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(54) **ANTIBACTERIAL FIBER AND RESIN AND PRODUCTION THEREOF.**

(57) This invention relates to: (1) antibacterial polyacrylonitrile or polyester fiber and resin containing 1 to 1,000 ppm, preferably 10 to 1,000 ppm, of silver in the form of silver sulfonate, (2) a method of producing the antibacterial polyacrylonitrile or polyester fiber or resin by reacting polyacrylonitrile or polyester fiber or resin having sulfo and/or sulfonate groups in its structure with a water-soluble silver compound in water, characterized in that said reaction is carried out at a temperature above the glass transition point of the polyacrylonitrile or polyester, (3) a method of producing the antibacterial polyacrylonitrile or polyester fiber or resin characterized by reacting polyacrylonitrile or polyester fiber or resin having sulfo and/or sulfonate group in its structure with a water-soluble silver compound in water at a temperature above the glass transition hint of the polyacrylonitrile or polyester and treating the reaction product with a reducing agent, and (4) antibacterial polyacrylonitrile or polyester fiber and resin produced by the above method (2) or (3).

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ANTIMICROBIAL FIBER, RESIN, AND METHOD FOR PRODUCTION THEREOF

Technical Field

This invention relates to an antimicrobial polyacrylonitrile or polyester fiber or resin, and to a method in which a polyacrylonitrile or polyester fiber or resin is processed to provide antimicrobial properties.

5 To date, antimicrobial materials have even been propagated and utilized everywhere in life. Further, they are becoming more indispensable to food industries such as meat industries, areas such as medical treatment, and manufacturing industries such as medical supplies. Furthermore, they may be considered that as society is aging, their importance will increase even more in the future.

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Background Art

Polyacrylonitrile fibers or resins (hereinafter referred to as PAN) are highly general-purpose, and have been widely used in, needless to say, clothes, and other life amenities including toiletry products. Consequently, studies concerning the antimicrobial processing of PAN are active, and various methods have been proposed, but there has not yet been a conclusive method. An idea wherein a PAN which has sulfonic group and/or sulfonate group in the structure thereof is treated with metallic silver or a silver compound to impart antimicrobial properties thereto has been well-known for a long time. However, because the reaction of a silver ion looks like proceeding fast, no literature can be found which investigates the reaction conditions in detail. As a result, in the prior art technique, its effectiveness can be proven only by increasing the amount of silver to be adhered by using a fiber with an increased amount of sulfonic group and/or sulfonate group, or by increasing the amount of carboxyl group in the fiber by partial hydrolysis of the PAN. On the other hand, polyester fibers and resins (hereinafter referred to as PET) are also highly general-purpose materials, being extensively utilized in various industrial fields, not to mention clothes. With reference to the PET, there is almost no effective method for imparting antimicrobial properties to the material by surface treatment after molding, thus the development of such a technique has long been desired.

In Japanese Patent Laid-Open (KOKAI) No. 52-92,000 (1977), a method for providing antimicrobial properties to mainly PAN is described. According to this, the useful silver concentration range is not less than 0.1 milliequivalent (meq)/g fiber, and 0.69 meq/g fiber of silver is used in its working example. This means that a large amount of silver, i.e. 1% and 7% by weight per fiber is used, respectively. This contains a practical problem from the economic viewpoint.

When antimicrobial properties are provided to PAN, it was required for the prior art techniques to prepare fibers in a special form or to perform a treatment such as hydrolysis previously. These treatment are not only complicated procedures, but also seriously affect the strength and physical properties of the fiber. Further, a use of a large amount of silver, as described above, is also a problem. The inventors have further found in the research on the PANs to which silver is adhered by means of the conventional method that the silver is unevenly adhered to them, especially the silver separated out as metallic silver aggregates to form particles of large diameter. Accordingly, it turned out that the specific surface area of the silver adhered to the PAN is small, and a large portion of the silver particle will be easily fallen off by several repetitions of washing. It has been also understood that, due to uneven adhering, no stable effect can be obtained without using a large amount of silver.

On the other hand, the PET has no chemically active group in the structure thereof. In only a certain case, there exist those having sulfonic group and/or sulfonate group in the structure thereof in which sulfonic group and/or sulfonate group is introduced for the purpose of improving dyeing properties, i.e., so-called cationic dye dyeable type polyester fibers or resins (hereinafter referred to as CDPET). However, only a quite small amount of sulfonic group and/or sulfonate group can be introduced without adversely affecting the performance of the fibers or resins. Consequently, in prior art technique has not been considered the surface treatment of fibers or resins with silver or a silver compound as a practical method, so as severely limited method that an antimicrobial compound is kneaded into PET to provide antimicrobial properties has been employed hitherto.

As described above, PETs having sulfonic group and/or sulfonate group in the fiber (CDPET) for the purpose of improving the dyeing properties have been known. However, if carrying out the treatment for adhering or bonding to them a silver compound or metallic silver by the conventional manner, almost no silver is adhered to the fiber or resin, otherwise even if silver is adhered, silver is adhered in an uneven

form, the specific surface area of silver is small and the aggregated silver is easily separated off with washing and the like, resulting in an insufficient antimicrobial activity and failure to show a continuous effect.

