

SPECIFICATION

Title of Invention: Method for Producing Polyvinyl Alcohol Resin

Technical Field

[0001]

The present invention relates to a method for producing a polyvinyl alcohol resin comprising a washing step of continuously washing polyvinyl alcohol particles.

Background Art

[0002]

Polyvinyl alcohol (PVA) is a water-soluble synthetic resin widely used in various fields such as fibers, films, dispersants, and adhesives. PVA is typically produced by saponifying polyvinyl acetate obtained by polymerizing vinyl acetate monomer, with an alkali catalyst such as sodium hydroxide. Therefore, the saponified PVA contains sodium acetate, which is a residue of the saponification catalyst. However, if a large amount of sodium acetate is present, the PVA is prone to thermal decomposition and discoloration when heated, and thus there are applications where the presence of such impurities is undesirable. Therefore, methods for removing sodium acetate from the saponified PVA have been investigated.

[0003]

For example, Patent Literature 1 has described a method for reducing a sodium acetate content of polyvinyl alcohol obtained by saponifying a polyvinyl

ester, by washing with a washing liquid containing methyl acetate, methanol, and water in a specific ratio. The examples describe a batch production method comprising forming a slurry containing a PVA and a washing liquid, then filtering the slurry to obtain a PVA cake, and then drying the cake. Thus, if the PVA particles are so fine that they form a cake after filtration, a washing efficiency is improved, but the need to handle the cake makes the method less workable, and thus a batch production is unavoidable.

[0004]

Patent Literature 2 has described a method for washing a PVA resin, using an apparatus comprising a vertical moving bed apparatus and an inclined screw conveyor, wherein the lower part of the vertical moving bed apparatus is connected to the vicinity of the lower part of the inclined screw conveyor, feeding a slurry containing the solid PVA resin from the upper part of the vertical moving bed apparatus, conveying it through the lower part to the upper part of the inclined screw conveyor while feeding a washing liquid from the vicinity of the upper part of the inclined screw conveyor and discharging the washing liquid from the vicinity of the upper part of the vertical moving bed apparatus, to remove impurities in the resin. While this method enables continuous washing of the PVA resin, the apparatus is large and complex. Furthermore, the PVA washed in the examples contains 0.1 to 0.3% (1000 to 3000 ppm) of sodium acetate, making it difficult to thoroughly wash the resin.

Citation List

Patent Literature

[0005]

Patent Literature 1: JP 2011-178964 A

Patent Literature 2: JP 2007-245432 A

Summary of Invention

Technical Problem

[0006]

The present invention has been devised to solve the above problems, and an object of the present invention is to provide a method for producing a polyvinyl alcohol resin, whereby an alkali catalyst residue contained in the saponified PVA particles can be continuously and efficiently removed.

Solution to Problem

[0007]

The present inventors have conducted extensive studies to solve the above problems and have completed the present invention, which relates to the following [1] to [11].

[0008]

[1] A method for producing a polyvinyl alcohol resin comprising a washing step of continuously washing polyvinyl alcohol particles, wherein

the washing step comprises at least a first washing step and a second washing step;

the polyvinyl alcohol particles subjected to the first washing step are obtained by saponifying a polyvinyl ester using an alkali catalyst;

in the first washing step, the polyvinyl alcohol particles are mixed with a first washing liquid containing 50% by mass or more of methanol and 0.1 to

10% by mass of an acid to form a slurry and thus to reduce a content of the alkali catalyst residue in the polyvinyl alcohol particles;

the slurry after the first washing step is continuously fed to the second washing step; and

in the second washing step, the slurry is brought into contact with a second washing liquid containing 50% by mass or more of methanol and having an acid concentration of less than 0.1% by mass to reduce an acid content in the polyvinyl alcohol particles.

[0009]

[2] The method for producing a polyvinyl alcohol resin according to [1], wherein the second washing step is performed in a tower type vessel; and the slurry after the first washing step is continuously introduced into an upper part of the tower type vessel while the second washing liquid is continuously introduced into a lower part of the tower type vessel.

[3] The method for producing a polyvinyl alcohol resin according to [1] or [2], wherein the washing liquid after the second washing step is recovered for reuse as the first washing liquid.

[4] The method for producing a polyvinyl alcohol resin according to any one of [1] to [3], wherein the acid contained in the first washing liquid is a carboxylic acid.

[5] The method for producing a polyvinyl alcohol resin according to [4], wherein the carboxylic acid is acetic acid.

