DESCRIPTION

Title of the Invention: POROUS FILM AND METHOD FOR PRODUCING POROUS FILM

TECHNICAL FIELD

[0001]

The present invention relates to a porous film and a method for producing a porous film.

BACKGROUND ART

[0002]

In the related art, various porous films have been used in applications such as filters that are separation films for a gas or a liquid. In addition, in recent years, porous films have also been applied to separators for secondary batteries such as lithium batteries.

[0003]

For example, a method for producing a polyimide porous film has been known, in which the porous film is formed by coating a substrate with varnish containing silica particles dispersed in a solution of a polyamic acid or a polyimide, heating the coating film in case of needs to obtain a polyimide film containing the silica particles, and removing the silica in the polyimide film through elution with hydrogen fluoride water (see Patent Document 1).

Citation List

Patent Documents

[0004]

Patent Document 1: Japanese Patent No. 5605566

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0005]

As the above-described porous film, a porous film having a small pore diameter is required. For example, in the production of semiconductors, porous films are used as filters for removing foreign matter contained in cleaning liquids, coating liquids, or the like. As miniaturization of semiconductors progresses, the size of foreign matter that causes defects also decreases. In order to collect small foreign matter, a porous film having a small pore diameter is required. The porous film having a small pore diameter can be produced by using a porous film-producing composition (varnish) containing fine particles having a small particle diameter such as silica. However, the reduction of the pore diameter of the porous film causes decrease in permeability (liquid permeability and air permeability) of the porous film to lower a flow rate of a liquid or a gas that permeates the porous film.

[0006]

The present invention has been made in view of the above circumstances, and an object thereof is to provide a porous film capable of reducing a pore diameter and improving a flow

rate, and a method for producing the porous film.

Means for Solving the Problems

[0007]

The present inventors conducted intensive studies to overcome the above difficulties. As a result, the present inventors have found that the above difficulties can be solved by providing a porous film containing: at least one resin component (A) selected from the group consisting of a polyimide, a polyamide imide, and a polyether sulfone; and a solvent (S), wherein the solvent (S) contains a nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher at atmospheric pressure, and a content of the nitrogen-containing polar solvent (S1) in the porous film is 10 ppm or more and 2,000 ppm or less. Specifically, the present invention provides the following.

[0008]

[1] A porous film containing: at least one resin component (A) selected from the group consisting of a polyimide, a polyamide imide, and a polyether sulfone; and a solvent (S),

the solvent (S) containing a nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher at atmospheric pressure,

a content of the nitrogen-containing polar solvent (S1) in the porous film being 10 ppm or more and 2,000 ppm or less.

[0009]

[2] The porous film as described in aspect [1], in which the nitrogen-containing polar solvent (S1) is at least one

selected from the group consisting of a nitrogen-containing heterocyclic compound which optionally has a substituent and an aromatic hydrocarbon substituted with a nitrogen-containing group.

[0010]

[3] The porous film as described in aspect [2], in which the nitrogen-containing polar solvent (S1) is at least one selected from the group consisting of 1,3-dimethyl-2-imidazolidinone, N-methylpyrrolidone, N-ethyl-2-pyrrolidone, and nitrobenzene.

[0011]

[4] The porous film as described in any one of aspects [1] to [3], in which the solvent (S) contains an organic solvent (S2) having a boiling point of lower than 200°C at atmospheric pressure.

[0012]

[5] The porous film as described in aspect [4], in which the organic solvent (S2) is an aliphatic amide-based solvent.

[0013]

[6] The porous film as described in aspect [5], in which the organic solvent (S2) is dimethylacetamide.

[0014]

[7] The porous film as described in any one of aspects [1] to [6], in which a content of the solvent (S) in the porous film is 10 ppm or more and 2,100 ppm or less.

[0015]

[8] A method for producing the porous film as described in any

one of aspects [1] to [7], including:

a composite film forming step of forming, on a substrate, a composite film made of a porous film-producing composition containing at least one resin component selected from the group consisting of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and a polyether sulfone, fine particles (B), and a solvent (S);

a heating step of heating the composite film; and

a fine particle removing step of removing the fine particles (B) from the composite film after the heating step,

wherein the solvent (S) contains the nitrogen-containing polar solvent (S1), and

in the heating step, a part of the solvent (S) is removed from the composite film such that a content of the nitrogen-containing polar solvent (S1) in the porous film to be produced is 10 ppm or more and 2,000 ppm or less.

Effects of the Invention

[0016]

According to the present invention, it is possible to provide a porous film capable of having a reduced pore diameter and an improved flow rate, and a method for producing the porous film.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0017]

Hereinafter, embodiments of the present invention will be described in detail, but the present invention is not limited

to the following embodiments, and can be carried out with appropriate modifications within the scope of the object of the present invention.

[0018]

«Porous Film»

A porous film contains at least one resin component (A) selected from the group consisting of a polyimide, a polyamide imide, and a polyether sulfone, and a solvent (S). The solvent (S) contained in the porous film contains a nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher at atmospheric pressure. A content of the nitrogen-containing polar solvent (S1) in the porous film is 10 ppm or more and 2,000 ppm or less.

[0019]

The polyimide, the polyamide imide, and the polyether sulfone as the resin component (A) contained in the porous film are not particularly limited and can be appropriately selected according to an application of the porous film.

[0020]

The solvent (S) contained in the porous film contains a nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher at atmospheric pressure (hereinafter, also simply referred to as "boiling point"). The boiling point of the nitrogen-containing polar solvent (S1) may be 200°C or higher, may be 210°C or higher, and may be 220°C or higher. Examples of the nitrogen-containing polar solvent (S1) include nitrogen-containing heterocyclic compounds which may have a

substituent and aromatic hydrocarbons substituted with a nitrogen-containing group. Examples of the nitrogen-containing heterocyclic compound which may have a substituent as the nitrogen-containing polar solvent (S1) include 1,3-dimethyl-2-imidazolidinone (boiling point of 220°C), N-methylpyrrolidone (boiling point of 202°C), and N-ethyl-2-pyrrolidone (boiling point of 218°C). Examples of the nitrogen-containing group include a nitro group. Examples of the aromatic hydrocarbon substituted with a nitrogen-containing group as the nitrogen-containing polar solvent (S1) include nitrobenzene (210°C). The nitrogen-containing polar solvent (S1) may be one type or two or more types.

[0021]

A content of the nitrogen-containing polar solvent (S1) in the porous film is 10 ppm or more and 2,000 ppm or less. In this way, the porous film contains the nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher in an amount of 10 ppm or more and 2,000 ppm or less, so that the porous film can have a reduced pore diameter and an improved (increased) flow rate as shown in Examples described later.

[0022]

On the other hand, when the content of the nitrogen-containing polar solvent (S1) is less than 10 ppm, the flow rate decreases. In addition, when the content of the nitrogen-containing polar solvent (S1) exceeds 2,000 ppm, pores of the porous film become large.

[0023]

The content of the nitrogen-containing polar solvent (S1) in the porous film is preferably 10 ppm or more and 1,500 ppm or less, and more preferably 150 ppm or more and 1,000 ppm or less.

[0024]

The solvent (S) contained in the porous film may contain an organic solvent (S2) having a boiling point of lower than 200°C at atmospheric pressure. The boiling point of the organic solvent (S2) may be lower than 200°C, but is preferably 180°C or lower, and more preferably 170°C or lower. The boiling point of the organic solvent (S2) is preferably 100°C or higher, and more preferably 120°C or higher. Examples of the organic solvent (S2) include aliphatic amide-based solvents. Examples of the aliphatic amide-based solvent as the organic solvent (S2) include dimethylacetamide (boiling point of 165°C). The organic solvent (S2) may be one type or two or more types.

[0025]

A content of the solvent (S) in the porous film is not particularly limited, but is preferably 10 ppm or more and 2,100 ppm or less, and more preferably 550 ppm or more and 2,000 ppm or less.