5 Disclosure of Invention

The inventors have studied about a method for uniformly adhering or bonding to PAN or CDPET silver with avoiding the aggregation. As a result, the present invention has been accomplished.

This invention relates to:

- 10 (1) an antimicrobial fiber or resin of polyacrylonitrile or polyester containing 1 to 1,000 ppm, preferably 10 to 1,000 ppm, of silver in the form of silver sulfonate,
- (2) a process for producing an antimicrobial fiber or resin of polyacrylonitrile or polyester comprising reacting a fiber or resin of polyacrylonitrile or polyester having a sulfonic group and/or a sulfonate group in the structure thereof with a water-soluble silver compound in water at a temperature not lower than the
15 glass transition temperature of the polyacrylonitrile or the polyester,
- (3) a process for producing an antimicrobial fiber or resin of polyacrylonitrile or polyester comprising reacting a fiber or resin of polyacrylonitrile or polyester having a sulfonic group and/or a sulfonate group in the structure thereof with a water-soluble silver compound in water at a temperature not lower than the glass transition temperature of the polyacrylonitrile or the polyester, and then treating it with a reducing
20 agent,
- (4) the process of the above-mentioned (2) or (3), wherein the fiber or resin of polyacrylonitrile or polyester is reacted with the water-soluble silver compound in water at a pH not higher than 5, and
- (5) an antimicrobial fiber or resin of polyacrylonitrile or polyester obtained by the process of the above-mentioned (2), (3), or (4).

25 As the PANs (polyacrylonitrile fibers and resins) for use in this invention, it is possible to use the fibers or resins with the amount of sulfonic group and/or sulfonate group especially increased, but it is sufficient to use commercially available PANs having a sulfonic group and/or a sulfonate group such as Cashmilon, Toraylon, Exlan, Beslon, Vonnell, and Kanekalon. In addition to the fiber in the form of yarn, cloth and the like, resin in various forms such as sheet, powder and granule may be used as the PAN, and the PAN in
30 any form may be treated in accordance with the method of this invention.

The PANs which are used in this invention usually are copolymers comprising at least 60 mol% of acrylonitrile and unsaturated compounds containing vinyl group copolymerizable with the acrylonitrile. Any PAN can be used in this invention as long as the PAN contains such an amount of sulfonic group and/or sulfonate group that 1 to 1,000 ppm or more of silver can be adhered or bonded thereto when the treatment
35 of the above-mentioned (2), (3) or (4) is carried out.

As the CDPETs (polyester fibers and resins having sulfonic group and/or sulfonate group in the structure thereof) for use in this invention, it is possible to use the fibers or resins with the amount of sulfonic group and/or sulfonate group especially increased, and commercially available cationic dye dyeable type polyesters (CDPET) or polyester cloths or yarns mixed with raw CDPET yarns can be used. Also,
40 resins in various forms such as sheet, powder and granule can be used.

Usually the CDPETs are polyester fibers or resins which are obtained mainly by the dehydrating polycondensation reaction of terephthalic acid and/or phthalic acid (derivatives) with polyhydric alcohols and have sulfonic group and/or sulfonate group in the structure thereof. Any CDPET can be used as long as the CDPET contains such an amount of sulfonic group and/or sulfonate group that 1 to 1,000 ppm or more of
45 silver can be adhered or bonded thereto when the treatment of the above-mentioned item (2), (3) or (4) is carried out. Phthalic acid, isophthalic acid, p-hydroxybenzoic acid, 2-sulfoterephthalic acid, 5-sulfoisophthalic acid, and the like, are used as the phthalic acid (derivatives), and ethylene glycol, pentaerythritol, oligoethylene glycols and the like are used as the polyhydric alcohols.

The water-soluble silver compound to be used is usually silver nitrate, but other compounds such as
50 silver fluoride, silver perchlorate, silver sulfate, silver lactate, silver tetrafluoroborate and silver acetate may also be used.

The glass transition temperature of the PAN depends on the kind of PAN, but generally is in the range of 60 to 90°C. Therefore, when the PAN is used, a temperature not lower than the glass transition temperature of the PAN may be obtained by setting a reaction temperature (a treating bath temperature) to
55 not lower than 90°C in general. The reaction may also be carried out at normal pressure, while boiling the treating bath. There is also no problem in carrying out the reaction at a temperature of not lower than 100°C under pressure. The reaction temperature is not specifically limited as long as it is not lower than the glass transition temperature of the PAN, but in order not to impair the characteristics of the PAN, it is

preferably not higher than 130 °C, especially in the range of the glass transition temperature to 100 °C.

