DESCRIPTION
RESIN POWDER

[Technical Field]
[0001]
The present invention relates to a resin powder.
[Background Art]
[0002]
A vinyl alcohol polymer (hereinafter, may be also referred to as “PVA”) is a synthetic resin obtained by saponifying a polyvinyl ester (hereinafter, may be also referred to as “PVAc”). The PVA possesses water solubility and is used in applications such as raw materials for synthetic fibers, raw materials for films, emulsifying and dispersing agents, and adhesives.
[0003]
The PVA is typically obtained by radical polymerization of vinyl acetate in a methanol solvent to give a methanol solution of a vinyl acetate polymer, followed by saponification by adding an alkali catalyst. A resin powder of the PVA is obtained by subjecting, to a treatment such as drying, a PVA composition containing a solvent or the like, obtained through saponification (see, Patent Document 1, etc.)
[PRIOR ART DOCUMENTS]
[Patent Documents]
[0004]
Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2013-28712
[SUMMARY OF THE INVENTION]
[Problems to be Solved by the Invention]
[0005]
Conventional resin powders comprising PVA are generally disadvantageous due to being inferior in drying efficiency. In order to reduce production costs by shortening a drying process time and saving energy during the production, etc., of resin powders, improvement in the drying efficiency of resin powders is desired. Furthermore, there are cases in which a PVA resin powder obtained through drying is subjected to a treatment using a liquid (for example, the synthesis of modified PVA, etc., i.e., “post-modification”, as generally referred to) and then re-dried, or cases in which a PVA resin powder that has absorbed moisture is re-dried as necessary. Even when performing such re-drying, the drying efficiency of the PVA resin powder being high is desired.
[0006]
An object of the present invention is to provide a resin powder which comprises a vinyl alcohol polymer and which exhibits improved drying efficiency.
[0007]
The object described above can be achieved by:
(1) A resin powder: comprising a vinyl alcohol polymer; having an average particle diameter of 100 to 2,000 μm; and the number of particles having bubbles of 1 μm or larger being 10 or more, among 100 particles arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm in the resin powder;
(2) The resin powder according to (1), wherein the vinyl alcohol polymer has a viscosity-average degree of polymerization being 200 to 5,000, and a degree of saponification being 35 to 99.99 mol%;
(3) The resin powder according to (1) or (2), wherein a content of the particles having a particle diameter of 106 to 1,000 μm is 50% by mass or more;

(4) The resin powder according to any one of (1) to (3), wherein a bulk density is 0.4 to 0.7 g/mL;
(5) The resin powder according to any one of (1) to (4), wherein a product of the average particle diameter (μm) and a bulk density (g/mL) is 700 μm·g/mL or less;
(6) The resin powder according to any one of (1) to (5), wherein an organic volatile content is 3.0% by mass or less.

[Effects of the Invention]

[0008]

According to the present invention, a resin powder can be provided, which comprises a vinyl alcohol polymer and which exhibits improved drying efficiency.

[Description of Embodiments]

[0009]

As referred to herein, a numerical range described by using "to" means a range including the numerical values described before and after "to" as the lower limit value and the upper limit value, respectively.

[0010]

Resin Powder

A resin powder according to one embodiment of the present invention comprises a vinyl alcohol polymer (PVA: polyvinyl alcohol), has an average particle diameter of 100 to 2,000 μm, and the number of particles having bubbles of 1 μm or larger is 10 or more, among 100 particles arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm. Hereinafter, the "particles having bubbles of 1 μm or larger" may be also referred to as "bubble-containing particles". The "bubbles of 1 μm or larger" as referred to herein mean bubbles having a bubble size of 1 μm or more, as described later. The bubble size may be also referred to as a diameter of the bubble. Moreover, "the number of particles having bubbles of 1 μm or larger (bubble-containing particle), among 100 particles arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm" may be also referred to as "bubble-containing particle number". The resin powder is an assembly of a plurality of particles (PVA particles), and these plurality of particles (PVA particles) comprise a plurality of bubble-containing particles. The resin powder may be constituted only from these plurality of particles (PVA particles).

[0011]

The resin powder according to one embodiment of the present invention exhibits improved drying efficiency as compared with conventional resin powders. Although the reason for this feature is not necessarily clear, it is presumed that the resin powder includes a sufficient amount of bubble-containing particles, thereby resulting in an increase in the surface area, and/or the like. Furthermore, in cases of particles not having bubbles, the center of each particle is less likely to be sufficiently heated during drying by heating, making it difficult for volatile components in the center of the particles to volatilize. To the contrary, in cases of the bubble-containing particles, suppression of such a phenomenon due to the presence of the bubbles is also presumed to be the reason for the improved drying efficiency.

[0012]

It is to be noted that the ease of drying a resin powder which comprises PVA is significantly influenced by physical properties of the PVA per se (degree of saponification, degree of polymerization, presence or absence of modified species, and the amount of modification, etc.), the particle diameter of the resin powder, and the like. Therefore, as referred to herein, "improved drying efficiency" means a case in which the drying time period is sufficiently shortened, as compared to a resin powder with substantially the same particle diameter provided by using the same type of PVA. The "same type of PVA" as

referred to herein means PVA having the degree of saponification, the degree of polymerization, the presence or absence of modified species, and the amount of modification, being the same. In addition, the "modified species" as referred to herein means other monomer aside from vinyl esters. The "amount of modification" as referred to herein means the content of monomer units derived from the other monomers, with respect to total monomer units in the PVA.

[0013]

Moreover, the resin powder according to one embodiment of the present invention has a low content of organic volatiles, and a high rate of dissolution in water. The reason for this feature is also presumed to be sufficiently increased surface area, and the like, as a result of the resin powder comprising a sufficient amount of bubble-containing particles. Furthermore, it is also believed that the resin powder is also favorable in the reactivity in performing post-modification, etc., since the surface area is sufficiently increased.