[0026]

The porous film may have an IPA flow rate of, for example, 0.06 mL/(min·cm^2) or more, and 0.22 mL/(min·cm^2) or more, as measured by the method described in [IPA flow rate (FR)]

described later. In addition, the porous film may have a bubble point of, for example, 90 psi or more, or 95 psi or more, as measured by the method described in [Bubble Point (BP)] described later. The bubble point is an index of a pore diameter of a communication pore, and the higher the bubble point, the smaller the pore diameter. The porous film to be produced may have a tensile strength of, for example, 27 MPa or more, or 29 MPa or more, as measured by a method described in [Tensile strength] described later.

[0027]

The porous film has a structure in which spherical pores communicate with one another (hereinafter, abbreviated as communication pores). An opening in the porous film is a portion in a surface of the porous film where the communication pore is opened.

[0028]

A sphere related to a shape of the pore is a concept including a true sphere, but is not necessarily limited to a true sphere. The spherical shape may be substantially a true spherical shape, and the spherical shape includes a shape that can be recognized as a substantially true spherical shape when an enlarged image of the pore is visually confirmed. Specifically, in the spherical pore, a surface defining the pore may be a curved surface, and a spherical or substantially spherical pore may be defined by the curved surface.

[0029]

Each of spherical pores is typically a pore formed by

removing fine particles (B) present in a composite film (resin-fine particle composite film) in a fine particle removing step, which is a subsequent step, in a method for producing a porous film described in detail later. The communication pore is formed by removing the plurality of fine particles (B) present in contact with the resin-fine particle composite film in the fine particle removing step, which is a subsequent step, in the method for producing a porous film. A portion where the spherical pores in the communication pore communicate with one another is derived from a portion where the plurality of fine particles (B) before being removed come into contact with one another.

[0030]

A diameter of the opening of the porous film may be appropriately changed, for example, in a range of 100 nm or more and 5,000 nm or less according to the use application of the porous film. The diameter of the opening is equal to or substantially equal to the diameter of the spherical pores constituting the communication pore. The communication pore formed by the continuous spherical pores having such a diameter allows a fluid to satisfactorily pass through the porous film. The porous film has a communication pore as a fluid flow path therein, the communication pore penetrating through the porous film in a thickness direction. Accordingly, a fluid can permeate from one main surface of the porous film to the other main surface thereof. When a laminate is used as a filter, the fluid passes through the inside of the porous

film while being in contact with the curved surface defining the spherical pores. A contact area of the fluid inside the porous film is considerably large due to provision of the communication pore formed of spherical pores. Therefore, it is considered that when the fluid passes through the laminate including the porous film, minute substances present in the fluid are likely to be adsorbed to the spherical pores in the porous film.

[0031]

«Method for Producing Porous Film»

The porous film described above can be produced by a method for producing a porous film, including: a composite film forming step of forming, on a substrate, a composite film made of a porous film-producing composition containing at least one resin component selected from the group consisting of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and a polyether sulfone, fine particles (B), and a solvent (S);

a heating step of heating the composite film; and

a fine particle removing step of removing the fine particles (B) from the composite film after the heating step, in which

the solvent (S) contains a nitrogen-containing polar solvent (S1), and

in the heating step, a part of the solvent (S) is removed from the composite film such that a content of the nitrogen-containing polar solvent (S1) in the porous film to be

produced is 10 ppm or more and 2,000 ppm or less. In addition, the method for producing a porous film may include a firing step in which the resin component contained in the porous film-producing composition contains at least one of a polyamic acid or a polyamide imide precursor, and the composite film is fired during the heating step or after the heating step and before the fine particle removing step. Each step will be described in detail below.

[0032]

[Composite Film Forming Step (Production of Unfired Composite Film)]

In the composite film forming step, a composite film made of the porous film-producing composition is formed on a substrate. The porous film-producing composition (hereinafter also referred to as "varnish") contains at least one resin component (a) selected from the group consisting of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and a polyether sulfone, fine particles (B), and a solvent (S). The solvent (S) contains the nitrogen-containing polar solvent (S1) and preferably contains the organic solvent (S2).

[0033]

[Resin Component (a)]

As described above, the porous film-producing composition contains at least one resin component (a) selected from the group consisting of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and a polyether sulfone.

When the porous film-producing composition contains a polyamic acid or a polyimide, the porous film contains the polyimide as the resin component (A). When the porous film-producing composition contains a polyamide imide precursor or a polyamide imide, the porous film contains the polyamide imide as the resin component (A). When the porous film-producing composition contains a polyether sulfone, the porous film contains the polyether sulfone as the resin component (A). Hereinafter, these resin components (a) will be described.

[0034]

<Polyamic Acid>

As the polyamic acid, a product obtained by polymerizing any tetracarboxylic dianhydride and a diamine can be used without particular limitation. Amounts of the tetracarboxylic dianhydride and the diamine used are not particularly limited, but the diamine is preferably used in an amount of 0.50 mol to 1.50 mol, more preferably 0.60 mol to 1.30 mol, and particularly preferably 0.70 mol to 1.20 mol per 1 mol of the tetracarboxylic dianhydride.

[0035]

The tetracarboxylic dianhydride can be appropriately selected from tetracarboxylic dianhydrides used as a synthetic raw material of polyamic acid in the related art. The tetracarboxylic dianhydride may be an aromatic tetracarboxylic dianhydride or an aliphatic tetracarboxylic dianhydride, and from the viewpoint of heat resistance of the obtained polyimide resin, it is preferable to use an aromatic

tetracarboxylic dianhydride. The tetracarboxylic dianhydrides may be used alone or in combination of two or more types thereof.

[0036]

Preferable specific examples of the aromatic tetracarboxylic dianhydride include pyromellitic dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride, 2,2,6,6-biphenyltetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl) propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, bis(2,3-dicarboxyphenyl)ether dianhydride, 2,2',3,3'-benzophenone tetracarboxylic dianhydride, 4,4-(p-phenylenedioxy)diphthalic dianhydride, 4,4-(m-phenylenedioxy)diphthalic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 2,3,6,7-naphthalene tetracarboxylic dianhydride, 1,2,3,4-benzene tetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 2,3,6,7-anthracene tetracarboxylic dianhydride, 1,2,7,8-

phenanthrene tetracarboxylic dianhydride, 9,9-bis phthalic anhydride fluorene, and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride. Examples of the aliphatic tetracarboxylic dianhydride include ethylene tetracarboxylic dianhydride, butane tetracarboxylic dianhydride, cyclopentane tetracarboxylic dianhydride, cyclohexane tetracarboxylic dianhydride, 1,2,4,5-cyclohexane tetracarboxylic dianhydride, and 1,2,3,4-cyclohexane tetracarboxylic dianhydride. Among them, 3,3',4,4'-biphenyl tetracarboxylic dianhydride and pyromellitic dianhydride are preferable from the viewpoint of price and availability. The tetracarboxylic dianhydride may be used alone or in a combination of two or more types thereof.

[0037]

The diamine can be appropriately selected from the diamine used as a synthetic raw material of polyamic acid in the related art. The diamine may be an aromatic diamine or an aliphatic diamine, and an aromatic diamine is preferable from the viewpoint of heat resistance of the obtained polyimide resin. These diamines may be used alone or in combination of two or more types thereof.

[0038]

Examples of the aromatic diamine include diamino compounds which have one phenyl group or in which about 2 to 10 phenyl groups are bonded to each other. Specific examples thereof include phenylenediamine and derivatives thereof, diaminobiphenyl compounds and derivatives thereof, diaminodiphenyl compounds and derivatives thereof,

diaminotriphenyl compounds and derivatives thereof, diaminonaphthalene and derivatives thereof, aminophenylaminoindane and derivatives thereof, diaminotetraphenyl compounds and derivatives thereof, diaminohexaphenyl compounds and derivatives thereof, and cardo-type fluorene diamine derivatives.

[0039]

Phenylenediamine is m-phenylenediamine or p-phenylenediamine, and as the phenylenediamine derivative, a diamine to which an alkyl group such as a methyl group or an ethyl group is bonded, for example, 2,4-diaminotoluene or 2,4-triphenylenediamine is used.

[0040]

In the diaminobiphenyl compound, two aminophenyl groups are bonded to each other. Examples thereof include 4,4'-diaminobiphenyl and 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl.