[6] The method for producing a polyvinyl alcohol resin according to any one of [1] to [5], wherein the first washing liquid further contains methyl acetate and a mass ratio of methyl acetate to methanol is 0.05 to 0.8.

[7] The method for producing a polyvinyl alcohol resin according to any one of [1] to [6], wherein the first washing liquid further contains water and a mass ratio of water to methanol is 0.005 to 0.2.

[8] The method for producing a polyvinyl alcohol resin according to any one of [1] to [7], wherein an average sphere-equivalent diameter of the polyvinyl alcohol particles is 1 to 10 mm.

[9] The method for producing a polyvinyl alcohol resin according to any one of [1] to [8], wherein the alkali catalyst is sodium hydroxide.

[10] The method for producing a polyvinyl alcohol resin according to any one of [1] to [9], further comprising a deliquoring step and a drying step after the washing step.

[11] The method for producing a polyvinyl alcohol resin according to any one of [1] to [10], wherein a content of sodium acetate in the polyvinyl alcohol resin obtained is 500 ppm or less.

Advantageous Effects of Invention

[0010]

In accordance with a method for producing a polyvinyl alcohol resin of the present invention, it is possible to continuously and efficiently remove an alkali catalyst residue contained in the saponified PVA particles, and to, in the second washing step, remove an acid incorporated into the PVA particles in the first washing step.

Brief Description of Drawings

[0011]

[FIG. 1] FIG. 1 schematically shows the apparatus used for producing dried PVA chips in Examples.

Description of Embodiments

[0012]

A production method of the present invention comprises a washing step of continuously washing polyvinyl alcohol particles containing an alkali catalyst residue, and furthermore, the washing step comprises at least a first washing step and a second washing step. By these two washing steps, sodium acetate contained in the saponified PVA particles can be continuously and efficiently removed. There will be specifically described a production method of the present invention.

[0013]

[Polymerization step]

A polyvinyl ester is produced by polymerization of a vinyl ester using a polymerization initiator. Examples of the vinyl ester include vinyl acetate, vinyl formate, vinyl propionate, vinyl caprylate, and vinyl versatate; among these vinyl acetate is preferable from an industrial standpoint. These can be used alone or in combination of two or more.

[0014]

During polymerization, other monomers besides vinyl esters can be copolymerized without departing from the objective of the present invention. Examples of such other monomers include α -olefins such as ethylene, propylene, n-butene, and isobutylene; (meth)acrylic acid and salts thereof; (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, n-

propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate, and octadecyl (meth)acrylate; (meth)acrylamide-based compounds such as (meth)acrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, diacetone(meth)acrylamide, (meth)acrylamidopropanesulfonic acid and salts thereof, (meth)acrylamidopropyldimethylamine and its salts or quaternary salts, and N-methylol(meth)acrylamide and its derivatives; 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; nitriles such as acrylonitrile and methacrylonitrile; vinyl halides such as vinyl chloride and vinyl fluoride; vinylidene halides such as vinylidene chloride and vinylidene fluoride; allyl compounds such as allyl acetate and allyl chloride; unsaturated dicarboxylic acids such as maleic acid, itaconic acid, and fumaric acid, and their salts or esters; vinylsilyl compounds such as vinyltrimethoxysilane; and isopropenyl acetate. These can be used alone or in combination of two or more. The amount of other monomers involved in copolymerization is usually 10 mol% or less, or 5 mol% or less. Herein, in the present specification, "(meth)acryl" is a collective term for methacryl and acryl.

[0015]

The polymerization initiator used in the polymerization can be, but not limited to, known polymerization initiators, such as azo polymerization initiators, peroxide polymerization initiators, and redox polymerization initiators, which can be selected depending on the polymerization method. Examples of azo polymerization initiators include 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-

azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMV), and 2,2'-azobis(2,4-dimethylvaleronitrile). Examples of peroxide polymerization initiators include percarbonate compounds such as diisopropyl peroxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, and diethoxyethyl peroxydicarbonate; perester compounds such as t-butyl peroxyneodecanate and α -cumyl peroxyneodecanate; acetylcyclohexylsulfonyl peroxide; and 2,4,4-trimethylpentyl-2-peroxyphenoxyacetate. Potassium persulfate, ammonium persulfate, hydrogen peroxide, or the like can be combined with the above polymerization initiator to form a polymerization initiator. These polymerization initiators can be used alone or in combination of two or more. In the light of increasing a polymerization velocity and achieving a higher polymerization ratio in a short time, a polymerization initiator is preferably an azo polymerization initiator or peroxide polymerization initiator, whose 10-hour half-life temperature is 66°C or lower. Examples of an azo polymerization initiator or peroxide polymerization initiator whose 10-hour half-life temperature is 66°C or lower include AIBN, AMV, 2,2'-azobis(2,4-dimethylvaleronitrile), and di-2-ethylhexyl peroxydicarbonate. The amount of the polymerization initiator is, but not limited to, usually preferably 0.1 to 20 parts by mass, more preferably 0.2 to 10 parts by mass, further preferably 0.3 to 5.0 parts by mass based on 100 parts by mass of the vinyl ester. The polymerization initiator can be added all at once at the initiation of the polymerization, or can be added at the initiation of the polymerization and then further added during polymerization.

[0016]

The polymerization type can be any of batch polymerization, semi-batch polymerization, continuous polymerization, or semi-continuous polymerization.

The polymerization method can be adopted from any of known polymerization methods, such as bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization. Among these, bulk polymerization, in which polymerization is carried out in the absence of a solvent, and solution polymerization, in which polymerization is carried out in the presence of a solvent, are preferred. Examples of solvents used in the solution polymerization include alcoholic solvents such as methanol, ethanol, and n-propanol, with methanol being particularly preferred. The solvents can be used alone or in combination of two or more. In the light of increasing a polymerization efficiency, the amount of the solvent is, but not limited to, usually preferably 10 to 150 parts by mass, more preferably 20 to 120 parts by mass, further preferably 30 to 90 parts by mass, particularly preferably 30 to 80 parts by mass, based on 100 parts by mass of the vinyl ester.

[0017]

A polymerization temperature is, but not limited to, usually preferably 0°C or higher and 200°C or lower, more preferably 30°C or higher and 140°C or lower, further preferably 30°C or higher and 100°C or lower, particularly preferably 30°C or higher and 90°C or lower. If the polymerization temperature is lower than 0°C, a sufficient polymerization velocity tends not to be achieved. If the polymerization temperature is higher than 200°C, it tends to be difficult to obtain a target polymer. There are no particular restrictions to a pressure during polymerization, and can be increased as needed, or can be an atmospheric pressure.

[0018]

A polymerization rate of the vinyl ester is, but not limited to, preferably 10

to 90%. If the polymerization rate is less than 10%, productivity of PVA may decrease. The polymerization rate is more preferably 20% or more, further preferably 50% or more. Meanwhile, if the polymerization rate exceeds 90%, viscosity of the resulting polyvinyl ester may become too high, which may decrease productivity of PVA and may also deteriorate the hue of the resulting PVA. The polymerization rate is more preferably 85% or less, further preferably 80% or less.

[0019]

[Saponification step]

The polyvinyl ester thus obtained is saponified using an alkali catalyst. For example, it can be saponified by alcoholysis or hydrolysis using an alkali catalyst such as sodium hydroxide, potassium hydroxide, or sodium methoxide. Among these, the alkali catalyst is preferably sodium hydroxide. When sodium hydroxide is added to a reaction solution as a saponification catalyst, some or all of it is converted to sodium acetate, remaining in the PVA particles as a catalyst residue. Examples of solvents used in the saponification reaction include alcohols such as methanol and ethanol; esters such as methyl acetate and ethyl acetate; ketones such as acetone and methyl ethyl ketone; and aromatic hydrocarbons such as benzene and toluene. These solvents can be used alone or in combination of two or more. Among these, preferred is a method in which saponification is carried out using methanol or a methanol/methyl acetate mixed solution as the solvent and sodium hydroxide as the catalyst. The amount of the alkali catalyst, expressed as a molar ratio to the vinyl ester units in the polyvinyl ester, is preferably 0.001 to 0.5, more preferably 0.002 to 0.2, further preferably 0.003 to 0.1. There are no particular

restrictions to a saponification temperature, which is preferably within the range of 20 to 70°C. As the saponification reaction proceeds, a gel-like product precipitates, which is then pulverized. Thus, there is obtained polyvinyl alcohol (PVA) particles containing sodium acetate as the catalyst residue and the solvent. The PVA particles thus obtained can be introduced into the first washing step.