[0014]

The PVA is, typically, a main component of the resin powder according to one embodiment of the present invention. It is to be noted that main component as referred to herein means a component, the content of which is the highest on mass basis. The lower limit of the content of the PVA in nonvolatiles of the resin powder is preferably 50% by mass, more preferably 70% by mass, and still more preferably 90% by mass, or may be even more preferably 99% by mass. The upper limit of the content of the PVA in nonvolatiles of the resin powder may be 100% by mass. The lower limit of the content of the PVA in the resin powder is preferably 60% by mass, more preferably 70% by mass, and still more preferably 90% by mass, or may be even more preferably 99% by mass. The upper limit of the content of the PVA in the resin powder may be 100% by mass, or may be 99.9% by mass.

[0015]

The PVA is a polymer having a vinyl alcohol unit as a monomer unit. The PVA is typically obtained by saponifying a polyvinyl ester. The lower limit of the content of the vinyl alcohol unit with respect to total monomer units in the PVA is preferably 35 mol%, more preferably 50 mol%, and still more preferably 70 mol%, or may be 80 mol%, 85 mol%, 90 mol%, or 95 mol%. When the content of the vinyl alcohol unit in the PVA is high, a time period needed for drying generally tends to be prolonged. Therefore, in the case in which the present invention is applied to a resin powder comprising a PVA having a high content of the vinyl alcohol unit, the advantage of improving the drying efficiency is particularly likely to be remarkably obtained. On the other hand, the upper limit of the content of the vinyl alcohol unit may be 100 mol%, preferably 99.99 mol%, and more preferably 99 mol%, or may be 98 mol%, 95 mol%, or 90 mol%. In the case in which the content of the vinyl alcohol unit in the PVA is equal to or less than the upper limit, contemplating shortening of the drying time period, and the like are enabled.

[0016]

The lower limit of the degree of saponification of the PVA is preferably 35 mol%, more preferably 50 mol%, and still more preferably 70 mol%, or may be 80 mol%, 85 mol%, 90 mol%, or 95 mol%. When the degree of saponification of the PVA is high, a time period needed for drying generally tends to be prolonged. Therefore, in the case in which the present invention is applied to a resin powder comprising a PVA having a high degree of saponification, the advantage of improving the drying efficiency is particularly likely to be remarkably obtained. On the other hand, the upper limit of the degree of saponification may be 100 mol%, preferably 99.99 mol%, and more preferably 99 mol%, or may be 98 mol%, 95 mol%, or 90 mol%. In the case in which the degree of saponification of the PVA is equal to or less than the upper limit described above,

contemplating shortening of the drying time period, and the like are enabled. The degree of saponification is a value measured by a method in accordance with JIS K6726: 1994.
[0017]

The PVA may also have an other monomer unit aside from the vinyl alcohol unit and the vinyl ester unit. Examples of the monomer (modified species) that gives the other monomer unit include: α-olefins such as ethylene, propylene, 1-butene, isobutene, and 1-hexene; acrylic acid and methacrylic acid; acrylic acid esters such as methyl acrylate, and ethyl acrylate; methacrylic acid esters such as methyl methacrylate and ethyl methacrylate; maleic acid and derivatives thereof such as maleic acid, and monomethyl maleate and dimethyl maleate; acrylamide derivatives such as N-methylacrylamide and N-ethylacrylamide; methacrylamide derivatives such as N-methylmethacrylamide and N-ethylmethacrylamide; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, and n-butyl vinyl ether; hydroxy group-containing vinyl ethers such as ethylene glycol vinyl ether, 1,3-propanediol vinyl ether, and 1,4-butanediol vinyl ether; allyl acetate; allyl ethers such as propyl allyl ether, butyl allyl ether, and hexyl allyl ether; monomers each having an oxyalkylene group; isopropenyl acetate; hydroxy group-containingα-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; monomers each having a silyl group such as vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyldimethylmethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, vinyldimethylethoxysilane, 3-(meth)acrylamidepropyltrimethoxysilane, and 3-(meth)acrylamidepropyltriethoxysilane; and the like. Of these, α-olefins, acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, maleic acid, and derivatives of maleic acid are preferred.
[0018]

The upper limit of the content (modification amount) of the other monomer unit with respect to total monomer units in the PVA may be preferably 20 mol%, and may be more preferably 10 mol%. The upper limit of the content of the other monomer unit may be 5 mol%, 3 mol%, 1 mol%, or 0.1 mol%. On the other hand, the lower limit of the content of the other monomer unit may be, for example, 0.1 mol%, or may be 1 mol%.
[0019]

The viscosity-average degree of polymerization of the PVA is not particularly limited, and the lower limit thereof is preferably 200, more 250, still more preferably 400, and particularly preferably 600, or may be 1,000, 1,500, or 2,000. When the viscosity-average degree of polymerization of the PVA is high, a time period needed for drying generally tends to be prolonged. Therefore, in the case in which the present invention is applied to a resin powder comprising a PVA having a high viscosity-average degree of polymerization, the advantage of improving the drying efficiency is particularly likely to be remarkably obtained. The upper limit of the viscosity-average degree of polymerization is preferably 5,000, more preferably 4,500, and still more preferably 3,500, or may be 3,000, 2,500, or 2,000. In the case in which the viscosity-average degree of polymerization of the PVA is equal to or less than the upper limit described above, contemplating shortening of the drying time period, and the like are enabled. It is to be noted that viscosity-average degree of polymerization is a value measured in accordance with JIS K6726: 1994. More specifically, after the PVA is resaponified such that a degree of saponification becomes 99.5 mol% or more and then purified, the viscosity-average degree of polymerization can be determined according to the following equation, from the limiting viscosity [η] (unit: liter/g) measured in water at 30 °C.

