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(54) POLYVINYL ALCOHOL FIBER AND METHOD FOR PRODUCING SAME

(57) [Problem to be solved] A polyvinyl alcohol fiber that is excellent in secondary processability and water solubility, particularly water solubility at a low temperature is provided.

[Solution] the present invention relates to a polyvinyl alcohol fiber comprising polyvinyl alcohol A having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol% and polyvinyl alcohol B having a degree of saponification satisfying the following formula (1).

$$0 < \alpha_A - \alpha_B \leq 20 \quad (1)$$

In the formula (1), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

Description

TECHNICAL FIELD

[0001] The present invention relates to a polyvinyl alcohol fiber containing polyvinyl alcohols having different degrees of saponification, a long fiber nonwoven fabric made of the fiber, and a method for producing the fiber or the long fiber nonwoven fabric. More specifically, the present invention relates to a polyvinyl alcohol fiber containing ethylene-modified polyvinyl alcohol and polyvinyl alcohol having a degree of saponification within a specific range, a long fiber nonwoven fabric made of the fiber, a method for producing the above fiber by melt spinning and a method for producing the long fiber nonwoven fabric made of the fiber.

BACKGROUND ART

[0002] In polyvinyl alcohol fibers, hydroxyl groups in polyvinyl alcohol molecules form intramolecular and intermolecular hydrogen bonds, and these bonds are extremely strong. Therefore, the polyvinyl alcohol fibers have high strength and excellent mechanical strength. Taking advantage of such excellent mechanical strength, the polyvinyl alcohol fibers are used in a wide variety of applications such as packaging, wound dressings and textile materials.

[0003] On the other hand, the polyvinyl alcohol fibers have excellent solubility in water and are useful as water-soluble fibers or water-soluble packaging materials. Since such water-soluble fibers or water-soluble packaging materials dissolve in water, they place less of a burden on the environment when disposed of and are expected to have further expanded uses.

[0004] Normally, the polyvinyl alcohol fibers are produced using a wet spinning method in which they are dissolved in a solvent and spun, but since the wet spinning method uses a solvent and the like, a process for removing the solvent is required, which may complicate the production process.

[0005] Further, trace amounts of solvent may remain on the fibers, and it may be necessary to remove the remaining solvent when disposing of the fibers.

[0006] On the other hand, since the melt spinning method does not use a solvent, the step of removing the solvent is omitted and no solvent remains on the fibers. Therefore, it is desired to develop polyvinyl alcohol suitable for melt spinning rather than wet spinning.

[0007] Ethylene-modified polyvinyl alcohol has been proposed as one of the polyvinyl alcohols suitable for the melt spinning method (for example, Patent Documents 1 and 2).

[0008] Patent Document 1 discloses a fiber consisting of α-olefin-modified polyvinyl alcohol (A) as a melt-spun resin and an alkali metal ion (B), in which the content ratio of component (B) to 100 parts by mass of component (A) is 0.0003 to 1 part by mass, wherein the α-olefin-modified polyvinyl alcohol (A) has a degree of polymerization of 200 to 500, a degree of saponification of 90 to 99.99 mol%, a mole fraction of the central hydroxyl group of three chains of hydroxyl groups expressed as a triad relative to the vinyl alcohol unit of 70 to 99.9 mol% and a melting point of 160°C to 230°C.

[0009] Patent Document 2 discloses a thermoplastic polyvinyl alcohol fiber containing at least one component polyvinyl alcohol having a content of 1,2-glycol bonds of 1.8 mol% to 3.5 mol%.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0010]

Patent Document 1: JP-A 2000-234214
Patent Document 2: JP-A 2001-248014

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0011] The ethylene-modified polyvinyl alcohol described in these documents needs to have a high degree of saponification in order to improve melt spinnability. However, secondary processability of fibers made of the ethylene-modified polyvinyl alcohol with a high degree of saponification tends to be lower than that of non-ethylene-modified polyvinyl alcohol.

[0012] Further, the ethylene-modified polyvinyl alcohol with the high degree of saponification has a reduced solubility in water, particularly low-temperature water, and when made into fibers, its water solubility is reduced. Therefore, it may be necessary to treat it with high-temperature water when disposing of it.

[0013] An object of the present invention is to provide a polyvinyl alcohol fiber that is excellent in secondary processability and water solubility, particularly water solubility at a low temperature and a long fiber nonwoven fabric made of the fiber.

[0014] The present inventors found that secondary processability and water solubility were improved by using a polyvinyl alcohol fiber containing two types of polyvinyl alcohol and a long fiber nonwoven fabric made of the fibers, thereby completing the present invention.

MEANS FOR SOLVING THE PROBLEM

[0015] That is, the present invention relates to:

[1] A polyvinyl alcohol fiber comprising polyvinyl alcohol A having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol% and polyvinyl alcohol B having a degree of saponification satisfying the following formula (1).

$$0 < \alpha_A - \alpha_B \leq 20 \quad (1)$$

[0016] In the formula (1), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

[0017] Further, as a preferred embodiment of the present invention, the present invention relates to:

[2] The polyvinyl alcohol fiber in the above-mentioned item [1], wherein a difference between a melting point and a decomposition temperature of the polyvinyl alcohol fiber is 40°C or more;
[3] The polyvinyl alcohol fiber in the above-mentioned item [1] or [2], wherein the polyvinyl alcohol A has a degree of polymerization of 200 to 600;
[4] The polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [3], wherein the polyvinyl alcohol B has a degree of polymerization of 200 to 600;
[5] The polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [4], wherein the degree of saponification of the polyvinyl alcohol B is 80 mol% or more;
[6] The polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [5] containing the polyvinyl alcohol B in an amount of 15% by mass or more and 95% by mass or less, where a total mass of the polyvinyl alcohol A and the polyvinyl alcohol B is 100% by mass; and
[7] The polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [6] having a fusing temperature in water of 70°C or less.