[0020]

Alternatively, the saponification reaction can be further carried out while contacting the PVA particles with methanol or a methanol/methyl acetate mixed solution at 30 to 70°C. In this case, a slurry in which the PVA particles are dispersed in the mixed solvent is obtained, and thus the filtrate is removed from the slurry using a solid-liquid separator to obtain the PVA particles. The solid-liquid separator can be any apparatus capable of separating the PVA particles from the solvent, and a continuous sieving apparatus such as an ultrascreen is preferably used. By contacting the PVA particles with the solvent, a portion of the alkali catalyst residue contained in the PVA particles is removed, but the remainder remains in the PVA particles.

[0021]

[PVA particles]

The PVA particles obtained through the saponification step contain the solvent consisting of methanol or a methanol/methyl acetate mixed solution and the alkali catalyst residue. The content of the solvent in the PVA particles is usually 20 to 400 parts by mass, preferably 30 to 300 parts by mass, and more preferably 50 to 200 parts by mass, based on 100 parts by mass of PVA. The content of methyl acetate in the mixed solvent is usually 50 parts by mass or

less, preferably 20 parts by mass or less, and further preferably 10 parts by mass or less, based on 100 parts by mass of methanol. The content of the alkali catalyst residue in the PVA particles is usually 5000 ppm or more based on 100 parts by mass of PVA. There are no particular restrictions to the shape of the PVA particles, and it can be chips, pellets, granules or the like. Its shape can be rectangular, spherical, cylindrical, or irregular. An average sphere-equivalent diameter of the PVA particles is preferably 1 to 10 mm. If the average sphere-equivalent diameter is too small, it becomes difficult to continuously separate the particles from the liquid, which may result in a decrease in productivity. The average sphere-equivalent diameter is preferably 2 mm or more, more preferably 3 mm or more. Meanwhile, if the average sphere-equivalent diameter is too large, a washing rate decreases. The average sphere-equivalent diameter is preferably 7 mm or less, more preferably 5 mm or less. Here, a sphere-equivalent diameter refers to the diameter of a sphere having the same volume as the PVA particles. An average value is calculated, excluding a fine powder with a sphere-equivalent diameter of less than 0.5 mm.

[0022]

[First washing step]

In the production method of the present invention, the PVA particles containing a large amount of the alkali catalyst residue obtained as described above are washed in two washing steps: a first washing step and a second washing step. In the first washing step, the PVA particles are mixed with a first washing liquid containing 50% by mass or more of methanol and 0.1 to 10% by mass of an acid to form a slurry, thereby reducing a content of an alkali catalyst

residue in the PVA particles. Furthermore, the alkali catalyst residue is extracted and removed from the PVA particles that come into contact with the washing liquid by the acid contained in the first washing liquid, thereby terminating the saponification reaction.

[0023]

The first washing liquid contains 50% by mass or more of methanol and 0.1 to 10% by mass of an acid. By containing 0.1% by mass or more of an acid, the washing liquid can extract the alkali catalyst residue in the PVA particles, effectively reducing a content of the alkali catalyst residue in the PVA particles. There are no particular restrictions to the type of the acid, and it has preferably pKa at 25 °C of 3 to 5.5, more preferably 4 to 5. The type of the acid is preferably a carboxylic acid, particularly preferably acetic acid. A content of the acid in the first washing liquid is preferably 0.16% by mass or more. Meanwhile, if the acid content is too high, the PVA particles contain a large amount of the acid, making it difficult to remove the acid in the second washing step. The content of the acid in the first washing liquid is preferably 5% by mass or less, more preferably 2% by mass or less, further preferably 1% by mass or less. Here, the acid contained in the first washing liquid can be the same as or different from the acid contained in the second washing liquid described below.

[0024]

It is preferable that the first washing liquid further contains methyl acetate. Methyl acetate is a by-product of alcoholysis during the saponification reaction and is contained in the reaction solvent after saponification. As the solvent is repeatedly recovered and reused, a ratio of methyl acetate to methanol

increases. It is, therefore, preferable to use a washing liquid containing methyl acetate at a predetermined ratio to methanol in the light of recyclability and operation costs. A mass ratio of methyl acetate to methanol (methyl acetate/methanol) in the first washing liquid is preferably 0.05 to 0.8. The mass ratio is more preferably 0.1 to 0.5, and further preferably 0.15 to 0.4.

[0025]

It is also preferable that the first washing liquid further contains water. By containing water, the first washing liquid can easily extract sodium acetate from the PVA pellets. If the water content is too low, efficiency of removing catalyst residues may decrease. Meanwhile, if the water content is too high, extra energy may be required to separate and remove water from the recovered solvent. A mass ratio of water to methanol (water/methanol) in the first washing liquid is preferably 0.005 to 0.2. The mass ratio is more preferably 0.008 to 0.1, and further preferably 0.01 to 0.05.