[0041]

The diaminodiphenyl compound is a compound in which two amino phenyl groups are bonded to each other via another group. Examples of the bond include an ether bond, a sulfonyl bond, a thioether bond, a bond based on alkylene or a derivative group thereof, an imino bond, an azo bond, a phosphine oxide bond, an amide bond, and a ureylene bond. The number of carbon atoms of the alkylene bond is about 1 to 6. The derivative group of the alkylene group is an alkylene group substituted with one or more halogen atoms or the like.

[0042]

Examples of the diaminodiphenyl compound include 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfide, 3,3'-diaminodiphenylketone, 3,4'-diaminodiphenyl ketone, 2,2-bis(p-aminophenyl)propane, 2,2'-bis(p-aminophenyl)hexafluoropropane, 4-methyl-2,4-bis(p-aminophenyl)-1-pentene, 4-methyl-2,4-bis(p-aminophenyl)-2-pentene, imino dianiline, 4-methyl-2,4-bis(p-aminophenyl)pentane, bis(p-aminophenyl)phosphine oxide, 4,4'-diaminoazobenzene, 4,4'-diaminodiphenylurea, 4,4'-diaminodiphenylamide, 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 4,4'-bis(4-aminophenoxy)biphenyl, bis[4-(4-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.

[0043]

Among them, p-phenylenediamine, m-phenylenediamine, 2,4-diaminotoluene, and 4,4'-diaminodiphenyl ether are preferable in terms of price, availability, and the like.

[0044]

The diaminotriphenyl compound is a compound in which two aminophenyl groups and one phenylene group are bonded to one

another via another group. As the other group, a group the same as the diaminodiphenyl compound is selected. Examples of the diaminotriphenyl compound include 1,3-bis(m-aminophenoxy)benzene, 1,3-bis(p-aminophenoxy)benzene, and 1,4-bis(p-aminophenoxy)benzene.

[0045]

Examples of diaminonaphthalene include 1,5-diaminonaphthalene and 2,6-diaminonaphthalene.

[0046]

Examples of aminophenylaminoindane include 5 or 6-amino-1(p-aminophenyl)-1,3,3-trimethylindane.

[0047]

Examples of the diaminotetraphenyl compound include 4,4'-bis(p-aminophenoxy)biphenyl, 2,2'-bis[p-(p'-aminophenoxy)phenyl]propane, 2,2'-bis[p-(p'-aminophenoxy)biphenyl]propane, and 2,2'-bis[p-(m-aminophenoxy)phenyl]benzophenone.

[0048]

Examples of the cardo-type fluorene diamine derivative include 9,9-bisaniline fluorene.

[0049]

The number of carbon atoms of the aliphatic diamine may be, for example, about 2 to 15. Specific examples of the aliphatic diamine include pentamethylene diamine, hexamethylene diamine, and heptamethylene diamine.

[0050]

The diamine may be a compound in which the hydrogen atom

is substituted with at least one substituent selected from the group consisting of a halogen atom, a methyl group, a methoxy group, a cyano group, and a phenyl group.

[0051]

Examples of a method for producing a polyamic acid include, but are not particularly limited to, a known method such as a method of reacting an acid and a diamine component in a solvent.

[0052]

A reaction between the tetracarboxylic dianhydride and the diamine is usually performed in a solvent. The solvent used for the reaction between the tetracarboxylic dianhydride and the diamine is not particularly limited as long as the solvent can dissolve the tetracarboxylic dianhydride and the diamine and does not react with the tetracarboxylic dianhydride and the diamine. The solvent may be used alone or in combination of two or more types thereof.

[0053]

Examples of the solvent used for the reaction between the tetracarboxylic dianhydride and the diamine include nitrogen-containing polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N-methylcaprolactam, and N,N,N',N'-tetramethylurea; lactone-based polar solvents such as β-propiolactone, γ-butyrolactone, γ-valerolactone, δ-valerolactone, γ-caprolactone, and ε-caprolactone; dimethylsulfoxide; acetonitrile; fatty acid esters such as

ethyl lactate and butyl lactate; ethers such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, dioxane, tetrahydrofuran, methyl cellosolve acetate, and ethyl cellosolve acetate; and phenolic solvents such as cresols and xylene mixed solvents. These solvents may be used alone or in combination of two or more types thereof. An amount of the solvent used is not particularly limited, but it is desirable that a content of the polyamic acid to be produced is 5 mass% to 50 mass%.

[0054]

As the solvent used for the reaction between the tetracarboxylic dianhydride and the diamine, the solvent (S) contained in the varnish, specifically, the nitrogen-containing polar solvent (S1) and the organic solvent (S2) contained as necessary are preferably used. When neither the nitrogen-containing polar solvent (S1) contained in the varnish nor the organic solvent (S2) contained as necessary is used as the solvent used for the reaction between the tetracarboxylic dianhydride and the diamine, the solvent may be substituted with the nitrogen-containing polar solvent (S1) or the organic solvent (S2) after the reaction.

[0055]

A polymerization temperature is generally -10°C to 120°C, preferably 5°C to 30°C. A polymerization time varies depending on the raw material composition used, but is usually 3 hours to 24 hours. The polyamic acid may be used alone or in combination of two or more types thereof.

[0056]

<Polyimide>

A structure and a molecular weight of the polyimide are not limited, and a known polyimide can be used. The polyimide may have, in a side chain, a condensable functional group, such as a carboxy group, or a functional group which promotes a crosslinking reaction or the like at the time of firing. In addition, a soluble polyimide soluble in the nitrogen-containing polar solvent (S1) contained in the varnish and the organic solvent (S2) contained as necessary is preferable.

[0057]

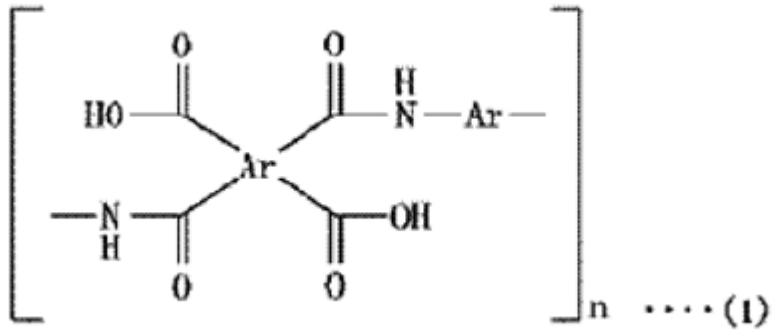
In order to obtain a polyimide which is soluble in the nitrogen-containing polar solvent (S1) and the organic solvent (S2) contained as necessary, it is effective to use a monomer for introducing a flexible bending structure into a main chain, for example, aliphatic diamines such as ethylene diamine, hexamethylene diamine, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, and 4,4'-diaminodicyclohexylmethane; aromatic diamines such as 2-methyl-1,4-phenylenediamine, o-tolidine, m-tolidine, 3,3'-dimethoxybenzidine, and 4,4'-diaminobenzanilide; polyoxyalkylene diamines such as polyoxyethylene diamine, polyoxypropylene diamine, and polyoxybutylenediamine; polysiloxane diamines; 2,3,3',4'-oxydiphthalic anhydride; 3,4,3',4'-oxydiphthalic anhydride; and 2,2-bis(4-hydroxyphenyl)propane dibenzoate-3,3',4,4'-tetracarboxylic dianhydride. In addition, it is also effective to use a monomer having a functional group that improves

solubility in a solvent, for example, a fluorinated diamine such as 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl or 2-trifluoromethyl-1,4-phenylenediamine. Further, in addition to the monomer for improving the solubility of the polyimide, a monomer the same as the monomer described in the above section on the polyamic acid may be used in combination as long as the solubility is not inhibited. The polyimide and the monomer thereof may be used alone or in combination of two or more types thereof.

