DESCRIPTION

Lint-Free Wiper

Technical Field

The present invention relates to a lint-free wiper formed from a non-woven fabric of thermoplastic poly(vinyl alcohol)-based long fibers.

Background Art

Wipers for use in a clean room to wipe off liquids, etc., or clean walls or floors of the clean room have been required to be highly lint-free, i.e., less generate fine dusts or fuzz of wiper materials, as well as to have a good water absorption, an good oil absorption and a good flexibility, i.e., easily drape with or follow the contours of the objects, such as walls or floors, to be cleaned.

In order to minimize the lints, the wipers must be free from the generation of dusts and the falling-off of minute fibers therefrom. In particular, minute fibers should be prevented from falling off from a cut surface or its periphery which are formed in the production of the wipers by cutting a sheet material. To attain this, it is important to produce the non-woven fabric from long fibers, preferably by a so-called spun-bonding method in which a thermoplastic polymer is melt-spun, and the resulting long fibers are directly formed into a non-woven fabric.

At present, many wipers for use in the clean room have been produced from a non-woven fabric mainly made of cellulose fibers. Although the cellulose fibers are suitable raw materials having a high water absorption, these fibers are not thermoplastic so that the spun-bonding method is inapplicable thereto. Fibers made of a thermoplastic polymer can be prevented from falling off from the non-woven fabric by heat-fusing the fibers together. However, this technique cannot be applied to cellulose fibers.

As the thermoplastic fibers, polyester fibers, etc. have been used.

However, since the polyester fibers, etc., show a low water absorption, these fibers must be made into hydrophilic by a treatment. Even though the water absorption is improved by the treatment, the wipers produced from such fibers subjected to the hydrophilic treatment produce another problem of increasing the amount of the substance being eluted therefrom when used for wiping organic solvent, etc.

Disclosure of Invention

An object of the present invention is to provide a lint-free wiper exhibiting a high affinity to water expressed by water absorption, hydrophilicity and water-swelling ability.

In accordance with the present invention, a lint-free wiper showing an excellent hydrophilicity is produced from poly(vinyl alcohol)-based non-woven fabric exhibiting a high affinity to water expressed by water absorption, hydrophilicity and water-swelling ability by a production technique used in producing a spun-bond non-woven fabric by melt-spinning method.

More specifically, the lint-free wiper of the present invention is formed from a non-woven fabric of thermoplastic poly(vinyl alcohol)-based long fibers having a viscosity-average polymerization degree of 200 to 700 and a melting point of 160 to 230°C.

Best Mode for Carrying Out the Invention

The poly(vinyl alcohol) used as the material for the non-woven fabric made of the poly(vinyl alcohol)-based long fibers according to the present invention include, in addition to vinyl alcohol homopolymer, a modified poly(vinyl alcohol) having another functional group incorporated by copolymerization, terminal modification, or post-reaction after polymerization.

The poly(vinyl alcohol) suitably used in the present invention (hereinafter occasionally referred to merely as "PVA") has a viscosity-average polymerization degree of 200 to 700, preferably 230 to 600, more preferably 250

to 500. When the viscosity-average polymerization degree is less than 200, the poly(vinyl alcohol) does not show a sufficient spinnability, thereby failing to make the polymer into fibers. When the viscosity-average polymerization degree exceeds 700, the melt-viscosity becomes too high so that the polymer is incapable of being stably extruded through a spinning nozzle.

The polymerization degree (P) of PVA was measured according to JIS-K6726. Specifically, PVA was completely re-saponified and purified to measure an intrinsic viscosity [η] (dl/g) at 30°C in water. The polymerization degree (P) of PVA was calculated from the measured intrinsic viscosity [η] according to the following formula:

$$P = ([\eta] \times 10^3/8.29)^{(1/0.62)}$$

When the polymerization degree lies within the above range, the effects of the present invention are fully achieved.

PVA used in the present invention preferably has a saponification degree of 90 to 99.99 mol%, more preferably 93 to 99.98 mol%, still more preferably 94 to 99.97 mol%, and most preferably 95 to 99.96 mol%. When the saponification degree is less than 90 mol%, PVA has a poor heat stability, which results in thermal decomposition or gelation of PVA to make it difficult to efficiently melt-spin PVA into fibers. Also, PVA having a saponification degree of more than 99.99 mol% is difficult to produce in a stable manner. Therefore, it is also difficult to form PVA fibers stably and, as a result thereof, a satisfactory non-woven fabric of long fibers cannot be obtained. Further, because of a reduced water absorption, the wipers made of such PVA fibers fail to show satisfactory properties required for wipers. s

The PVA used in the present invention has a melting point (Tm) of 160 to 230°C, preferably 170 to 227°C, and more preferably 180 to 220°C. When the melting point is lower than 160°C, the PVA shows a low crystallizability so that PVA fibers as well as the non-woven fabric made thereof become poor in mechanical strength. In some cases, PVA fails to have a spinnability sufficient for melt-spinning and causes severe thermal decomposition, thereby failing to

form a non-woven fabric. Further, the non-woven fabric produced from such PVA creates many fuzzes and lints, failing to show satisfactory properties as the wipers. When the melting point is higher than 230°C, the melt-spinning temperature of PVA must increase to ensure a suitable melt viscosity. Since the melt-spinning temperature reaches much closer to the decomposition temperature of PVA, it becomes difficult to melt-spin PVA stably and produce a non-woven fabric stably.