[0026]

There are no particular restrictions to the washing apparatus for the first washing step. It is sufficient that the PVA particles containing a large amount of the alkali catalyst residue and the first washing liquid can be continuously fed and the washed PVA particles can be continuously discharged. The washing apparatus is preferably a tower type vessel because it is simple, requires little energy, and enables uniform washing. In this case, it is preferred that the PVA particles containing a large amount of the alkali catalyst residue are continuously introduced into the upper part of the tower type vessel while the first washing liquid is continuously introduced into the lower part of the tower type vessel. This allows countercurrent contact between the PVA particles

gradually descending by gravity and the ascending first washing liquid, thereby efficiently removing methyl acetate from the PVA particles. The first washing liquid introduced into the lower part of the tower type vessel can be introduced into the tower type vessel from only one pipe or from multiple pipes. When the first washing liquid is introduced into the tower type vessel from multiple pipes, the composition of the first washing liquid is that of the combined first washing liquid. The PVA particles descending within the tower type vessel are continuously taken out as a slurry together with the washing liquid from the lower part of the tower type vessel and are continuously fed to the second washing step. The washing liquid containing sodium acetate after washing is discharged from the upper part of the tower type vessel to the outside of the system, recovered, and purified as necessary for reuse.

[0027]

[Second washing step]

The slurry after the first washing step is continuously fed to the second washing step, in which the PVA particles contained in the slurry are brought into contact with a second washing liquid containing 50% by mass or more of methanol and having an acid concentration of less than 0.1% by mass, thereby reducing an acid content in the PVA particles.

[0028]

The second washing liquid contains 50% by mass or more of methanol and has an acid concentration of less than 0.1% by mass. With an acid concentration of less than 0.1% by mass, the acid in the PVA particles can be extracted into the washing liquid, thereby effectively reducing the acid content in the PVA particles. The acid concentration of the second washing liquid is

preferably 0.05% by mass or less. There are no particular restrictions to the lower limit of the acid concentration of the second washing liquid, and it can be 0.0001% by mass. In one embodiment, it is more preferable that an acid concentration of the second washing liquid is 0% by mass, i.e., the second washing liquid is substantially acid-free. The amount of methanol contained in the second washing liquid is preferably 70% by mass or more, more preferably 90% by mass or more. The second washing liquid can contain methyl acetate or water, but the total content of these is 50% by mass or less, preferably 30% by mass or less, and further preferably 10% by mass or less.

[0029]

There are no particular restrictions to a washing apparatus for the second washing step. It is sufficient that it can continuously feed a slurry containing PVA particles containing a relatively large amount of acid and a washing liquid, and the second washing liquid, and continuously discharge the washed PVA particles. As with the first washing step, the washing apparatus is preferably a tower type vessel because it is simple, requires little energy, and enables uniform washing. In this case, it is preferred that the slurry containing PVA particles containing an acid and a washing liquid is continuously introduced into the upper part of the tower type vessel, while the second washing liquid is continuously introduced into the lower part of the tower type vessel. This allows countercurrent contact between the PVA particles gradually descending by gravity and the ascending second washing liquid, thereby efficiently removing the acid from the PVA particles. The second washing liquid introduced into the lower part of the tower type vessel can be introduced into the tower type vessel from only one pipe or from multiple pipes. When the

second washing liquid is introduced into the tower type vessel from multiple pipes, the composition of the second washing liquid is that of the combined second washing liquid. It is also preferable to use the washing liquid recovered in the solid-liquid separator after the second washing step as part of the second washing liquid. In this case, it is also preferable to add methanol to the recovered washing liquid to form the second washing liquid. The PVA particles descending within the tower type vessel are continuously taken out as a slurry together with the washing liquid from the lower part of the tower type vessel and are continuously fed to the deliquoring step. Furthermore, the washing liquid after the second washing step is taken out from the upper part of the tower type vessel. It is also preferable to recover the washing liquid after the second washing step and reuse it as the first washing liquid.

