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

(11) EP 2 458 082 A1

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

(43) Date of publication:
30.05.2012 Bulletin 2012/22

(21) Application number: **10802210.4**

(22) Date of filing: **15.07.2010**

(51) Int Cl.:
D06M 11/63 *(2006.01)* ***D01F 6/18*** *(2006.01)*
D06M 11/00 *(2006.01)* ***D06M 101/28*** *(2006.01)*

(86) International application number:
PCT/JP2010/061937

(87) International publication number:
WO 2011/010590 (27.01.2011 Gazette 2011/04)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **22.07.2009 JP 2009170867**

(71) Applicant: **JAPAN EXLAN COMPANY LIMITED**
Osaka-shi
Osaka 530-0004 (JP)

(72) Inventors:
- **YAMAUCHI, Takao**
  Okayama-shi
  Okayama 704-8510 (JP)
- **TANAKA, Koji**
  Okayama-shi
  Okayama 704-8510 (JP)

(74) Representative: **Patentanwälte**
Ruff, Wilhelm, Beier, Dauster & Partner
Kronenstrasse 30
70174 Stuttgart (DE)

(54) MOISTURE-ABSORBING FIBER DYEABLE WITH ACID DYES AND METHOD FOR PRODUCING SAME

(57) The conventional crosslinked acrylic acid fiber has such characteristics that the harmonic functions such as pH buffer property, antistatic property and water-holding property and also high moisture-absorption rate, high moisture-absorption velocity, high moisture-absorption rate difference or temperature adjusting and humidity adjusting functions derived therefrom, but there is still a problem for its dyeing property. The present invention provides a fiber having the above characteristics and making a practical dyeing with an acid dye possible. To be more specific, the present invention provides a moisture-absorptive fiber dyeable with an acid dye, comprising a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group, wherein the saturation dye uptake of the acid dye to the fiber weight is 3.5 to 10% by weight and the carboxyl group content is 1.0 to 10 mmol/g.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field of the Invention

[0001] The present invention relates to a fiber which is dyeable with an acid dye and has moisture-absorption property and also to a method of manufacturing the same.

Background Art

[0002] A crosslinked acrylic acid fiber has been known to have harmonic functions such as pH buffer property, antistatic property and water-holding property and also high moisture-absorption rate, high moisture-absorption velocity, high moisture-absorption rate difference or temperature adjusting and humidity adjusting functions derived therefrom and has been used in the fields of clothing and industrial materials. However, the crosslinked acrylic acid fiber has a problem in its dyeing property and that is a main cause for suppressing the development of its use.

[0003] Since the crosslinked acrylic acid fiber has a carboxyl group which functions as a dyeing site for a cationic dye, it is possible to add the color thereto using a cationic dye in principle. However, since the ionic bond formed between the cationic dye and the carboxyl group is weak, the cationic dye is apt to be liberated by, for example, a change in pH. In addition, swelling property of the fiber in water is high and, therefore, the liberated cationic dye is easily eluted therefrom. Accordingly, it is not possible to give a color fastness which is in a level of being durable against practical use by mere dyeing using common formulations.

[0004] For solving the problem for the dyeing property as such, Patent Documents 1 and 2 propose a dyeing method for a crosslinked acrylic acid fiber using a reactive dye. Although the color fastness is improved by the use of a reactive dye in such a method, it is necessary that the pH upon dyeing is made under a strongly acidic condition and there is a problem that it is necessary to restrict the mixed fiber used together and to cope with the device such as countermeasure for corrosion. Further, in dyeing a fiber structure mixed with a cellulose fiber, there may be the case where the difference is resulted in the hue from the cellulose fiber and there is a weakness in a practical color matching.

[0005] In Patent Document 3, there is a proposal for a fiber into which sulfonic group is introduced by impregnating a monomer having sulfonic group into a material fiber having carboxyl group followed by polymerizing. Since this fiber has many sulfonic groups which function as a dyeing site for a cationic dye, coloration using a cationic dye is possible but it is difficult to achieve sufficient coloring property or color fastness and hue stability. In addition, since there is adopted a means where sulfonic group is introduced by impregnating a monomer having sulfonic group into a material fiber followed by polymerizing, there is a problem that complicated operations are necessary, which results in high production cost.

Prior Art Documents

Patent Documents

[0006]

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. 2003-278079
Patent Document 2: Japanese Patent Application Laid-Open (JP-A) No. 2006-70421
Patent Document 3: Japanese Patent Application Laid-Open (JP-A) No. 2008-174849

Disclosure of the Invention

Problem that the Invention is to Solve

[0007] As mentioned hereinabove, the conventional crosslinked acrylic acid fiber has such characteristics that the harmonic functions such as pH buffer property, antistatic property and water-holding property and also high moisture-absorption rate, high moisture-absorption velocity, high moisture-absorption rate difference or temperature adjusting and humidity adjusting functions derived therefrom, but there is still a problem for its dyeing property. The present invention has been achieved under such current circumstances and its object is to provide a fiber where a practical dyeing with an acid dye is possible while the characteristics of the crosslinked acrylic acid fiber such as high moisture-absorption property or high moisture-absorption rate difference are still available.

Means for Solving the Problem

[0008] The present inventors have carried out intensive investigations for achieving the above object and resulted in the present invention as shown below.

[0009]

(1) A moisture-absorptive fiber dyeable with an acid dye, comprising a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group, wherein the saturation dye uptake of the acid dye to the fiber weight is 3.5 to 10% by weight and the carboxyl group content is 1.0 to 10 mmol/g.

(2) The moisture-absorptive fiber dyeable with an acid dye according to (1), wherein the polymer having a functional group acting as a dyeing site for acid dye is such a polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component.

(3) The moisture-absorptive fiber dyeable with an acid dye according to (1), wherein the polymer having a functional group acting as a dyeing site for acid dye is such a polymer which is produced by subjecting a polymer where acrylonitrile is a main component to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule.

(4) The moisture-absorptive fiber dyeable with an acid dye according to (1), wherein the polymer having a crosslinked structure and a carboxyl group is such a polymer which is produced by subjecting a polymer where acrylonitrile is a main component to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment.