The melting point of PVA means a peak top temperature of an endothermic curve of PVA measured using a differential scanning calorimeter (DSC) by heating a sample to 250°C at a temperature rise rate of 10°C/min in nitrogen gas atmosphere, cooling to room temperature, and heating again to 250°C at a temperature rise rate of 10°C/min.

PVA is produced by saponifying vinyl ester units of a corresponding vinyl ester polymer. Vinyl monomers forming the vinyl ester units may include vinyl formate, vinyl acetate, vinyl propionate, vinyl valerate, vinyl caprate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate, and vinyl versatate. Of these vinyl monomers, vinyl acetate is preferred.

As described above, polymers for producing the PVA-based long fibers according to the present invention may be either PVA homopolymer or modified PVA having copolymerized units incorporated. Of these, the modified PVA having copolymerized units is preferred in view of the melt-spinnability and the fiber properties. Examples of the copolymerizable monomers include α-olefins such as ethylene, propylene, 1-butene, isobutene and 1-hexene; acrylic acid and salts thereof; acrylates such as methyl acrylate, ethyl acrylate, n-propyl acrylate and i-propyl acrylate; methacrylic acid and salts thereof; methacrylates such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate and i-propyl methacrylate; acrylamide; acrylamide derivatives such as N-methylacrylamide and N-ethylacrylamide; methacrylamide; methacrylamide derivatives such as N-methylmethacrylamide and N-ethylmethacrylamide; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether,

n-propyl vinyl ether, i-propyl vinyl ether and n-butyl vinyl ether; hydroxy-containing vinyl ethers such as ethylene glycol vinyl ether, 1,3-propan-diol vinyl ether and 1,4-butan-diol vinyl ether; allyl ethers such as allyl acetate, propyl allyl ether, butyl allyl ether and hexyl allyl ether; oxyalkylene-containing monomers; vinylsilyl compounds such as vinyltrimethoxysilane; isopropenyl acetate; hydroxy-containing α-olefins such as 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, 7-octen-1-ol, 9-decen-1-ol and 3-methyl-3-buten-1-ol; N-vinylamides such as N-vinylformamide, N-vinylacetamide and N-vinylpyrrolidone; monomers having carboxyl derived from fumaric acid, maleic acid, itaconic acid, maleic anhydride, phthalic anhydride, trimellitic anhydride, and itaconic anhydride; monomers having sulfonic group derived from ethylenesulfonic acid, allylsulfonic acid, metallylsulfonic acid, and 2-acrylamide-2-methylpropanesulfonic acid; and monomers having cationic group derived from vinyloxyethyltrimethylammonium chloride, vinyloxybutyltrimethylammonium chloride, vinyloxyethyldimethylamine, vinyloxymethyldiethylamine, N-acrylamidomethyltrimethylammonium chloride, N-acrylamidoethyltrimethylammonium chloride, N-acrylamidodimethylamine, allyltrimethylammonium chloride, metallyltrimethylammonium chloride, dimethylallylamine, allylethylamine and derivatives thereof. The content of the copolymerized monomer in the modified PVA is usually 25 mol% or lower.

Of these monomers, in view of easy availability, preferred are α-olefins such as ethylene, propylene, 1-butene, isobutene and 1-hexene; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether and n-butyl vinyl ether; hydroxy-containing vinyl ethers such as ethylene glycol vinyl ether, 1,3-propan-diol vinyl ether and 1,4-butan-diol vinyl ether; allyl ethers such as allyl acetate, propyl allyl ether, butyl allyl ether and hexyl allyl ether; N-vinylamides such as N-vinylformamide, N-vinylacetamide and N-vinylpyrrolidone; oxyalkylene-containing monomers; and hydroxy-containing α-olefins such as 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, 7-octen-1-ol, 9-

decen-1-ol and 3-methyl-3-buten-1-ol.

Further, in view of copolymerizability, melt-spinnability and high affinity to water such as water absorption and water-swelling ability of fibers, more preferred are α-olefins having 4 or less carbon atoms such as ethylene, propylene, 1-butene and isobutene; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether and n-butyl vinyl ether; and N-vinylamides such as N-vinylformamide, N-vinylacetamide and N-vinylpyrrolidone. The constitutional units derived from the α-olefins having 4 or less carbon atoms, the vinyl ethers and the N-vinylamides are preferably present in PVA in an amount of 0.1 to 20 mol%, more preferably 1 to 15 mol%.

Since a modified PVA having ethylene units enhances the fiber properties, particularly preferred is a modified PVA containing ethylene units in an amount of 3 to 20 mol%, preferably 5 to 18 mol%.

