repeatedly washed. Thus, the functional fibers afforded by this method are also low in washing fastness. In fact, when the latter method is practiced using a zinc compound as the metal compound in the same manner as above to obtain deodorant fibers, the deodorant properties become halved or lower if the fibers are repeatedly washed about 10 times.

25 Further Unexamined Japanese Patent Publication SHO 55-137210 discloses bactericidal fibers prepared by attaching copper ion to an ion exchange group present in the surface layer of fibers having ion exchange ability, and causing the copper ion to form a water-insoluble compound as incorporated in the surface layer. Nevertheless, the invention of the publication is not applicable as it is to natural cellulose fibers since the hydroxyl group of natural cellulose fibers has no ion exchange ability. When we treated natural cellulose fibers according to the invention as disclosed in the publication by impregnating the fibers with a water-soluble metal salt, drying the fibers and washing the fibers with water, we found that almost all the metal ions were washed away. This indicates that the disclosed technique is unable to basically overcome the conventional drawback.

30 An object of the present invention is to provide natural cellulose fibers capable of retaining for a prolonged period of time functions imparted thereto by various metal compounds.

35 Another object of the invention is to provide a process for producing such natural cellulose fibers.

Other features of the invention will become apparent from the following description.

40 The present invention provides a natural cellulose fiber having a water-insoluble inorganic metal compound incorporated therein and having at least one heat-treated polycarboxylic acid combined therewith, the polycarboxylic acid being selected from the group consisting of polycarboxylic acids and partial salts thereof. It also provides a process for producing a natural cellulose fiber having a water-insoluble inorganic metal compound incorporated therein, the process comprising the steps of impregnating a natural cellulose fiber with a treating solution containing a water-soluble inorganic metal compound and a polycarboxylic acid, heating the fiber and insolubilizing the water-soluble inorganic metal compound incorporated in the fiber.

45 The natural cellulose fiber of the present invention is characterized in that the cellulose fiber has an inorganic metal compound incorporated therein. With the prior art, fibers are coated with a resin containing a particulate metal compound admixed therewith, or a third substance, such as tannic acid, which is adsorbable by or reactive with fibers and which is caused to form a complex with a metal ion, hence the necessity of using an intermediary substance. The present invention, however, does not require any support medium such as resin or other chemical substance because the natural cellulose fiber has incorporated therein an insoluble metal compound as converted from a metal ion within the fiber. The metal compound incorporating cellulose fiber of the present invention is less likely to release the metal compound even when repeatedly washed. The metal compound is not merely deposited on the cellulose fiber but behaves as if enclosed in the noncrystalline structure of the fiber.

50 Examples of natural cellulose fibers for use in the present invention are cotton and hemp fibers. Such fibers may

be in the form of a blend with polyester or like synthetic fibers. The fibers are not limited specifically in form but can be in any form such as yarns, woven fabrics, knitted fabrics or nonwoven fabrics.

The inorganic metal compound to be incorporated into cellulose fibers is not limited specifically insofar as it is insoluble in water. Examples of useful inorganic metal compounds are hydroxides, carbonates, phosphates, silicates, aluminates and zirconates of metals such as copper, silver, zinc zirconium iron, cobalt, nickel, manganese, cerium, magnesium tin and antimony. At least one of these metal compounds is incorporated into the cellulose fiber.

According to the invention, 0.01 to 10 wt. %, preferably 0.1 to 5 wt. %, of the metal compound is incorporated in the cellulose fiber.

The natural cellulose fiber of the present invention is produced by causing a metal ion to penetrate into a natural cellulose fiber and converting the metal ion to a water-insoluble inorganic metal compound. Depending on the kind of metal compound to be incorporated into the fiber, the particulars of the process differ as will be described below.

The process generally comprises a first bath treatment for impregnating the cellulose fiber to be treated with a water-soluble metal salt and a second bath treatment for insolubilizing the water-soluble metal salt in the fiber.

In the first bath treatment, the fiber is treated with an aqueous solution of the water-soluble metal salt so as to be impregnated with the metal salt. The fiber is treated with the metal salt solution, for example, by dipping, padding, spraying or coating. The dipping or padding method is suitable to practice.

More specifically, the dipping method is practiced by dipping the fiber in an aqueous solution containing the metal salt in an amount of 0.01 to 10 wt. % calculated as the metal concerned at room temperature to 100°C for 3 seconds to 10 minutes. The treatment conditions differ with the kind of fiber, and optimum conditions for the fiber to be treated are used. While the dipped fiber is subjected to the second bath treatment, the fiber may be washed with water and dried before the second bath treatment. Since the metal salt is soluble in water according to the invention, it is desired that the dipping treatment be changed over to the second bath treatment by way of the drying step only.