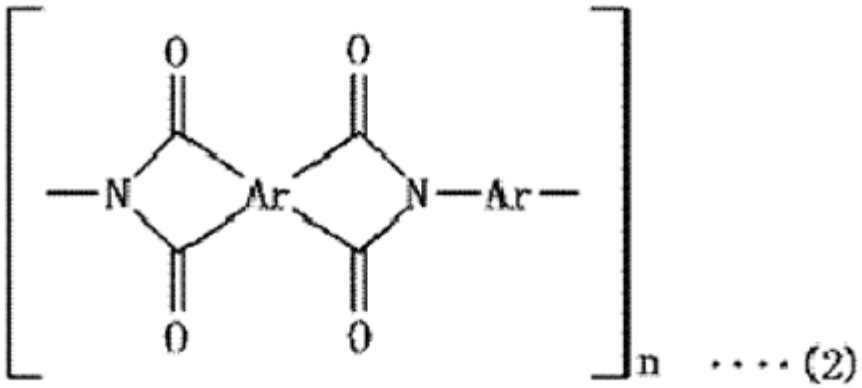
[0058]

The method for producing the polyimide is not particularly limited. For example, a known method such as a method in which a polyamic acid is chemically imidized or heated and imidized can be used. Examples of such a polyimide include aliphatic polyimides (full-aliphatic polyimides) and aromatic polyimides, and aromatic polyimides are preferable. Examples of the aromatic polyimide include polyimides obtained by subjecting a polyamic acid having a repeating unit represented by Formula (1) to a closed ring reaction by a thermal or chemical method, and polyimides having a repeating unit represented by Formula (2). In the formula, Ar represents an aryl group. The polyimides may be then dissolved in the nitrogen-containing polar solvent (S1) to be used or the organic solvent (S2) contained as necessary.

[Chem. 1]



[Chem. 2]



[0059]

<Polyamide Imide and Polyamide Imide Precursor>

A structure and a molecular weight of the polyamide imide are not limited, and a known polyamide imide can be used. The polyamide imide may have, in a side chain, a condensable functional group, such as a carboxy group, or a functional group which promotes a crosslinking reaction or the like at the time of firing. In addition, a soluble polyamide imide soluble in the nitrogen-containing polar solvent (S1) contained in the varnish and the organic solvent (S2) contained as necessary is preferable.

[0060]

As the polyamide imide, (i) a resin obtained by reacting

diisocyanate with an acid having a carboxy group and an acid anhydride group in one molecule such as trimellitic anhydride, (ii) a resin obtained by imidizing a precursor polymer (polyamide imide precursor) obtained by a reaction of a diamine with a reactive derivative of the acid such as trimellitic anhydride chloride, and the like can be generally used without particular limitation.

[0061]

Examples of the acid or a reactive derivative thereof include trimellitic anhydride halogenates such as trimellitic anhydride and trimellitic anhydride chloride, and trimellitic anhydride esters.

[0062]

Examples of the diamine include the diamine exemplified in the description of the polyamic acid. A diaminopyridine compound can also be used.

[0063]

Examples of the diisocyanate include, but are not particularly limited to, diisocyanate compounds corresponding to the diamine, and specific examples thereof include o-tolidine diisocyanate, p-phenylenediisocyanate, m-phenylenediisocyanate, 4,4'-oxy bis(phenyl isocyanate), 4,4'-diisocyanate diphenylmethane, bis[4-(4-isocyanatephenoxy)phenyl]sulfone, 2,2'-bis[4-(4-isocyanatephenoxy)phenyl]propane, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate,

3,3'-dimethyl diphenyl-4,4'-diisocyanate, 3,3'-diethyl diphenyl-4,4'-diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexyl methane diisocyanate, m-xylene diisocyanate, p-xylene diisocyanate, and naphthalene diisocyanate.

[0064]

As the raw material monomer of the polyamide imide, compounds described as general formulae in JPS63-283705A and JPH02-198619A can also be used in addition to the above. The imidization in the method (ii) may be either thermal imidization or chemical imidization. In the chemical imidization, a method of immersing the composite film (unfired composite film) formed using varnish containing a polyamide imide precursor or the like in acetic anhydride or a mixed solvent of acetic anhydride and isoquinoline can be used. The polyamide imide precursor may also be referred to as a polyimide precursor from the viewpoint of being a precursor before imidization.

[0065]

The polyamide imide contained in the varnish may be, for example, (1) a polymer obtained by reacting an acid such as trimellitic anhydride with diisocyanate, or (2) a polymer obtained by imidizing a precursor polymer obtained by reacting a reactive derivative of the acid such as trimellitic anhydride chloride with a diamine. In the present description and claims, the "polyamide imide precursor" means a polymer (precursor polymer) before imidization. Each of the polyamide

imide and the polyamide imide precursor may be used alone or in combination of two or more types thereof. Regarding the polyamide imide, each of the polymer, the raw material monomer, and the oligomer may be used alone or in combination of two or more types thereof.

[0066]

<Polyether Sulfone>

The polyether sulfone is not particularly limited as long as it is soluble in the nitrogen-containing polar solvent (S1) used in the varnish and the organic solvent (S2) contained as necessary. The polyether sulfone can be appropriately selected depending on the application of the porous film to be produced, and may be hydrophilic or hydrophobic. In addition, the polyether sulfone may be an aliphatic polyether sulfone or an aromatic polyether sulfone. A mass average molecular weight thereof is, for example, 5,000 to 1,000,000, and preferably 10,000 to 300,000.

[0067]

[Fine Particles (B)]

A material of the fine particles (B) is not particularly limited as long as it is insoluble in the solvent (S) contained in the varnish and may be removed from the composite film (resin-fine particle composite film) later, and any known material may be adopted. Examples of an inorganic material include metal oxides such as silica (silicon dioxide), titanium oxide, and alumina (Al_2O_3), and examples of an organic material include organic high-molecular-weight fine particles

such as a high-molecular-weight olefin (polypropylene, polyethylene, and the like), polystyrene, an epoxy resin, cellulose, polyvinyl alcohol, polyvinyl butyral, polyester, and polyether.

[0068]

Specific examples of the fine particles (B) include colloidal silica. Among these, monodisperse spherical silica particles are preferably selected because uniform pores can be formed.

[0069]

The fine particles (B) preferably have a high sphericity and a small particle diameter distribution index. The fine particles (B) satisfying these conditions are excellent in dispersibility in the varnish and can be used in a state where the fine particles do not aggregate with each other. An average particle diameter of the fine particles (B) to be used is, for example, preferably 10 nm or more and 500 nm or less, more preferably 50 nm or more and 300 nm or less, and still more preferably 70 nm or more and 150 nm or less. In the present description, the average particle diameter of the fine particles (B) is D50, and means the particle diameter at an integrated value of 50% in a volume-based particle size distribution determined by a laser diffraction/scattering method. The size of the pores derived from the fine particles (B) formed in the porous film is the same as or close to the average particle diameter of the fine particles (B). The fine particles (B) may be used alone or in combination of two or

more types thereof.

[0070]

[Solvent (S)]

The solvent (S) contained in the varnish contains the above-described nitrogen-containing polar solvent (S1). It is preferable that the solvent (S) contained in the varnish contains the above-described organic solvent (S2). The boiling points and specific examples of the nitrogen-containing polar solvent (S1) and the organic solvent (S2) are as described in «Porous Film» given above.

[0071]

In order to form a porous film, the solvent (S), the nitrogen-containing polar solvent (S1), and the organic solvent (S2) contained in the varnish are solvents that can dissolve the resin component (a) composed of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and/or a polyether sulfone contained in the varnish and do not dissolve the fine particles (B).

[0072]

In the varnish, when the solvent (S) contains the nitrogen-containing polar solvent (S1) and a solvent other than the nitrogen-containing polar solvent (S1) such as the organic solvent (S2), a ratio of a mass of the nitrogen-containing polar solvent (S1) to a mass of the solvent (S) is preferably 1 mass% or more and 95 mass% or less, more preferably 5 mass% or more and 90 mass% or less, and still more preferably 10 mass% or more and 80 mass% or less. A

content of the nitrogen-containing polar solvent (S1) in the varnish is preferably 100 parts by mass or more and 900 parts by mass or less, more preferably 200 parts by mass or more and 800 parts by mass or less, and still more preferably 300 parts by mass or more and 700 parts by mass or less with respect to 100 parts by mass of the resin component (a).