[0018] Further, the present invention relates to:
A method for producing the polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [7], the method comprising:

melting a composition comprising polyvinyl alcohol A having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol% and polyvinyl alcohol B having a degree of saponification satisfying the following formula (2);
discharging the molten composition from a nozzle; and
cooling the discharged composition.

$$0 < \alpha_A - \alpha_B \leq 20 \quad (2)$$

[0019] In the formula (2), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

[0020] Furthermore, the present invention relates to:

[9] A long fiber nonwoven fabric made of the polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [7]; and
[10] A method for producing a long fiber nonwoven fabric by depositing the polyvinyl alcohol fiber in any one of the above-mentioned items [1] to [7] to form a nonwoven fabric web.

EFFECTS OF THE INVENTION

[0021] According to the present invention, it is possible to provide a polyvinyl alcohol fiber and a long fiber nonwoven fabric, which are excellent in secondary processability and water solubility, particularly water solubility at a low temperature and methods for producing the polyvinyl alcohol fiber and the long fiber nonwoven fabric.

MODE FOR CARRING OUT THE INVENTION

[0022] Polyvinyl alcohol A in the present invention is an ethylene-modified polyvinyl alcohol having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol%.

[0023] Examples of the ethylene-modified polyvinyl alcohol include an ethylene-vinyl alcohol copolymer obtained by saponifying an ethylene-vinyl ester copolymer obtained by copolymerizing ethylene and vinyl ester. The ethylene-vinyl alcohol copolymer may be an ethylene-vinyl alcohol copolymer obtained by saponifying a copolymer of ethylene, a monomer other than ethylene that can be copolymerized with the vinyl ester as described below and vinyl ester. The ethylene-modified polyvinyl alcohol may also be a so-called polyvinyl acetal resin in which a portion hydroxyl groups of the ethylene-vinyl alcohol copolymer are crosslinked with aldehydes such as formalin, butyraldehyde and benzaldehyde.

[0024] One kind or two or more kinds of vinyl esters may be used in the production of ethylene-modified polyvinyl alcohol, and it is preferable to use one kind of vinyl ester.

[0025] Examples of vinyl esters include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate, vinyl versatate and the like. Among these, vinyl acetate is preferred.

[0026] Examples of monomers copolymerizable with the vinyl ester include olefins having 3 to 30 carbon atoms such as propylene, 1-butene, and isobutene; acrylic acid or its salt; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, and octadecyl acrylate; methacrylic acid or its salts; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, and octadecyl methacrylate; acrylamide, N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, diacetone acrylamide, acrylamide propanesulfonic acid or salts thereof, acrylamidopropyldimethylamine or its salts; acrylamide derivatives such as N-methylolacrylamide or derivatives thereof; methacrylamide derivatives such as methacrylamide, N-methylmethacrylamide, N-ethylmethacrylamide, methacrylamidepropanesulfonic acid or its salts, methacrylamidepropyldimethylamine or its salts, N-methylolmethacrylamide or its derivatives; N-vinyl amides such as N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, n-butyl vinyl ether, i-butyl vinyl ether, t-butyl vinyl ether, dodecyl vinyl ether and stearyl vinyl ether; vinyl cyanides such as acrylonitrile and methacrylonitrile; vinyl halides such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride; allyl compounds such as allyl acetate and allyl chloride; maleic acid or its salts, esters or acid anhydrides; itaconic acid or its salts, esters or acid anhydrides; vinylsilyl compounds such as vinyltrimethoxysilane; isopropenyl acetate; and the like.

[0027] Among these, olefins having 3 to 30 carbon atoms are preferred, and propylene, 1-butene, 1-pentene and 1-hexene are preferred.

[0028] The degree of saponification of the polyvinyl alcohol A is 90 mol% or more. From the viewpoint of mechanical strength of the resulting polyvinyl alcohol fiber, the degree of saponification of the polyvinyl alcohol A is preferably 95 mol% or more, more preferably 98 mol% or more. The degree of saponification of the polyvinyl alcohol A is usually 100 mol% or less, preferably 99.5 mol% or less, and more preferably 99 mol% or less.

[0029] The degree of saponification of the polyvinyl alcohol A refers to the ratio (mol%) of the number of moles of vinyl alcohol units to the total number of moles of structural units that can be converted into vinyl alcohol units by saponification, typically vinyl ester monomer units and vinyl alcohol units.

[0030] The degree of saponification of polyvinyl alcohol can be measured according to the description in JIS K 6726-1994.

[0031] The ethylene modification rate of the polyvinyl alcohol A is 4 to 15 mol% from the viewpoint of water solubility and strength. The ethylene modification rate is the ratio of structural units derived from ethylene to all structural units, assuming that the total structural units constituting polyvinyl alcohol A are 100 mol%.

[0032] Based on the number of moles of all structural units constituting a vinyl ester polymer, the ethylene modification rate is preferably 12 mol% or less, more preferably 9 mol% or less. Further, from the viewpoint of strength, the ethylene modification rate is preferably 6 mol% or more, more preferably 7 mol% or more.

[0033] The ethylene modification rate is determined, for example, from 1H-NMR of an ethylene-vinyl ester copolymer which is a precursor or re-esterified product of ethylene-modified polyvinyl alcohol. Specifically, the ethylene modification rate can be determined using a peak derived from main chain methylene of vinyl ester in the range of 4.7 to 5.2 ppm and a peak derived from main chain methylene of ethylene, vinyl esters and other monomers copolymerizable with vinyl esters in the range of 0.8 to 1.6 ppm.

[0034] A difference between a melting point and a decomposition temperature of the polyvinyl alcohol A is preferably 40°C or higher from the viewpoint of melt spinnability. The difference between the melting point and the decomposition temperature of the polyvinyl alcohol A is more preferably 50°C or more. When the difference between the melting point and the decomposition temperature of the polyvinyl alcohol A is equal to or greater than the above lower limited value, the melt spinnability of the polyvinyl alcohol A is excellent. Further, there is no particular restriction on the upper limited value of the difference between the melting point and the decomposition temperature of the polyvinyl alcohol A, but it is preferably 150°C or less.