The padding method is especially suited to woven fabrics and knitted fabrics. Stated more specifically when the padding method is resorted to, the fiber is treated as immersed in an aqueous solution containing the metal salt in an amount of 0.01 to 10 wt. % calculated as the metal at room temperature to 100°C for 3 seconds to 10 minutes, and is thereafter squeezed as by a mangle to a predetermined uniform ratio. This treatment is conducted under conditions optimum for the fiber and suitably selected. The padded fiber may be washed with water and dried prior to the second bath treatment to be subsequently conducted. Like the dipping method, the padding method is preferably followed by the drying step only before the second bath treatment.

In the second bath treatment, an aqueous solution of alkali, acid or alkali metal salt is caused to act on the water-soluble metal salt impregnating the fiber or deposited thereon to convert the water-soluble metal salt to a water-insoluble metal compound. This treatment can be carried out also by dipping, padding, spraying, coating or like method. The dipping or padding method is suitable to practice. The dipping method is usable for fibers of any form, while the padding method is suited to woven or knitted fabrics.

More specifically, the padding method is practiced by dipping the fiber subjected to the first bath treatment in an aqueous solution containing 0.01 to 10 wt. % of an alkali, acid or alkali metal salt at room temperature to 70°C for 3 seconds to 5 minutes, and thereafter squeezing the dipped fiber as by a mangle to a predetermined uniform ratio. The treatment is conducted under suitably selected conditions which are optimum for the fiber.

The padded and squeezed fiber is then soaped or washed with water to completely remove the alkali, acid or alkali metal salt, and is thereafter dried, whereby a natural cellulose fiber of the invention is prepared which has a water-insoluble inorganic metal compound incorporated therein as if enclosed in the amorphous region of the fiber.

In the case where the metal of the metal compound to be incorporated into the fiber is a transition metal, such as copper, silver, iron, cobalt, nickel, manganese, zinc, titanium, zirconium, cerium, vanadium, molybdenum or tungsten, germanium, aluminum or magnesium, the water-soluble metal salt present in the first bath is preferably in the form of the chloride, oxychloride, sulfate, nitrate or like mineral acid salt of the metal, or the acetate, formate or like organic acid salt of the metal, while an aqueous solution of alkali is used as the second bath. Examples of useful alkalis are hydroxides of alkali metals, hydroxides of alkaline earth metals, ammonium hydroxide and the like, among which sodium hydroxide is preferred.

In the case where the metal of the metal compound to be incorporated into the fiber is a metal element such as zinc, titanium, zirconium, vanadium, molybdenum, tungsten, aluminum, silicon, tin or antimony, it is desirable to use as the first bath an aqueous solution which contains as an anion the oxide of the metal element prepared by dissolving the element or a salt thereof with an alkali hydroxide or ammonium hydroxide, and to use an aqueous solution of acid as the second bath. Examples of useful acids are hydrochloric acid, sulfuric acid and like mineral acids, formic acid, acetic acid and like water-soluble organic acids, etc., among which acetic acid is desirable.

Alternatively, the natural cellulose fiber to be treated can be impregnated with a water-soluble metal salt using the first bath and thereafter passed through an aqueous solution of another water-soluble metal salt serving as the second bath to form a water-insoluble inorganic metal salt in the fiber. The water-soluble metal salt for use in the first bath is any water-soluble metal salt other than the salts of alkali metals. The water-soluble metal salt for use in the second

bath is any inorganic metal salt which becomes insoluble in water when reacting with the metal salt of the first bath. Examples of such salts are alkali salts of carbonic acid, phosphoric acid, pyrophosphoric acid, metasilicic acid, silicic acid, zincic acid, aluminic acid, titanitic acid, molybdic acid, vanadic acid, zirconic acid and the like, alkali sulfides, etc.

The metal compound incorporated in the fiber imparts to the fiber deodorizing, antibacterial and fungicidal effects when the compound is, for example, a zinc or copper compound, a deodorizing effect when the compound is an aluminum or magnesium compound, effects to accumulate heat, block ultraviolet rays and radiate far infrared rays when the compound is a zirconium compound, or flame retardant effect when the compound is an antimony compound.

An enhanced deodorant effect is available when at least one member selected from polycarboxylic acids and partial salts thereof is used in combination with the water-soluble inorganic metal compound. The term "partial salt of polycarboxylic acid" used herein refers to a salt thereof having at least one free carboxyl group remaining after the reaction of all carboxyl groups with a base.

Examples of useful polycarboxylic acids are straight-chain or branched-chain aliphatic polycarboxylic acids, alicyclic polycarboxylic acids, aromatic polycarboxylic acids, etc. These acids may be those having a hydroxyl group, halogen atom, carbonyl group or carbon-carbon double bond.