(5) A method for manufacturing the moisture-absorptive fiber dyeable with an acid dye mentioned in (1), **characterized in that,** a surface layer area of a fiber comprising a polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment.

(6) A method for manufacturing the moisture-absorptive fiber dyeable with an acid dye mentioned in (1), wherein a fiber comprising a polymer where acrylonitrile is a main component is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and, after that, to a hydrolyzing treatment, **characterized in that**, the range to which the hydrolyzing treatment is applied is made smaller than the range to which the crosslinking treatment is applied.

Advantages of the Invention

[0010] The moisture-absorptive fiber dyeable with an acid dye according to the present invention comprises a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group. As a result thereof, a practical dyeing with an acid dye is now possible and its moisture-absorption property becomes high as well. Therefore, in the moisture-absorptive fiber dyeable with an acid dye according to the present invention, its restriction concerning the color is little and it also can be developed to the use such as the use where color is regarded to be important, for which the development by the conventional crosslinked acrylic acid fiber has been difficult.

Best Mode for Carrying Out the Invention

[0011] The moisture-absorptive fiber dyeable with an acid dye according to the present invention comprises a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group.

[0012] The region of a polymer having a crosslinked structure and a carboxyl group in the moisture-absorptive fiber dyeable with an acid dye according to the present invention is an area which mainly plays a role of a moisture-absorption property which is one of the big characteristics of the fiber. As mentioned already, carboxyl group existing in such a region can form an ionic bond to cationic dye but, since ion exchange easily takes place, the resulting color fastness is bad and the dyeing in a practical level is not possible. In the fiber of the present invention, there is provided a region of a polymer having a functional group acting as a dyeing site for acid dye, which region is different from the above-mentioned region whereby the dyeing in a practical level with acid dye is made possible.

[0013] As to the polymer having a functional group acting as a dyeing site for acid dye, there are exemplified a polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component and a polymer which is produced by subjecting a polymer where acrylonitrile is a main component to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule. Incidentally, in the invention of the present invention, the polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component may also be expressed as an acrylonitrile polymer having cationic group and the polymer where acrylonitrile is a main component may also be expressed as an acrylonitrile polymer.

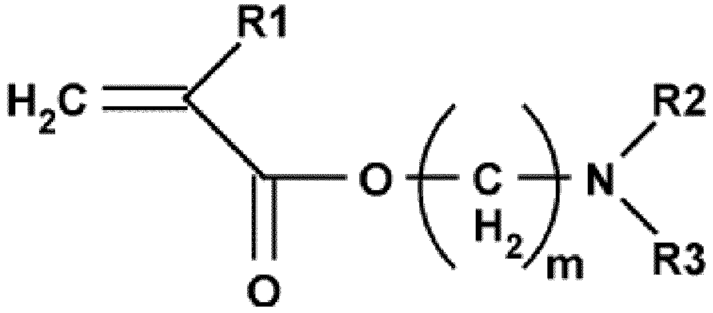
[0014] Although there is no particular limitation for the functional group acting as a dyeing site for acid dye, examples thereof include a cationic group such as primary amino group, secondary amino group, tertiary amino group or quaternary ammonium group.

[0015] The expression reading "acrylonitrile is a main component" means that, in any of the above cases, the polymer contains 40 to 100% by weight of acrylonitrile monomer unit. With regard to the monomer component other than acrylonitrile, there is no particular limitation and examples thereof include the monomers such as a (meth)acrylate compound (e.g., methyl (meth)acrylate, ethyl (meth)acrylate and butyl (meth)acrylate), a sulfonic group-containing monomer (e.g., metallylsulfonic acid and p-styrenesulfonic acid) and a salt thereof; styrene and vinyl acetate. When a vinyl monomer having cationic group is used as a copolymerizing component, the cationic group of said monomer functions as a dyeing site for acid dye.

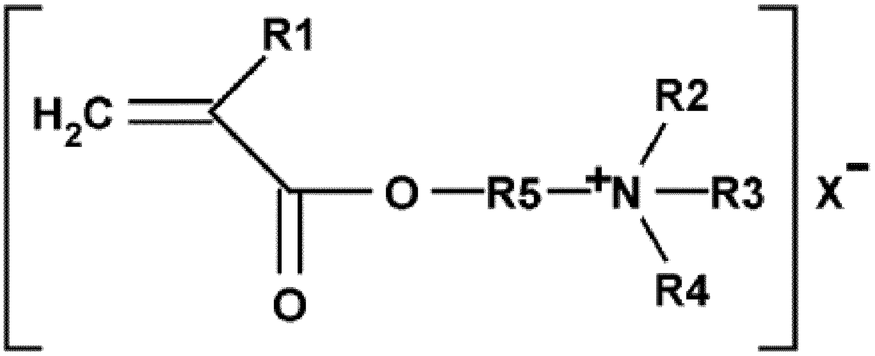
[0016] Examples of the vinyl monomer having cationic group as such include the monomers represented by the following formulas 1 to 3. In the formulas 1 to 3, R1 is hydrogen or an alkyl group of C4 or less; each of R2, R3 and R4 is an alkyl group of C4 or less; R5 is an alkylene group or a hydroxyalkylene group of C4 or less; R6 is an alkylene group of C4 or less; X is Cl, Br, I, CH_3COO, CH_3SO_4 or SCN; m is an integer of 2 to 4; and n is an integer of 0 or 1.