[0035] The melting point of the polyvinyl alcohol A is preferably 180°C or higher, more preferably 190°C or higher, from the viewpoint of the melt spinnability. Further, the melting point of the polyvinyl alcohol A is preferably 220°C or lower, more preferably 210°C or lower, from the viewpoint of secondary processability when made into a fiber.

[0036] Further, the decomposition temperature of the polyvinyl alcohol A is preferably 250°C or higher, more preferably 260°C or higher, from the viewpoint of melt spinnability. Further, there is no particular restriction on the upper limited value of the decomposition temperature of the polyvinyl alcohol A, but it is preferably 350°C or lower.

[0037] The melting point is a peak temperature of a main endothermic peak observed with a differential scanning calorimeter (DSC), and the decomposition temperature is a temperature at which a weight decreases by 3% when the temperature is increased at a rate of 10°C/min in thermogravimetry (TG).

[0038] A degree of polymerization (viscosity average degree of polymerization) of the polyvinyl alcohol A is preferably 600 or less, more preferably 500 or less, from the viewpoint of melt spinnability. If the degree of polymerization of the polyvinyl alcohol A is too large, the melt viscosity may be too high to discharge the polymer from a spinning nozzle. In addition, from the viewpoint of suppressing deterioration in stringiness during spinning and interfiber adhesion and maintaining mechanical performance and quality of the fiber and the fiber structure, the degree of polymerization is preferably 200 or more, more preferably 300 or more.

[0039] Note that the degree of polymerization means the average degree of polymerization measured in accordance with the description of JIS K 6726-1994. In this specification, the degree of polymerization is determined by the following formula (3) from the intrinsic viscosity [η] (unit: deciliter/g) measured in water at 30°C after resaponifying the remaining acetate groups of the polyvinyl alcohol A and purifying it.

$$\text{Degree of polymerization } P = ([\eta]\times 10^{4}/8.29)^{(1/0.62)} \qquad (3)$$

[0040] Polyvinyl alcohol B in the present invention is polyvinyl alcohol having a degree of saponification satisfying the following formula (1).

$$0 < \alpha_A - \alpha_B \leq 20 \qquad (1)$$

[0041] In the above formula (1), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

[0042] It is preferable that the degree of saponification of polyvinyl alcohol B satisfies the following formula (4) from the viewpoint of secondary processability and water solubility of the resulting fiber.

$$0 < \alpha_A - \alpha_B \leq 15 \qquad (4)$$

[0043] In the above formula (4), αA and αB represent the same meanings as above.

[0044] The degree of saponification of polyvinyl alcohol B satisfies the above formula (4) from the viewpoint of secondary processability and water solubility of the resulting fiber and is preferably 80 mol% or more, more preferably 85 mol% or more. When the degree of saponification of the polyvinyl alcohol B is as described above, the degree of saponification of the polyvinyl alcohol A is preferably 95 mol% or more, more preferably 98 mol% or more.

[0045] The polyvinyl alcohol B only needs to have the degree of saponification that satisfies the formula (1) and may be the same kind of ethylene-modified polyvinyl alcohol as the polyvinyl alcohol A or may be a saponified product of the vinyl ester polymer. Further, the polyvinyl alcohol B may be a copolymer of vinyl ester and a copolymerizable monomer.

[0046] Examples of vinyl esters and monomers copolymerizable with the vinyl esters include ethylene and the same kind of vinyl esters and monomers as the vinyl ester and the monomer exemplified above for the polyvinyl alcohol A, and preferred vinyl esters and monomers are also the same as above.

[0047] The polyvinyl alcohol B is preferably an ethylene-unmodified polyvinyl alcohol whose the degree of saponification satisfies the formula (1) and is not modified with ethylene. Examples of ethylene-unmodified polyvinyl alcohols include a polyvinyl alcohol that is a saponified product of a polymer of the vinyl ester, or a polyvinyl alcohol that is a saponified product of a copolymer of a vinyl ester and a monomer other than ethylene that can be copolymerized with the vinyl ester. Among the ethylene-unmodified polyvinyl alcohols, a polyvinyl alcohol which is a saponified product of the vinyl ester polymer is preferred.

[0048] Examples of the vinyl esters and the monomers copolymerizable with the vinyl esters include the same vinyl esters and monomers as those exemplified for the polyvinyl alcohol A, and preferred vinyl esters and monomers are also the same as above except for ethylene.

[0049] A difference between a melting point and a decomposition temperature of the polyvinyl alcohol B is preferably 40°C or higher from the viewpoint of melt spinnability. The difference between the melting point and the decomposition temperature of the polyvinyl alcohol B is more preferably 50°C or more. When the difference between the melting point and the decomposition temperature of the polyvinyl alcohol B is equal to or greater than the above lower limited value, the melt spinnability of the polyvinyl alcohol B is excellent. Further, there is no particular restriction on the upper limited value of the difference between the melting point and the decomposition temperature of the polyvinyl alcohol B, but it is preferably 150°C or less.

[0050] The melting point of the polyvinyl alcohol B is preferably 170°C or higher, more preferably 180°C or higher, from the viewpoint of the melt spinnability. Further, the melting point of the polyvinyl alcohol B is preferably 200°C or lower, more preferably 190°C or lower, from the viewpoint of secondary processability when made into a fiber.

[0051] Further, the decomposition temperature of the polyvinyl alcohol A is preferably 250°C or higher, more preferably 260°C or higher, from the viewpoint of melt spinnability. Further, there is no particular restriction on the upper limited value of the decomposition temperature of the polyvinyl alcohol A, but it is preferably 350°C or lower.