On the other hand, the glass transition temperature of the commercially available CDPET depends on the kind of CDPET, but is generally in the range of 70 to 90 °C. Therefore, when the CDPET is used, a temperature not lower than the glass transition temperature of the CDPET may be obtained by setting the reaction temperature (a treating bath temperature) to not lower than 90 °C in general. The reaction may be carried out at normal pressure, while boiling the treating bath. There is also no problem carrying out the reaction at a temperature of not lower than 100 °C under a pressure. The reaction temperature is not specifically limited as long as it is not lower than the glass transition temperature of the CDPET but in order not to impair the characteristics of the CDPET, it is preferably not higher than 200 °C, especially in the range of 90 to 140 °C.

In the explanation hereinafter, the term "PAN" and the term "CDPET" are referred to collectively as "CDFR".

For carrying out the process of the present invention, generally the CDFR is added to an aqueous solution of the water-soluble silver compound, and the reaction is performed by heating it to a temperature not lower than the glass transition temperature of the CDFR added, with stirring. The reaction may also be carried out by preheating an aqueous solution of the water-soluble silver compound to a temperature not lower than the glass transition temperature of the CDFR, and then adding the CDFR. The bath ratio (CDFR: the aqueous solution of the water-soluble silver compound) is suitably in the range of 1 : 10 to 40 (weight ratio). The heat treatment period is not specifically limited, but generally it is sufficient to carry out the heat treatment for 10 to 60 minutes.

The amount of the water-soluble silver compound to be added depends on the amount of silver desired to be adhered, kind of CDFR, and the reaction conditions. In the case of CDFRs which are generally commercially available, the water-soluble silver compound may be used in such an amount as 1 to 5 times the amount of silver desired to be adhered or bonded to the CDFR. When the PAN is used, it is preferable in order not to impair the characteristics of the PAN, such as the feeling of the fiber, to pay attention to the control of the bath temperature after the treatment. To be specific, it is preferred to cool the bath gradually until the bath temperature becomes lower than 60 °C.

By the method as described above, an antimicrobial CDFR of the present invention having silver sulfonate group can be obtained.

The antimicrobial CDFR of the present invention having silver sulfonate group has less coloration, and has almost no tendency to color change by sunlight and reduction by detergent, thus it is very advantageous considering practical application to living hygienic fields.

In particular, when the coloration causes a problem, such as in the case of white cloth, it is preferable to carry out the reaction in an acidic aqueous solution by adjusting the pH value. The pH adjustment can be performed by the use of a buffer, an acid or the like, but the use of a compound which reacts with silver to form a precipitate such as hydrochloric acid is not preferable. Generally the pH value is adjusted with acetic acid, lactic acid, or an acetic acid buffer. The pH level preferably ranges from 1 to 5.

When an acid is used alone, the concentration of the acid is defined by the pH. The concentration of the buffer solution is not specifically limited, but generally it is sufficient to be 0.01 mol/l (acetic acid buffer) more or less. The antimicrobial CDFR thus obtained, if necessary, can be further reduced to provide CDFR with fine silver particles adhered thereto. If the reduction treatment is carried out, a reducing agent having a relatively strong reducing power is preferably used. For example, hydroxylamine, hydrazine, glucose-caustic alkali, sodium boron hydride, or the like may be used as the reducing agent. The reduction treatment can be carried out by the use of an aqueous solution of the reducing agent, preferably in a concentration in the range of 0.05 to 5% by weight preferably in an amount of 2 to 30 times the weight of the antimicrobial CDFR having silver sulfonate, and preferably heating to 95 to 100 °C for five minutes or more. The antimicrobial CDFR having silver sulfonate and the antimicrobial CDFR with fine silver particles adhered thereto thus obtained have a sufficient antimicrobial effect, even when silver content is a low content in the range of 1 to 1,000 ppm, preferably 10 to 1,000 ppm. As described above, in the prior art, it was required for providing antimicrobial properties to fibers that the fibers contain silver at a high content of 1% or 7%. In contrast, according to the present invention, the resins or the fibers unexpectedly exhibit strong antimicrobial effects, and excel in wash fastness, in spite of a low content of silver in the range of 1 to 1,000 ppm. This is because, in the antimicrobial CDFR of the present invention, silver is uniformly adhered or bonded onto the fibers or resins and silver separated as metallic silver does not aggregate but exists as fine particles.

Those in which silver is reduced to fine particles according to the present invention are pale yellow, whereas the conventional ones become dark brown, thus the fibers and the resins obtained by the present invention are advantageous in this aspect.

The antimicrobial CDFR having silver sulfonate and the pale yellow CDFR with fine silver particles adhered thereto according to the present invention can be dyed with a cationic dye in a suitable color tone by a known method. Otherwise, the CDFR may be dyed with a cationic dye by the conventional method at first, and then antimicrobial properties can be provided thereto according to the method of the present invention. Furthermore, the antimicrobial properties can be provided according to the present invention simultaneously with the dyeing using a cationic dye from which halogen ions contained have been removed carefully.