[0017]

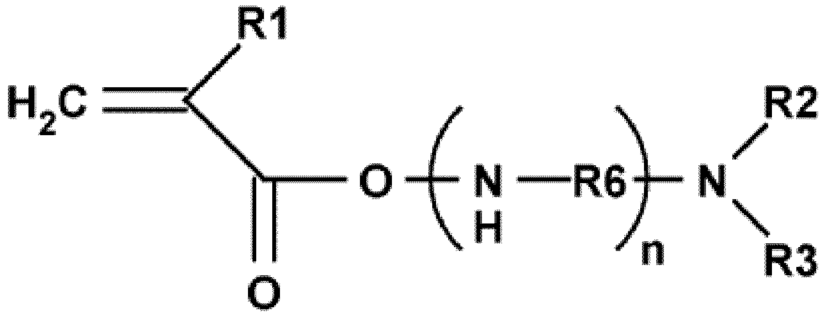
[Formula 1]



[Formula 2]



[Formula 3]



[0018] Specific examples of the vinyl monomer having cationic group as such include dimethylaminoethyl (meth) acrylate and diethylaminoethyl (meth)acrylate.

[0019] When the acrylonitrile polymer is subjected to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule, a crosslinked structure is formed in the polymer by the reaction of the functional group in the nitrogen-containing compound with nitrile group derived from acrylonitrile. It is likely that the functional group in the nitrogen-containing compound which did not react with the nitrile group, the functional group which was by-produced from failure of formation of crosslinked structure when the functional group in the nitrogen-containing compound reacted with the nitrile group or the like functions as a functional group acting as the dyeing site for acid dye.

[0020] With regard to the nitrogen-containing compound having two or more nitrogen atoms in a molecule, an amino compound and a hydrazine compound having two or more primary amino groups are preferred. Although there is no particular upper limitation for the numbers of the nitrogen atoms in a molecule, 12 or less is preferred, 6 or less is more preferred, and 4 or less is particularly preferred. When the numbers of the nitrogen atoms in a molecule exceeds the above upper limit, molecule of the crosslinking agent becomes big and there may be the case where the crosslinking is hardly introduced into the polymer.

[0021] Examples of the amino compound having two or more primary amino groups include a diamine compound such as ethylenediamine or hexamethylenediamine; a triamine compound such as diethylenetriamine, 3,3'-iminobis (propylamine) or N-methyl-3,3'-iminobis(propylamine); a tetramine compound such as triethylenetetramine, N,N'-bis(3-aminopropyl)-1,3-propylenediamine or N,N'-bis(3-aminopropyl)-1,4-butylene-diamine; and polyamine compound such as polyvinylamine and polyallylamine having two or more primary amino groups.

[0022] Examples of the hydrazine compound include hydrazine hydrate, hydrazine sulfate, hydrazine hydrochloride, hydrazine hydrobromide and hydrazine carbonate.

[0023] Examples of the polymer having a crosslinked structure and a carboxyl group include the polymer which is produced by subjecting an acrylonitrile polymer to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment. In the former treatment, the nitrogen-containing compound is made to react with a nitrile group derived from acrylonitrile whereupon a crosslinked structure is formed in the polymer while, in the latter treatment, nitrile group is hydrolyzed to form a carboxyl group. As a result, a polymer having a crosslinked structure and a carboxyl group is produced.

[0024] Examples of the acrylonitrile polymer and the nitrogen-containing compound having two or more nitrogen atoms in a molecule include those which are already mentioned hereinabove. In the hydrolyzing treatment, there may be used an alkali metal salt compound such as alkali metal hydroxide, alkali earth metal hydroxide or alkali metal carbonate.

[0025] With regard to the above-exemplified polymer having a crosslinked structure and a carboxyl group, although the acrylonitrile polymer is subjected to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule the same as in the case of the polymer exemplified as the polymer having a functional group which acts as a dyeing site for acid dye, it is not possible to conduct a practical dyeing using an acid dye. That is likely due to the fact that, although a functional group which acts as a dyeing site for acid dye is once formed by the crosslinking treatment, said functional group changes by the hydrolyzing treatment conducted thereafter whereupon it no longer functions as a dyeing site for acid dye.

[0026] Further, the moisture-absorptive fiber dyeable with an acid dye according to the present invention may also be constituted only from the region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group as mentioned above. Still further, besides those regions, a region where the polymers constituting those regions exist in a mixed state or a region constituted from a polymer being different from the polymers constituting those regions may exist. Representative examples of the alignment of those regions include a core-sheath structure where a region of a polymer having a functional group acting as a dyeing site for acid dye is a central area while a region of a polymer having a crosslinked structure and a carboxyl group is a surface layer area; a multi-layered structure where a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group are alternately layered; and islands-in-a-sea structure where one of a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group is a sea area while another is an island area.

[0027] With regard to the ratio of the region of a polymer having a functional group acting as a dyeing site for acid dye to a region of a polymer having a crosslinked structure and a carboxyl group, a fiber having higher moisture-absorption rate is produced when the rate of the region of a polymer having a crosslinked structure and a carboxyl group is higher but, on the other hand, the rate of the region of a polymer having a functional group acting as a dyeing site for acid dye becomes lower whereupon the color-developing property tends to lower. In order to manufacture a fiber where both moisture-absorption property and color-developing property are well-balanced, it is desirable that an area of 20 to 80% and more preferably 30 to 70% of the cross-sectional area of the fiber in a dry state is occupied by the region of a polymer having a functional group acting as a dyeing site for acid dye.

[0028] The above-mentioned area ratio can be calculated by such a manner that the fiber which is subjected to a dyeing treatment with an acid dye followed by cutting and the resulting fiber section is observed under an optical microscope. Thus, the dyed region is a region of the polymer having the functional group acting as a dyeing site for acid dye while the region which is not dyed or the region where dyeing cannot be confirmed is a region of the polymer having a crosslinked structure and a carboxyl group.

[0029] As to the carboxyl group content in the present invention, it is preferred to be 1.0 to 10 mmol/g and more preferred to be 2.0 to 6.0 mmol/g to the fiber weight. When the carboxyl group content is less than 1.0 mmol/g, there may be the case where no sufficient moisture-absorption property is achieved while, when it is more than 10 mmol/g, the region of the polymer having a crosslinked structure and a carboxyl group becomes weak upon absorption of moisture or water resulting in the detachment of the polymer whereupon there may be the case where fiber shape and moisture-absorption property cannot be maintained.