Specific examples of these polycarboxylic acids are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, corresponding branched fatty acids, maleic acid, fumaric acid, cyclohexanedicarboxylic acid and corresponding position isomers and like aliphatic dibasic acids; tetrahydrophthalic acid, nadic acid and like alicyclic dibasic acids; tricarbaryl acid, aconitic acid, methylcyclohexanetricarboxylic acid and like tribasic acids; butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, tetrahydrofuran-tetracarboxylic acid, an ene adduct of methyltetrahydrophthalic acid with maleic acid and like tetrabasic acids; malic acid, tartaric acid, citric acid and like hydroxy-fatty acids; trimellitic acid, pyromellitic acid, biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, diphenylsulfonetetracarboxylic acid and like aromatic polycarboxylic acids; etc. Of these polycarboxylic acids, butanetetracarboxylic acid is preferred.

Useful metal ions constituting a partial salt of polycarboxylic acid are sodium, potassium, ammonium, etc.

When a polycarboxylic acid or partial salt thereof is used in combination with the water-soluble metal compound, the polycarboxylic acid or partial salt is impregnated into and deposited on the cellulose fiber together with the water-soluble metal compound and heat-treated and then the water-soluble metal compound is insolubilized, or alternatively the water-soluble metal compound is insolubilized first and the treated cellulose fiber is dipped in an aqueous solution of polycarboxylic acid or the like, followed by heat treatment.

The present invention provides natural cellulose fibers capable of retaining for a prolonged period of time the functions imparted thereto by various metal compounds. The natural cellulose fiber of the present invention, which has the insoluble inorganic metal compound incorporated therein, is excellent in washing fastness, therefore less likely to release the metal compound even if washed repeatedly and capable of retaining the function imparted by the metal compound for a prolonged period of time. The natural cellulose fiber of the invention is fully satisfactory also in hand.

The invention will be described in greater detail with reference to the following examples, Reference examples and comparative examples.

#### Reference Example 1

A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 1.16% of zinc chloride, thereafter squeezed with a mangle and dried at 100° C to incorporate zinc chloride into the cotton fabric. The fabric was subsequently dipped in an aqueous solution containing 1.0% of sodium hydroxide for 3 seconds, then squeezed with the mangle, washed with water immediately after squeezing and dried to obtain a cotton fabric having zinc hydroxide incorporated therein. The fabric was found to contain 4100 mg/kg of zinc hydroxide by the atomic absorption method.

#### Comparative Example 1

The same cotton fabric as in Reference Example 1 was treated in the same manner as in Reference Example 1 except that the treating solution was free from zinc chloride.

#### Example 1

A polyester/cotton blended yarn fabric weighing 150 g/m<sup>2</sup> was bleached in the usual manner, then dyed, dipped in an aqueous solution containing 1.6% of zinc chloride and thereafter squeezed with a mangle. Subsequently, the fabric was dipped in an aqueous solution containing 1.0% of sodium hydroxide for 3 seconds, then squeezed with the mangle, further dipped in an aqueous solution containing 6.9% of butanetetracarboxylic acid and 1.2% of sodium carbonate and thereafter squeezed with the mangle. The fabric was dried at 120° C and cured at 160° C for 2 minutes

to obtain a butanetetracarboxylic acid crosslinked fabric having zinc hydroxide incorporated therein. The fabric was found to contain 3100 mg/kg of zinc hydroxide by the atomic absorption method.

Comparative Example 2

5 The same fabric as in Example 1 was treated in the same manner as in Example 1 except that the treating solutions were free from zinc chloride or butanetetracarboxylic acid.

Reference Example 2

10 A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 10% of aluminum chloride, thereafter squeezed with a mangle and dried at 60°C to incorporate aluminum chloride into the fabric. Subsequently, the fabric was dipped in an aqueous solution containing 1.0% of sodium hydroxide for 3 seconds, then squeezed with the mangle, washed with water immediately after squeezing and  
15 dried to obtain a cotton fabric having aluminum hydroxide incorporated therein. The weight of the fabric measured indicated that the fabric contained 18500 mg/kg of aluminum hydroxide.

Comparative Example 3

20 The same cotton fabric as used in Reference Example 2 was treated in the same manner as in Reference Example 2 except that the treating solution was free from aluminum chloride.

Reference Example 3

25 A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 20% of zirconium oxychloride, thereafter squeezed with a mangle and dried at 50°C to incorporate zirconium oxychloride into the fabric. Subsequently, the fabric was dipped in an aqueous solution containing 1.0% of sodium hydroxide for 3 seconds, then squeezed with the mangle, washed with water immediately after squeezing and  
30 dried to obtain a cotton fabric having zirconium hydroxide incorporated therein. The weight of the fabric measured indicated that the fabric contained 43000 mg/kg of zirconium hydroxide.

Comparative Example 4

35 The same cotton fabric as used in Reference Example 3 was treated in the same manner as in Reference Example 3 except that the treating solution was free from zirconium oxychloride.

Example 2

40 A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 0.45% of magnesium chloride hexahydrate and thereafter squeezed with a mangle. Subsequently, the fabric was dipped in an aqueous solution containing 0.5% of sodium hydroxide for 3 seconds, further dipped in an aqueous solution containing 2.5% of butanetetracarboxylic acid and 0.45% of sodium carbonate and thereafter squeezed with the mangle. The fabric was dried at 120°C and cured at 160°C for 2 minutes to obtain a  
45 butanetetracarboxylic acid crosslinked fabric having magnesium hydroxide incorporated therein. The fabric was found to have a magnesium hydroxide content of 1200 mg/kg by the atomic absorption method.