Since the antimicrobial CDFR of the present invention exhibits highly antimicrobial effects, in spite of a markedly low content of silver, it is sufficient to use a small amount of silver, and still does not adversely affect human body. The antimicrobial CDFR of the present invention can be utilized as an antimicrobial material in any place which has a possibility to be contaminated with harmful microorganisms. For example, as for the antimicrobial PAN, microbially clean state can be maintained by making a bath mat, a toilet mat, a toilet seat cover, a carpet, a mop, an air filter, a towel, and a dish towel. The antimicrobial PAN may be used further as work gloves or work clothings in food processing or production. As for the antimicrobial CDPET, it can be used in, for example, a white overall for the operation, a curtain in hospital, a bed, a sofa, a pillow cover or a backing of a slipper equipped in hospital, or a diaper cover, a sanitary tampon and the like.

The antimicrobial CDFR of the present invention may be used alone or used together with other fibers as mixed or union fabric of a cloth, a knitted product, or a nonwoven material.

Best Mode for Carrying Out the Invention

Now, the present invention will be described more precisely with reference to the working examples. The present invention, however, should not be limited to these examples. The test for antimicrobial activity was carried out by adhering bacterium, *Staphylococcus aureus* or *Klebsiella pneumoniae*, having been suspended in a standard bouillon medium, to a test strip, maintaining it at 37°C for 18 hours, and then counting the number of the living bacterium on the test strip. The test for washing fastness was carried out by measuring the antimicrobial effect of a test strip which was subjected to the procedure according to JIS L 0217 103 repeatedly thirty times, and measuring the amount of remaining silver by atomic absorption spectrometry.

Example A1

100 parts by weight of Cashmilon (PAN available from Asahi Kasei Co., Ltd.) was soaked in 3000 parts by weight of water containing 0.126 part by weight of silver nitrate. It was heated to a boil, and maintained in the boiling state for 30 minutes. Then the heating was stopped, and it was left standing until it cooled down to 50°C, after which Cashmilon was taken out. It was thoroughly washed with water and then dried, to obtain a Cashmilon having silver-sulfonate group.

Evaluation of Antimicrobial Activity

0.2 g of the treated cloth obtained in the above-mentioned manner was sampled, then 0.2 ml of a standard bouillon suspension of *Staphylococcus aureus* ATCC 6538P (the number of bacterium; 8×10^5 /ml) was applied thereon. This was maintained at 37°C for 18 hours, and then it was extracted with 20 ml of physiological saline buffer containing phosphate. The extract was inoculated into a standard agar medium, and the number of bacterium was counted. As a result, the extract from the treated cloth according to the present invention was found to contain 18 bacterium/ml. In contrast, the extract from an untreated control cloth not containing silver was found to contain 9×10^3 bacterium/ml.

Example A2

A testing cloth (a treated cloth) was obtained by following the procedure of Example A1, except that 100 parts by weight of Toraylon (PAN available from Toray Co., Ltd.) instead of Cashmilon and 0.063 part by weight of silver nitrate instead of 0.126 part by weight were used. As a result of carrying out antimicrobial

test in the manner of Example A1 using the resultant Toraylon, 35 bacterium/ml were detected from the extract and 7×10^3 bacterium/ml were detected from the extract from an untreated cloth not containing silver.

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Examples A3 and A4

Testing cloths (treated cloths) were obtained by following the procedure of Example A1, except that the amounts of silver nitrate were changed to 0.032 part by weight, and 0.008 part by weight respectively, and
10 the test was carried out in a similar manner.

The results of Example A1 to A4 are shown in Table A1.

Table A1

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Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
A1	805 ppm	18 bacterium/ml
A2	397 ppm	35 bacterium/ml
A3	195 ppm	25 bacterium/ml
A4	52 ppm	93 bacterium/ml

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Examples A5 to A8

100 parts by weight of the cloths obtained in Examples A1 to A4 were respectively soaked in 500 parts by weight of water in which 0.5 part by weight of sodium boron hydride had been suspended, and then heated to a boil for 30 minutes. After washing with water and drying, were obtained cloths to which silver was adhered as metallic silver by reducing silver ion. Each of them was evaluated in a similar manner to Example A1. The results are shown in Table A2.

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Table A2

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
A5 (A1)	780 ppm	8 bacterium/ml
A6 (A2)	367 ppm	25 bacterium/ml
A7 (A3)	188 ppm	34 bacterium/ml
A8 (A4)	48 ppm	51 bacterium/ml

Examples A9 to A12

The cloths to which silver was adhered or bonded, and which were obtained in Examples A1, A3, A5, and A7, were washed repeatedly thirty times according to the procedure of JIS L 0217 103. Respectively, the amount of silver remaining and the results of the antimicrobial activity tests carried out in the same manner as in Example A1 are shown in Table A3.