Viscosity-average degree of polymerization = $([\eta] \times 10{,}000/8.29)^{(1/0.62)}$
[0020]

The resin powder according to one embodiment of the present invention may comprise a component other than the PVA. Nonvolatiles other than the PVA which may be comprised in the resin powder are exemplified by resins other than the PVA, additives such as a surfactant and a plasticizer, each compound used in the production, and the like.

[0021]

The upper limit of the content of the organic volatiles in the resin powder according to one embodiment of the present invention may be, for example, 5.0% by mass or 4.0% by mass, and is preferably 3.0% by mass. When the content of organic volatiles is equal to or less than the upper limit described above, handleability, and the like can be improved. The lower limit of the content of the organic volatiles may be, for example, 0.1% by mass, or may be 0.5% by mass, 1.0% by mass, or 1.5% by mass.

[0022]

The upper limit of the content of the volatiles in the resin powder according to one embodiment of the present invention may be, for example, 5.0% by mass or 4.0% by mass, and is preferably 3.0% by mass. When the content of the volatiles is equal to or less than the upper limit described above, handleability, and the like can be improved. The lower limit of the content of the volatiles may be, for example, 0.1% by mass, or may be 0.5% by mass, 1.0% by mass, or 1.5% by mass.

[0023]

The content of each of the organic volatiles and volatiles in the resin powder according to one embodiment of the present invention can be measured in accordance with JIS K6726: 1994. It is to be noted that in the case in which the content of the volatiles measured in accordance with the standard described above in the resin powder is, for example, 3.0% by mass, it is clear that the content of organic volatiles is 3.0% or less by mass.

[0024]

The lower limit of the average particle diameter of the resin powder according to one embodiment of the present invention may be 100 μm, preferably 150 μm, more preferably 300 μm, and still more preferably 400 μm. When the average particle diameter is equal to or more than the lower limit, ease in preparing a solution such as an aqueous solution due to enhanced wettability of the resin powder, inhibition of scattering and adhesion to wall surfaces, etc., lowered risk of dust explosion, and the like enable the handleability to be improved. Furthermore, when the average particle diameter of the resin powder increases, a time period needed for drying generally tends to be prolonged. Therefore, in the case in which the resin powder having a comparatively large average particle diameter is applied to the present invention, the advantage of improving the drying efficiency is particularly likely to be remarkably obtained. On the other hand, the upper limit of the average particle diameter may be 2,000 μm, preferably 1,500 μm, more preferably 1,000 μm, and still more preferably 850 μm. When the average particle diameter is equal to or less than the upper limit described above, contemplating shortening of the drying time period, and the like are enabled. The average particle diameter of the resin powder is a value measured in accordance with the method described in JIS K7369: 2009.

[0025]

The resin powder according to one embodiment of the present invention comprises particles having a particle diameter of 106 to 1,000 μm. The lower limit of the number of bubble-containing particles (bubble-containing particle number), among 100 particles arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm comprised in the resin powder, may be 10, preferably 15, more preferably 20, still more preferably 30, and yet more preferably 40, 45 or 50. The bubble-containing particle

number being equal to or more than the lower limit enables improving the drying efficiency, and the like. The upper limit of the bubble-containing particle number may be 100, or may be 90, 80, 70, or 60. It is to be noted that the bubble-containing particles can be obtained by, for example, introducing a gas into the slurry or solid comprising the PVA in the saponifying step or the step that follows, as described later. Furthermore, the bubble-containing particle number can be adjusted by the amount of the gas to be introduced, and the like.

[0026]

The lower limit of the average bubble size in the bubble-containing particles of the resin powder according to one embodiment of the present invention may be 1 μm, preferably 10 μm, more preferably 30 μm, still more preferably 40 μm, and even further preferably 50 μm. The average bubble size being equal to or more than the lower limit enables more improving the drying efficiency, and the like. On the other hand, the upper limit of the average bubble size is preferably 200 μm, and more preferably 100 μm. When the average bubble size is equal to or less than the upper limit described above, the productivity of the resin powder can be enhanced. The average bubble size as referred to herein means an average value of the size (bubble size) of bubbles of 1 μm or more comprised in the bubble-containing particles. The average bubble size can be adjusted by, for example, the air hole diameter, etc., of the filter used when the gas is introduced into the slurry or solid comprising the PVA.

[0027]

The number and the average bubble size of the bubble-containing particles of the resin powder may be determined by the following method. One hundred particles are arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm in the resin powder. The particles having a particle diameter of 106 to 1,000 μm can be selected in sieving, as particles which passed through a sieve mesh having a nominal mesh opening size of 1,000 μm (16 mesh), but did not passed through a sieve mesh having a nominal mesh opening size of 106 μm (150 mesh). The mechanical sieving can be carried out by a method described in JIS K7369: 2009, for example. On each particle extracted, observation of the presence or absence of bubbles and measurement of the bubble size (the diameter of the bubble) are performed by using a microscope. The observation and the measure of each particle by using a microscope are performed from directly above in a state in which each particle is disposed on a horizontal plane. In a case in which a bubble is circular, the bubble size is defined as the diameter of the circle, and in a case in which the bubble is elliptical, the bubble size is defined as the major axial length. The average bubble size is defined as an average value of the bubble sizes of bubbles having a bubble size of 1 μm or more included in the bubble-containing particles observed. The "bubbles" include not only completely closed bubbles (existing inside the particle) but also bubbles that are not completely closed (those having a surface shape recessed in a circular or elliptical shape considered to be derived from a bubble). Even for bubbles that are not completely closed (having a surface shape recessed in a circular or elliptical shape considered to be derived from a bubble), the diameter or major axial length thereof is defined as the bubble size.