[0052] A degree of polymerization (viscosity average degree of polymerization) of the polyvinyl alcohol B is preferably 600 or less, more preferably 500 or less, from the viewpoint of melt spinnability. If the degree of polymerization of the polyvinyl alcohol B is too large, the melt viscosity may be too high to discharge the polymer from the spinning nozzle. In addition, from the viewpoint of suppressing deterioration in stringiness during spinning and interfiber adhesion and maintaining mechanical performance and quality of the fiber and the fiber structure, the degree of polymerization is preferably 200 or more, more preferably 300 or more.

[0053] The polyvinyl alcohol fiber of the present invention contains the polyvinyl alcohol A and the polyvinyl alcohol B.

[0054] The polyvinyl alcohol fiber of the present invention preferably contains the polyvinyl alcohol B in an amount of 15% by mass or more and 95% by mass or less, where the total mass of the polyvinyl alcohol A and the polyvinyl alcohol B is 100% by mass.

[0055] When the content of the polyvinyl alcohol B is within the above range, the fiber has an excellent balance between low-temperature solubility in water and secondary processability.

[0056] The content of the polyvinyl alcohol B is more preferably 30% by mass or more and 80% by mass or less, where the total mass of polyvinyl alcohol A and the polyvinyl alcohol B is 100% by mass.

[0057] The melting point of the polyvinyl alcohol fiber of the present invention is preferably 190°C or more and 210°C or less from the viewpoint of secondary processability. The upper limited value of the melting point is more preferably 208°C or lower, and even more preferably 205°C or lower. Further, from the viewpoint of secondary processability, the difference between the melting point and the decomposition temperature of the polyvinyl alcohol fiber is preferably 40°C or higher, more preferably 50°C or higher, and even more preferably 60°C or higher.

[0058] The melting point and the decomposition temperature of the polyvinyl alcohol fiber can be obtained by spinning the polyvinyl alcohol A and the polyvinyl alcohol B by the method described below and measuring the fiber obtained by the method described above.

[0059] By adjusting the ethylene modification rate and the degree of saponification of the polyvinyl alcohol A and the degree of saponification and the content of the polyvinyl alcohol B within the above ranges, the melting point and the decomposition temperature of the resulting fiber can be set within the above ranges.

[0060] From the viewpoint of secondary processability, a tensile strength of the polyvinyl alcohol fiber of the present invention is preferably 1 cN/dtex or more, more preferably 3 cN/dtex or more. There is no particular limit to the upper limited value of the tensile strength, but it is usually 25 cN/dtex or less.

[0061] The tensile strength of the polyvinyl alcohol fiber can be adjusted to a desired tensile strength by controlling drawing conditions such as a drawing temperature and a drawing ratio in the method for producing the fiber described below.

[0062] A fusing temperature of the polyvinyl alcohol fiber of the present invention in water is preferably as low as possible, and from the viewpoint of reducing environmental load, it is preferably 70°C or lower, more preferably 50°C or lower, and even more preferably 30°C or lower. Further, from the viewpoint of handling the fiber, the melting temperature is preferably 5°C or higher.

[0063] The fusing temperature is a temperature at which the fiber fuses and a load drops when the load of 2 mg/dtex is applied to a fiber with a length of 100 mm, the fiber is maintained in water and the water temperature is raised at a rate of 2°C/min.

[0064] The fusing temperature can be set to a desired fusing temperature by adjusting the ethylene modification rate of the polyvinyl alcohol A in the polyvinyl alcohol fiber, the ratio of the polyvinyl alcohol B, the degree of saponification of the polyvinyl alcohol A or the polyvinyl alcohol B and the like within the above ranges.

[0065] From the viewpoint of water solubility, a degree of crystallinity of the polyvinyl alcohol fiber of the present invention is preferably 50% or less, more preferably 40% or less. Further, from the viewpoint of fiberization and mechanical strength, the degree of crystallinity of the polyvinyl alcohol fiber is preferably 15% or more, more preferably 25% or more.

[0066] The degree of crystallinity of the fiber can be controlled by the degree of polymerization, the degree of saponification, the kind and content of functional groups, and the like of the polyvinyl alcohol A and the polyvinyl alcohol B.

[0067] The degree of crystallinity of the fiber can be determined by the following method. Using a differential scanning calorimeter (DSC-20) manufactured by Mettler, an endothermic amount ΔH (J/g) at an endothermic peak was measured when 10 mg of the fiber sample was heated at a rate of 10°C/min in a nitrogen atmosphere, and the degree of crystallinity was calculated using the following formula (6) from the ratio to 174.5 J/g which is the heat of fusion of perfect crystals of the polyvinyl alcohol.

$$\text{Degree of crystallinity (\%)} = \Delta H(J/g)/174.5\ (J/g)\times 100 \quad (6)$$

[0068] In addition to the above, various commonly used additives such as plasticizers, crosslinkers, antioxidants, stabilizers, lubricants, processing aids, antistatic agents, colorants, impact aids and blowing agents may be added to the polyvinyl alcohol fiber of the present invention. When added, the total amount of the polyvinyl alcohol A and the polyvinyl alcohol B in the polyvinyl alcohol fiber is preferably 60% by mass or more, more preferably from 70 to 99% by mass.

[0069] The polyvinyl alcohol fiber of the present invention can be produced by any method including wet spinning, dry spinning, or melt spinning, but the melt spinning method is preferable from the viewpoint of simplifying the spinning process and reducing the environmental load by not using a solvent during the process.

[0070] In the melt spinning method, the polyvinyl alcohol as a raw material is melted, and a yarn discharged from a spinning nozzle is taken and spun. The melt spinning method also includes a melt blow method or a spunbond method in which the fiber discharged from the spinning nozzle are directly formed into a sheet. The melt blow method is preferred because it yields a nonwoven fabric with fine fibers and fine mesh.