PVA used in the present invention can be produced by known methods such as bulk polymerization, solution polymerization, suspension polymerization and emulsion polymerization. Of these methods, bulk polymerization in the absence of solvent and solution polymerization in the presence of solvent such as alcohol may be ordinarily used. Examples of alcohol used in the solution polymerization are lower alcohols such as methyl alcohol, ethyl alcohol and propyl alcohol. The initiators used for the copolymerization may be known azo or peroxide initiators such as α,α'-azobisisobutylonitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), benzoyl peroxide and n-propylperoxycarbonate. The polymerization temperature is not particularly limited, and suitably 0 to 200°C.

PVA for producing the non-woven fabric wiper according to the present invention preferably contains an alkali metal ion (B) in an amount of 0.00001 to 0.05 part by mass, more preferably 0.00005 to 0.04 part by mass, still more preferably 0.0001 to 0.03 part by mass, and most preferably 0.0002 to 0.02 part by mass in terms of sodium ion on the basis of 100 parts by mass of the PVA (A). PVA having an alkali metal ion content of less than 0.00001 part by mass is

difficult to industrially produce. When the alkali metal ion content exceeds 0.05 part by mass, PVA tends to suffer from thermal decomposition or gelation during the melt-spinning, thereby failing to produce a satisfactory non-woven fabric. In addition, the amount of the metal ion eluted from the non-woven fabric is increased, thereby rendering the non-woven fabric wipers unusable in the clean room. Examples of the alkali metal ion include potassium ion and sodium ion.

The method of incorporating a specific amount of the alkali metal ion (B) into PVA is not particularly limited. For example, an alkali metal ion-containing compound may be added to PVA after polymerization. Alternatively, a vinyl ester polymer is saponified in a solvent in the presence of an alkali metal ion-containing alkaline substance as a saponification catalyst to incorporate the alkali metal ion into PVA, followed by washing PVA as a saponified product with a cleaning solution to control the alkali metal ion content. The latter method is preferred. The alkali metal ion content may be determined by an atomic absorption method.

Examples of the alkaline substance used as the saponification catalyst include potassium hydroxide and sodium hydroxide. The alkaline substance as the saponification catalyst may be used preferably in an amount of 0.004 to 0.5 mole, more preferably 0.005 to 0.05 mole per mole of vinyl ester units. The saponification catalyst may be added all at once at the initial stage of the saponification reaction, or in parts in the course of the saponification reaction.

Examples of the solvent for the saponification reaction include methanol, methyl acetate, dimethylsulfoxide and dimehtylformamide. Of these solvents, preferred is methanol, more preferred is methanol having a water content of 0.001 to 1 mass %, still more preferred is methanol having a water content of 0.003 to 0.9 mass %, and most preferred is methanol having a water content of 0.005 to 0.8 mass %. Examples of the cleaning solution include methanol, acetone, methyl acetate, ethyl acetate, hexane, water, etc. Of these cleaning solutions, preferred are methanol, methyl acetate, water and mixed solutions

thereof.

The amount of the cleaning solution used is not particularly restricted as long as the content of the alkali metal ion (B) in PVA meets the above range, and is preferably 300 to 10,000 parts by mass, more preferably 500 to 5,000 parts by mass based on 100 parts by mass of PVA. The washing temperature is preferably 5 to 80°C, more preferably 20 to 70°C, and the washing time is preferably 20 minutes to 100 hours, more preferably 1 to 50 hours.

PVA (A) used in the present invention may contain an acid (C) having an acid radical of pKa 5.0 or less at 25°C in an amount that makes the ratio, α, defined by the following formula:

α = (content (mass %) of acid (C) in PVA)/(content (mass % of alkali metal ion (B) in PVA),

preferably from 0.01 to 1, more preferably from 0.03 to 0.8, and most preferably 0.05 to 0.6. In the above formula, the content of acid (C) was measured by neutralization titration and expressed in terms of acetic acid. The term, pKa, is defined by the formula:

$$pKa = -\log Ka$$

wherein Ka is a dissociation constant of the acid.

When the pKa of the acid radical of the acid (C) exceeds 5.0 or when the content of the acid (C) cannot make the α value from 0.01 to 1, PVA tend to suffer from severe decomposition, gelation and breaking in the production of the spun-bond non-woven fabric, thereby failing to be stably formed into fibers. Examples of the acid (C) having an acid radical of pKa 5.0 or less at 25°C include acetic acid, phosphoric acid and monobasic sodium phosphate.

The method of incorporating a specific amount of the acid (C) into PVA is not particularly limited. For example, PVA obtained by saponifying a vinyl ester polymer in a solvent is blended with the acid (C), and then washed with a cleaning solution to regulate the content of the acid (C) within the range specified above. Alternatively, the incorporation may be carried out by treating dried PVA with a solvent containing the acid (C), or adding a specific

amount of the acid (C) to PVA during the pelletization of PVA.

The content of the acid (C) in PVA can be determined by extracting the acid (C) with methanol from PVA, and subjection the methanol extract to neutralization titration with an aqueous solution of sodium hydroxide.