[0028]

The gas to be contained in the bubbles of the bubble-containing particles preferably contains an inert gas, in light of safety and the like. Furthermore, in light of handleability and the like, the gas to be contained in bubbles of the bubble-containing particles is preferably an inorganic substance. From these viewpoints and in light of the production cost, the gas to be contained in the bubbles of the bubble-containing particles is preferably the air or nitrogen, and more preferably nitrogen. The content of nitrogen in

the gas to be contained in bubbles of the bubble-containing particles is preferably 78 volume% or more, more preferably 80 volume% or more, and still more preferably 90 volume% or more.

[0029]

In the resin powder according to one embodiment of the present invention, the content of the particles having a particle diameter of 106 to 1,000 μm is not particularly limited, and the lower limit thereof is preferably 50% by mass, more preferably 60% by mass, and still more preferably 70% by mass. On the other hand, the upper limit of the content of the particles having a particle diameter of 106 to 1,000 μm may be 100% by mass, or may be 99% by mass or 95% by mass. When the content of the particles having a particle diameter of 106 to 1,000 μm falls within the above range, the drying efficiency is more improved. The content of the particles having a particle diameter of 106 to 1,000 μm in the resin powder can be determined in accordance with the method described in JIS K7369: 2009 using a sieve mesh having a nominal opening size of 1,000 μm (16 mesh) and a sieve mesh having a nominal mesh opening size of 106 μm (150 mesh).

[0030]

In the resin powder according to one embodiment of the present invention, the bulk density is not particularly limited, and the upper limit thereof is preferably 0.7 g/mL, more preferably 0.6 g/mL, and still more preferably 0.55 g/mL. When the bulk density is equal to or less than the upper limit described above, the drying efficiency may be more improved. On the other hand, the lower limit of the bulk density is preferably 0.4 g/mL. The bulk density in the resin powder is measured under conditions involving 25 °C and 50% RH, by placing the resin powder into a 100 mL graduated cylinder up to 100 mL, and calculating from this volume (100 mL) and the mass (unit: g) of the resin powder placed in the graduated cylinder.

[0031]

In the resin powder according to one embodiment of the present invention, the upper limit of the product of the average particle diameter (μm) and the bulk density (g/mL) thereof is preferably 700 μm·g/mL, more preferably 500 μm·g/mL, still more preferably 400 μm·g/mL, and even more preferably 350 μm·g/mL, 320 μm·g/mL, or 300 μm·g/mL. The product of the average particle diameter and the bulk density (g/mL) of the resin powder (μm) being equal to or less than the upper limit described above means that the bulk density is low relative to the size of the particles. Therefore, the smaller the value of the product, the larger the surface area, and thus, the drying efficiency tends to be more improved. The lower limit of the product may be, for example, 100 μm·g/mL, or may be 150 μm·g/mL or 200 μm·g/mL.

[0032]

The resin powder according to one embodiment of the present invention can be used for a variety of intended usages. Examples are presented below, but not limited thereto.

(1) Vinyl chloride dispersant usages: dispersion stabilizers and dispersion aids for suspension polymerization of vinyl chloride or vinylidene chloride

(2) Coating material usages: sizing agents, fiber processing agents, leather finishers, paints, anti-fogging agents, metal corrosion inhibitors, gloss agents for galvanized material, and antistatic agents

(3) Adhesive/binder usages: adhesives, agglutinants, remoistenable adhesives, various binders, and additives for cements, mortars, etc.

(4) dispersion stabilizer usages: dispersion stabilizers for organic/inorganic pigments such as paints and adhesives, dispersion stabilizers for emulsion polymerization of various types of vinyl compounds, post-emulsifying agents for bitumen, etc.

(5) paper processing usages: paper strength-enhancing agents, oil/solvent resistance-imparting agents, smoothness-improving agents, surface gloss-improving agents, sizing agents, barrier agents, light resistance-imparting agents, water resistance-imparting agents, dye/developer dispersants, adhesion-improving agents, binders

(6) Agricultural usages: binders for pesticides, spreaders for pesticides, agricultural coating materials, soil improving agents, erosion inhibitors, and dispersants for pesticides

(7) Medical/cosmetic usages: granulate binders, coating agents, emulsifying agents, skin patches, binding agents, bases for film formulations, and film-forming agents

(8) Viscosity adjusting agent usages: thickening agents, rheology-adjusting agents

(9) Aggregating agent usages: agents for aggregating solids suspended in water and for dissolved matter, and metal aggregating agents

(10) Film usages: water-soluble films, polarized films, barrier films, films for wrapping textile products, seed germination sheets, vegetation sheets, seed tapes, and hygroscopic films

(11) Molded article usages: fibers, pipes, tubes, anti-leak films, water-soluble fibers for chemical laces, and sponges

(12) Usages as raw materials for resins: raw materials for polyvinyl butyral, raw materials for photosensitive resins, raw materials for graft polymers, and raw materials for various gels

(13) Post-reaction usages: post-reaction usages with low-molecular organic compounds, high-molecular organic compounds, and inorganic compounds

[0033]

Method for Producing Resin Powder

The method for producing a resin powder of the present invention is not particularly limited, but it is preferred that the bubbles are included in the particles in any of steps of polymerization, saponification, washing, drying, pulverization, etc., which are general steps in producing a PVA. In the method for production, a solid which comprises the PVA and has bubbles formed is obtained by introducing a gas into a system. It is to be noted that (into a/the) "system" may refer to a liquid, gelatinous, or solid mixture comprising the PVA. The expression, (into a/the) "system", may refer to a liquid, gelatinous, or solid mixture, comprising at least one of a reactant and a product during the production of the PVA. For example, (into a/the) "system" in the saponifying step (saponification reaction) may refer to a reaction liquid during the saponification reaction. A part of a reaction liquid in the saponification reaction liquid may be gelatinous or in a solid state. The gas is introduced in to the system, preferably in the saponifying step. More specifically, it is preferred that the gas is introduced into the reaction liquid when the vinyl ester polymer is saponified to obtain the PVA.