[0030] Although the carboxyl group may be that of an H type or of a salt type, or they may be present in a mixed state, it is desirable that the carboxyl group is in an H type so as to make the process such as spinning easy in the stage of after the manufacture of the fiber while, in the stage of after dyeing or of the final product, it is desirable that 50% or more of the carboxyl group is in a salt type so as to achieve the high moisture-absorption rate.

[0031] Examples of the cation which constitutes such a salt-type carboxyl group include cations of alkali metal such as Li, Na and K, alkali earth metal such as Be, Mg, Ca and Ba, metal such as Cu, Zn, Al, Mn, Ag, Fe, Co and Ni, NH_4 and amine and a plurality of cations may be present in a mixed state.

[0032] With regard to the saturation dye uptake of the acid dye in the present invention, it is preferred to be 3.5 to 10% by weight and more preferred to be 4 to 9% by weight to the fiber weight. When such a saturation dye uptake is less than 3.5%, there may be the case where dyeing in dark color is not possible and its application into the practical use is not suitable while, when it is more than 10%, a dyeing speed is quick and uneven dyeing is apt to happen. Incidentally, the saturation dye uptake as such is calculated by the method which will be mentioned later.

[0033] In the moisture-absorptive fiber dyeable with an acid dye according to the present invention, its color fastness is improved as compared with the conventional crosslinked acrylic acid fiber and it is desirable that the color fastness to perspiration evaluated by the following evaluating method is the third or higher grade.

(Evaluation Method) A sample is poured into a bath containing an acid dye (Supranol Black VLG; manufactured by DyStar) in 5% by weight to the sample weight, the pH thereof is adjusted to 4 using acetic acid and the fiber is dipped at 100˚C for 30 minutes and subjected to soaping, washing with water and drying. The resulting fiber is subjected to the evaluation for color fastness to perspiration according to JIS-L-0848.

[0034] Although the saturated moisture-absorption rate of the moisture-absorptive fiber dyeable with an acid dye according to the present invention under the atmosphere of 20˚C temperature and 65% relative humidity cannot be unconditionally determined since the required moisture-absorption rate is different depending upon the use, it is preferred to be 15% by weight or more and more preferred to be 20% by weight or more.

[0035] In the moisture-absorptive fiber dyeable with an acid dye according to the present invention, its degree of swelling is preferred to be not more than 2 g/g and more preferred to be not more than 1.8 g/g. When the degree of swelling is more than 2 g/g, there may be the case where the fiber properties lower or the operability becomes bad.

[0036] Several methods may be listed as a method for the manufacture of the moisture-absorptive fiber dyeable with an acid dye according to the present invention mentioned hereinabove. An example is a method where an acrylonitrile fiber comprising an acrylonitrile polymer having a cationic group is used as a material fiber and said fiber is partially subjected to a crosslinking treatment and a hydrolyzing treatment. In such a method, a part of the acrylonitrile polymer having a cationic group is converted to a region of a polymer having a crosslinked structure and a carboxyl group by the crosslinking treatment and the hydrolyzing treatment while the part which is not converted becomes a region of a polymer having a functional group acting as a dyeing site for acid dye.

[0037] In the acrylonitrile fiber comprising an acrylonitrile polymer having a cationic group, it is desirable to have not less than 0.15 mmol/g and preferably not less than 0.17 mmol/g of cationic group to the fiber weight. When the cationic group is less than 0.15 mmol/g, there may be the case where the region of a polymer having a crosslinked structure and a carboxyl group needs to be made small in order to achieve a sufficient color-developing property. Although there is no particular limitation for the upper limit, it is desirable to be not more than 0.40 mmol/g in view of the homogeneity of the dyeing.

[0038] Further, it is also possible to adopt a method where an acrylonitrile fiber comprising an acrylonitrile polymer is used as a material fiber and said fiber is subjected to a crosslinking treatment by a nitrogen-containing compound having two or more nitrogen atoms in a molecule followed by subjecting to a hydrolyzing treatment, wherein the range to which the hydrolyzing treatment is applied is made smaller than the range to which the crosslinking treatment is applied. In such a method, the region comprising a polymer having a functional group acting as a dyeing site for acid dye is firstly formed together with a crosslinked structure by means of a crosslinking treatment and, as a result of the hydrolyzing treatment thereafter, a part of said region is converted to a region of a polymer having a crosslinked structure and a carboxyl group. Incidentally, it goes without saying that, in such a method, an acrylonitrile polymer having a cationic group may also be used as an acrylonitrile polymer.

[0039] Still further, it is also possible to adopt a method where an acrylonitrile fiber comprising an acrylonitrile polymer having no functional group acting as a dyeing site for acid dye is used as a material fiber and, after a functional group acting as a dyeing site for acid dye is introduce therein, the resulting one is partially subjected to a crosslinking treatment and a hydrolyzing treatment and a method where an acrylonitrile fiber containing a polymer having a functional group acting as a dyeing site for acid dye other than the acrylonitrile polymer is used as a material fiber and is partially subjected to a crosslinking treatment and a hydrolyzing treatment.

[0040] Incidentally, it is preferred in the above-listed manufacturing methods that the rate of the acrylonitrile polymer in the acrylonitrile fiber to be used as a material fiber is 80 to 100% by weight regardless of the presence or the absence of the functional group acting as a dyeing site for acid dye.

[0041] It is also preferred that the acrylonitrile fiber to be used as a material fiber comprises at least two types of acrylonitrile polymers where the contents of acrylonitrile are different from each other and that the difference in said contents is 2% by weight or more. As a result thereof, a difference is resulted in the easiness of the crosslinking and of the hydrolysis whereby the region of the polymer having a functional group acting as a dyeing site for acid dye and the region of the polymer having a crosslinked structure and carboxyl group are apt to be formed.

[0042] Although the acrylonitrile fiber as such may be either a fiber where the two types of acrylonitrile polymers are conjugated side-by-side or are randomly mixed, a fiber in a three-layered structure comprising the layers A-B-A or a fiber in a core-sheath structure is more preferred. It is preferred that the area of the layer B or the core contains much acrylonitrile and also contains many cationic groups. To be more specific, the acrylonitrile content in the area of the layer B or the core is 82% by weight or more, preferably 85% by weight or more, and more preferably 90% by weight or more while the cationic group content therein is 0.15 mmol/g or more and preferably 0.17 mmol/g or more.