PVA may further contain, if required, various additives such as stabilizers such as copper compounds, colorants, ultraviolet light absorbers, light stabilizers, antioxidants, antistatic agents, flame retardants, plasticizers, lubricants and crystallization retardants unless the addition of these additives adversely affect the objects and effects of the present invention. The additives may be added to PVA either during the polymerization reaction or in the subsequent steps. In particular, the addition of a heat stabilizer, e.g., organic stabilizers such as hindered phenol, halogenated copper compounds such as copper iodide and halogenated alkali metal compounds such as potassium iodide, is preferable to enhance the melt-dwelling stability during the fiber formation.

Further, PVA may be added with, if required, fine particles having an average particle size of 0.01 to 5 μm in an amount of 0.05 to 10 mass % during the polymerization reaction or in the subsequent steps. The fine particles to be added are not particularly limited, and include, for example, inert fine particles of silica, alumina, titanium oxide, calcium carbonate, barium sulfate, etc. These fine particles may be used alone or in combination of two or more. Of these fine particles, inorganic fine particles having an average particle size of 0.02 to 1 μm are especially preferred because it improves the spinnability and the drawing properties.

The process for producing the non-woven fabric made of PVA long fibers for use as the lint-free wiper according to the present invention is explained below. The non-woven fabric made of long fibers according to the present invention is effectively produced by a method employed in producing a spun-bond non-woven fabric in which the melt-spun fibers are directly formed into the non-woven fabric.

More specifically, after the PVA is melt-kneaded in an extruder, the molten polymer is introduced to a spinning head and extruded through a spinning nozzle while metering its flow rate. The extruded strands are cooled by a cooling device and then attenuated by air jet stream at a speed corresponding to a take-off rate of 1,000 to 6,000 m/min using an aspirator having air jet nozzles so that the thickness of the strands is reduced to a desired fineness. Then, the strands are split and deposited on a moving collecting surface to form a non-woven fabric web. Successively, the web is partially pressed and wound up into a roll to obtain the non-woven fabric of PVA-based long fibers.

In the production of the non-woven fabric according to the present invention, the spinneret temperature for melt-spinning PVA is required to be within the range from Tm + 10°C to Tm + 80°C, wherein Tm represents a melting point of the polymer. When the spinneret temperature is lower than Tm + 10°C, the melt viscosity of the polymer is too high, coming to resistant to the spinning and drawing by air jet. When the spinneret temperature is higher than Tm + 80°C, PVA undergoes thermal decomposition, thereby failing to stably spin the polymer.

The melting point, Tm, of PVA referred to herein means a peak temperature of a main endothermic peak as observed by a differential scanning calorimeter (DSC), for example, TA3000 available from Mettler Corp.

In the present invention, it is important to attenuate the extruded strands by air jet using an aspirator having air jet nozzles at a speed corresponding to a take-off rate of 1,000 to 6,000 m/min. The take-off conditions of the strands by the aspirator is selected depending on the melt viscosity of the molten polymer being extruded through the spinning nozzle, the extrusion rate, the temperature of the spinning nozzle, the cooling conditions, etc. If less than 1,000 m/min, the extruded strands are cooled and solidified too slowly so that adjacent strands are likely to fuse together. In addition, because of delayed orientation and crystallization, the non-woven fabric being produced is coarse and poor in mechanical strength. When the take-off rate is larger than 6,000

m/min, the extruded strands are broken to prevent the stable production of the non-woven fabric because the rate is too high beyond their spinnability and drawing properties.

In the present invention, the PVA-based non-woven fabric web is partially hot-pressed to fuse the fibers together, thereby allowing the web to retain its shape. More specifically, the web is passed between a heated metal roll having embossed patterns thereon (embossed roll) and a heated flat roll. This allows the long fibers to be partially hot-pressed to fuse together, thereby retaining the shape of the non-woven fabric. The temperatures of the heated rolls, the heat-pressing force, the treating speed, the embossed patterns, etc. employed in the above heat-fusion step may be appropriately selected according to the requirements.

The PVA-based long fibers constructing the non-woven fabric according to the present invention is active to water so that the apparent melting point thereof is decreased in the presence of water. For this reason, by adding water to the web before the heat-fusion step, the temperatures of the heated rolls may be lowered.

If the spun-bonded non-woven fabric is unsuitable as the wiper because of it high solubility to water, the non-woven fabric may be heat-treated to control the solubility. This is because the heat treatment promotes the crystallization of fiber-forming resin. The heat treatment may be performed either during the production of the non-woven fabric or after winding up the fabric into a roll.

Further, the non-woven fabric may be heat-treated by any suitable method using hot air, hot plate or hot roll, as long as the fabric is prevented from being directly exposed to water, e.g., being immersed in water bath.

The non-woven fabric of PVA-based long fibers used in the present invention preferably exhibits a water absorption length of 2 cm or more, more preferably 2.5 cm or more, still more preferably 3 cm or more, and most preferably 3.5 cm or more when measured at 20°C for one minute. When the water absorption length is less than 2 cm, the water absorption is poor and the

non-woven fabric is functionally unsuitable as the wiper.