[0034]

In the polymerizing step, a vinyl ester monomer is polymerized to obtain a vinyl ester polymer. The procedure for polymerizing a vinyl ester monomer is exemplified by a well-known procedure such as a bulk polymerization procedure, a solution polymerization procedure, a suspension polymerization procedure, an emulsion polymerization procedure, and the like. Of these procedures, the bulk polymerization procedure performed without a solvent and the solution polymerization procedure performed with a solvent such as an alcohol or the like are preferred, and the solution polymerization procedure in which the polymerization is performed in the presence of a lower alcohol is more preferred. The lower alcohol is preferably an alcohol having 3 or fewer carbon atoms; more preferably methanol, ethanol, n-propanol, or isopropanol; and still more preferably methanol. In carrying out a polymerization reaction by the bulk

polymerization procedure or the solution polymerization procedure, in terms of a reaction system, either of a batchwise system or a continuous system can be employed.
[0035]

Examples of the vinyl ester monomer include vinyl formate, vinyl acetate, vinyl propionate, vinyl valerate, vinyl caprate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate, vinyl versatate, and the like. Of these, vinyl acetate is preferred.
[0036]

Examples of the initiator for use in the polymerization reaction include well-known initiators, e.g.,: azo-based initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile); organic peroxide-based initiators such as benzoyl peroxide and n-propyl peroxycarbonate; and the like. A polymerization temperature in carrying out the polymerization reaction is not particularly limited, and a range of 5 °C or more and 200 °C or less is appropriate.
[0037]

When the vinyl ester monomer is polymerized, an other copolymerizable monomer may be further copolymerized within the range not leading to impairment of the principles of the present invention. Examples of such other monomer include monomers (modified species) that give the other monomer units described above. The upper limit of the amount of these other monomers used may vary depending on the purpose and intended usage thereof, and the like, and is preferably 20 mol%, and more preferably 10 mol%, with respect to total monomers. The upper limit of the amount of the other monomer unit used may be 5 mol%, 3 mol%, 1 mol%, or 0.1 mol%. On the other hand, the lower limit of the amount of the other monomer used may be, for example, 0.1 mol%, or may be 1 mol%.
[0038]

During polymerization of the vinyl ester monomer, a chain transfer agent may also be present for the purpose of adjusting the degree of polymerization of the resulting PVA, and the like. Examples of the chain transfer agent include: aldehydes such as acetaldehyde, propionaldehyde, butylaldehyde, and benzaldehyde; ketones such as acetone, methyl ethyl ketone, hexanone, and cyclohexanone; mercaptans such as 2-hydroxyethanethiol; thiocarboxylic acids such as thioacetic acid; halogenated hydrocarbons such as trichloroethylene and perchloroethylene; and the like. Of these, aldehydes and ketones may be suitably used. The amount of the chain transfer agent added may be predetermined according to: the chain transfer constant of the chain transfer agent to be added; and the degree of polymerization of the PVA intended, and in general, the amount of 0.1 to 10% by mass with respect to the vinyl ester used is preferred.
[0039]

In the saponifying step, the vinyl ester polymer is saponified in an alcohol solution by using an alkali catalyst to give the PVA. For the saponification reaction of the vinyl ester polymer, an alcoholysis or hydrolysis reaction in which a conventionally well-known basic catalyst such as sodium hydroxide, potassium hydroxide, or sodium methoxide can be employed. Examples of the solvent for use 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; aromatic hydrocarbons such as benzene and toluene; and the like. These may be used either alone, or in combination of two or more thereof. Of these, using methanol, or a mixed solution of methanol and methyl acetate as a solvent to carry out the saponification reaction in the presence of sodium hydroxide is preferred due to convenience.
[0040]

As described above, it is preferred that the gas is introduced into the system (reaction liquid) in the saponifying step to obtain a solid which comprises the PVA and has bubbles formed. A procedure for introducing the gas into the system in the saponifying step may be exemplified by: a procedure of mixing while entraining a gas during the mixing of the vinyl ester polymer and the alkali catalyst; a procedure of directly introducing bubbles into a mixture of the vinyl ester polymer and the alkali catalyst immediately before a PVA gel is formed; and the like. It is to be noted that to continue introducing the gas into the system from the beginning to the end of the saponifying step is not necessary, and the gas may be introduced into the system in at least a part of the saponifying step.

[0041]

The gas to be introduced into the system, i.e., the gas to be contained in the bubbles formed, is not particularly limited, and the air, nitrogen, carbon dioxide, and the like are exemplified, and nitrogen is preferred.

[0042]

The bubble-containing particle number in the resin powder to be obtained can be adjusted by, for example, the amount of the gas introduced into the system, and the like. Moreover, the gas can be introduced into the system by passing through a filter for foaming having a predetermined pore size. Such a process allows for easy adjustment of the size of the bubbles formed. The pore size of the filter is, for example, preferably 1 to 300 μm, and more preferably 5 to 200 μm.