[0073]

[Dispersant]

In order to uniformly disperse the fine particles (B) in the varnish, a dispersant may be further added to the fine particles (B). By adding the dispersant, the fine particles (B) can be further uniformly mixed in the varnish, and furthermore, the fine particles (B) can be uniformly distributed in the film formed by the varnish. As a result, dense openings can be provided in a surface of the finally obtained porous film, and front and rear surfaces can efficiently communicate with one another, so that the air permeability of the porous film is improved. Further, by adding the dispersant, the drying property of the varnish is likely to be improved, and the releasability of the formed unfired composite film from the substrate or the like is likely to be improved.

[0074]

The dispersant is not particularly limited, and a known dispersant can be used. Examples thereof include, but are not limited to, anionic surfactants such as coconut fatty acid salts, salts of sulfonated castor oil, lauryl sulfate salts,

polyoxyalkylene allylphenyl ether sulfate salts, alkylbenzene sulfonic acids, alkylbenzene sulfonates, alkyldiphenyl ether disulfonates, alkylnaphthalenesulfonates, dialkyl sulfosuccinate salts, isopropyl phosphate, polyoxyethylene alkyl ether phosphate salts, polyoxyethylene allyl phenyl ether phosphate salts; cationic surfactants such as oleylamine acetate, laurylpyridinium chloride, cetylpyridinium chloride, lauryltrimethylammonium chloride, stearyltrimethylammonium chloride, behenyltrimethylammonium chloride, and didecyldimethylammonium chloride; amphoteric surfactants such as coconut alkyldimethylamine oxide, fatty acid amidopropyldimethylamine oxide, alkylpolyaminoethylglycine hydrochloride, amidobetaine-type surfactants, alanine-type surfactants, and lauryliminodipropionic acid; nonionic surfactants of polyoxyalkylene primary alkyl ethers or polyoxyalkylene secondary alkyl ethers such as polyoxyethylene octyl ether, polyoxyethylene decyl ether, polyoxyethylene lauryl ether, polyoxyethylene lauryl amine, polyoxyethylene oleylamine, polyoxyethylene polystyryl phenyl ether, and polyoxyalkylene polystyryl phenyl ether, and other polyoxyalkylene nonionic surfactants such as polyoxyethylene dilaurate, polyoxyethylene laurate, polyoxyethylene castor oil, polyoxyethylene hardened castor oil, sorbitan lauric acid ester, polyoxyethylene sorbitan lauric acid ester, and fatty acid diethanolamide; aliphatic alkyl esters such as octyl stearate and trimethylolpropane tridecanoate; and polyether polyols such as polyoxyalkylene butyl ether, polyoxyalkylene

oleate ether, and trimethylolpropane tris(polyoxyalkylene)ether. The dispersants may be used in combination of two or more types thereof.

[0075]

A content of the dispersant in the varnish is preferably 0.01 mass% or more and 5 mass% or less, more preferably 0.05 mass% or more and 1 mass% or less, and still more preferably 0.1 mass% or more and 0.5 mass% or less with respect to the mass of the fine particles (B), for example, from the viewpoint of film formability.

[0076]

A method for producing the composition (varnish) for producing a porous film is not particularly limited. The varnish is typically produced by a fine particle dispersion preparation step of dispersing the fine particles (B) in a solvent, a step of preparing a resin solution containing the resin component (a), and a kneading step of kneading the fine particle dispersion and the resin solution to adjust the concentration.

[0077]

The varnish preferably has a viscosity at 25°C of 0.1 Pa·s or more and 3 Pa·s or less, and preferably has a solid content concentration of 10 mass% or more and 50 mass% or less. The varnish is produced by kneading for preferably 2 minutes or longer and 10 hours or shorter, and more preferably 2 minutes or longer and 60 minutes or shorter. The viscosity of the varnish is measured by an E-type viscosity meter. For the

kneading of the varnish, a planetary centrifugal mixer (trade name: Awatori Rentaro (ARE), manufactured by THINKY CORPORATION), a planetary mixer, a bead mill, or the like can be used. In addition, in the kneading step, a dispersion treatment may be performed in which a dispersion device including a flow path having a cross-sectional area of 1,960 μm^2 or more and 785,000 μm^2 or less is used, and a mixed solution (slurry) containing the fine particle dispersion and the resin solution in a state of being pressurized to 50 MPa or more is passed through the flow path. As a method of performing the dispersion treatment of causing the mixed solution to pass through such a flow path, a method described in JP2020-104105A is exemplified.

[0078]

A composite film (hereinafter also referred to as "unfired composite film") may be directly formed on a substrate, or may be formed on a lower layer film different from the unfired composite film. In addition, an upper layer film different from the unfired composite film may be further formed as an upper layer after forming an unfired composite film using the varnish (porous film-producing composition). In the present application, a method of providing a lower layer film on a substrate and a method of forming an upper layer film different from the unfired composite film on an upper layer after forming the unfired composite film using the varnish are included in the method of forming an unfired composite film on a substrate. However, in the case where the resin component

(a) contained in the varnish is a polyamic acid or a polyamide imide precursor, and a material not requiring a firing step is used for the upper layer film, the upper layer film may be formed on the resin-fine particle composite film after firing. The composite film (unfired composite film) made of the varnish is preferably formed as a single-layer film on the substrate. Examples of the substrate include a PET film, a SUS substrate, and a glass substrate.

[0079]

Examples of the lower layer film (or upper layer film) include a lower layer (or upper layer) unfired composite film formed using a varnish for a lower layer (or upper layer) film containing a resin component composed of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and/or a polyether sulfone, fine particles, and a solvent, the content of the fine particles being more than 40 vol% and 81 vol% or less with respect to the total of the resin component and the fine particles. The lower layer (or upper layer) unfired composite film may be formed on the substrate. Since when the content of the fine particles is more than 40 vol%, the particles are uniformly dispersed, and when the content of the fine particles is 81 vol% or less, the particles are dispersed without being aggregated with one another, pores can be uniformly formed in the porous film. In addition, in a case where the content of the fine particles is within the above range, when the lower layer (or upper layer) unfired composite film is formed on the substrate, the releasability after film

formation is easily secured even if a release layer is not provided in advance on the substrate.

[0080]

The fine particles used in the varnish for the lower layer (or upper layer) film and the fine particles (B) used in the varnish may be the same as or different from each other. In order to make the pores in the lower layer (or upper layer) unfired composite film denser, the fine particles used in the varnish for the lower layer (or upper layer) film preferably have a smaller particle diameter distribution index or the same particle diameter distribution index as that of the fine particles (B) used in the above-described varnish. Alternatively, the fine particles used in the varnish for the lower layer (or upper layer) film preferably have a lower sphericity or the same sphericity as the fine particles (B) used in the above-described varnish.

[0081]

An average particle diameter of the fine particles used in the varnish for the lower layer (or upper layer) film may be the same as or different from the average particle diameter of the fine particles (B) of the above-described varnish. The average particle diameter may be appropriately set in a range of 10 nm or more and 5,000 nm or less according to the application. When a varnish for a lower layer (or upper layer) film is used, it is preferable to use a varnish for a lower layer film having a different average particle diameter of fine particles, a different particle diameter distribution

index, or the like in combination with the above-described varnish as an upper layer.

[0082]

A content of the fine particles in the varnish for forming a lower layer (or upper layer) film may be larger or smaller than that of the above-described varnish. Preferable examples of the components such as the resin component, the fine particles, and the solvent contained in the varnish for forming a lower layer (or upper layer) film are the same as those in the above-described varnish. The varnish for forming a lower layer (or upper layer) film can be prepared by the same method as that for the above-described varnish. The lower layer unfired composite film can be formed by, for example, coating a substrate with the varnish for forming a lower layer film and drying the varnish at a normal pressure or under vacuum at 0°C to 100°C, preferably a normal pressure at 10°C to 100°C. The same applies to the film formation conditions of the upper layer unfired composite film.

[0083]

Examples of the lower layer (or upper layer) film include a lower layer film made of a fibrous material such as a cellulose-based resin or a nonwoven fabric (for example, polyimide nonwoven fabric, having
a fiber diameter of, for example, about 50 nm to about 3,000 nm) and a polyimide film.