The water absorption length of the non-woven fabric was measured according to JIS L 1018-70 "Testing Methods for Knitted Fabrics" (water absorption test method B (Byreck method), KRT, No. 411-2). Specifically, a non-woven fabric specimen of 2.5 cm x 17 cm loaded at its lower end was immersed in an aqueous ink (ink/water = 1/5) by 1 cm from the lower end and kept for one minute to measure the height of water absorbed by the capillary action.

Thus, the lint-free wiper of the present invention can be provided with a water absorption or a tenacity of intended level according to the requirements by appropriately selecting PVA and the conditions for the production of the non-woven fabric.

The important features of the wiper according to the present invention reside in that the wiper is produced from the non-woven fabric of PVA-based long fibers which is produced by melt-spinning method and exhibits reasonable hydrophilic and lint-free characteristics. Therefore, in the present invention, the fineness and cross-sectional shape of the long fibers, the basis weight of the non-woven fabric, its mechanical properties such as tensile strength, tensile elongation and tear strength, its configurations such as thickness and bulkiness and other properties such as flexibility are not particularly limited and may be appropriately selected from the ranges ordinarily employed in the art.

EXAMPLES

The present invention will be described in more detail by reference to the following examples. However, these examples are only illustrative and not intended to limit the present invention thereto. In the following examples and comparative examples, the respective properties and characteristics were measured by the following methods, and "part" and "%" represent "part by mass" and "mass %", respectively, unless otherwise specified.

1. Analysis of PVA

PVA was analyzed by the method described in JIS K 6726, unless otherwise specified.

The modification degree of a modified poly(vinyl ester) or a modified PVA was determined by 500MHz, ^{1}H NMR (JEOL GX-500).

The alkali metal ion content was determined by an atomic absorption method.

2. Melting Point

The melting point of PVA was expressed by the peak top temperature of an endothermic curve of PVA measured using a differential scanning calorimeter (TA3000 available from Mettler Corp.) by heating a sample to 250°C at a temperature rise rate of 10°C/min in nitrogen gas atmosphere, cooling to room temperature, and heating again to 250°C at a temperature rise rate of 10°C/min.

3. Moldability

The states of the melt-spinning and the resultant non-woven fabric were observed visually and by touch, and evaluated according to the following ratings:

A: Excellent; B: Good; C: Slightly poor; and D: Poor.

4. Basis Weight and Thickness

The basis weight and thickness of the non-woven fabric were measured according to JIS L 1906 "Test methods for non-woven fabrics made of filament yarn".

5. Tenacity

The basis weight and thickness of the non-woven fabric were measured according to JIS L 1906 "Test methods for non-woven fabrics made of filament yarn".

6. Water absorption length

The water absorption length of the non-woven fabric was measured according to JIS L 1018-70 "Testing Methods for Knitted Fabrics" (water absorption test method B (Byreck method), KRT, No. 411-2).

Namely, a non-woven fabric specimen of 2.5 cm x 17 cm loaded at its lower end was immersed in an aqueous ink (ink/water = 1/5) by 1 cm from the lower end and kept for one minute to measure the height of water absorbed by the capillary action.

7. Water retention

After drying completely, an accurately weighed non-woven fabric of 20 cm x 20 cm was immersed in 50 cc of pure water at 20°C for 5 minutes. Then, the non-woven fabric was taken out of water and kept above the water surface for 30 seconds. At the time when water no longer dropped from the non-woven fabric, the whole weight thereof was measured to calculate the water retention.

8. Miswiped amount

One gram of distilled water was placed in a watch glass of 9 cm diameter. A non-woven fabric of 5 cm x 5 cm was immersed in the distilled water for 5 seconds and removed therefrom to measure the amount of water left in the watch glass.

9. Fall-off of fuzzes or lints

A non-woven fabric of 15 cm x 15 cm was circularly rubbed by a circular urethane sheet of 7 cm diameter 10 times (one clockwise circuit and one counterclockwise circuit for each run). The amount of fibers fallen off from the fabric was visually observed. The results were classified into five ranks of 1 to 5 where 1 is severe fall-off and 5 is substantially no fall-off.

10. Lint-free property of non-woven fabric in water

A non-woven fabric of 20 cm x 20 cm was immersed in 500 cc of 20°C pure water in a flask. The flask was laid on its side and shaken up and down 100 times. Thereafter, the amount of lints in water was visually observed. The results were classified into five ranks of 1 to 5 where 1 is heavy lint formation and 5 is substantially no lint formation.

PRODUCTION OF ETHYLENE-MODIFIED PVA

A 100 liter pressure reactor equipped with a stirrer, a nitrogen inlet, an ethylene inlet and an initiator inlet was charged with 29.0 kg of vinyl acetate

and 31.0 kg of methanol. After heating the contents of the reactor to 60°C, the reaction system was purged with nitrogen by bubbling nitrogen for 30 minutes. Ethylene was introduced into the reactor until the inside pressure reached 5.9 kg/cm^2 (5.8×10^5 Pa).

Separately, a 2.8 g/l methanol solution of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMV) as the initiator was prepared and purged by nitrogen bubbling. After the inside temperature of the reactor was adjusted to 60°C, 170 ml of the initiator solution was poured into the reactor to initiate the polymerization. During the polymerization, the inside pressure of the reactor was maintained at 5.9 kg/cm^2 (5.8×10^5 Pa) by introducing ethylene and the inside temperature was maintained at 60°C while continuously feeding the initiator solution at a rate of 610 ml/hr.