Table A3

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
A9 (A1)	713 ppm	25 bacterium/ml
A10 (A3)	168 ppm	61 bacterium/ml
A11 (A5)	699 ppm	38 bacterium/ml
A12 (A7)	162 ppm	30 bacterium/ml

Examples A13 to A16

The antimicrobial activity tests were carried out in the same manner as in Example A1, except that 0.2 ml of a standard bouillon suspension of *Klebsiella pneumoniae* ATCC 4352 (number of bacterium: 9×10^5 /ml) in place of *Staphylococcus aureus* was applied on each of the cloths to which silver was adhered or bonded and which were obtained in Examples A1, A3, A5 and A7. The results are shown in Table A4. The extract from the untreated control cloth not containing silver contained 1×10^4 bacterium/ml.

Table A4

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
A13 (A1)	805 ppm	25 bacterium/ml
A14 (A3)	195 ppm	31 bacterium/ml
A15 (A5)	780 ppm	42 bacterium/ml
A16 (A7)	188 ppm	38 bacterium/ml

Example A17

The antimicrobial activity test was examined for the testing strip obtained in the same manner as in Example A1 except that 0.124 part by weight of silver lactate was used in place of silver nitrate. The results obtained were substantially the same as those of Example A1.

Examples A18 and A19

A testing cloth was obtained in the same manner as in Example A5, except that 2.5 parts by weight of hydroxyl amine or 2.5 parts by weight of hydrazine was used in place of sodium boron hydride, and the antimicrobial activity test was examined. In each case, the results obtained were substantially the same as those of Example A5.

Example A20

100 parts by weight of Exlan (PAN available from Nihon Exlan Co., Ltd.) having sulfonate group was soaked in 2,500 parts by weight of an aqueous 500 ppm acetic acid solution (pH = 3.4) containing 0.063 part by weight of silver nitrate, and heated to 100°C with stirring. After stirring at 120°C for one hour, it was allowed to cool, thoroughly washed with water, dried, to obtain a polyacrylonitrile cloth having silver sulfonate. The content of silver in this polyacrylonitrile cloth was 368 ppm.

Example A21

A polyacrylonitrile cloth having silver sulfonate was obtained by following the procedure of Example A20, except that treatment was performed using 2,500 parts by weight of water (pH = 6.5) containing 0.063 part by weight of silver nitrate instead of the aqueous 500 ppm acetic acid solution containing 0.063 part by weight of silver nitrate. The content of silver in this polyacrylonitrile cloth was 374 ppm.

Both of the polyacrylonitrile cloths obtained in Example A20 and in Example A21 exhibited antimicrobial effects similar to those of Examples A1 to A4.

Example A22

Color difference between the polyacrylonitrile cloth obtained in Example A20 or in Example A21 and an untreated polyacrylonitrile cloth was measured by the use of a color difference meter. The results are given in Table A5.

Table A5

	Acetic acid Concentration (ppm)	pH	ΔL	Δa	Δb
Example A20	500	3.4	-0.10	0.11	0.09
Example A21	0	6.5	-2.02	0.98	3.27

In Table A5 given above, ΔL , Δa , and Δb represent lightness difference, hue difference, and saturation difference between the treated cloth and the untreated cloth, respectively.

It is clear from the results shown in Table A5 that though the color tone of the polyacrylonitrile cloth obtained in Example A20 is little different from that of the untreated polyacrylonitrile cloth, the polyacrylonitrile cloth obtained in Example A21 decreases in lightness and has a higher value both for Δa , and Δb , in comparison with those of the untreated polyacrylonitrile cloth. An increase in Δa means that the cloth becomes tinted with red, and an increase of Δb means that the cloth becomes tinted with yellow. The difference between the results obtained in Example A20 and in Example A21 is due to the pH value of the treating solution. Especially when coloration causes a problem in such a case where a white polyacrylonitrile cloth is desired, an antimicrobial polyacrylonitrile cloth without any color tone variation can be obtained by conducting the reaction in an acidic aqueous solution by adjusting the pH value.

Example A23

120 parts by weight of Toraylon (PAN available from Toray Co., Ltd.) having sulfonate group was soaked in 3,600 parts by weight of water in which 0.24 part by weight of silver nitrate was dissolved. It was then gradually heated to a boil, maintained for 30 minutes, and then the Toraylon was taken out and washed with water.

Subsequently, 0.4 part of a cationic dye, Kayacryl light blue 4GSL, was dissolved in 3,000 parts by weight of water. In this was again soaked the Toraylon treated with the aqueous silver nitrate solution in the above step. After the addition of 10 parts by weight of 10% acetic acid, it was heated to a boil. After maintaining 20 minutes, it was allowed to cool down to 50°C or less gradually, after which the Toraylon was taken out, thoroughly washed with water, and then dried to obtain a blue dyed Toraylon having silver-sulfonate group.

Evaluation of Antimicrobial Activity

0.2 g of a test strip was sampled from the cloth obtained in the above-mentioned manner, and 0.2 ml of a standard bouillon suspension of *Klebsiella pneumoniae* ATCC4352 (the number of bacterium; 9×10^5 /ml) was applied thereon. This was maintained at 37 °C for 18 hours, and then it was extracted with 20 ml of physiological saline buffer containing phosphate. As a result, the extract from the treated cloth according to the present invention was found to contain 43 bacterium/ml. In contrast, the extract from an untreated control cloth not containing silver was found to contain 1×10^4 bacterium/ml.