[0030]

[Deliquoring step]

It is preferable to comprise a deliquoring step after the second washing step, in which the washing liquid is mechanically removed from the PVA particles. When the second washing step is performed in the tower type vessel, the slurry taken out from the lower part of the tower type vessel is continuously fed to a solid-liquid separator, where it is separated into PVA particles and a washing liquid. There are no particular restrictions to the solid-liquid separator as long as it can separate the PVA particles from the washing liquid. It is preferable to use a centrifugal deliquoring machine as the solid-liquid separator, because it can effectively remove the washing liquid adhering to the surface of the PVA particle and reduce the energy required in the subsequent drying step. It is preferable to recover the washing liquid

separated in the deliquoring step and use it as part of the second washing liquid.

[0031]

[Drying step]

After the deliquoring step, the PVA particles are dried in a drying step. There are no particular restrictions to the drying apparatus, and hot air drying is preferred. A drying temperature is preferably 40 to 130°C, more preferably 80 to 120°C. A drying time is preferably 1 to 20 hours, more preferably 1.5 to 6 hours. The drying step usually reduces a solvent content in the PVA particles to 8% by mass or less.

[0032]

The dried PVA particles thus obtained have a low sodium acetate content and a low acid content. A sodium acetate content in the dried PVA particles is preferably 500 ppm or less, more preferably 100 ppm or less, and further preferably 50 ppm or less. Meanwhile, since thorough washing increases washing costs, the dried PVA particles usually contain 1 ppm or more of sodium acetate. An acid content in the dried PVA particles is preferably 1000 ppm or less, more preferably 700 ppm or less, and further preferably 500 ppm or less. Meanwhile, since thorough washing increases washing costs, the dried PVA particles usually contain 10 ppm or more of an acid.

[0033]

A saponification degree of the PVA contained in the dried PVA particles is usually, but not limited to, 70 mol% or more, preferably 80 mol% or more, more preferably 90 mol% or more, and further preferably 95 mol% or more. Meanwhile, the saponification degree is usually 99.9 mol% or less. A saponification degree is determined in accordance with JIS K 6726 (1994).

Here, a saponification degree of the PVA after the saponification step is substantially the same as a saponification degree of the PVA contained in the dried PVA particles.

[0034]

A viscosity-average polymerization degree of the PVA contained in the dried PVA particles is usually, but not limited to, 100 to 5000, preferably 200 to 4000, and more preferably 300 to 3000. A viscosity-average polymerization degree is determined in accordance with JIS K 6726 (1994). Specifically, when the saponification degree is less than 99.5 mol%, a viscosity-average polymerization degree (P) is calculated by the following formula using a limiting viscosity $[\eta]$ (liters/g) of polyvinyl alcohol saponified to a saponification degree of 99.5 mol% or more, as measured in water at 30°C. Here, a saponification degree of PVA after the saponification step and a viscosity-average polymerization degree of PVA contained in the dried PVA particles are substantially the same.

$$P = ([\eta] \times 10000/8.29)^{(1/0.62)}$$

[0035]

The PVA particles thus obtained can be used in a variety of applications. The PVA particles can be dissolved in water to prepare an aqueous solution, which can be used in a wide range of applications such as films, fibers, coating agents, dispersants, emulsifiers, and adhesives. Instead of preparing an aqueous solution, the particles can also be melt-molded. In this case, it is preferable to add a plasticizer such as glycerin before melt-molding. The dried PVA particles of the present invention have a low sodium acetate content, resulting in suppressing discoloration and melt viscosity variation during heating

to melt. Furthermore, a low acid content can also prevent the acid from volatilizing and generating odor.

Examples

[0036]

[Example 1]

Dried polyvinyl alcohol (PVA) chips 18 were produced using the apparatus shown in Figure 1. First, to a mixture of 48 parts by mass of polyvinyl acetate and 52 parts by mass of methanol was added 2.0 parts by mass of a solution of sodium hydroxide in methanol (concentration: 120 g/L), and a saponification reaction was allowed to proceed at 36°C. After 15 minutes, the resulting solid was pulverized to obtain polyvinyl alcohol (PVA) chips containing methanol.

[0037]

The PVA chips obtained by pulverization were introduced into a tower type reactor (unshown) containing methanol, and the saponification reaction was further carried out at 64°C for 1.5 hours. Subsequently, a slurry 1 containing the PVA chips and methanol was filtered through an ultrascreen 2 to remove a filtrate 3, to obtain PVA chips 4 containing an alkali catalyst residue. The resulting PVA chips 4 were of a rectangular shape with an average dimension of 5.0 to 6.0 mm in length and width, a thickness of approximately 1.0 mm, and an average spherical-equivalent diameter of 3.6 to 4.1 mm. The PVA had a saponification degree of 99 mol% and a viscosity-average polymerization degree of 370.