Comparative Example 5

50 The same cotton fabric as used in Example 2 was treated in the same manner as in Example 2 except that the treating solutions were free from magnesium chloride or butanetetracarboxylic acid.

Reference Example 4

55 A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped for 3 minutes in an aqueous solution of sodium zincate which was prepared in advance by mixing together 5% zinc carbonate and 30% sodium hydroxide with stirring. The fabric was squeezed with a mangle and dried at 100°C to obtain a cotton fabric having sodium zincate incorporated therein. Subsequently, the fabric was dipped in 0.4% aqueous solution of acetic acid for 3 seconds, squeezed with the mangle, washed with water and dried to obtain a cotton fabric having zinc

hydroxide incorporated therein. The fabric was found to have a zinc hydroxide content of 25700 mg/kg by the atomic absorption method.

Comparative Example 6

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The same cotton fabric as used in Reference Example 4 was treated in the same manner as in Reference Example 4 except that the treating solution was free from sodium zincate.

Reference Example 5

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A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 1% of cupric chloride, thereafter squeezed with a mangle and dried at 80°C to incorporate cupric chloride into the fabric. Subsequently, the fabric was dipped in an aqueous solution containing 1.0% of sodium silicate for 3 seconds, then squeezed with the mangle, washed with water immediately after squeezing and dried to obtain a cotton fabric having cupric silicate incorporated therein. The fabric was found to have a cupric silicate content of 4800 mg/kg by the atomic absorption method.

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Comparative Example 7

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The same cotton fabric as used in Reference Example 5 was treated in the same manner as in Reference Example 5 except that the treating solution was free from cupric chloride.

Reference Example 6

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A cotton fabric weighing 120 g/m<sup>2</sup> was scoured, bleached and mercerized. The fabric was then dipped in an aqueous solution containing 8% of zinc chloride, thereafter squeezed with a mangle and dried at 80° C to incorporate zinc chloride into the fabric. Subsequently, the fabric was dipped in an aqueous solution containing 1.0% of sodium aluminate for 3 seconds, then squeezed with the mangle, washed with water immediately after squeezing and dried to obtain a cotton fabric having incorporated therein zinc aluminate (aluminum oxide zinc oxide hydrate). The fabric was found to have a zinc aluminate content of 38100 mg/kg by the atomic absorption method.

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Comparative Example 8

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The same cotton fabric as used in Reference Example 6 was treated in the same manner as in Reference Example 6 except that the treating solutions were free from zinc chloride or sodium aluminate.

Comparative Example 9

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The same cotton fabric as used in Reference Examples 1 to 6 and Example 2 was mercerized to prepare an untreated fabric 1. A polyester/cotton blended yarn fabric the same as the one used in Example 1 was mercerized to prepare an untreated fabric 2.

Comparative Example 10

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The untreated fabric 1 was dipped in an aqueous solution containing 1.16% of zinc chloride, squeezed with a mangle and dried at 100°C to obtain a cotton fabric having zinc chloride incorporated therein. The fabric was found to have a zinc chloride content of 5600 mg/kg by the atomic absorption method.

Washing Conditions

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The fabrics obtained in Examples 1 and 2, those obtained in Comparative Examples 1 to 8 and Reference Examples 1 to 6 and the untreated fabrics 1 and 2 were washed in a household washing machine under the following conditions. For the sake of convenience, washing the fabric in water at ordinary temperature for 10 minutes using 2 g/liter of a household detergent (brand name: NEW BEADS, product of Kao Soap Co., Ltd.) was regarded as one washing cycle. The washing cycle was repeated 10 times for 100 minutes, or 30 times for 300 minutes, or 50 times for 500 minutes, followed by rinsing with water, dewatering and drying to obtain 10- cycle washing (L-10), 30-cycle washing (L-30) or 50-cycle washing (L-50). The fabrics obtained in Reference Example 3 and Comparative Example 4 were laundered under the same conditions as above except that a detergent (brand name: MONOGEN UNI, product of P & G) free

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from any fluorescent agent was used.

Evaluation of Deodorizing Ability

5 The following test was conducted to determine the deodorizing ability of the fabrics obtained in Examples 1 and 2 and Reference Examples 1, 2 and 4 to 6 and the fabrics obtained in Comparative Examples 1 to 3, 5 to 8 and 10, the untreated fabrics 1 and 2, and the 10-cycle washing, 30-cycle washing and 50-cycle washing of each of these fabrics.