[0043]

The solid comprising the PVA obtained via the saponifying step may be subjected to, typically, washing, drying, and pulverizing, whereby the resin powder can be obtained. The washing can be executed by using an alcohol such as methanol, for example. Conditions for the drying are not particularly limited, and the drying temperature can be, for example, 50 °C or more and 120 °C or less, or may be 60 °C or more and 100 °C or less. The drying time period can be, for example, 1 hour or more and 24 hours or less, may be 2 hours or more and 20 hours or less, 16 hours or less, or may be 12 hours or less, or 6 hours or less.

EXAMPLES

[0044]

The present invention will be specifically described by way of the following Examples, but the present invention is not in any how limited to these Examples. It is to be noted that each measuring method adopted in the following Examples and Comparative Examples is indicated below.

[0045]

Viscosity-Average Degree of Polymerization of PVA

The viscosity-average degree of polymerization of PVA (comprising modified PVA) was measured in accordance with JIS K6726: 1994. Specifically, in the case in which the degree of saponification of the PVA is less than 99.5 mol%, saponification was performed until the degree of saponification reached 99.5 mol% or more, and in regard to the PVA thus obtained, the viscosity-average degree of polymerization was determined according to the following equation using a limiting viscosity [η] (liter/g) measured in water at 30 °C.

$$\text{Viscosity-average degree of polymerization} = ([\eta] \times 10{,}000/8.29)^{(1/0.62)}$$

[0046]

Degree of Saponification of PVA

The degree of saponification of the PVA (comprising a modified PVA) was determined according to the method described in JIS K6726: 1994.

[0047]

Content of Organic Volatiles

The content of the organic volatiles of the resin powder was determined according to the method described in JIS K6726: 1994.

[0048]

Average Particle Diameter of Resin Powder, and Content of Particles Having a Particle Diameter of 106 to 1,000 μm

Using a JIS standard sieve, the average particle diameter of the resin powder and the content of the particles having a particle diameter of 106 to 1,000 μm were determined according the method described in JIS K7369: 2009.

[0049]

Bubble-Containing Particle Number and Average Bubble Size

Particles having a particle diameter of 106 to 1,000 μm were selected by the sieving described above, and from these particles, arbitrary 100 particles were extracted. With respect to these particles, the bubble-containing particle number and the average bubble size were measured, based on an image with an enlargement ratio of 100 times using a digital microscope VHX-900 manufactured by Keyence Corporation.

[0050]

Bulk Density

The bulk density was determined under conditions involving 25 °C and 50% RH by placing the resin powder into a 100 mL graduated cylinder up to 100 mL, and calculating from the volume (100 mL) and the mass (unit: g) of the resin powder placed in the graduated cylinder.

[0051]

Example 1: Production of PVA1

Into a 3 L reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet tube, and an initiator addition port, 1,125 g of vinyl acetate and 375 g of methanol (75% by mass vinyl acetate and 25% by mass methanol) were charged, and replacement with nitrogen in the system was carried out for 30 min while bubbling nitrogen. Elevation of the temperature in the reaction vessel was started, and when the internal temperature became 60 °C, 0.5 g of 2,2'-azobisisobutyronitrile (AIBN) was added to start polymerization. When the rate of polymerization became 50%, the polymerization was stopped by cooling. The solid content concentration when the polymerization was stopped was 37.0%. Subsequently, unreacted vinyl acetate monomers were removed while adding methanol at intervals at 30 °C under a reduced pressure to give a methanol solution (concentration: 35%) of polyvinyl acetate (PVAc). Furthermore, 1,429 g of a methanol solution of PVAc (PVAc in the solution: 500 g) was prepared by adding methanol thereto, and 46.5 g of an alkali solution (10% methanol solution of sodium hydroxide) was added to the solution, whereby saponification was conducted (PVAc concentration in the saponification solution: 30%; molar ratio of sodium hydroxide to vinyl acetate units in PVAc: 0.02 mol%). About 3 min later since the alkali solution was added, nitrogen was introduced at 0.3 L/min into a reaction liquid during the saponification reaction, through a filter having a pore size of 40 μm. Thereafter, since the solid (gelatinous matter) was produced about 1 min later, the solid was pulverized with a grinder. After the pulverized matter was left to stand at 40 °C for 1 hour to allow the saponification to proceed, 50 kg of methyl acetate was added thereto, whereby remaining alkali was neutralized. After completion of neutralization was ascertained by using a phenolphthalein indicator, the mixture was filtered off to obtain a white solid. To this white solid was added 1,000 g of methanol, and the mixture was left to stand at room temperature for 3 hours to permit washing. After the washing operation was performed

three times, a white solid obtained by deliquoring through centrifugation was dried in a dryer at 70 °C for 16 hours. Thus resulting crude powder was charged into a juicer mixer, and the particles were pulverized at room temperature in a nitrogen atmosphere to give the resin powder of Example 1 (resin powder of PVA 1).

The viscosity-average degree of polymerization of PVA1 was 1,700, and the degree of saponification thereof was 98.5 mol%. As for the resin powder of PVA1: the organic volatile content was 2.7% by mass; the average particle diameter was 550 μm; the content of the particles (specified particles) having a particle diameter of 106 to 1,000 μm was 85% by mass; the bubble-containing particle number was 55; the average bubble size was 50 μm; the bulk density was 0.49 g/mL; and the product of the average particle diameter and the bulk density was 269.5 μm·g/mL.

Furthermore, for the evaluation of drying efficiency described later, the PVAc obtained by the above method was subjected to saponification without introducing nitrogen, and thereafter a similar treatment was performed to give a resin powder of PVA 1'. The viscosity average degree of polymerization and the degree of saponification of PVA 1', as well as the average particle diameter and the content of the particles having a particle diameter of 106 to 1,000 μm of the resin powder of PVA 1', were substantially equal to those of PVA 1 and the powder of PVA 1. The organic volatile content of the resin powder of PVA 1' was 6.1% by mass, and the bubble-containing particle number was less than 5.