[0084]

Further, a firing step of firing the unfired composite

film or a laminated film of the unfired composite film and the lower layer (or upper layer) film to obtain a polyimide-fine particle composite film is started. When the unfired composite film or the lower layer unfired composite film is formed on the substrate, the unfired composite film or the lower layer unfired composite film may be fired as it is, or the unfired composite film or the laminated film of the unfired composite film and the lower layer unfired composite film may be peeled off from the substrate before the firing step.

[0085]

When the lower layer (or upper layer) film in the laminated film is a lower layer (or upper layer) unfired composite film formed using a varnish for a lower layer (or upper layer) film, and the composition of the varnish for a lower layer (or upper layer) film is the same as the composition of the above-described varnish, the laminated film of the composite film (unfired composite film) and the lower layer (or upper layer) film is substantially one layer (single layer), but is referred to as a laminated film in the present description.

[0086]

When the composite film (unfired composite film) or the laminate film of the unfired composite film and the lower layer (or upper layer) unfired composite film is to be peeled off from the substrate, a substrate provided with a release layer in advance may be used in order to further enhance the peeling property of the film. When a release layer is to be

provided on the substrate in advance, a release agent is applied onto the substrate before applying the varnish, followed by drying or firing. As the release agent used here, a known release agent such as an ammonium alkylphosphate, fluorine, or silicon can be used without particular limitation. At the time of peeling off the unfired composite film from the substrate, the release agent slightly remains on a peeled surface of the unfired composite film, which causes discoloration and a bad influence on electrical characteristics during firing, and thus it is preferable to remove the release agent as much as possible. For the purpose of removing the release agent, a cleaning step of cleaning the unfired composite film or the laminated film of the unfired composite film and the lower layer unfired composite film peeled off from the substrate using an organic solvent may be introduced.

[0087]

On the other hand, when the substrate is used as it is without being provided with a release layer in the formation of the unfired composite film or the lower layer unfired composite film, the step of forming a release layer and the cleaning step can be omitted. In the production of the unfired composite film, an immersion step in a solvent containing water, a press step, and a drying step after the immersion step may be provided as freely selected steps.

[0088]

[Heating Step]

In the heating step, the composite film (unfired composite film) is heated to remove a part of the solvent (S) from the composite film such that the content of the nitrogen-containing polar solvent (S1) in the produced porous film is 10 ppm or more and 2,000 ppm or less. The heating step may be referred to as a drying step because the solvent is removed. The content of the nitrogen-containing polar solvent (S1) in the produced porous film can be adjusted to 10 ppm or more and 2,000 ppm or less by controlling the conditions of the heating step in accordance with the components contained in the varnish and the amount thereof. A heating temperature is, for example, preferably 40°C or higher and 170°C or lower, and more preferably 60°C or higher and 145°C or lower. The heating step may be performed under a normal pressure, a reduced pressure, or vacuum.

[0089]

[Firing Step (Production of Resin-Fine Particle Composite Film)]

The firing step is a step of firing the composite film during the heating step or after the heating step and before the fine particle removing step. The firing step may be performed after the heating step (drying step), or may be performed during the heating step. That is, heating in the firing step may also serve as heating (drying) in the heating step.

[0090]

When the resin component (a) contained in the varnish

contains a polyamic acid and/or a polyamide imide precursor, a composite film (resin-fine particle composite film) composed of a resin composed of a polyimide and/or a polyamide imide and fine particles (B) is formed by subjecting the composite film (unfired composite film) to the firing step. When the resin component contained in the varnish is a polyimide, a polyamide imide, or a polyether sulfone, the firing step may be included, but the firing step may be omitted.

[0091]

When the unfired composite film is formed on a lower layer film different from the unfired composite film in the composite film forming step, the lower layer film is also fired together with the unfired composite film in the firing step.

[0092]

A firing temperature in the firing step is preferably 120°C or higher and 450°C or lower, more preferably 150°C or higher and 420°C or lower, although it varies depending on a structure of the composite film and the lower layer film and presence or absence of a condensation agent. When an organic material is used for the fine particles (B), it is necessary to set a temperature lower than a thermal decomposition temperature thereof. When the resin component (a) contained in the varnish is a polyamic acid, the imidization is preferably completed in the firing step.

[0093]

Firing conditions may be, for example, a method in which

the temperature is increased to a room temperature or higher and 400°C or lower for 3 hours and then held at 400°C for 20 minutes, or a stepwise drying-thermal imidization method in which the temperature is increased in a stepwise manner from a room temperature to 400°C at intervals of 50°C (held for 20 minutes in each step) and finally held at 400°C for 20 minutes. When an unfired composite film is formed on a substrate and the unfired composite film is once peeled off from the substrate, a method of fixing an end of the unfired composite film to a mold made of SUS or the like to prevent deformation may be employed.

[0094]

A film thickness of the obtained resin-fine particle composite film can be obtained by measuring thicknesses of a plurality of portions with, for example, a micrometer and averaging the thicknesses. The preferable average film thickness varies depending on the application of the porous film, but for example, when used for a separator or the like, the average film thickness is preferably 5 μm or more and 500 μm or less, more preferably 10 μm or more and 100 μm or less, and still more preferably 15 μm or more and 30 μm or less. When used for a filter or the like, the average film thickness is preferably 5 μm or more and 500 μm or less, more preferably 10 μm or more and 300 μm or less, and still more preferably 20 μm or more and 150 μm or less.

[0095]

[Fine Particle Removing Step (Pore Formation of Resin-Fine

Particle Composite Film)]

In the fine particle removing step, the fine particles (B) are removed from the composite film after the heating step (when firing step is performed, composite film (resin-fine particle composite film) after firing step). By selecting an appropriate method to remove the fine particles (B), a porous film can be produced with good reproducibility.

[0096]

When silica, for example, is adopted as the material of the fine particles (B), it is possible to dissolve and remove the silica by treating the resin-fine particle composite film with low-concentration hydrogen fluoride water or the like.

[0097]

An organic material can also be selected as the material of the fine particles (B). The organic material is not particularly limited as long as it is decomposed at a lower temperature than the resin contained in the resin-fine particle composite film. Examples thereof include resin fine particles made of a linear polymer or a known depolymerizable polymer. A typical linear polymer is a polymer in which molecular chains of the polymer are randomly cleaved during thermal decomposition, and a depolymerizable polymer is a polymer in which the polymer is decomposed into a monomer during thermal decomposition. Both of the typical linear polymer and the depolymerizable polymer disappear from the porous film by being decomposed into low-molecular-weight substances or CO_2. A decomposition temperature of the resin

fine particles used is preferably 230°C or higher and 320°C or lower.

[0098]

An overall film thickness of the porous film is not particularly limited, but for example, when the porous film is used for a separator or the like, the overall film thickness thereof is preferably 5 μm or more and 500 μm or less, more preferably 10 μm or more and 100 μm or less, and still more preferably 15 μm or more and 30 μm or less. When used for a filter or the like, the overall film thickness thereof is preferably 5 μm or more and 500 μm or less, more preferably 10 μm or more and 300 μm or less, and still more preferably 20 μm or more and 150 μm or less. The film thickness can be obtained by, for example, measuring thicknesses of a plurality of portions with a micrometer or the like and averaging the thicknesses, as in the measurement of the resin-fine particle composite film.

[0099]

When the porous film is formed of two or more types of compositions for producing a porous film, a ratio in a thickness direction of a region formed by each porous film-producing composition may be appropriately set according to the application of the porous film. In the case of a porous film having two regions of a layer (I) formed by a porous film-producing composition and a layer (II) formed by another porous film-producing composition, a ratio in the thickness direction of each region ((I):(II)) is, for example, in a

range of 1:99 to 99:1, and preferably in a range of 5:95 to 95:5. The thickness of each layer can be calculated by observing a plurality of portions of a cross section of the porous film with a scanning electron microscope (SEM) or the like and averaging them.

[0100]

[Resin Removing Step]

The method for producing a porous film may include a resin removing step of removing at least a part of a resin portion of the resin-fine particle composite film before the fine particle removing step, or removing at least a part of the porous film after the fine particle removing step. By removing at least a part of the resin portion of the resin-fine particle composite film or at least a part of the porous film, the porosity of the porous film of the final product may be improved as compared with the case where neither at least a part of the resin portion of the resin-fine particle composite film nor at least a part of the porous film is removed.