[0043] As to a method for manufacturing an acrylonitrile fiber in the three-layered structure comprising the layers A-B-A, a method which is mentioned in JP-A-2000-045126 or the like may be adopted. In that case, it is preferred that the dope viscosity of the component A is made lower than the dope viscosity of the component B so that exposure of the component B onto the fiber surface is made little.

[0044] With regard to a method of manufacturing a moisture-absorptive fiber dyeable with an acid dye according to the present invention which is illustrated hereinabove, the following method is preferred in view of the manufacturing facilities and costs. It is such a method where an acrylonitrile fiber comprising an acrylonitrile polymer having a cationic group is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule followed by subjecting to a hydrolyzing treatment with an aqueous solution of alkali metal salt or is subjecting to those treatments at the same time whereupon the region of the polymer having a crosslinked structure and a carboxyl group is formed on the surface layer area of the fiber while the region of the acrylonitrile polymer having a cationic group is remained in the core area.

[0045] In such a method, the acrylonitrile fiber comprising the acrylonitrile polymer having a cationic group is subjected to a treatment of introducing a crosslinking with an aqueous solution containing a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment with an aqueous solution containing an alkali metal salt compound as mentioned above. Those treatments may be carried out by such a separate manner that the hydrolyzing treatment is done after the crosslinking treatment or by such a simultaneous treatment using an aqueous solution in which both of the nitrogen-containing compound having two or more nitrogen atoms in a molecule and the alkali metal salt compound are co-existing. In any of the cases, a crosslinked structure is formed by the reaction of the nitrogen-containing compound having two or more nitrogen atoms in a molecule with the nitrile group in the acrylonitrile polymer on the surface layer area of the acrylonitrile fiber while a carboxyl group is formed by the reaction of the aqueous solution of the alkali metal salt compound with the nitrile group whereupon conversion to the polymer having a crosslinked structure and carboxyl group takes place.

[0046] As to a specific method for the above-mentioned crosslinking treatment and hydrolyzing treatment, a method where the reaction is carried out under the state where the fiber is dipped in an aqueous solution used for the treatments may be adopted. Further, in any of the separate treatment and the simultaneous treatment, concentration of the nitrogen-containing compound having two or more nitrogen atoms in a molecule is preferred to be 0.1 to 5% by weight and more preferred to be 0.1 to 3% by weight. When the concentration is too low, there may be the case where the effect of suppressing the elution for the polymer having the crosslinked structure and the carboxyl group cannot be achieved. On the other hand, in order to limit introduction of the crosslinked structure to the surface layer area of the fiber, the concentration is preferred to be made 5% by weight or less. With regard to the concentration of the alkali metal salt compound, it is preferred to be 0.5 to 5% by weight and more preferred to be 0.5 to 4% by weight. When the concentration of the alkali metal salt compound is too low, there may be the case where the content of the resulting carboxyl group is insufficient. On the other hand, when the concentration is suppressed to an extent of 5% by weight or less, it is possible that the introduction of carboxyl group is limited to the surface area of the fiber while the region of the acrylonitrile polymer having cationic group is remained in the core area.

[0047] With regard to the reaction temperature and time, their appropriate ranges vary depending upon the concentration(s) of the nitrogen-containing compound having two or more nitrogen atoms in a molecule and/or the alkali metal salt compound. In the case of the simultaneous treatment where the concentration of the nitrogen-containing compound having two or more nitrogen atoms in a molecule is about 0.5 to 2% by weight and the concentration of the alkali metal salt compound is about 1 to 2% by weight, the condition of at 90 to 100˚C for about 2 hours is recommended.

[0048] In the case of the above separate treatment, the fiber subjected to the crosslinking treatment may be subjected to a treatment with an acid before the hydrolyzing treatment. As a result of the treatment with an acid as such, coloring of the fiber can be made hypochromic. Examples of the acid used hereinabolve include an aqueous solution of mineral acid such as nitric acid, sulfuric acid, hydrochloric acid, and an organic acid although there is no particular limitation therefor. An example of the treating condition is that a fiber to be treated is dipped in an aqueous solution at the temperature of 50 to 120˚C for 0.5 to 10 hour(s) where an acid concentration is 5 to 20% by weight and preferably 7 to 15% by weight. However, such a treatment with an acid has an effect of progressing the hydrolysis and of decreasing the region of the acrylonitrile polymer to be remained in the finally-prepared fiber or, in other words, the region of the polymer having a functional group acting as a dyeing site for acid dye. Accordingly, it is important to set the condition by taking such an effect into consideration.

[0049] The above-prepared fiber after the hydrolyzing treatment or after the simultaneous crosslinking and hydrolyzing treatments may be utilized as it is for the moisture-absorptive fiber dyeable with an acid dye of the present invention, but it also may be further washed with an acidic aqueous solution. As a result thereof, a fiber in more white degree can be prepared. Examples of the above acidic aqueous solution include an aqueous solution of mineral acid such as nitric acid, sulfuric acid, hydrochloric acid, and an organic acid although there is no particular limitation therefor.

[0050] As mentioned above, in the stage after the manufacture of the fiber, it is desirable that a carboxyl group is in an H type so as to make the process such as spinning easy while, in the stage of after dyeing or of the final product, it is desirable that the carboxyl group is converted to the desired salt type or H type or that the different salt types are made to exist in a mixed state. Adjustment of such a type of the carboxyl group can be carried out by applying an ion exchange treatment using a metal salt such as nitrate, sulfate or hydrochloride or by a pH adjusting treatment using a buffer or the like. In case a high moisture-absorption rate is aimed, it is desirable that 50% or more of the carboxyl group is made into an salt type.