10 A sample of the fabric, 10 cm x 10 cm, was placed into a 600-ml Erlenmeyer flask, which was then closed with a stopper. A gaseous or liquid compound releasing an offensive odor and having a specified concentration was then injected into the flask from its top using a microsyringe and allowed to stand for 60 minutes. The compound, when liquid, was evaporated by heating with a hot air gun and thereafter allowed to stand. The same gas or liquid was also injected into a flask containing no fabric sample and allowed to stand. After standing, the gas concentration was measured using a Kitagawa gas sensor tube.

15 Conditions for Injecting Odor-Releasing Compound Ammonia: A 20-ml quantity of 35% ammonia water was placed into a 100-ml Erlenmeyer flask and heated to produce ammonia gas. The gas was collected from an upper portion of the flask with a gastight syringe, and a 0.2-ml portion thereof was injected into the flask for use in the test. Isovaleric acid: A 0.5- $\mu$ l quantity of isovaleric acid was injected into the flask with a microsyringe and heated for evaporation.

20 The odor-releasing compound removal efficiency was calculated from the following equation.

$$\text{Removal efficiency(\%)} = \frac{A-B}{A} \times 100$$

25 wherein A is the gas concentration (ppm) in the flask containing no fabric, and B is the gas concentration (ppm) in the flask containing the fabric to be tested.

The fabrics of the examples and comparative examples and the untreated fabrics were tested for deodorizing ability before and after the washing, and the results are listed in Table 1. The fabrics of Examples 1 and 2 and Reference Examples 1 to 6 and Comparative Example 10 were also checked for the content of metal compound incorporated therein before and after the washing. Table 2 shows the results.

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Table 1

Removal efficiency (%)	Ammonia				Isovaleric acid			
	L-0	L-10	L-30	L-50	L-0	L-10	L-30	L-50
Reference Example 1	85	80	75	73	100	95	91	90
Comp. Ex. 1	55	56	51	54	50	45	45	45
Untreated 1	45	46	45	46	45	47	45	47
Example 1	100	97	95	95	100	92	90	85
Comp. Ex. 2	41	40	40	35	33	35	33	35
Untreated 2	40	35	38	40	35	38	35	35
Reference Example 2	60	65	60	57	70	75	60	50
Comp. Ex. 3	44	40	43	45	38	35	33	35
Example 2	100	95	93	90	95	90	81	75
Comp. Ex. 5	42	40	45	45	45	32	35	30
Reference Example 4	75	70	70	65	100	98	95	95
Comp. Ex. 6	45	43	40	35	33	30	35	37
Reference Example 5	55	50	50	45	81	75	70	65
Comp. Ex. 7	45	42	40	43	30	33	32	30
Reference Example 6	75	70	70	65	100	98	95	93
Comp. Ex. 8	40	43	45	42	35	35	30	34
Comp. Ex. 10	85	50	45	45	78	50	45	46



Table 2

mg/kg	Metal compound incorporated	L-0	L-10	L-30	L-50
Reference Example 1	Zinc hydroxide	4100	3900	3600	3400
Example 1	Zinc hydroxide	3100	2900	2500	2400
Reference Example 2	Aluminum hydroxide	18500	15500	12700	12100
Reference Example 3	Zirconium hydroxide	43000	38900	36100	34300
Example 2	Magnesium hydroxide	1200	1000	900	900
Reference Example 4	Zinc hydroxide	25700	23100	21700	19900
Reference Example 5	Cupric silicate	4800	4600	4200	4000
Reference Example 6	Zinc aluminate	38100	34800	32200	31200
Comp. Ex. 10	Zinc chloride	5 00	3	0	0

Evaluation of Antibacterial Property

The fabrics obtained in Example 1, 1 and Reference Examples 1 and 4 to 6, and the fabrics obtained in Comparative Examples 1, 2 and 6 to 8 were tested for antibacterial property by the 5 following method.

5 Test bacterium: Staphylococcus aureus IAM12082,

Test method: Clear zone test was conducted according to AATCC TEST METHOD 90. The number of cells was measured according to AATCC TEST METHOD 100.

10 Table 3 shows the result of the clear zone test. Table 4 shows the result of cell number measurement.

Table 3

	Diameter of clear zone (mm)				
	Reference Ex.1	Ex.1	Reference Ex.4	Reference Ex.5	Reference Ex.6
L-0	3.5	3.0	4.0	3.0	3.5
L-10	3.0	3.0	3.5	3.0	3.0

	Diameter of clear zone (mm)				
	Comp. Ex.1	Comp. Ex.2	Comp. Ex.6	Comp. Ex.7	Comp. Ex.8
L-0	0	0	0	0	0
L-10	0	0	0	0	0

Table 4

5	Untreated fabric 1	Number of cells collected immediately after inoculation (= Number A) $1.38 \times 10^5$	logB/A = 3.09 > 2
10	Untreated fabric 1	Number of cells collected after incubation (= Number B) $1.70 \times 10^{10}$	