[0071] Since the polyvinyl alcohol fiber of the present invention contains the polyvinyl alcohol A and the polyvinyl alcohol B, a composition containing predetermined amounts of the polyvinyl alcohol A and the polyvinyl alcohol B may be prepared in advance and the composition may be melt-spun, or the polyvinyl alcohol A and the polyvinyl alcohol B may be melted separately and combined into one fiber when discharged from the spinning nozzle.

[0072] In the case of the composition containing a predetermined amount of the polyvinyl alcohol A and the polyvinyl alcohol B, once the composition containing both polyvinyl alcohols is taken out in a melt-kneading machine, it may be melt-spun, or it may be melt-kneaded in a melt-spinning machine and then spun as it is without being taken out.

[0073] When the polyvinyl alcohol A and the polyvinyl alcohol B are melted and extruded separately, by controlling an extrusion amount and the like, the content of the polyvinyl alcohol A and the polyvinyl alcohol B in the polyvinyl alcohol fiber can be set to a predetermined amount.

[0074] In the case of melt spinning, the polyvinyl alcohol is melted at a temperature higher than its melting temperature and lower than its decomposition temperature. Preferably, the polyvinyl alcohol is melted at a temperature that is 10°C or more higher than the melting temperature of the polyvinyl alcohol and 20°C or more lower than the decomposition temperature.

[0075] In the present invention, the melting temperature may be higher than the melting temperature of the higher one of the polyvinyl alcohol A and the polyvinyl alcohol B and lower than the lower decomposition temperature of the polyvinyl alcohol A and the polyvinyl alcohol B, and it is preferable to melt in the range of 220°C or more and 240°C or less.

[0076] The temperature of the spinning nozzle during discharge from the spinning nozzle is 10°C or more higher than the melting temperature of the polyvinyl alcohol.

[0077] In the present invention, it is sufficient to discharge at a temperature higher than the melting temperature of the higher one of the polyvinyl alcohol A and the polyvinyl alcohol B and lower than a temperature higher than the melting temperature by 10°C or more, and it is preferable to discharge at a temperature of 230°C or higher and 240°C or lower.

[0078] The yarn discharged from the spinning nozzle may be taken off as is without being drawn or may be drawn subsequently. Drawing is carried out at a temperature higher than a glass transition point (Tg) of the polyvinyl alcohol and at a temperature higher than the higher Tg of the polyvinyl alcohol A and the polyvinyl alcohol B.

[0079] From the viewpoint of the strength of the fiber obtained, a drawing ratio is preferably 2 times or more, more preferably 3 times or more.

[0080] The drawing is usually carried out by hot drawing, and the hot drawing may be carried out using hot air, a hot plate, a hot roller, a water bath, or the like.

[0081] The drawing temperature is usually about 70 to 100°C. Further, when heating and drawing is performed using a noncontact type heater such as a heating tube, it is preferable to set the temperature condition to an even higher temperature of about 110 to 150°C.

[0082] In addition, in the case of the melt spinning method, a cross section of the fiber can be circular, hollow, or irregularly shaped depending on the shape of the spinning nozzle. A perfect circle is preferable from the viewpoint of passability in the process of fiberization and weaving.

[0083] Although the fineness of the single fiber of the polyvinyl alcohol fiber of the present invention is not particularly limited, the fineness is preferably 0.01 dtex or more, more preferably 0.1 dtex or more, and even more preferably 0.2 dtex or more. Further, the fineness is preferably 1000 dtex or less, more preferably 100 dtex or less, and even more preferably 10 dtex or less. Fineness of 0.1 to 1000 dtex, especially 0.2 to 100 dtex and more preferably 0.5 to 10 dtex can be widely used.

[0084] Although there is no particular limitation on the cross-sectional shape of the polyvinyl alcohol fiber, simple substantially circular fiber are preferable to complex shapes in terms of water dispersibility, product homogeneity and the like.

[0085] The polyvinyl alcohol fiber of the present invention has excellent mechanical properties such as strength and is also excellent in water solubility, so that any fibrous structure can be obtained by using the fiber. For example, it can be processed into fibrous structures such as cut fibers, filaments, spun yarns, fabrics such as woven and knitted fabrics or dry nonwoven fabrics, ropes, and string-like articles. Moreover, such a fabric may be formed into a desired shape. At this time, other fibers may be used in combination, but in order to efficiently obtain the effects of the present invention, it is preferable that the polyvinyl alcohol fiber of the present invention accounts for 40% by mass or more, further 60% by mass or more, particularly 80 to 100% by mass of the fiber structure. Note that other fibers include water-soluble fibers, water-insoluble fibers, and polyvinyl alcohol fibers other than those of the present invention. It may also be used in combination with other materials such as metal or film.

[0086] A fiber length of the polyvinyl alcohol fiber of the present invention may be set appropriately depending on the application, but for example, when processing into a short fiber nonwoven fabric such as paper or spun yarn, the fiber length is preferably about 1 to 100 mm. The obtained short fiber can be made into a nonwoven fabric by a dry method.

[0087] On the other hand, when the polyvinyl alcohol fiber of the present invention are used as a long fiber to form a long fiber nonwoven fabric, the fiber length may be from several meters to several hundred meters and used for the nonwoven fabric. As for the method for producing the long fiber nonwoven fabric, the long fiber obtained by the above method are opened and deposited on a collecting surface to form a nonwoven fabric web, and then this web is partially crimped and rolled up to form a nonwoven fabric by a spunbond method or a melt blow method.

[0088] Although the polyvinyl alcohol fiber and the fiber structure of the present invention can be used for various purposes, but taking advantage of water-solubility and secondary processability thereof, it can be particularly suitably used as a process aid for textile products and as a base fabric for embroidery of chemical lace.

[0089] When using the fiber structure of the present invention as a base fabric for embroidery, it is preferable to use at least a fabric from the viewpoint of mechanical performance. The basis weight of such a fabric is preferably 50 g/m^2 or more, particularly 100 g/m^2 or more from the viewpoint of mechanical performance, and preferably 300 g/m^2 or less, more preferably 200 g/m^2 or less from the viewpoint of production efficiency. Further, from the viewpoint of mechanical performance, the tearing length of the fabric is preferably 2.5 N/25 mm or more, more preferably 2.6 N/25 mm or more.