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Example A24

120 parts by weight of Toraylon (PAN available from Toray Co., Ltd.) having sulfonate group was dyed red at 100 °C by the use of 0.3 part of Kayacryl red GL. The bath ratio was 1 : 30.

Then, the red dyed cloth was soaked in 1200 parts by weight of water-containing 0.2 part by weight of silver nitrate. It was then gradually heated, and boiled for 30 minutes. Thereafter, it was thoroughly washed with boiling water.

Further, it was incorporated into 1200 parts by weight of 0.4% hydroxylamine sulfate solution, and boiled for 30 minutes. After the liquid cooled down to 50 °C or below, the treated cloth was taken out, thoroughly washed with water, and then dried.

When the antimicrobial activity test of the red cloth thus obtained, to which adhered fine silver particles, was carried out using *Klebsiella pneumoniae*, it had a strong activity.

25 Example A25

The treatment of Example A1 was repeated except that particles of polyacrylonitrile having sulfonate group were treated instead of Cashmilon in Example A1. The treated polyacrylonitrile particle exhibited antimicrobial effect similar to those of Example A1.

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Example B1

100 parts by weight of a cationic dye dyeable type polyester cloth having sulfonate group (standard dyeing temperature 120 °C) was soaked in 3000 parts by weight of boiling water containing 0.18 part by weight of silver nitrate, and maintained at this state for 30 minutes. After being cooled, the treated cloth was taken out, thoroughly washed with water, and dried to obtain a polyester cloth having silver sulfonate group. When the silver content was measured by atomic absorption spectrometry method, it was found to contain 840 ppm of silver.

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Evaluation of Antimicrobial Activity

0.2 g of the cloth obtained in the above-mentioned manner was sampled and 0.2 ml of a standard bouillon suspension of *Staphylococcus aureus* ATCC 6583P (the number of bacterium; 8×10^5 /ml) was applied thereto. This was maintained at 37 °C for 18 hours, and then it was extracted with 20 ml of physiological saline buffer containing phosphate. The extract was inoculated into a standard agar medium, and the number of bacterium was counted. As a result, the extract from the treated cloth according to the present invention was found to contain 120 bacterium/ml. In contrast, the extract from an untreated control cloth not containing silver was found to contain 6×10^8 bacterium/ml.

Examples B2 to B4

Treated cloths respectively containing specific amount of silver were obtained by following the procedure of Example B1, except that 0.09 part by weight, 0.045 part by weight, and 0.01 part by weight of silver nitrate were respectively used instead of 0.18 part by weight of silver nitrate. They were evaluated in a similar manner as in Example B1. The results are shown in Table B1.

Table B1

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
B1	840 ppm	120 bacterium/ml
B2	414 ppm	95 bacterium/ml
B3	193 ppm	145 bacterium/ml
B4	67 ppm	135 bacterium/ml

Examples B5 to B8

100 parts by weight of the cloths obtained in Examples B1 to B4 were respectively soaked in 500 parts by weight of aqueous 0.5% hydroxylamine solution, and then boiled for 30 minutes. Subsequent washing with water and drying gave cloths to which adhered silver as metallic silver by reducing silver ion. Each of them was evaluated in a similar manner as in Example B1. The results are shown in Table B2.

Table B2

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
B5 (B1)	823 ppm	85 bacterium/ml
B6 (B2)	400 ppm	120 bacterium/ml
B7 (B3)	195 ppm	98 bacterium/ml
B8 (B4)	57 ppm	160 bacterium/ml

Examples B9 to B12

The cloths to which silver was adhered or bonded, and which were obtained in Examples B1, B3, B5, and B7, were washed repeatedly thirty times according to the procedure of JIS L 0217 103. The amounts of the remaining silver and the results of the antimicrobial activity test in the same manner as in Example B1 are shown in Table B3.

Table B3

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
B9 (B1)	780 ppm	115 bacterium/ml
B10 (B3)	177 ppm	156 bacterium/ml
B11 (B5)	764 ppm	98 bacterium/ml
B12 (B7)	180 ppm	135 bacterium/ml

Examples B13 to B16

The antimicrobial activity tests were carried out in the same manner as in Example B1, except that 0.2 ml of a standard bouillon suspension of *Klebsiella pneumoniae* ATCC 4352 (number of bacterium: 9×10^5 /ml) in place of *Staphylococcus aureus* was applied on each of the treated cloths obtained in Examples B1, B3, B5 and B7. The extract from the untreated control cloth not containing silver contained 8×10^8 bacterium/ml. The results are shown in Table B4.