When the rate of polymerization reached 70% after 10 hours, the reactor was cooled to terminate the polymerization. After releasing ethylene by opening the reactor, the reaction mixture was bubbled with nitrogen to completely remove ethylene. Then, the unreacted vinyl acetate monomer was removed under reduced pressure to obtain a methanol solution of poly(vinyl acetate).

The resultant methanol solution of poly(vinyl acetate) was mixed with an additional amount of methanol to adjust the concentration to 50%. Into 200 g of the resultant methanol solution of poly(vinyl acetate) (containing 100 g poly(vinyl acetate)), were added 46.5 g of a 10% NaOH solution in methanol (molar ratio (MR) of NaOH to vinyl acetate units was 0.10), thereby saponifying poly(vinyl acetate). The gelation occurred 2 minutes after the addition of the alkali solution. After pulverizing the gel by a mill, the mixture was allowed to stand at 60°C for one hour to proceed the saponification. The saponified mixture was added with 1,000 g of a water/methanol (20/80) mixed solution containing 0.5% of acetic acid to neutralize the residual alkali. After the completion of the neutralization was confirmed using phenolphthalein indicator, the reaction mixture was filtered to obtain PVA as white solids, which

was mixed with 2,000 g of a water/methanol (20/80) mixed solution and allowed to stand at room temperature for 3 hours for washing PVA. After repeating the washing procedure 3 times, PVA was further mixed with 1,000 g of methanol and allowed to stand at room temperature for 3 hours for washing. Thereafter, the liquid phase was removed by centrifugation and the separated PVA was kept in a dryer at 70°C for 2 days, thereby obtaining dried PVA (PVA-1). The saponification degree of the ethylene-modified PVA was 98.4 mol%.

The modified PVA was ashed and dissolved in an acid for determining the sodium content by an atomic absorption spectrophotometer. The result showed that it was 0.0005 part by mass based on 100 parts by mass of the modified PVA.

Further, the methanol solution of poly(vinyl acetate) obtained by removing the unreacted vinyl acetate monomer from the polymerization reaction mixture was added to n-hexane to precipitate poly(vinyl acetate). The precipitated poly(vinyl acetate) was dissolved in acetone, and the resultant solution was added again to n-hexane to precipitate poly(vinyl acetate). This reprecipitation and purification procedure was repeated three times, and then the poly(vinyl acetate) precipitate was dried under reduced pressure at 80°C for three days, thereby obtaining a purified poly(vinyl acetate). The purified poly(vinyl acetate) was dissolved in d6-DMSO and analyzed by 500MHz, ^{1}H NMR (JEOL GX-500) at 80°C. The result showed that the ethylene content was 10 mol%.

The methanol solution of poly(vinyl acetate) obtained above was saponified at an alkali–vinyl acetate unit molar ratio of 0.5, pulverized by a mill, and allowed to stand at 60°C for five hours to proceed the saponification. The saponification mixture was extracted with methanol using Soxhlet's extractor for three days, followed by drying the extract under reduced pressure at 80°C for three days to obtain a purified ethylene-modified PVA. The average polymerization degree of the ethylene-modified PVA measured by an ordinary method according to JIS K 6726 was 330.

The purified ethylene-modified PVA was dissolved in water to prepare an aqueous 5% solution, which was cast to form a 10 μm-thick film. After drying the film under reduced pressure at 80°C for one day, the melting point of PVA was measured by the method described above using a DSC (TA3000 available from Mettler Corp.). As a result thereof, the melting point of PVA was 206°C.

In the same manner, ethylene-modified PVAs, PVA-2 to PVA-20, were prepared. The characteristics thereof are shown in Table 1.

Table 1

	Polymerization degree	Saponification degree (mol%)	Tm (°C)
PVA-1	330	98.4	206
PVA-2	560	98.2	192
PVA-3	230	98.9	207
PVA-4	330	99.7	216
PVA-5	290	94.1	188
PVA-6	350	98.3	222
PVA-7	450	98.7	208
PVA-8	320	98.1	179
PVA-9	280	98.2	195
PVA-10	330	98.4	206
PVA-11	330	98.4	206
PVA-12	330	98.4	206
PVA-13	290	88.0	178
PVA-14	450	98.7	208
PVA-15	380	98.3	176
PVA-16	230	98.9	207
PVA-17	1050	97.8	206
PVA-18	150	98.6	207
PVA-19	350	99.8	234
PVA-20	410	99.0	153

Table 1 (contd.)