[0090] The method for producing such a fabric is not particularly limited, but from the viewpoint of texture, flexibility and the like, it is preferable to use a dry nonwoven fabric obtained by treating a fibrous web. A preferred method for producing the dry nonwoven fabric is, for example, a method in which a web is formed by opening the polyvinyl alcohol fiber filament and the like using a repulsive action of frictional electrification or by opening crimped or cut staples with a card or the like and then this is thermally bonded using a hot air dryer at 150°C to 200°C

[0091] Another method for producing the dry nonwoven fabric includes, for example, a method for producing a nonwoven fabric by performing an interlacing treatment using needle punching. In this case, a dry nonwoven fabric with excellent strength and flexibility can be produced by using a known needle punch machine and adjusting conditions such as needle density, needle type, needle depth, and number of punches according to the properties of the fibers. If needed, entanglement may be optimized through multiple needle punch machines.

EXAMPLES

[0092] Hereinafter, the present invention will be described in more detail below with reference to examples, but the present invention is not limited to these examples.

[Ethylene modification rate]

[0093] An ethylene-vinyl ester copolymer was purified by reprecipitation three times or more with n-hexane/acetone and then dried under reduced pressure at 80°C for 3 days to produce an ethylene-vinyl ester copolymer for analysis. The obtained polymer was dissolved in DMSO-d6 and measured at 80°C using 500 MHz 1H-NMR. An ethylene modification rate was calculated using a peak derived from the main chain methylene of vinyl ester in the range of 4.7 to 5.2 ppm and a peak derived from ethylene and vinyl ester in the range of 0.8 to 1.6 ppm.

[Degree of Polymerization]

[0094] Based on JIS K 6726-1994, the degree of polymerization was calculated by the following formula (7) from the measured value of the intrinsic viscosity [η] of an aqueous solution at 30°C. In this regard, P is an average degree of polymerization of the polyvinyl alcohol.

$$\text{Degree of polymerization } P = ([\eta] \times 10^{4}/8.29)^{(1/0.62)} \quad (7)$$

[Degree of Saponification (mol%)]

[0095] Measured according to JIS K 6726-1994.

[Tensile strength (cN/dtex)]

[0096] Tensile strengths of the fibers were measured according to JIS L 1013.

[Fusing temperature of fiber in water (°C)]

[0097] A load of 2 mg/dtex was applied to an end of the fibers with a length of 100 mm, and the fibers were held in water with the load facing down. Thereafter, when the water temperature was raised at a rate of 2°C/min, the temperature at which the fibers fused and the load dropped was measured. The fusing temperature in water is the fusing temperature at the fiber diameter at the time of measurement.

[0098] In the case of the long fiber nonwoven fabrics, the nonwoven fabric was cut into pieces of 50 mm in length and 50 mm in width, and when the water temperature was raised at a rate of 2°C/min while stirring in water, the temperature at which the nonwoven fabric collapsed and dispersed in the water was measured.

[Secondary processability of fiber]

[0099] The fibers were formed into a web and heat treated at 160°C for 1 minute using a hot air dryer to produce a thermal bonded nonwoven fabric with a basis weight of 100 g/m^2. At that time, samples that could not be processed into nonwoven fabrics were labeled C, samples whose breaking strength was 2.5 N/25 mm or less were labeled B, and samples whose breaking strength exceeded 2.5 N/25 mm were labeled A.

[0100] In the case of the long fiber nonwoven fabrics, samples in which a nonwoven fabric could not be obtained were labeled C, samples in which a nonwoven fabric with a basis weight of about 40 g/m^2 was obtained and a breaking strength of 3.0 N/25 mm or less was labeled B, and samples in which a nonwoven fabric with a basis weight of about 40 g/m^2 was obtained and a breaking strength exceeded 3.0 N/25 mm were labeled A.

[Thickness of nonwoven fabric (mm)]

[0101] Thicknesses of the long fiber nonwoven fabrics were measured according to JIS L 1913.

<Example 1>

[0102] A polyvinyl alcohol composition was prepared by mixing 90% by mass of polyvinyl alcohol with a degree of saponification of 98.5 mol%, a degree of polymerization of 380 and a degree of ethylene modification of 8 mol% as polyvinyl alcohol A and 10% by mass of polyvinyl alcohol with a degree of saponification of 88 mol% and a degree of polymerization of 300 as polyvinyl alcohol B. The obtained polyvinyl alcohol composition was discharged from a round hole nozzle at 230°C and spun using a melt spinning machine. The spun yarn was dry heat drawn at a magnification of 2.7 times using a hot air oven to obtain a multifilament of 50 dtex/24 filaments. The spinnability was good after 6 hours with no fiber breakage, and the drawability was good with no fluff or sticking, and there were no problems.

<Examples 2 to 9>

[0103] Polyvinyl alcohol fibers were obtained in the same manner as in Example 1, except that the ratio of the polyvinyl alcohol A and the polyvinyl alcohol B was changed as shown in Table 1. The results are shown in Table 1.

<Example 10>

[0104] A polyvinyl alcohol fiber was obtained in the same manner as in Example 1, except that the polyvinyl alcohol composition was prepared by mixing 70% by mass of polyvinyl alcohol with a degree of saponification of 98.5 mol%, a degree of polymerization of 380 and a degree of ethylene modification of 8 mol% as the polyvinyl alcohol A and 30% by mass of polyvinyl alcohol with a degree of saponification of 80 mol% and a degree of polymerization of 300 as the polyvinyl alcohol B. The results are shown in Table 1.