Table B4

Example	Amount of Silver on Treated Cloth (atomic absorption spectrometry)	The number of Bacterium after treatment at 37°C for 18 hrs
B13 (B1)	840 ppm	93 bacterium/ml
B14 (B3)	193 ppm	150 bacterium/ml
B15 (B5)	823 ppm	100 bacterium/ml
B16 (B7)	195 ppm	142 bacterium/ml

Example B17

The antimicrobial activity test was carried out on the strip obtained in the same manner as in Example B1 except that 0.17 part by weight of silver lactate was used in place of silver nitrate in Example B1. The results obtained were substantially the same as those of Example B1.

Examples B18 and B19

A test cloth was obtained in the same manner as in Example B5, except that 500 parts by weight of an aqueous 0.5% hydrazine solution or 500 parts by weight of 0.5% sodium boron hydride suspension was used in place of hydroxylamine in Example B5, and the antimicrobial activity test was carried out. In each case, the results obtained were substantially the same as those of Example B5.

Example B20

100 parts by weight of a cationic dye dyeable type polyester having sulfonate group (a standard dyeing temperature: 105 °C) was soaked in 2,500 parts by weight of water containing 0.05 part of silver nitrate, and heated to boil with stirring. After stirring for another 20 minutes, it was allowed to cool, thoroughly washed with water, and dried to obtain a polyester cloth having silver sulfonate group. When the content of silver in this polyester cloth was measured by atomic absorption spectrometry, it was found to contain 301 ppm of silver. The silver content in the polyester cloth after washing 30 times as in Example B9 was 290 ppm. As a result of carrying out the evaluation of antimicrobial activity on the unwashed polyester cloth and the polyester cloth after washing 30 times, the extract from the unwashed cloth was found to contain 135 bacterium/ml and the extract from the polyester cloth after washing 30 times was found to contain 118 bacterium/ml, while the untreated polyester cloth for control which did not contain silver was found to contain 7×10^8 bacterium/ml.

Example B21

100 parts by weight of a cationic dye dyeable type polyester (a standard dyeing temperature: 120 °C)

was soaked in 1,500 parts by weight of an aqueous 100 ppm acetic acid solution (pH = 3.8) containing 0.063 parts by weight of silver nitrate, and heated to 120 °C under pressure with stirring. After stirring at 120 °C for 1 hour, it was allowed to cool, thoroughly washed with water, and dried to obtain a polyester cloth having silver sulfonate group. The content of silver in this polyester cloth was 344 ppm.

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Example B22

A polyester cloth having silver sulfonate group was obtained by following the procedure of Example B21, except that treatment was performed using 1,500 parts by weight of water (pH = 6.5) containing 0.063 part by weight of silver nitrate instead of 1,500 parts by weight of aqueous 100 ppm acetic acid solution containing 0.063 part by weight of silver nitrate. The content of silver in this polyester cloth was 354 ppm.

Both of the polyester cloths obtained in Example B21 and in Example B22 exhibited antimicrobial effects similar to those of Example B20.

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Example B23

Color difference between the polyester cloth obtained in Example B21 or in Example B22 and an untreated polyester cloth was measured by the use of a color difference meter. The results are given in Table B5.

Table B5

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	Acetic acid Concentration (ppm)	pH	ΔL	Δa	Δb
Example B21	100	3.8	-0.26	0.31	0.17
Example B22	0	6.5	-2.68	0.70	3.96

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In Table B5, ΔL , Δa , and Δb represent lightness difference, hue difference, and saturation difference between the treated cloth and the untreated cloth, respectively.

It is clear from the results shown in Table B5 that though the color tone of the polyester cloth obtained in Example B21 is little different from that of the untreated polyester cloth, the polyester cloth obtained in Example B22 decreases in lightness and has a higher value both for Δa , and Δb , in comparison with those of the untreated polyester cloth. The difference between the results obtained in Example B21 and in Example B22 is due to the pH value of the treating solution. Especially when coloration causes a problem in such a case where a white polyester cloth is desired, an antimicrobial polyester cloth without any color tone variation can be obtained by conducting the reaction in an acidic aqueous solution by adjusting the pH value.

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Example B24

120 parts by weight of a cationic dye dyeable polyester jersey having sulfonate group was first dyed red at 120 °C using 0.3 part by weight of a cationic dye Kayacryl Red GL. The bath ratio was 1 : 30.

Then, the red dyed cloth was soaked in 1,200 parts by weight of water containing 0.2 part by weight of silver nitrate, and gradually heated to a boil, and maintained for 30 minutes. Thereafter, it was thoroughly washed with boiling water and then dried to obtain a polyester having silver-sulfonate group.

The polyester thus treated also had a high antimicrobial activity against *Staphylococcus aureus* and *Klebsiella pneumoniae*.

5 Example B25

35 parts by weight of the cationic dye dyeable polyester with fine particles of silver adhered thereon obtained in Example B5 was soaked in 400 parts by weight of water in which 0.07 part by weight of a cationic dye, Kayacryl blue 4GSL, had been dissolved. It was heated to 120 °C in an autoclave, and
10 maintained for 40 minutes to carry out dyeing. After cooling, the dyed cloth was taken out, and thoroughly washed with water to obtain a blue dyed polyester cloth. The antimicrobial activity was retained.