20		Number of cells collected after incubation	Difference of vial counts	anti-bacterial effect	
25	Reference Example 1	L-0	0	$\infty$	Yes
		L-10	0	$\infty$	Yes
30	Comp. Ex. 1	L-0	$2.1 \times 10^8$	-0.21	No
		L-10	$1.8 \times 10^8$	-0.06	No
35	Example 1	L-0	0	$\infty$	Yes
		L-10	0	$\infty$	Yes
	Comp. Ex. 2	L-0	$3.1 \times 10^8$	-0.60	No
40		L-10	$2.3 \times 10^8$	-0.30	No
	Reference Example 4	L-0	0	$\infty$	Yes
		L-10	0	$\infty$	Yes
45	Comp. Ex. 6	L-0	$1.9 \times 10^8$	-0.12	No
		L-10	$1.5 \times 10^8$	0.43	No
	Reference Example 5	L-0	0	$\infty$	Yes
50		L-10	0	$\infty$	Yes
	Comp. Ex. 7	L-0	$1.2 \times 10^8$	0.35	No
55		L-10	$1.6 \times 10^8$	0.06	No

Table 4 (continued)

		Number of cells collected after incubation	Difference of vial counts	anti-bacterial effect
Reference Example 6	L-0	0	$\infty$	Yes
	L-10	0	$\infty$	No
Comp. Ex. 8	L-0	$1.5 \times 10^8$	0.12	No
	L-10	$1.8 \times 10^8$	-0.06	No

#### Evaluation of Ultraviolet Ray Blocking Property

The following method was used for evaluating the ultraviolet ray blocking effect of the fabrics obtained in Reference Example 3 and Comparative Example 4. Used as a UV light source was a short-long wavelength change-over type UV hand lamp UV-GL-58 (product of San Gabriel, U.S.A.). A UV intensity meter (UM-1, product of Minolta Camera Co., Ltd.) was placed immediately below the lamp, with the sensor portion of the meter covered with the fabric to be tested, and the intensity of ultraviolet rays passing through the fabric was measured. The UV sensors used were UM-36 for long wavelengths and UM-25 for short wavelengths to measure the intensity in the respective wavelength ranges. The transmittance (%) was calculated from the following equation.

$$\text{Transmittance (\%)} = \frac{I_1}{I_2} \times 100$$

wherein  $I_1$  is the intensity of ultraviolet rays (mw/cm<sup>2</sup>) passing through the fabric, and  $I_2$  is the intensity of ultraviolet rays (mw/cm<sup>2</sup>) impinging on the sensor in the absence of fabric.

Table 5 shows the result obtained.

Table 5

	UM-25		UM-36	
	L-0	L-10	L-0	L-10
Reference Example 3	7.8	8.2	30.1	31.2
Comp. Ex. 4	16.0	17.9	44.8	45.9
Untreated 1	16.7	17.6	45.1	46.2

#### Evaluation of Heat Accumulating Property

The fabrics obtained in Reference Example 3 and Comparative Example 4 were checked for heat accumulating effect by the following method. Each of the fabrics was placed in a constant-temperature chamber at 20°C 60% RH and irradiated with light by a 500-W photographic white lamp at a distance of 1.5 m from the fabric. Five minutes after the start of irradiation, the surface temperature of the fabric on one side thereof opposite to the irradiate side was measured with an IR noncontact surface thermometer. Table 6 shows the result.

Table 6

Surface temperature (°C)	L-0	L-10
Reference Example 3	27.5	27.2
Comp. Ex. 4	25.6	25.4

Table 6 (continued)

Surface temperature (°C)	L-0	L-10
Untreated 1	25.5	25.3

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**Claims**

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1. A natural cellulose fiber having a water-insoluble inorganic metal compound incorporated therein and having at least one heat-treated polycarboxylic acid combined therewith, the polycarboxylic acid being selected from the group consisting of polycarboxylic acids and partial salts thereof.

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2. A natural cellulose fiber according to claim 1 which is a cotton or hemp fiber or a blend of the cotton or hemp fiber with a synthetic fiber.

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3. A natural cellulose fiber according to claim 1 or 2 wherein the water-insoluble inorganic metal compound is at least one compound selected from the group consisting of hydroxides, carbonates, phosphates, silicates, aluminates and zirconates of metals selected from copper, silver, zinc, zirconium, iron, cobalt, nickel, manganese, cerium, magnesium, tin and antimony.

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4. A natural cellulose fiber according to claim 1 or 2 wherein the water-insoluble inorganic metal compound is at least one compound selected from the group consisting of zinc hydroxide and magnesium hydroxide.

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5. A natural cellulose fiber according to any one of claims 1-4 wherein the polycarboxylic acid is at least one compound selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, corresponding branched fatty acids, maleic acid, fumaric acid, cyclohexanedicarboxylic acid and corresponding position isomers, tetrahydrophthalic acid, nadic acid, tricarboxylic acid, aconitic acid, methylcyclohexanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, tetrahydrofuran-tetracarboxylic acid, an ene adduct of methyltetrahydrophthalic acid with maleic acid, malic acid, tartaric acid, citric acid, trimellitic acid, pyromellitic acid, biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid and diphenylsulfonetetracarboxylic acid.