<Example 11>

[0105] A polyvinyl alcohol composition described in Example 1 was discharged from a round hole nozzle at 260°C using a melt blowing machine to obtain a long fiber nonwoven fabric having a basis weight of about 40 g/m^2. The results are shown in Table 2.

<Examples 12 and 13>

[0106] A long fiber nonwoven fabric was obtained in the same manner as in Example 11, except that the ratio of the polyvinyl alcohol A and the polyvinyl alcohol B was changed as shown in Table 2. The results are shown in Table 2.

<Example 14>

[0107] A long fiber nonwoven fabric was obtained in the same manner as in Example 11, except that the polyvinyl alcohol composition described in Example 10 was used. The results are shown in Table 2.

<Comparative Example 1>

[0108] A polyvinyl alcohol fiber was obtained in the same manner as in Example 1, except that the polyvinyl alcohol B used in Example 1 was not used and only the polyvinyl alcohol A was used. The results are shown in Table 1. The melting point of the obtained fiber was high and it was impossible to process them into nonwoven fabrics.

<Comparative Example 2>

[0109] A polyvinyl alcohol fiber was obtained in the same manner as in Example 1, except that the polyvinyl alcohol A used in Example 1 was not used and only the polyvinyl alcohol B was used. The results are shown in Table 1. The strength of the obtained fibers was low and it was impossible to process them into nonwoven fabrics.

<Comparative Example 3>

[0110] A polyvinyl alcohol fiber was obtained in the same manner as in Example 1, except that polyvinyl alcohol with a degree of saponification of 74 mol% and a degree of polymerization of 500 was used as the polyvinyl alcohol B instead of the polyvinyl alcohol B used in Example 1 and the ratio of the polyvinyl alcohol A and the polyvinyl alcohol B was changed as shown in Table 1. The results are shown in Table 1. The resulting fiber had a high fusing temperature in water.

<Comparative Example 4>

[0111] The polyvinyl alcohol A used in Example 1 was not used, but polyvinyl alcohol with a degree of saponification of 88 mol% and a degree of polymerization of 1700 was used as the polyvinyl alcohol B, and a stock solution was prepared by dissolving only the polyvinyl alcohol B in DMSO at 90°C to a concentration of 20% by mass. This stock solution was passed through a nozzle with 3000 holes and a hole diameter of 0.08 mm and wet-spun with a composition of methanol/DMSO in a mass ratio of 7/3 in a solidification bath at 5°C at a bath draft of 0.5 times. Subsequently, DMSO was extracted with methanol at 20°C while applying wet drawing at a drawing ratio of 3 times. And then, the yarn was immersed in a bath containing 10% by mass of glycerin as an additive, 45% by mass of methyl isobutyl ketone (hereinafter abbreviated as MIBK) and a remaining part consisting of methanol so that the amount of glycerin applied was 10% by mass based on the polyvinyl alcohol in the spun yarn and dried at 150° C to obtain a spun yarn. This spun yarn was dry heat drawn at 160°C so that the total drawing ratio was 6 times and then wound up. The melting point of the obtained fiber was high and it was impossible to process them into nonwoven fabrics. The results are shown in Table 1.

<Comparative Example 5>

[0112] A polyvinyl alcohol fiber was obtained in the same manner as in Example 3, except that polyvinyl alcohol with a degree of saponification of 98 mol% and a degree of polymerization of 500 was used as the polyvinyl alcohol A. Since the polyvinyl alcohol A was not ethylene-modified, the resulting fiber had a high melting point and was difficult to process into a nonwoven fabric. The results are shown in Table 1.

[Table 1]

	Blend ratio of polyvinyl alcohol B1) (%)	Degree of saponification α_A of polyvinyl alcohol A (mol%)	Ethylene modification rate of polyvinyl alcohol A (mol%)	Degree of saponification α_B of polyvinyl alcohol B (mol%)	Difference of degree of saponification α_A-α_B (mol%)	Polyvinyl alcohol fiber					
						Melting point (°C)	Decomposition temperature (°C)	Strength (cN/dtex)	Fusing temperature in water (°C)	Secondary processability evaluation	Nonwoven fabric breaking strength (N/25mm)
Example 1	10	98.5	8	88	10.5	209	292	3.6	67	B	2.5
Example 2	20	98.5	8	88	10.5	206	290	3.6	48	A	2.7
Example 3	30	98.5	8	88	10.5	202	287	3.3	18	A	2.8
Example 4	40	98.5	8	88	10.5	202	284	3.1	7	A	2.9
Example 5	50	98.5	8	88	10.5	199	232	2.3	6	A	3.0
Example 6	60	98.5	8	88	10.5	197	279	2.3	5	A	3.0
Example 7	70	98.5	8	88	10.5	195	276	2.0	5	A	3.1
Example 8	80	98.5	8	88	10.5	193	273	1.7	5	A	3.2
Example 9	90	98.5	B	88	10.5	191	271	1.4	5	A	3.4
Example 10	30	98.5	8	80	10.5	205	257	3.3	6	A	3.0
Comparative Example 1	0	98.5	8	-	-	211	295	4.5	80	C	-
Comparative Example 2	100	-	-	88	-	189	268	0.9	5	C	-
Comparative Example 3	30	98.5	8	74	24.5	209	235	3.5	74	A	3.0
Comparative Example 4	100	-	0	88	-	220	290	4.0	5	C	-
Comparative Example 5	30	98.5	0	88	10.5	214	269	3.4	10	C	-

1) Blend ratio (%): Mass of polyvinyl alcohol B × 100/(mass of polyvinyl alcohol A + mass of polyvinyl alcohol B)

<Comparative Example 6>

[0113] A long fiber nonwoven fabric was obtained in the same manner as in Example 11, except that the polyvinyl alcohol B used in Example 1 was not used and only the polyvinyl alcohol A was used. The results are shown in Table 2.