	Modifier	Modification degree (mol%)	Sodium ion (part by mass)	$\alpha^{1)}$
PVA-1	ethylene	10	0.0005	0.04
PVA-2	ethylene	18	0.003	0.1
PVA-3	ethylene	11	0.0008	0.09
PVA-4	ethylene	10	0.002	0.07
PVA-5	ethylene	5	0.0004	0.2
PVA-6	–	–	0.003	0.1
PVA-7	propylene	3	0.001	0.08
PVA-8	ethyl vinyl ether	6	0.003	0.2
PVA-9	N-vinylacetamide	3	0.002	0.1
PVA-10	ethylene	10	0.03	0.08
PVA-11	ethylene	10	0.00005	0.4
PVA-12	ethylene	10	0.0009	0.9
PVA-13	ethylene	5	0.0001	0.2
PVA-14	propylene	3	0.07	0.09
PVA-15	ethylene	28	0.01	1.2
PVA-16	ethylene	11	0.006	0.007
PVA-17	ethylene	7	0.0006	0.1
PVA-18	ethylene	10	0.005	0.2
PVA-19	–	–	0.001	0.07
PVA-20	ethyl vinyl ether	10	0.002	0.1

$^{1)}\alpha$ = (acetic acid content)/(sodium ion content) of PVA

EXAMPLE 1

PVA-1 was melt-kneaded at 225°C in a melt extruder. The molten polymer was introduced into a spinning head extruded through a spinneret having 24 orifices each having a diameter of 0.25 mm. The spun strands were introduced into a cylindrical air-jet aspirator while cooling by 20°C cooling air, where the strands were attenuated at a take-off rate of about 3,500 m/min. The attenuated strands were broken into discrete fibers and collected in layer on a moving conveyor to form a web of long fibers. The web was passed between an unevenly patterned emboss roll and a flat roll both heated to 180°C under a linear pressure of 20 kgf/cm to heat-fuse the fibers at embossed portions. The web was further heat-treated by passing through a hot-air dryer at 200°C for 2 minutes, thereby obtaining a non-woven fabric of 34 g/m^2 basis weight made of long fibers having a monofilament fineness of 4.4 dtex.

The process conditions for producing the non-woven fabric and the moldability of PVA are shown in Table 2, and the results of the evaluation of the produced non-woven fabric in basis weight, thickness, lateral tenacity, water retention, water-absorption length, miswiped amount, fall-off of fuzzes or lints, and lint-free property in water are shown in Table 3.

EXAMPLES 2 to 16

Non-woven webs of PVA long fibers were produced in the same manner as in Example 1 except for using PVA-2 to PVA-16 shown in Table 1 instead of PVA-1 and changing the production conditions as shown in Table 2. The obtained non-woven webs were embossed and heat-treated at the temperatures shown in Table 2, thereby obtaining non-woven fabrics of long fibers. The results of the evaluation of the produced non-woven fabric in basis weight, thickness, lateral tenacity, water retention, water-absorption length, miswiped amount, fall-off of fuzzes or lints, and lint-free property in water are shown in Table 3.

COMPARATIVE EXAMPLES 1 to 4

Non-woven webs of PVA long fibers were produced in the same manner as in Example 1 except for using PVA-17 to PVA-20 shown in Table 1 instead of PVA-1 and changing the production conditions as shown in Table 2. The obtained non-woven webs were embossed and heat-treated at the temperatures shown in Table 2, thereby obtaining non-woven fabrics of long fibers.

In Comparative Example 1 using PVA-17, the melt viscosity of PVA was too high to stably extrude the molten polymer through spinning nozzles, thereby failing to obtain a non-woven web. Although the apparent melt viscosity was reduced when the spinning head was heated to 280°C, the thermal decomposition and gelation occurred to bring about more undesirable results.

In Comparative Example 2 using PVA-18, the melt viscosity of PVA was too low so that the molten polymer was dripping during the extrusion from spinneret, thereby failing to stably produce fibers and a non-woven web.

In Comparative Example 3 using PVA-19, the melt viscosity of PVA was too high at a spinning temperature of 240°C because it was much closer to the melting point. Although the apparent melt viscosity was reduced when the spinning head was heated to 255°C, the thermal decomposition and gelation occurred to bring about more undesirable results.

In Comparative Example 4 using PVA-20, adjacent spun filaments were fused to each other because of their reduced crystallization. The fused filaments could not be split into discrete fibers, resulting in formation of a coarse non-woven web.

Table 2

	PVA	Plasticizer (part by mass)	Production Conditions			
			spinning temp. (°C)	take-off rate (m/min)	emboss temp. (°C)	heat-treating temp. (°C)
Examples						
1	PVA-1	–	225	3500	180	200
2	PVA-2	–	220	3000	170	–
3	PVA-3	–	225	3500	180	200
4	PVA-4	–	235	3500	190	200
5	PVA-5	–	210	3000	170	180
6	PVA-6	DG* (3)	240	2500	200	200
7	PVA-7	–	230	3500	190	200
8	PVA-8	–	200	3500	160	180
9	PVA-9	–	215	3500	170	180
10	PVA-10	–	225	3500	180	200
11	PVA-11	–	225	3500	180	200
12	PVA-12	–	225	3500	180	200
13	PVA-13	–	200	2500	160	180
14	PVA-14	–	230	2000	190	200
15	PVA-15	–	195	2000	150	–
16	PVA-16	–	225	2500	180	200
Comparative Examples						
1	PVA-17	–	280	1000	–	–
2	PVA-18	–	220	–	–	–
3	PVA-19	DG* (3)	255	–	–	–
4	PVA-20	–	175	2500	120	140

*DG = Diglycerol

Table 2 (contd.)