[0051] It is also a preferred method where the above-mentioned acrylonitrile fiber comprising the acrylonitrile polymer is used as a material fiber and is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule followed by subjecting to a hydrolyzing treatment, wherein the range to which the hydrolyzing treatment is applied is made smaller than the range to which the crosslinking treatment is applied. In such a method, the crosslinking treatment is firstly applied using a solution where the concentration of the nitrogen-containing compound having two or more nitrogen atoms in a molecule is set high and then the hydrolyzing treatment is carried out so that the range to which the crosslinking treatment is applied is made broader than the range to which the hydrolysis treatment is applied. In the case of making into a core-sheath structure for example, concentration of the nitrogen-containing compound is made preferably 7 to 20% by weight or, more preferably, 10 to 20% by weight for applying the crosslinking treatment to whole fiber. With regard to the condition of the hydrolyzing treatment for the surface layer area of the fiber after the above treatment, the above-mentioned condition may be adopted and, if necessary, the treatment with an acid and the adjustment of the carboxyl group type may be carried out in the same way.

Examples

[0052] The present invention will now be specifically illustrated by using the following Examples although the present invention is not limited thereto. The terms "part (s) " and "percent (s) " used in the Examples are those by weight unless otherwise stipulated. The method for evaluating the characteristics in the Examples are as follows.

(1) Carboxyl group content

[0053] A well-dried sample (about 1 g) is precisely weighed (A[g]), 200 ml of water is added thereto, a 1 mol/L aqueous solution of hydrochloric acid is added to the resulting mixture together with heating at 50˚C to adjust to pH 2 and, after that, a titration curve is determined according to the conventional method using a 0.1 mol/L aqueous solution of sodium hydroxide. Amount of the aqueous solution of sodium hydroxide consumed by the carboxyl group (B[ml]) is determined from the titration curve and the carboxyl group content is calculated by the following formula.

$$\text{Carboxyl group content [mmol/g]} = 0.1 \times B/A$$

(2) Cationic group content in a material fiber

[0054] well-dried sample (about 0.5 g) is precisely weighed (C[g]) and dipped into a beaker containing a 0.1 mol/L aqueous solution of hydrochloric acid (D[ml]) (which is such an amount that ion exchange is sufficiently carried out). The sample is filtered and a phenolphthalein solution is added to the filtrate as an indicator. The filtrate is then titrated with a 0.1 mmol/L aqueous solution of sodium hydroxide to quantify the residual hydrochloric acid. The cationic group content is calculated by the following formula where E [ml] is the titrated amount of sodium hydroxide.

$$\text{Cationic group content [mmol/g]} = (0.1 \times D - 0.1 \times E)/C$$

(3) Saturated moisture-absorption rate

[0055] The sample (about 5.0 g) is dipped in water, an aqueous solution of sodium hydroxide is added thereto so that the degree of neutralization to the carboxyl group is made 70%, the dipping treatment is done at 70˚C for 1 hour and, after that, washing with water and dehydration are conducted followed by drying with air for 24 hours. The sample being subjected to a neutralizing treatment is dried at 105˚C for 16 hours in a hot-air drier and the resulting weight is measured (F [g]). After that, the sample is placed for 24 hours in a constant-temperature and constant-humidity container adjusted to the condition of 20˚C and 65% relative humidity. Weight of the sample moisturized as such is measured (G[g]). Saturated moisture-absorption rate is calculated by the following formula using the above measured result.

$$\text{Saturated moisture-absorption rate [\%]} = (G - F)/F \times 100$$

(4) Degree of swelling

[0056] A sample (about 3 g) is dried at 70˚C for 3 hours in a hot-air drier to measure the weight (H[g]). After that, the sample is dipped for 30 minutes in a beaker containing 300 ml of water, the swollen sample is dehydrated with a portable centrifugal dehydrator (160G × 5 minutes) and the weight of the sample is measured (J[g]). Degree of swelling is calculated by the following formula using the above measured result.

$$\text{Degree of swelling [g/g]} = (J - H)/H$$

(5) Dyeing property

[0057] A sample is poured into a bath containing an acid dye (Supranol Black VLG; manufactured by DyStar) in 5% by weight to the sample weight, the pH thereof is adjusted to 3.5 using acetic acid and the fiber is dipped at 100˚C for 30 minutes and subjected to soaping, washing with water and drying. The resulting fiber is subjected to the evaluation for dyeing property by naked eye according to the following judging standards.

○: sufficiently dyeable
△: dyeable in light color

×: hardly dyeable or hue is abnormal

(6) Color fastness to perspiration

[0058] The fiber which is dyed by the same manner as mentioned in "(5) Dyeing property" is evaluated for the color fastness to perspiration according to JIS-L-0848.

(7) Cross section ratio of the region of the acrylonitrile polymer

[0059] The fiber which is dyed by the same manner as mentioned in " (5) Dyeing property" is cut and the fiber section is observed under an optical microscope whereupon the cross section ratio of the region of the acrylonitrile polymer is calculated.

(8) Saturation dye uptake

[0060] A mother liquor for dyeing is prepared in a bath ratio of 1:200 containing 20% of acid dye (Sandolan Fast Blue P-L 125%; manufactured by Sandoz) to the weight of the sample to be poured thereinto and being adjusted to pH 3 with acetic acid. Then, the absorbance of the mother liquor for dyeing to the light of 590 nm wavelength is measured. After that, a sample is poured into the mother liquor for dyeing and treated at 100˚C for 30 minutes. After a gradual cooling, the dyeing bath is adjusted to pH 7 with sodium carbonate and treated at 70˚C for 30 minutes. Then water which was evaporated during the treatment is supplemented to the dyeing bath, the bath ratio is adjusted to 1:200 once again and the absorbance of the residual liquor for dyeing at the light of 590 nm wavelength is measured. From the above measuring result, the saturation dye uptake to the fiber weight is calculated using the following formula.

$$\text{Saturation dye uptake (\%)} = \{[(\text{Absorbance of mother liquor for dyeing}) - (\text{Absorbance of residual liquor for dyeing})]/[\text{Absorbance of mother liquor for dyeing}]\} \times 20$$

Each absorbance of the mother liquor for dyeing and the residual liquor for dyeing is measured using the liquor diluted to an extent of 20-fold and U-1100 Spectrophotometer (manufactured by Hitachi).