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6. A natural cellulose fiber according to any one of claims 1-4 wherein the polycarboxylic acid is butanetetracarboxylic acid.

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7. A natural cellulose fiber according to any one of claims 1-6 wherein the partial salt of polycarboxylic acid is a sodium salt, potassium salt or ammonium salt of polycarboxylic acid.

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8. A process for preparing the natural cellulose fiber of any one of claims 1-7, the process comprising the steps of impregnating a natural cellulose fiber with a treating solution containing a water-soluble inorganic metal compound and a polycarboxylic acid, heating the fiber and insolubilizing the water-soluble inorganic metal compound incorporated in the fiber.

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9. A process for preparing the natural cellulose fiber of any one of claims 1-7, the process comprising the steps of impregnating a natural cellulose fiber with a treating solution containing a water-soluble inorganic metal compound, insolubilizing the water-soluble inorganic metal compound incorporated in the fiber, impregnating the treated fiber with a treating solution containing a polycarboxylic acid and heating the fiber.

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10. A process according to claim 8 or 9 wherein the water-soluble inorganic metal compound is zinc chloride or magnesium chloride.

11. A process according to claim 8 or 9 wherein the water-soluble inorganic metal compound is zinc chloride and the polycarboxylic acid is butanetetracarboxylic acid.

**Patentansprüche**

1. Natürliche Cellulosefaser mit einer darin eingelagerten wasserunlöslichen anorganischen Metallverbindung und

mindestens einer hitzebehandelten Polycarbonsäure, die damit kombiniert ist, wobei die Polycarbonsäure ausgewählt wird aus der Gruppe Polycarbonsäuren und teilweise Salzen davon.

- 5 2. Natürliche Cellulosefaser nach Anspruch 1, die eine Baumwoll- oder Hanffaser oder ein Gemisch der Baumwoll- oder Hanffaser mit einer synthetischen Faser ist.
- 10 3. Natürliche Cellulosefaser nach Anspruch 1 oder 2, wobei die wasserunlösliche anorganische Metallverbindung mindestens eine Verbindung ist, ausgewählt aus der Gruppe von Hydroxiden, Carbonaten, Phosphaten, Silicaten, Aluminaten und Zirkonaten von Metallen, ausgewählt aus Kupfer, Silber, Zink, Zirkonium, Eisen, Cobalt, Nickel, Mangan, Cer, Magnesium, Zinn und Antimon.
- 15 4. Natürliche Cellulosefaser nach Anspruch 1 oder 2, wobei die wasserunlösliche anorganische Metallverbindung mindestens eine Verbindung, ausgewählt aus Zinkhydroxid und Magnesiumhydroxid, ist.
- 20 5. Natürliche Cellulosefaser nach einem der Ansprüche 1 - 4, wobei die Polycarbonsäure mindestens eine Verbindung ist, ausgewählt aus der Gruppe von Oxalsäure, Malonsäure, Bernsteinsäure, Glutarsäure, Adipinsäure, Korksäure, Azelainsäure, Sebacinsäure, den entsprechenden verzweigten Fettsäuren, Maleinsäure, Fumarsäure, Cyclohexandicarbonsäure und den entsprechenden Stellungsisomeren, Tetrahydrophthalsäure, 5-Norbornen-2,3-dicarbonsäure (nadic acid), Tricarballylsäure, Aconitsäure, Methylcyclohexentricarbonsäure, Butantetracarbonsäure, Cyclopentantetracarbonsäure, Tetrahydrofuran-tetracarbonsäure, ein En-Addukt von Methyltetrahydrophthalsäure mit Maleinsäure, Äpfelsäure, Weinsäure, Citronensäure, Trimellitsäure, Pyromellitsäure, Biphenyltetracarbonsäure, Benzophenontetracarbonsäure und Diphenylsulfontetracarbonsäure.
- 25 6. Natürliche Cellulosefaser nach einem der Ansprüche 1 - 4, wobei die Polycarbonsäure Butantetracarbonsäure ist.
7. Natürliche Cellulosefaser nach einem der Ansprüche 1 - 6, in der das teilweise Salz der Polycarbonsäure ein Natriumsalz, Kaliumsalz oder Ammoniumsalz der Polycarbonsäure ist.
- 30 8. Verfahren zur Herstellung der natürlichen Cellulosefaser nach einem der Ansprüche 1 - 7, wobei das Verfahren die nachstehenden Schritte umfaßt: Tränken einer natürlichen Cellulosefaser mit einer Behandlungslösung, die eine wasserlösliche anorganische Metallverbindung und eine Polycarbonsäure enthält, Erhitzen der Faser und Unlöslichmachen der wasserlöslichen anorganischen Metallverbindung, die in die Faser eingelagert ist.
- 35 9. Verfahren zur Herstellung der natürlichen Cellulosefaser nach einem der Ansprüche 1 - 7, wobei das Verfahren die nachstehenden Schritte umfaßt: Tränken einer natürlichen Cellulosefaser mit einer Behandlungslösung, die eine wasserlösliche anorganische Metallverbindung enthält, Unlöslichmachen der wasserlöslichen anorganischen Metallverbindung, die in die Faser eingelagert ist, Tränken der behandelten Faser mit einer Behandlungslösung, die eine Polycarbonsäure enthält, und Erhitzen der Faser.
- 40 10. Verfahren nach Anspruch 8 oder 9, wobei die wasserlösliche anorganische Metallverbindung Zinkchlorid oder Magnesiumchlorid ist.
- 45 11. Verfahren nach Anspruch 8 oder 9, wobei die wasserlösliche anorganische Metallverbindung Zinkchlorid ist und die Polycarbonsäure Butantetracarbonsäure ist.