[0038]

The PVA chips 4 thus obtained were continuously introduced into a first washing tower 5 for washing (a first washing step). The first washing tower 5 is a tower type washing apparatus equipped with a flow path for introducing a washing liquid 6 containing water, acetic acid, methanol and methyl acetate, and a flow path for introducing a washing liquid 8 recovered from a second washing tower 7 as described later. A composition of the washing liquid (a first washing liquid) fed to the first washing tower 5 can be adjusted by regulating the flow rates of the respective washing liquids. In this example, continuous washing was performed while adjusting the composition of the first washing liquid to be in the range of 0.23 parts by mass of acetic acid, 75 to 80 parts by mass of methanol, 18 to 23 parts by mass of methyl acetate, and 1.5 to 2.0 parts by mass of water. Here, a pKa of acetic acid at 25°C is 4.56. Furthermore, the first washing tower 5 is equipped with a mechanism for discharging the washing liquid to an outside of the system, and the used washing liquid containing the alkali catalyst residue and the like is discharged to the outside of the system 9, purified in a solvent recovery step, and then reused. The PVA chips 4 containing the alkali catalyst residue were continuously introduced into the upper part of the first washing tower 5 and descended within the tower while contacting the washing liquid, and a slurry 10 containing the PVA chips and the washing liquid was taken out from the lower part of the tower. In the first washing tower 5, the alkali catalyst residue contained in the PVA chips that had come into contact with the washing liquid was extracted and removed by acetic acid contained in the washing liquid, thereby terminating the saponification reaction.

[0039]

Subsequently, the slurry 10 of the PVA chips and the washing liquid taken out from the first washing tower 5 was continuously introduced into a second washing tower 7 for washing (a second washing step). The second washing tower 7 is a tower type washing apparatus, and is equipped at its upper part with an inlet for introducing the PVA slurry 10 fed from the first washing tower 5 and an outlet for feeding the washing liquid 8 in the second washing tower 7 to the first washing tower 5. Furthermore, the second washing tower 7 is further equipped at its lower part with an outlet for feeding a slurry 11 containing the PVA chips that have come into contact with the washing liquid in the second washing tower 7 to a solid-liquid separator 12, and with an inlet for introducing methanol 13 and a washing liquid 14 recovered from the solid-liquid separator 12 into the second washing tower 7.

[0040]

The washing liquid (a second washing liquid 15) introduced from the lower part of the second washing tower 7 was a mixed liquid of the washing liquid 14 recovered from the solid-liquid separator 12 and methanol 13, and contains 90% by mass or more of methanol, and small amounts of methyl acetate and water, and less than 0.1% by mass of an acid. The washing liquid 15 flowed from the lower part to the upper part of the second washing tower 7, was taken out from the outlet at the upper part of the second washing tower 7 together with the washing liquid in the slurry introduced from the upper part, and was sent to the first washing tower 5 through a flow path and reused as the washing liquid 8. The PVA chips contained in the slurry 10 continuously introduced from the upper part of the second washing tower 7 descended to the lower part within the second washing tower 7 while coming into contact with the

washing liquid containing methanol as a main component. In terms of the washing liquid within the second washing tower 7, as the lower its position is, the higher a methanol concentration is and the lower an acetic acid concentration is. Thus, the PVA chips passing through the second washing tower 7 passed through a solution containing methanol as a main component. Therefore, the acetic acid contained in the PVA chips at the end of the first washing step was washed away in the second washing step.

[0041]

The slurry 11 taken out from the lower part of the second washing tower 7 was continuously sent to the solid-liquid separator 12 and separated into PVA chips 16 and the washing liquid 14 by a centrifugal deliquoring machine. The resulting PVA chips 16 were dried at 100°C in a dryer 17 to obtain dried PVA chips 18. A solvent content of the dried PVA chips 18 was 5% by mass or less. The washing liquid 14 recovered in the solid-liquid separator 12 was sent to the second washing tower 7 and reused as the washing liquid. The dried PVA chips 18 were sampled approximately every four hours and reduced to obtain a representative subsample. Then, a sodium acetate content in the chips was measured using an atomic absorption spectrophotometer and found to be 5 to 48 ppm. An acetic acid content in the dried PVA chips 18 was measured using gas chromatography and found to be 50 to 400 ppm. These results are summarized in Table 1.