Example 1

[0061] An acrylonitrile polymer (limiting viscosity [η] in dimethylformamide of 30˚C is 1.2) (10 parts) comprising 86% of acrylonitrile, 11% of methyl acrylate and 3% of dimethylaminoethyl (meth) acrylate was dissolved in 90 parts of a 48% aqueous solution of sodium rhodanate and the resulting spinning dope was spun and drafted according to a conventional method (total drafting rate: 10 times), dried in an atmosphere where dry bulb/wet bulb = 120˚C/60˚C and subjected to a moist heat treatment to give a material fiber (fiber length: 51 mm) having single fiber fineness of 2.2 dtex. The resulting material fiber was treated at 90˚C for 2 hours in an aqueous solution containing 0.4% of hydrazine hydrate and 2% of sodium hydroxide, washed with an aqueous solution of nitric acid having pH of 2 or lower, washed with water and dried to give the fiber of Example 1. Result of the evaluation of the resulting fiber is shown in Table 1.

Example 2

[0062] The material fiber of Example 1 was treated at 90˚C for 1.5 hours in an aqueous solution containing 0.4% of hydrazine hydrate and 2% of sodium hydroxide, washed with an aqueous solution of nitric acid having pH of 2 or lower, washed with water and dried to give the fiber of Example 2. Result of the evaluation of the resulting fiber is shown in Table 1.

Example 3

[0063] An acrylonitrile polymer (limiting viscosity [η] in dimethylformamide of 30˚C is 1.2) (10 parts) comprising 90% of acrylonitrile, 9.7% of methyl acrylate and 0.3% of sodium metallylsulfonate was dissolved in 90 parts of a 48% aqueous solution of sodium rhodanate and the resulting spinning dope was spun and drafted according to a conventional method (total drafting rate: 10 times), dried in an atmosphere where dry bulb/wet bulb = 120˚C/60˚C and subjected to a moist heat treatment to give a material fiber (fiber length: 51 mm) having single fiber fineness of 2.2 dtex. The resulting material fiber was treated at 110˚C for 1 hour in an aqueous solution containing 10% of hydrazine hydrate,treated at 100˚C for 1 hour in an aqueous solution containing 1.6% of sodium hydroxide, washed with an aqueous solution of nitric acid having pH of 2 or lower, washed with water and dried to give the fiber of Example 3. Result of the evaluation of the resulting fiber is shown in Table 1.

Example 4

[0064] The material fiber of Example 1 was treated at 110˚C for 1.5 hours in an aqueous solution containing 15% of hydrazine hydrate, treated at 100˚C for 1 hour in an aqueous solution containing 2% of sodium hydroxide, washed with an aqueous solution of nitric acid having pH of 2 or lower, washed with water and dried to give the fiber of Example 4. Result of the evaluation of the resulting fiber is shown in Table 1.

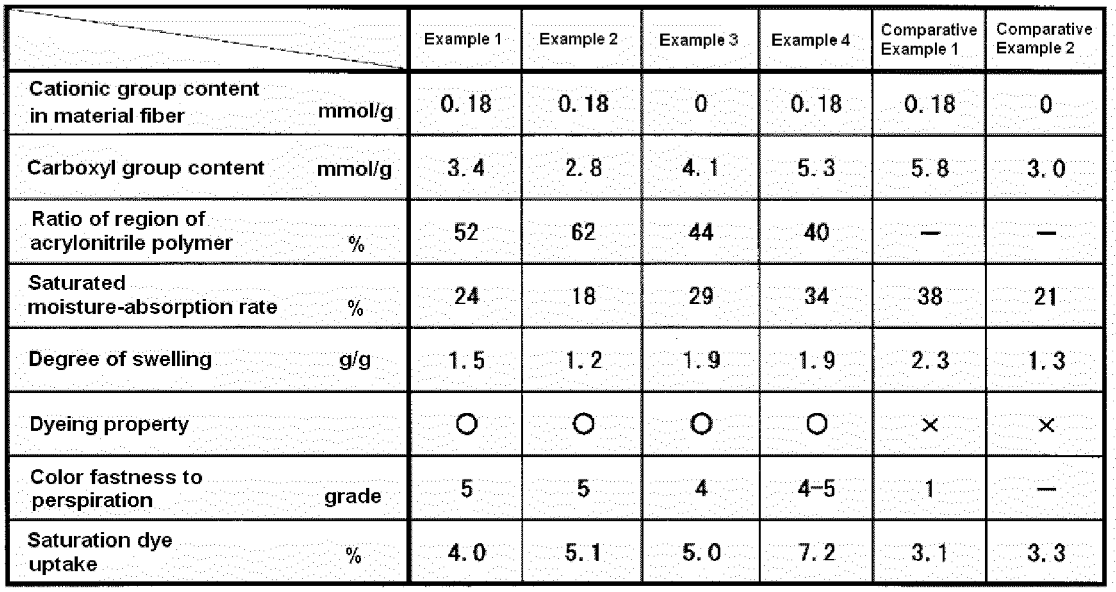
Comparative Example 1

[0065] The material fiber of Example 1 was treated at 110˚C for 3 hours in a 15% aqueous solution of hydrazine hydrate and washed. The resulting fiber was dipped in a 8% aqueous solution of nitric acid and treated at 100˚C for 1 hour. Then, it was treated at 100˚C for 1 hour in a 5% aqueous solution of sodium hydroxide, washed with an aqueous solution of nitric acid having pH of 2 or lower, washed with water and dried to give a moisture-absorptive fiber of Comparative Example 1. Result of the evaluation of the resulting fiber is shown in Table 1.

Comparative Example 2

[0066] The same operation as in Example 1 was carried out except that the material fiber of Example 3 was used as a material fiber to give a moisture-absorptive fiber of Comparative Example 2. Result of the evaluation of the resulting fiber is shown in Table 1.