[0052]

Evaluation of Drying Efficiency

Each 100 g of the resin powder of PVA1 and the resin powder of PVA1' was immersed in 500 mL of methanol at room temperature overnight so as to allow for swelling of each resin powder. Thus swollen each resin powder was dried in a dryer at 100 °C, and a time period until the methanol content of each resin powder became less than 3% by mass was measured as the drying time period. The drying time period (T) of the resin powder of PVA1 was 2.5 hours, and the drying time period (T') of the resin powder of PVA1' was 6.0 hours.

A ratio (T/T') of the drying time period (T) of the resin powder of PVA1 to the drying time period (T') of the resin powder of PVA1' employed as a standard was determined as an improvement index of the drying efficiency. The value of the ratio (T/T') in the resin powder of PVA1 was 0.42. Furthermore, the evaluation was made on the value of the ratio (T/T'), according to the following criteria. The resin powder of PVA1 was evaluated as falling under "A", whereby a superior effect of improving the drying efficiency due to comprising bubbles was identified.

(criteria)

A: less than 0.50

B: 0.50 or more and less than 0.65

C: 0.65 or more and less than 0.75

D: 0.75 or more

[0053]

Evaluation of Wettability

A 500 mL beaker was filled with 300 mL of distilled water, and a 30 mm rotation bar was set in the beaker. The beaker was placed on a magnetic stirrer, and stirring was performed at 100 rpm. Ten g of the resin powder of PVA1 was charged all at once into the beaker with stirring and the dispersion state of the particles was visually observed; as a result, 95% or more particles were dispersed in water. Furthermore, the dispersion state of the particles was evaluated according to the following criteria. The resin powder of PVA1 was evaluated as falling under "A", and the particles were likely to be dispersed in

water, accompanied by superior handleability as production of the aqueous solution was easy.

Criteria

A: 90% or more particles being dispersed in water

B: 50% or more and less than 90% particles being dispersed in water

C: less than 50% particles being dispersed in water

[0054]

Examples 2 to 5

Each resin powder of Examples 2 to 5 (each of the resin powders of PVA2 to PVA5) was obtained under conditions similar to those of Example 1, except that production conditions were changed to the conditions shown in Table 1. Furthermore, each of the resin powders of PVA2' to PVA5' was obtained by conducting saponification under the production conditions for each of the resin powders of PVA2 to PVA5, without introducing nitrogen. In each of the resin powders of PVA2' to PVA5' serving as the standard for the evaluation of drying efficiency, the bubble-containing particle number was less than 5 in all cases. Each of the resin powders of Examples 2 to 5 (each of the resin powders of PVA2 to PVA5) was subjected to the measurements and evaluations which were performed similarly to Example 1. The results are shown in Tables 2 and 3.

[0055]

Example 6

Into a 5 L pressure reaction vessel equipped with a stirrer, a nitrogen feed port, an ethylene feed port, an initiator addition port, and a delay solution addition port, 2,400 g of vinyl acetate and 600 g of methanol were charged, and after the temperature was elevated to 60 °C, replacement with nitrogen in the system was carried out for 30 min while bubbling nitrogen. Next, ethylene was introduced such that the pressure inside the reaction vessel was became 0.50 MPa. After the internal temperature of the reaction vessel was adjusted to 60 °C, 1.0 g of 2,2'-azobisisobutyronitrile (AIBN) was infused to start polymerization. During the polymerization, the polymerization temperature was maintained at 60 °C while adjusting the ethylene pressure, and 3 hours later when the rate of polymerization became 30%, the polymerization was stopped by cooling. Subsequently, saponification was conducted by a procedure similar to that of Example 1 and under the conditions shown in Table 1, whereby the resin powder of Example 6 (resin powder of PVA6) was produced. Furthermore, the resin powder of PVA6' was obtained under the production conditions for the resin powder of PVA6, without introducing nitrogen. In the resin powder of PVA6' serving as the standard for the evaluation of drying efficiency, the bubble-containing particle number was less than 5. The resin powder of Example 6 (resin powder of PVA6) was subjected to the measurements and evaluations which were performed similarly to Example 1. The results are shown in Tables 2 and 3. It is to be noted that PVA6 and PVA6' were ethylene-modified PVAs, and the modification amount was determined by ^{1}H-NMR.

[0056]

Example 7

Into a 3 L reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet tube, a comonomer-dripping port, and an initiator addition port, 1,200 g of vinyl acetate, 300 g of methanol, and 0.71 g of monomethyl maleate (MMM) were charged, and replacement with nitrogen in the system was carried out for 30 min while bubbling nitrogen. Furthermore, a comonomer solution as a delay solution was prepared by dissolving MMM in methanol at a concentration of 10% by mass, and replacement with nitrogen was carried out by bubbling a nitrogen gas. Elevation of the temperature in the reaction vessel was started, and when the internal temperature became 60 °C, 1.0 g of 2,2'-

azobisisobutyronitrile (AIBN) was added to start polymerization. After the polymerization was performed at 60 °C for 3 hours while the monomer composition (the proportion of vinyl acetate and MMM) in the polymerization solution was kept constant with adding the delay solution dropwise, the polymerization was stopped by cooling. Subsequently, saponification was conducted by a procedure similar to that of Example 1 and under the conditions shown in Table 1, whereby the resin powder of Example 7 (resin powder of PVA7) was produced. Furthermore, the resin powder of PVA7' was obtained under the production conditions for the resin powder of PVA7, without introducing nitrogen. In the resin powder of PVA7' serving as the standard for the evaluation of drying efficiency, the bubble-containing particle number was less than 5. The resin powder of Example 7 (resin powder of PVA7) was subjected to the measurements and evaluations which were performed similarly to Example 1. The results are shown in Tables 2 and 3. It is to be noted that PVA7 and PVA7' were MMM-modified PVAs, and the modification amount was determined by ^{1}H-NMR.