Example B26

15 The treatment of Example B1 was carried out except that a polyester resin particle having sulfonate group was used instead of the cationic dye dyeable polyester cloth in Example B1. The resultant polyester resin particle exhibited antimicrobial effects similar to those of Example B1.

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Industrial Applicability

The antimicrobial CDFR of the present invention, in spite of a smaller amount of silver to be adhered or bonded than that of the conventional one, exhibits strong antimicrobial effects, and excels in wash fastness.
25 The antimicrobial CDFR of the present invention also is very safe, and when incinerating it, it is free from generating any toxic substance derived from the substance used for providing antimicrobial activity. Further, the antimicrobial CDFR of the present invention has a markedly low stimulation on skin, thus it can also suitably be used in such an application as bringing it into contact with skin such as clothes.

Furthermore, according to the present invention, antimicrobial properties can be easily and economically provided to PAN and CDPET having sulfonic group and/or sulfonate group or fibers mixed or
30 combined with, PAN or CDPET. There is, in the present invention, substantially no problem of coloration of the fiber or resin due to adhering or bonding of silver.

35 Claims

1. An antimicrobial fiber or resin of polyacrylonitrile or polyester containing 1 to 1,000 ppm of silver in the form of silver sulfonate.
- 40 2. The fiber or resin according to claim 1, wherein the content of silver is 10 to 1,000 ppm.
3. A process for producing an antimicrobial fiber or resin of polyacrylonitrile or polyester, which comprises reacting fiber or resin of polyacrylonitrile or polyester having sulfonic group and/or sulfonate group in the structure thereof with a water-soluble silver compound in water at a temperature not lower than the
45 glass transition temperature of the polyacrylonitrile or the polyester.
4. A process for producing an antimicrobial fiber or resin of polyacrylonitrile or polyester, which comprises reacting a fiber or resin of polyacrylonitrile or polyester having sulfonic group and/or sulfonate group in the structure thereof with a water-soluble silver compound in water at a temperature not lower than the
50 glass transition temperature of the polyacrylonitrile or the polyester; and treating the thus reacted fiber or resin with a reducing agent.
5. The process according to claim 3 or 4, wherein the fiber or resin of polyacrylonitrile or polyester is reacted with the water-soluble silver compound in water at a pH not higher than 5.
- 55 6. The process according to any one of claims 3, 4 and 5, wherein the fiber or resin is polyacrylonitrile and the temperature of the reaction of the fiber or resin with the water-soluble silver compound in water is not lower than the glass transition temperature of the polyacrylonitrile.

7. The process according to claim 6, wherein the reaction temperature is in the range from the glass transition temperature to 100 ° C.
8. The process according to any one of claims 3, 4 and 5, wherein the fiber or resin is polyester and the temperature of the reaction of the fiber or resin with the water-soluble silver compound in water is not lower than the glass transition temperature of the polyester.
9. The process according to claim 8, wherein the reaction temperature is in the range from 90 to 140 ° C.
10. The process according to any one of claims 1 to 9, wherein the water-soluble silver compound is selected from the group consisting of silver nitrate, silver fluoride, silver perchlorate, silver sulfate, silver lactate, silver tetrafluoroborate and silver acetate.
11. An antimicrobial fiber or resin of polyacrylonitrile or polyester obtained by the process according to any one of claims 3 to 10.
12. The fiber or resin according to claim 11, wherein the content of the silver is 1 to 1,000 ppm.
13. The fiber or resin according to claim 12, wherein the content of the silver is 10 to 1,000 ppm.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00299

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ D06M11/83, D01F6/38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	D06M11/00 - 11/84, D06M23/00, D01F6/38	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
Kokai Jitsuyo Shinan Koho 1975 - 1990		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	JP, A, 52-92000 (Toray Industries, Inc.), 2 August 1977 (02. 08. 77), (Family: none)	1, 2, 11 - 13
X	JP, A, 56-148965 (Mitsubishi Rayon Co., Ltd.), 18 November 1981 (18. 11. 81), (Family: none)	1, 2, 11 - 13
Y	JP, A, 52-92000 (Toray Industries, Inc.), 2 August 1977 (02. 08. 77), (Family: none)	3 - 10
Y	JP, A, 56-148965 (Mitsubishi Rayon Co., Ltd.), 18 November 1981 (18. 11. 81), (Family: none)	3 - 10
Y	JP, A, 55-137210 (Mitsubishi Rayon Co., Ltd.), 25 October 1980 (25. 10. 80), (Family: none)	1 - 13
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
May 8, 1990 (08. 05. 90)	May 21, 1990 (21. 05. 90)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A

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6 October 1983 (06. 10. 83)
& EP, B1, 89593 & DE, A, 3209796
& DK, A, 8301239 & US, A, 4507257

1 - 13

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.