[0101]

The step of removing at least a part of the resin portion or the step of removing at least a part of the porous film can be performed by an ordinary chemical etching method, a physical removal method, or a combination thereof.

[0102]

Examples of the chemical etching method include a treatment using a chemical etching solution such as an inorganic alkali solution or an organic alkali solution. An

inorganic alkali solution is preferable. Examples of the inorganic alkali solution include hydrazine solutions containing hydrazine hydrate and ethylene diamine, a solution of an alkali metal hydroxide such as potassium hydroxide, sodium hydroxide, sodium carbonate, sodium silicate, and sodium metasilicate, an ammonia solution, and an etching solution containing alkali hydroxide, hydrazine, and 1,3-dimethyl-2-imidazolidinone as main components. Examples of the organic alkali solution include alkaline solutions of primary amines such as ethyl amine and n-propylamine; secondary amines such as diethyl amine and di-n-butyl amine; tertiary amines such as triethyl amine and methyl diethyl amine; alcoholic amines such as dimethyl ethanol amine and triethanol amine; quaternary ammonium salts such as tetramethylammonium hydroxide and tetraethylammonium hydroxide; and cyclic amines such as pyrrole and piperidine.

[0103]

As the solvent of each of the above solutions, pure water and alcohols can be appropriately selected. A solvent in which a surfactant is added in an appropriate amount may also be used. An alkali concentration is, for example, 0.01 mass% to 20 mass%.

[0104]

In addition, as the physical method, for example, dry etching by plasma (oxygen, argon, or the like), corona discharge, or the like, or a method of performing a surface treatment by dispersing a polishing agent (for example,

alumina (hardness of 9)) in a liquid and irradiating the surface of the film with the polishing agent at a speed of 30 m/s to 100 m/s can be used.

[0105]

The above-described method is preferably applicable to any resin removing step before or after the fine particle removing step.

[0106]

On the other hand, as a physical method applicable only to the resin removing step performed after the fine particle removing step, a method may be adopted in which the porous film is peeled off from a mount film (for example, polyester film such as PET film) after a target surface is pressed to the mount film wet with a liquid and then dried or not dried. Due to a surface tension or a static adhesive force of the liquid, the porous film is peeled off from the mount film in a state where only a surface layer of the porous film remains on the mount film.

[0107]

The method for producing a porous film described above makes it possible to improve (increase) the flow rate of the fluid (liquid or gas) that passes through the porous film, and thus to cope with both reduction in pore diameter and improvement in flow rate. Accordingly, it becomes possible to produce a porous film having a small pore diameter and a large flow rate.

EXAMPLES

[0108]

Although the present invention will be more specifically described below using Examples, the scope of the present invention is not limited to Examples below.

[0109]

[Examples 1 to 20 and Comparative Examples 1 to 8]

To a polyamic acid solution, a silica dispersion (including dispersant of 0.5 mass% with respect to silica described in Table 1) was added such that an amount of a polyamic acid was 30 mass% and a mass of the silica was 70 mass% with respect to a total of the mass of the polyamic acid (resin component (a)) and the mass of the silica (fine particles (B)). Further, as a solvent (S), a nitrogen-containing polar solvent (S1), an organic solvent (S2), and/or an organic solvent (S') corresponding to neither the nitrogen-containing polar solvent (S1) nor the organic solvent (S2) were added such that a composition of the solvent (S) in a final composition (porous film-producing composition (varnish)) as a whole was the mass% shown in Table 1. The obtained mixed solution was dispersed in a container having a capacity of 1,000 mL by stirring with a stirring blade at 4,000 rpm for 30 minutes. Thereafter, a dispersion treatment was performed 10 times using a dispersion device provided with a flow path having a diameter of 60 μm (cross-sectional area of 2,826 μm^2) manufactured by Yoshida Kikai Co., Ltd., in which the mixed solution was allowed to pass through the flow path

at 200 MPa, to prepare a composition (varnish) for producing a porous film having a solid content concentration of 30 mass%. A ratio of the polyamic acid to the silica (polyamic acid: silica) in the obtained varnish was 38:62 in volume ratio and 30:70 in mass ratio. The following polyamic acid solution, organic solvent, dispersant, and fine particles were used.

·Polyamic acid solution: reaction product of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether (solid content of 20 mass% (organic solvent: N,N-dimethylacetamide))

·Nitrogen-containing polar solvent (S1): N-methylpyrrolidone (NMP) or 1,3-dimethyl-2-imidazolidinone (DMI)

·Organic solvent (S2): N,N-dimethylacetamide (DMAc)

·Organic solvent (S'): γ-butyrolactone (GBL)

·Dispersant: polyoxyethylene secondary alkyl ether-based dispersant

·Fine particles (B): silica having an average particle diameter of 100 nm, silica having an average particle diameter of 80 nm, or silica having an average particle diameter of 50 nm

[0110]

The obtained porous film-producing composition was coated onto a polyethylene terephthalate (PET) film as a substrate using an applicator to form a composite film on the substrate (composite film forming step). Next, the composite film (unfired composite film) was heated at 90°C for 5 minutes to remove a part of the solvent (S) (heating step). The composite film after the heating step was placed in an oven and fired at

380°C for 15 minutes to complete imidization, thereby obtaining a resin-fine particle composite film (firing step). Then, the resin-fine particle composite film was peeled off from the substrate. The peeled resin-fine particle composite film was immersed in hydrogen fluoride (HF) for 10 minutes to remove silica fine particles contained in the film (fine particle removing step). Thereafter, the resin-fine particle composite film was washed with water and dried to obtain polyimide porous films of Examples 1 to 20 and Comparative Examples 1 to 8 each having a film thickness of 40 μm.

[0111]

For the obtained polyimide porous films of Examples and Comparative Examples, a content of the nitrogen-containing polar solvent (S1), an IPA flow rate (FR), a bubble point (BP), and a tensile strength were measured according to the following methods. The results are shown in Table 2.

[0112]

[Content of Nitrogen-Containing Polar Solvent (S1)]

Acetone (10 g) was added to 0.1 g of the polyimide porous film, followed by stirring for 3 hours to remove the polyimide porous film, thereby preparing a measurement solution. The measurement solution was measured by GC-MS (GC: 7820A, MS: 5977E, manufactured by Agilent) to determine the content of the nitrogen-containing polar solvent (S1).

[0113]

[IPA Flow Rate (FR)]

Each polyimide porous film was cut into a membrane filter

size having a diameter of 47 mm and attached to an in-line filter holder. Next, isopropyl alcohol (IPA) was pressurized with air of 0.1 MPa and filtered from a primary side (upstream side of flow path of porous film), and the flow rate thereof was measured. The measurement was performed at 25°C. In Table 2, the number of mL per minute per 1 cm^2 is displayed.

[0114]

[Bubble Point (BP)]

The bubble point (BP) was measured in accordance with ASTM F316-86 and JIS K 3832. Specifically, each polyimide porous film was cut into a membrane filter size having a diameter of 47 mm and attached to a bubble point measurement holder. A secondary side of the film (downstream side of flow path of porous film) was wet with a fluorine-based solvent (Novec 7200, manufactured by 3M, hydrofluoroether), and gradually pressurized with air from the primary side, to measure the pressure at which bubbles were generated on the secondary side. The measurement was performed at a room temperature (25°C).

[0115]

[Tensile Strength]

Each polyimide porous film was cut into a dumbbell shape No. 6 to prepare a test piece. A small desktop tester EZ Test EZ-SX (manufactured by Shimadzu Corporation) was used as a tester to measure a stress at break (tensile strength (MPa)) of the test piece under measurement conditions of 25°C and 5 mm/min in accordance with JIS K 7127.