[0057]

Comparative Example 1

The resin powder of Comparative Example 1 (resin powder of PVA8) was produced under conditions similar to those of Example 1, except that the amount of nitrogen introduced was changed to 0.05 L/min. The resin powder of Comparative Example 1 (resin powder of PVA8) was subjected to the measurements and evaluations which were performed similarly to Example 1. The results are shown in Tables 2 and 3. It is to be noted that the resin powder used as the standard in the evaluation of drying efficiency was the resin powder of PVA1', similarly to Example 1.

[0058]

Comparative Example 2

The resin powder of Comparative Example 2 (resin powder of PVA9) was produced under conditions similar to those of Example 2, except that the amount of nitrogen introduced was changed to 0.05 L/min. The resin powder of Comparative Example 2 (resin powder of PVA9) was subjected to the measurements and evaluations which were performed similarly to Example 1. The results are shown in Tables 2 and 3. It is to be noted that the resin powder used as the standard in the evaluation of drying efficiency was the resin powder of PVA2', similarly to Example 2.

[0059]

Table 1

	PVA	Polymerization conditions				Saponification conditions		
		vinyl acetate	Methanol	modified species (comonomer)	rate of polymerization	PVAc concentration	NaOH molar ratio	amount of nitrogen introduced
		mass%	mass%	type	%	mass%	mol%	L/min
Example 1	PVA1	75	25	-	50	30	0.02	0.30
Example 2	PVA2	75	25	-	50	30	0.008	0.30
Example 3	PVA3	75	25	-	50	30	0.005	0.30
Example 4	PVA4	85	15	-	40	25	0.02	0.30
Example 5	PVA5	90	10	-	25	20	0.02	0.30
Example 6	PVA6	80	20	ethylene	30	30	0.04	0.30
Example 7	PVA7	80	20	MMM	30	30	0.06	0.30
Comparative Example 1	PVA8	75	25	-	50	30	0.02	0.05
Comparative	PVA9	75	25	-	50	30	0.008	0.05

Example 2								

[0060]

Table 2

	PVA			Resin powder				
	viscosity-average degree of polymerization	degree of saponification	modification amount	organic volatiles	average particle diameter	content of specified particles (*1)	bubbles-containing particle number	average bubble size
	-	mol%	mol%	mass%	μm	mass%	particles	μm
Example 1	1700	98.5	-	2.7	550	85	55	50
Example 2	1700	88.0	-	2.3	600	90	40	60
Example 3	1700	80.0	-	2.1	720	92	20	40
Example 4	2400	98.5	-	2.8	420	80	52	60
Example 5	3200	98.5	-	2.9	460	75	53	80
Example 6	1750	98.5	4 (ethylene)	2.6	530	86	50	40
Example 7	1700	98.5	4 (MMM)	2.5	480	88	45	50
Comparative Example 1	1700	98.5	-	5.6	650	83	9	60
Comparative Example 2	1700	88.0	-	4.3	700	85	6	50

*1: Content of particles having a particle diameter of 106 to 1,000 μm

[0061]

Table 3

	Drying time period (T)	Drying time period of resin powder serving as standard (T')	Ratio (T/T')	Drying efficiency evaluation	Wettability evaluation
	hours	Hours	-	-	-
Example 1	2.5	6.0	0.42	A	A
Example 2	1.8	2.8	0.64	B	A
Example 3	1.6	2.3	0.70	C	B
Example 4	2.8	6.5	0.43	A	A
Example 5	3.1	7.2	0.43	A	A
Example 6	2.3	5.2	0.44	A	A
Example 7	2.2	4.5	0.49	A	B
Comparative Example 1	4.5	6.0	0.75	D	A
Comparative Example 2	2.3	2.8	0.82	D	B

[0062]

As shown in Tables 2 and 3, the drying efficiency of each of the resin powders of Examples 1 to 7 was evaluated as falling under “A” to “C”, thereby revealing results indicating sufficiently improved drying efficiency.

[INDUSTRIAL APPLICABILITY]

[0063]

The resin powder of the present invention exhibits improved drying efficiency, thereby leading to superior productivity, and thus can be used for a variety of intended usages such as synthetic fiber materials, film materials, emulsifying and dispersing agents, and adhesives.

CLAIMS:

[Claim 1]

A resin powder:

comprising a vinyl alcohol polymer;

having an average particle diameter of 100 to 2,000 μm; and

the number of particles having bubbles of 1 μm or larger being 10 or more, among 100 particles arbitrarily extracted from particles having a particle diameter of 106 to 1,000 μm in the resin powder.

[Claim 2]

The resin powder according to claim 1, wherein the vinyl alcohol polymer has a viscosity-average degree of polymerization being 200 to 5,000, and a degree of saponification being 35 to 99.99 mol%.

[Claim 3]

The resin powder according to claim 1 or claim 2, wherein a content of the particles having a particle diameter of 106 to 1,000 μm is 50% by mass or more.

[Claim 4]

The resin powder according to claim 1 or claim 2, wherein a bulk density is 0.4 to 0.7 g/mL.

[Claim 5]

The resin powder according to claim 1 or claim 2, wherein a product of the average particle diameter (μm) and a bulk density (g/mL) is 700 μm·g/mL or less.

[Claim 6]

The resin powder according to claim 1 or claim 2, wherein an organic volatile content is 3.0% by mass or less.