#### Revendications

- 50 1. Fibre de cellulose naturelle dans laquelle est incorporé un composé métallique inorganique insoluble dans l'eau et à laquelle est combiné au moins un acide polycarboxylique traité à chaud, l'acide polycarboxylique étant choisi dans le groupe consistant en acides polycarboxyliques et sels partiels de ceux-ci.
- 55 2. Fibre de cellulose naturelle suivant la revendication 1, qui est une fibre de coton ou de chanvre ou un mélange de la fibre de coton ou de chanvre avec une fibre synthétique.
3. Fibre de cellulose naturelle suivant les revendications 1 ou 2, dans laquelle le composé métallique inorganique insoluble dans l'eau est au moins un composé choisi dans le groupe consistant en hydroxydes, carbonates, phosphates, silicates, aluminates et zirconates de métaux choisis parmi le cuivre, l'argent, le zinc, le zirconium, le fer,

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le cobalt, le nickel, le manganèse, le cérium, le magnésium, l'étain et l'antimoine.

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4. Fibre de cellulose naturelle suivant les revendications 1 ou 2, dans laquelle le composé métallique inorganique insoluble dans l'eau est au moins un composé choisi dans le groupe consistant en hydroxyde de zinc et hydroxyde de magnésium.
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5. Fibre de cellulose naturelle suivant l'une quelconque des revendications 1 à 4, dans laquelle l'acide polycarboxylique est au moins un composé choisi dans le groupe consistant en acide oxalique, acide malonique, acide succinique, acide glutarique, acide adipique, acide subérique, acide azélaïque, acide sébacique, acides gras ramifiés correspondants, acide maléique, acide fumarique, acide cyclohexane dicarboxylique et isomères de position correspondants, acide tétrahydrophthalique, acide nadique, acide tricarbaryle, acide aconitique, acide méthylcyclohexène tricarboxylique, acide butane tétracarboxylique, acide cyclopentane tétracarboxylique, acide tétrahydrofurane tétracarboxylique, produit d'addition ène d'acide méthyltétrahydrophthalique avec l'acide maléique, acide malique, acide tartrique, acide citrique, acide trimellitique, acide pyromellitique, acide biphényl tétracarboxylique, acide benzophénone tétracarboxylique et acide diphénylsulfone tétracarboxylique.
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6. Fibre de cellulose naturelle suivant l'une quelconque des revendications 1 à 4, dans laquelle l'acide polycarboxylique est l'acide butane tétracarboxylique.
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7. Fibre de cellulose naturelle suivant l'une quelconque des revendications 1 à 6, dans laquelle le sel partiel d'acide polycarboxylique est un sel de sodium, un sel de potassium ou un sel d'ammonium d'acide polycarboxylique.
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8. Procédé pour préparer la fibre de cellulose naturelle suivant l'une quelconque des revendications 1 à 7, le procédé comprenant les étapes d'imprégnation d'une fibre de cellulose naturelle avec une solution de traitement contenant un composé métallique inorganique soluble dans l'eau et un acide polycarboxylique, de chauffage de la fibre et d'insolubilisation du composé métallique inorganique soluble dans l'eau incorporé dans la fibre.
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9. Procédé pour préparer la fibre de cellulose naturelle suivant l'une quelconque des revendications 1 à 7, le procédé comprenant les étapes d'imprégnation d'une fibre de cellulose naturelle avec une solution de traitement contenant un composé métallique inorganique soluble dans l'eau, d'insolubilisation du composé métallique inorganique soluble dans l'eau incorporé dans la fibre, d'imprégnation de la fibre traitée avec une solution de traitement contenant un acide polycarboxylique et de chauffage de la fibre.
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10. Procédé suivant les revendications 8 ou 9, dans lequel le composé métallique inorganique soluble dans l'eau est le chlorure de zinc ou le chlorure de magnésium.
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11. Procédé suivant les revendications 8 ou 9, dans lequel le composé métallique inorganique soluble dans l'eau est le chlorure de zinc et l'acide polycarboxylique est l'acide butane tétracarboxylique.

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