<Comparative Example 7>

[0114] A long fiber nonwoven fabric was obtained in the same manner as in Example 11, except that polyvinyl alcohol with a degree of saponification of 74 mol% and a degree of polymerization of 500 was used as the polyvinyl alcohol B instead of the polyvinyl alcohol B used in Example 1 and the ratio of the polyvinyl alcohol A and the polyvinyl alcohol B was changed as shown in Table 2. The results are shown in Table 2.

[Table 2]

	Blend ratio of polyvinyl alcohol B1) (%)	Degree of saponification α_A of polyvinyl alcohol A (mol%)	Ethylene modification rate of polyvinyl alcohol A (mol%)	Degree of saponification α_B of polyvinyl alcohol B (mol%)	Difference of degree of saponification α_A-α_B (mol%)	Polyvinyl alcohol long fiber nonwoven fabric					
						Melting point (°C)	Decomposition temperature (°C)	Fusing temperature in water (°C)	Secondary processability evaluation	Nonwoven fabric breaking strength (N/25mm)	Thickness of nonwoven fabric (mm)
Example 11	10	93.5	8	88	10.5	209	292	57	B	0.7	0.33
Example 12	30	98.5	8	88	10.5	202	287	5	A	4.5	0.38
Example 13	40	98.5	8	88	10.5	202	284	3	A	4.7	0.41
Example 14	30	93.5	8	80	18.5	205	257	6	A	4.6	0.36
Comparative Example 6	0	98.5	a	-	-	211	295	85	B	0.5	0.28
Comparative Example 7	30	98.5	8	74	24.5	209	235	-	C	-	-
1) Blend ratio (%): Mass of polyvinyl alcohol B × 100/(mass of polyvinyl alcohol A + mass of polyvinyl alcohol B)											

[0115] As is clear from Table 1, the polyvinyl alcohol fiber of the present invention has excellent water solubility and strength. Further, the polyvinyl alcohol fiber has excellent secondary processability such as nonwoven fabric processability. Furthermore, as is clear from Table 2, the polyvinyl alcohol fiber of the present invention is excellent in forming long fiber nonwoven fabric by melt blowing or the like and the obtained long fiber nonwoven fabric is also excellent in water solubility and mechanical performance.

[0116] Therefore, the fiber structure containing at least a portion of the vinyl alcohol fiber of the present invention can be suitably used as a water-soluble fiber or a water-soluble nonwoven fabric.

Claims

1. A polyvinyl alcohol fiber comprising polyvinyl alcohol A having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol% and polyvinyl alcohol B having a degree of saponification satisfying the following formula (1).

$$0 < \alpha_A - \alpha_B \leq 20 \qquad (1)$$

In the formula (1), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

2. The polyvinyl alcohol fiber as claimed in claim 1, wherein a difference between a melting point and a decomposition temperature of the polyvinyl alcohol fiber is 40°C or more.

3. The polyvinyl alcohol fiber as claimed in claim 1 or 2, wherein the polyvinyl alcohol A has a degree of polymerization of 200 to 600.

4. The polyvinyl alcohol fiber as claimed in any one of claims 1 to 3, wherein the polyvinyl alcohol B has a degree of polymerization of 200 to 600.

5. The polyvinyl alcohol fiber as claimed in any one of claims 1 to 4, wherein the degree of saponification of the polyvinyl alcohol B is 80 mol% or more.

6. The polyvinyl alcohol fiber as claimed in any one of claims 1 to 5 containing the polyvinyl alcohol B in an amount of 15% by mass or more and 95% by mass or less, where a total mass of the polyvinyl alcohol A and the polyvinyl alcohol B is 100% by mass.

7. The polyvinyl alcohol fiber as claimed in any one of claims 1 to 6 having a fusing temperature in water of 70°C or less.

8. A method for producing the polyvinyl alcohol fiber as claimed in any one of claims 1 to 7, the method comprising:

   melting a composition comprising polyvinyl alcohol A having a degree of saponification of 90 mol% or more and an ethylene modification rate of 4 to 15 mol% and polyvinyl alcohol B having a degree of saponification satisfying the following formula (2);
   discharging the molten composition from a nozzle; and
   cooling the discharged composition.

$$0 < \alpha_A - \alpha_B \leq 20 \qquad (2)$$

   In the formula (2), α_A represents the degree of saponification of the polyvinyl alcohol A and α_B represents the degree of saponification of the polyvinyl alcohol B.

9. A long fiber nonwoven fabric made of the polyvinyl alcohol fiber as claimed in any one of claims 1 to 7.

10. A method for producing a long fiber nonwoven fabric by depositing the polyvinyl alcohol fiber as claimed in any one of claims 1 to 7 to form a nonwoven fabric web.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/045689

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/50(2006.01)i; ***D01F 6/34***(2006.01)i; ***D04H 3/007***(2012.01)i
FI: D01F6/50 Z; D01F6/34 Z; D04H3/007

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)

D01F6/50; D01F6/34; D01F6/14; D04H1/00-18/04; C08K3/00-13/08; C08L1/00-101/14

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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.
A	JP 49-33945 A (THE NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD.) 28 March 1974 (1974-03-28) example 2, control example 1	1-10
A	JP 50-90717 A (NITIVY CO., LTD.) 21 July 1975 (1975-07-21) example 1	1-10
A	JP 2000-234214 A (KURARAY CO., LTD.) 29 August 2000 (2000-08-29) example 1	1-10

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

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"&" document member of the same patent family

Date of the actual completion of the international search **01 February 2023**	Date of mailing of the international search report **14 February 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/045689

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 49-33945 A	28 March 1974	(Family: none)	
JP 50-90717 A	21 July 1975	(Family: none)	
JP 2000-234214 A	29 August 2000	EP 1010783 A1 example 1 JP 2000-234215 A JP 2000-239926 A JP 2000-314067 A US 6552123 B1 TW 477836 B CA 2292234 A CN 1259594 A KR 10-2000-0052481 A CA 2292234 A1	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000234214 A **[0010]**
- JP 2001248014 A **[0010]**