[0116]

[Table 1]

	Porous film-producing composition				
	Fine particles (B)	Solvent (S)			
	Silica	Nitrogen-containing polar solvent (S1)		Organic solvent (S2)	Organic solvent (S')
	Average particle diameter	DMI	NMP	DMAc	GBL
		mass %	mass %	mass %	mass%
Example 1	100 nm	70	0	30	0
Example 2	100 nm	60	0	40	0
Example 3	100 nm	50	0	50	0
Example 4	100 nm	40	0	60	0
Example 5	100 nm	30	0	70	0
Example 6	100 nm	20	0	80	0
Example 7	100 nm	10	0	90	0
Example 8	100 nm	0	70	30	0
Example 9	100 nm	0	50	50	0
Example 10	100 nm	0	10	90	0
Example 11	100 nm	40	20	40	0
Example 12	100 nm	30	20	50	0
Example 13	100 nm	20	20	60	0
Example 14	100 nm	10	20	70	0
Example 15	100 nm	20	40	40	0
Example 16	100 nm	20	30	50	0
Example 17	100 nm	20	20	60	0
Example 18	100 nm	20	10	70	0
Example 19	80 nm	20	20	60	0
Example 20	50 nm	20	20	60	0
Comparative Example 1	100 nm	80	0	20	0
Comparative Example 2	100 nm	5	0	95	0
Comparative Example 3	100 nm	0	5	95	0
Comparative Example 4	100 nm	4	4	92	0
Comparative Example 5	100 nm	0	0	100	0
Comparative Example 6	100 nm	0	0	90	10
Comparative Example 7	80 nm	0	0	100	0
Comparative Example 8	50 nm	0	0	100	0

[0117]

[Table 2]

	Content in porous film				Evaluation result		
	Nitrogen-containing polar solvent (S1)		Organic solvent (S2)	Organic solvent (S')	IPA FR (mL/(min·cm^2))	BP (psi)	Film strength (MPa)
	DMI	NMP	DMAc	GBL			
	ppm by mass	ppm by mass	ppm by mass	ppm by mass			
Example 1	2000	0	100	0	0.28	90	33
Example 2	1500	0	200	0	0.27	95	32
Example 3	1000	0	400	0	0.26	100	31
Example 4	500	0	900	0	0.25	100	30
Example 5	300	0	1400	0	0.24	100	29
Example 6	100	0	1400	0	0.23	100	28
Example 7	20	0	1400	0	0.22	100	27
Example 8	0	1000	900	0	0.25	95	31
Example 9	0	500	1200	0	0.24	100	30
Example 10	0	10	1400	0	0.22	100	27
Example 11	500	50	200	0	0.27	95	38
Example 12	300	50	400	0	0.24	100	31
Example 13	100	50	900	0	0.23	100	29
Example 14	20	50	1400	0	0.22	100	27
Example 15	100	250	200	0	0.26	95	38
Example 16	100	150	400	0	0.24	100	31
Example 17	100	50	900	0	0.23	100	29
Example 18	100	10	1400	0	0.22	100	27
Example 19	100	50	900	0	0.12	150	40
Example 20	100	50	900	0	0.06	200	50
Comparative Example 1	2100	0	100	0	0.30	85	40
Comparative Example 2	5	0	1400	0	0.20	100	25
Comparative Example 3	0	5	1400	0	0.20	100	25
Comparative Example 4	4	4	920	0	0.20	100	25
Comparative Example 5	0	0	900	0	0.20	100	25
Comparative Example 6	0	0	900	100	0.20	100	25
Comparative Example 7	0	0	900	0	0.06	150	45
Comparative Example 8	0	0	900	0	0.03	200	55

[0118]

As shown in Tables 1 and 2, Examples 1 to 18, which are

produced using the fine particles (B) having an average particle diameter of 100 nm and in which the content of the nitrogen-containing polar solvent (S1) in the porous film is in the range of 10 ppm or more and 2,000 ppm or less, have the bubble points the same as or similar to that of Comparative Example 5, which is produced using the fine particles (B) having an average particle diameter of 100 nm and in which the porous film does not contain the nitrogen-containing polar solvent (S1). That is, it can be said that Examples 1 to 18 are porous films not containing the nitrogen-containing polar solvent (S1) and having a pore diameter as small as that of Comparative Example 5. In addition, Examples 1 to 18 have a higher IPA flow rate (FR) and a larger flow rate than those of Comparative Example 5. Accordingly, it can be said that the porous films of Examples 1 to 18 have small pore diameters and improved flow rates. Examples 1 to 18 have a higher film strength than that of Comparative Example 5. On the other hand, it is understood that the porous films of Comparative Examples 1 to 4, which are produced using the fine particles (B) having an average particle diameter of 100 nm and in which the content of the nitrogen-containing polar solvent (S1) in the porous film is out of the range of 10 ppm or more and 2,000 ppm or less, have a small flow rate or a large pore diameter. Example 19, which is produced using the fine particles (B) having an average particle diameter of 80 nm and in which the content of the nitrogen-containing polar solvent (S1) in the porous film is in the range of 10 ppm or more and

2,000 ppm or less, has a bubble point the same as or similar to that of Comparative Example 7, which is produced using the fine particles (B) having an average particle diameter of 80 nm and in which the porous film does not contain the nitrogen-containing polar solvent (S1). That is, it can be said that Example 19 is a porous film not containing the nitrogen-containing polar solvent (S1) and having a pore diameter as small as that of Comparative Example 7. In addition, Example 19 has a higher IPA flow rate (FR) and a larger flow rate than those of Comparative Example 7. Accordingly, it can be said that the porous film of Example 19 has a small pore diameter and an improved flow rate.

[0119]

Example 20, which is produced using the fine particles (B) having an average particle diameter of 50 nm and in which the content of the nitrogen-containing polar solvent (S1) in the porous film is in the range of 10 ppm or more and 2,000 ppm or less, has a bubble point the same as or similar to that of Comparative Example 8, which is produced using the fine particles (B) having an average particle diameter of 50 nm and in which the porous film does not contain the nitrogen-containing polar solvent (S1). That is, it can be said that Example 20 is a porous film not containing the nitrogen-containing polar solvent (S1) and having a pore diameter as small as that of Comparative Example 8. In addition, Example 20 has a higher IPA flow rate (FR) and a larger flow rate than those of Comparative Example 8. Accordingly, it can be said

that the porous film of Example 20 has a small pore diameter and an improved flow rate.

CLAIMS

[Claim 1]

A porous film comprising: at least one resin component (A) selected from the group consisting of a polyimide, a polyamide imide, and a polyether sulfone; and a solvent (S),

the solvent (S) containing a nitrogen-containing polar solvent (S1) having a boiling point of 200°C or higher at atmospheric pressure,

a content of the nitrogen-containing polar solvent (S1) in the porous film being 10 ppm or more and 2,000 ppm or less.

[Claim 2]

The porous film according to claim 1, wherein the nitrogen-containing polar solvent (S1) is at least one selected from the group consisting of a nitrogen-containing heterocyclic compound which optionally has a substituent and an aromatic hydrocarbon substituted with a nitrogen-containing group.

[Claim 3]

The porous film according to claim 2, wherein the nitrogen-containing polar solvent (S1) is at least one selected from the group consisting of 1,3-dimethyl-2-imidazolidinone, N-methylpyrrolidone, N-ethyl-2-pyrrolidone, and nitrobenzene.

[Claim 4]

The porous film according to claim 1, wherein the solvent (S) contains an organic solvent (S2) having a boiling point of

lower than 200°C at atmospheric pressure.

[Claim 5]

The porous film according to claim 4, wherein the organic solvent (S2) is an aliphatic amide-based solvent.

[Claim 6]

The porous film according to claim 5, wherein the organic solvent (S2) is dimethylacetamide.

[Claim 7]

The porous film according to claim 1, wherein a content of the solvent (S) in the porous film is 10 ppm or more and 2,100 ppm or less.

[Claim 8]

A method for producing the porous film according to any one of claims 1 to 7, comprising:

a composite film forming step of forming, on a substrate, a composite film made of a porous film-producing composition containing at least one resin component selected from the group consisting of a polyamic acid, a polyimide, a polyamide imide precursor, a polyamide imide, and a polyether sulfone, fine particles (B), and a solvent (S);

a heating step of heating the composite film; and

a fine particle removing step of removing the fine particles (B) from the composite film after the heating step,

wherein the solvent (S) contains the nitrogen-containing polar solvent (S1), and

in the heating step, a part of the solvent (S) is removed from the composite film such that a content of the nitrogen-

containing polar solvent (S1) in the porous film to be produced is 10 ppm or more and 2,000 ppm or less.