		Moldability		
		Spinning	Non-woven fabric	
Example				
1	PVA-1	A	A	–
2	PVA-2	A	B	–
3	PVA-3	A	A	–
4	PVA-4	A	A	–
5	PVA-5	A	B	–
6	PVA-6	B	B	–
7	PVA-7	A	A	–
8	PVA-8	A	A	–
9	PVA-9	A	A	–
10	PVA-10	A	A	–
11	PVA-11	A	A	–
12	PVA-12	A	A	–
13	PVA-13	B–C	B–C	slight decomposition odor
14	PVA-14	B–C	C	slight fiber breaking
15	PVA-15	B–C	C	slight fiber breaking
16	PVA-16	B–C	B–C	slight decomposition odor
Comparative Examples				
1	PVA-17	D	–	incapable of stable spinning by thermal decomposition
2	PVA-18	D	–	frequent fiber breaking
3	PVA-19	D	–	incapable of stable spinning by increased viscosity
4	PVA-20	D	D	severe fiber-to-fiber bonding

Table 3

	Results of Evaluation							
	basis weight (g/m^2)	thickness (mm)	lateral tenacity (N/2.5cm)	water-absorption length (cm)	water retention (%)	miswiped amount (g)	fall-off of fuzz	lint-free property in water
Examples								
1	34	0.25	32	5.6	1005	0.13	5.0	5.0
2	35	0.28	38	4.2	691	0.23	5.0	5.0
3	35	0.25	30	5.8	1029	0.11	5.0	4.5
4	32	0.20	31	4.9	955	0.16	5.0	5.0
5	37	0.31	28	7.5	1071	0.08	4.5	4.5
6	35	0.26	27	6.1	1038	0.10	4.5	4.5
7	28	0.17	30	5.7	993	0.14	5.0	5.0
8	34	0.23	32	5.4	971	0.15	5.0	5.0
9	32	0.27	33	5.9	1035	0.11	5.0	5.0
10	35	0.29	34	5.4	976	0.15	5.0	5.0
11	36	0.29	34	5.5	989	0.14	5.0	5.0
12	35	0.26	32	5.2	962	0.15	5.0	5.0
13	37	0.29	29	5.6	1065	0.09	4.5	4.5
14	34	0.20	23	5.2	961	0.13	4.5	4.5
15	28	0.18	25	2.9	382	0.29	4.5	4.0
16	37	0.29	28	5.5	987	0.15	4.5	4.5
Comparative Examples								
4	34	0.28	9	5.1	987	0.14	4.5	4.5

Industrial Applicability

In accordance with the present invention, a poly(vinyl alcohol)-based non-woven fabric exhibiting a high affinity to water such as water absorption, hydrophilicity and water swelling ability is produced by the melt-spinning method employed in the production of a spun-bonded non-woven fabric, thereby providing a lint-free wiper having an excellent hydrophilicity.

CLAIMS

1. A lint-free wiper comprising a non-woven fabric made of thermoplastic poly(vinyl alcohol)-based long fibers having a viscosity-average polymerization degree of 200 to 700 and a melting point of 160 to 230°C.

2. The lint-free wiper according to Claim 1, wherein the water-absorption length of the wiper is 2 cm or more when immersed in water for one minute at 20°C.

3. The lint-free wiper according to Claim 1 or 2, wherein the poly(vinyl alcohol) contains an alkali metal ion (B) in an amount of 0.00001 to 0.05 part by mass based on 100 parts by mass of the poly(vinyl alcohol) (A).

4. The lint-free wiper according to any one of Claims 1 to 3, wherein the poly(vinyl alcohol) (A) contains an acid (C) containing an acid radical having a pKa of 5.0 or less when measured at 25°C in such an amount that a ratio, α, of the poly(vinyl alcohol) defined by the formula:

α = (content (mass %) of acid (C))/(content (mass %) of alkali metal ion (B))

is in the range of 0.01 to 1.

5. The lint-free wiper according to any one of Claims 1 to 4, wherein a saponification degree of the poly(vinyl alcohol) (A) is 90 to 99.99 mol%.

6. The lint-free wiper according to any one of Claims 1 to 5, wherein the poly(vinyl alcohol) (A) is a modified poly(vinyl alcohol) containing at least one unit selected from the group consisting of α-olefin units having 4 or less carbon atoms, vinyl ether units and N-vinylamide units in a total amount of 0.1 to 20 mol%.

7. The lint-free wiper according to Claim 6, wherein the poly(vinyl alcohol) (A) is a modified poly(vinyl alcohol) containing ethylene units in an amount of 3 to 20 mol%.

ABSTRACT OF THE DISCLOSURE

A lint-free wiper of the present invention is formed from a non-woven fabric of long poly(vinyl alcohol)-based fibers having a viscosity-average polymerization degree of 200 to 700 and a melting point of 160 to 230°C, and exhibits not only an excellent lint-free property but also a high affinity to water such as water absorption, hydrophilicity and water swellability.