[Table 1]



	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Cationic group content in material fiber mmol/g	0. 18	0. 18	0	0. 18	0. 18	0
Carboxyl group content mmol/g	3. 4	2. 8	4. 1	5. 3	5. 8	3. 0
Ratio of region of acrylonitrile polymer %	52	62	44	40	–	–
Saturated moisture-absorption rate %	24	18	29	34	38	21
Degree of swelling g/g	1. 5	1. 2	1. 9	1. 9	2. 3	1. 3
Dyeing property	○	○	○	○	×	×
Color fastness to perspiration grade	5	5	4	4–5	1	–
Saturation dye uptake %	4. 0	5. 1	5. 0	7. 2	3. 1	3. 3

[0067] In Example 1, there was prepared a fiber having good dyeing property and color fastness to the dyeing with acid dye and also having good moisture-absorption property. Although the moisture-absorptive fiber of Example 2 had a broad region of the acrylonitrile polymer as compared with the moisture-absorptive fiber of Example 1, it still had a sufficient moisture-absorption property as a moisture-absorptive fiber and had good dyeing property and color fastness. In Example 3, although an acrylonitrile fiber comprising an acrylonitrile polymer having no functional group acting as a dyeing site for acid dye was used as a starting material, a moisture-absorptive fiber having good dyeing property and color fastness was prepared. That is probably due to the fact that a functional group acting as a dyeing site for acid dye derived from a crosslinking agent was introduced into the inner layer of the fiber as a result of making the crosslinking treatment condition strong. In Example 4, it is likely that a moisture-absorptive fiber having a high saturation dye uptake was prepared due to the following reasons that an acrylonitrile fiber comprising an acrylonitrile polymer having a cationic group was used as a material fiber and the crosslinking treatment condition was also made strong whereupon the functional group acting as a dyeing site for acid dye being effective for the dyeing becomes abundant.

[0068] On the other hand, in the fiber of Comparative Example 1, the saturation dye uptake was low, dyeing into an intended hue was not possible and the color fastness was also low. That is probably due to the fact that, since the hydrolyzing treatment condition was made strong, hydrolysis happened in whole fiber and many of cationic groups in the material fiber were lost. In addition, with regard to the functional group acting as a dyeing site for acid dye derived from the crosslinking agent, it is also likely that it changed to other functional group due to hydrolysis or, around the functional group, many carboxyl groups are formed due to the hydrolysis whereupon a structure which is apt to absorb water to swell is resulted and, even when the dye is attached, it is apt to be flown out upon contact with water, and accordingly that the functional group does not well function as a dyeing site for acid dye. In the fiber of Comparative Example 2, the crosslinking treatment and the hydrolyzing treatment to the material fiber having no functional acting as a dyeing site for acid dye are limited only to the surface layer area of the fiber whereupon it is likely that no functional group acting as a dyeing site for acid dye exits in the core and the surface layer area becomes the same structure as in the fiber of Comparative Example 1 whereby the dyeing property becomes poor. Incidentally, in the fibers of those Comparative Examples, it was not possible to conduct an appropriate dyeing whereby it was not possible to determine the cross section ratio of the region of the acrylonitrile polymer.

Industrial Applicability

[0069] The moisture-absorptive fiber dyeable with an acid dye according to the present invention has a high moisture-absorption property and is excellent in terms of dyeing property to an acid dye whereby a practical dyeing is possible. Accordingly, it is now possible to develop to the use which has been limited because of the fact that a practical dyeing was difficult with the conventional crosslinked acrylic acid fiber.

Claims

1. A moisture-absorptive fiber dyeable with an acid dye, comprising a region of a polymer having a functional group acting as a dyeing site for acid dye and a region of a polymer having a crosslinked structure and a carboxyl group, wherein the saturation dye uptake of the acid dye to the fiber weight is 3.5 to 10% by weight and the carboxyl group content is 1.0 to 10 mmol/g.

2. The moisture-absorptive fiber dyeable with an acid dye according to claim 1, wherein the polymer having a functional group acting as a dyeing site for acid dye is such a polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component.

3. The moisture-absorptive fiber dyeable with an acid dye according to claim 1, wherein the polymer having a functional group acting as a dyeing site for acid dye is such a polymer which is produced by subjecting a polymer where acrylonitrile is a main component to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule.

4. The moisture-absorptive fiber dyeable with an acid dye according to claim 1, wherein the polymer having a crosslinked structure and a carboxyl group is such a polymer which is produced by subjecting a polymer where acrylonitrile is a main component to a treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment.

5. A method for manufacturing the moisture-absorptive fiber dyeable with an acid dye mentioned in claim 1, **characterized in that**, a surface layer area of a fiber comprising a polymer where acrylonitrile is a main component and a vinyl monomer having at least a cationic group is a copolymerizing component is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and to a hydrolyzing treatment.

6. A method for manufacturing the moisture-absorptive fiber dyeable with an acid dye mentioned in claim 1, wherein a fiber comprising a polymer where acrylonitrile is a main component is subjected to a crosslinking treatment with a nitrogen-containing compound having two or more nitrogen atoms in a molecule and, after that, to a hydrolyzing treatment, **characterized in that**, the range to which the hydrolyzing treatment is applied is made smaller than the range to which the crosslinking treatment is applied.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/061937

A. CLASSIFICATION OF SUBJECT MATTER
D06M11/63(2006.01)i, *D01F6/18*(2006.01)i, *D06M11/00*(2006.01)i, *D06M101/28*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06M11/00-15/715, D01F6/00-6/96

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2009/057235 A1 (Japan Exlan Co., Ltd.), 07 May 2009 (07.05.2009), claims; paragraph [0031]; table 1 & JP 2009-114556 A	1,3,4,6 1-6
Y	JP 49-20251 B1 (Toray Industries, Inc.), 23 May 1974 (23.05.1974), column 2 (Family: none)	1-6

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 29 July, 2010 (29.07.10)	Date of mailing of the international search report 10 August, 2010 (10.08.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003278079 A **[0006]**
- JP 2006070421 A **[0006]**
- JP 2008174849 A **[0006]**
- JP 2000045126 A **[0043]**