[0042]

[Examples 2 to 5]

PVA chips were washed, deliquored and dried to obtain dried chips, which were analyzed, as described in Example 1, except that a proportion of

methanol, methyl acetate, water and acetic acid contained in the first washing liquid was changed as shown in Table 1. The results are summarized in Table 1.

[0043]

[Comparative Examples 1 and 2]

PVA chips were washed, deliquored and dried to obtain dried chips, which were analyzed, as described in Example 1, except that the first washing liquid was free from acetic acid and that a proportion of methanol, methyl acetate and water contained in the first washing liquid was changed as shown in Table 1. The results are summarized in Table 1.

[0044]

[Comparative Example 3]

Chips after the first washing step as described in Example 4 were collected and deliquored and dried to obtain dried PVA chips as described in Example 1, which were then analyzed as described in Example 1. The results are summarized in Table 1.

[0045]

[Table 1]

	First washing liquid				Second washing step	Dried PVA chips	
	Methanol	Methyl acetate	Water	Acetic acid		Sodium acetate	Acetic acid
	(parts by mass)	(parts by mass)	(parts by mass)	(parts by mass)		(ppm)	(ppm)
Example 1	75-80	18-23	1.5-2.0	0.23	Yes	5-48	50-400
Example 2	75-80	18-23	1.5-2.0	0.2	Yes	9-21	200-400
Example 3	78-83	15-20	1.0-1.5	0.18	Yes	3-35	200-400
Example 4	85-90	5-10	1.3-1.8	0.15	Yes	21-36	50-200
Example 5	85-90	8-13	1.3-1.8	0.14	Yes	34-48	50-200
Comparative Example 1	78-83	17-22	0.1-0.2	0	Yes	6400-10000	0
Comparative Example 2	80-85	15-20	1.5-2.0	0	Yes	7000-9000	0
Comparative Example 3	85-90	5-10	1.3-1.8	0.15	No	35	1190

Reference Signs List

[0046]

- 1, 10, 11 slurry
- 2 ultrascreens
- 3 filtrate
- 4, 16 PVA chips
- 5 first washing tower
- 6, 8, 14, 15 washing liquid
- 7 second washing tower
- 9 outside of the system
- 12 solid-liquid separator
- 13 methanol
- 17 dryer
- 18 dried PVA chips

CLAIMS

[Claim 1] A method for producing a polyvinyl alcohol resin comprising a washing step of continuously washing polyvinyl alcohol particles, wherein the washing step comprises at least a first washing step and a second washing step;

the polyvinyl alcohol particles subjected to the first washing step are obtained by saponifying a polyvinyl ester using an alkali catalyst;

in the first washing step, the polyvinyl alcohol particles are mixed with a first washing liquid containing 50% by mass or more of methanol and 0.1 to 10% by mass of an acid to form a slurry and thus to reduce a content of the alkali catalyst residue in the polyvinyl alcohol particles;

the slurry after the first washing step is continuously fed to the second washing step; and

in the second washing step, the slurry is brought into contact with a second washing liquid containing 50% by mass or more of methanol and having an acid concentration of less than 0.1% by mass to reduce an acid content in the polyvinyl alcohol particles.

[Claim 2] The method for producing a polyvinyl alcohol resin according to Claim 1, wherein the second washing step is performed in a tower type vessel; and the slurry after the first washing step is continuously introduced into an upper part of the tower type vessel while the second washing liquid is continuously introduced into a lower part of the tower type vessel.

[Claim 3] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein the washing liquid after the second washing step is

recovered for reuse as the first washing liquid.

[Claim 4] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein the acid contained in the first washing liquid is a carboxylic acid.

[Claim 5] The method for producing a polyvinyl alcohol resin according to Claim 4, wherein the carboxylic acid is acetic acid.

[Claim 6] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein the first washing liquid further contains methyl acetate and a mass ratio of methyl acetate to methanol is 0.05 to 0.8.

[Claim 7] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein the first washing liquid further contains water and a mass ratio of water to methanol is 0.005 to 0.2.

[Claim 8] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein an average sphere-equivalent diameter of the polyvinyl alcohol particles is 1 to 10 mm.

[Claim 9] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein the alkali catalyst is sodium hydroxide.

[Claim 10] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, further comprising a deliquoring step and a drying step after the washing step.

[Claim 11] The method for producing a polyvinyl alcohol resin according to Claim 1 or 2, wherein a content of sodium acetate in the polyvinyl alcohol resin obtained is 500 ppm or less.