adding an organic compound having a polar group, or a polymer having a polar group, either of which was indispensable in the production of a porous polyimide film according to PTL 1 and 2.

MEANS FOR SOLVING THE PROBLEMS

[0007]

The present invention includes the following aspects.

[1]

A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid); and

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, wherein each of the shrinkage ratios in the longitudinal direction and the transverse direction of the film after heat treatment is suppressed to 8% or lower, and the temperature rising rate in the temperature region of 200°C or higher in the heat treatment is 25°C/min or higher,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

[1a]

A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number, determined by the method of measurement according to paragraphs [0082] to [0085] of the description, of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid); and

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, wherein each of the shrinkage ratios, determined by the method of measurement according to paragraph [0086] of the description, in the longitudinal direction and the transverse direction of the film after heat treatment is suppressed to 8% or lower, and the temperature rising rate in the temperature region of 200°C or higher in the heat treatment is 25°C/min or higher,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value, determined by the method of measurement according to paragraph [0075] of the description, being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

[2]

The method for producing a porous polyimide film according to [1], wherein the

poly(amic acid) comprises at least one tetracarboxylic dianhydride selected from the group consisting of biphenyltetracarboxylic dianhydride and pyromellitic dianhydride; and at least one diamine selected from the group consisting of benzenediamine, diaminodiphenyl ether and bis(aminophenoxy)phenyl.

[3]

The method for producing a porous polyimide film according to [1] or [2], wherein the coagulating solvent comprising water as an essential component is water, or a mixed solution of 5% by mass or more and less than 100% by mass of water, and more than 0% by mass to 95% by mass or less, of an organic polar solvent.

[4]

The method for producing a porous polyimide film according to any one of [1] to [3], further comprising the step of subjecting at least one surface of the porous polyimide film obtained in the step (2) to plasma treatment.

[5]

A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid);

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, and

(3) subjecting at least one surface of the porous polyimide film obtained in the step (2) to plasma treatment,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a

plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

[5a]

A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number, determined by the method of measurement according to paragraphs [0082] to [0085] of the description, of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid);

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, and

(3) subjecting at least one surface of the porous polyimide film obtained in the step (2) to plasma treatment,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the

macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value, determined by the method of measurement according to paragraph [0075] of the description, being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

[6]

A porous polyimide film produced by the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid); and

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, wherein each of the shrinkage ratios in the longitudinal direction and the transverse direction of the film after heat treatment is suppressed to 8% or lower, and the temperature rising rate in the temperature region of 200°C or higher in the heat treatment is 25°C/min or higher,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

CLAIMS

1. A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number, determined by the method of measurement according to paragraphs [0082] to [0085] of the description, of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid); and

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, wherein each of the shrinkage ratios, determined by the method of measurement according to paragraph [0086] of the description, in the longitudinal direction and the transverse direction of the film after heat treatment is suppressed to 8% or lower, and the temperature rising rate in the temperature region of 200°C or higher in the heat treatment is 25°C/min or higher,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value, determined by the method of measurement according to paragraph [0075] of the description, being not more than 20 sec/100 cc, and a porosity being 60% to 95%.

2. The method for producing a porous polyimide film according to claim 1, wherein the poly(amic acid) comprises at least one tetracarboxylic dianhydride selected from the group consisting of biphenyltetracarboxylic dianhydride and pyromellitic dianhydride; and at least one diamine selected from the group consisting of benzenediamine, diaminodiphenyl ether and bis(aminophenoxy)phenyl.

3. The method for producing a porous polyimide film according to claim 1 or 2, wherein the coagulating solvent comprising water as an essential component is water, or a mixed solution of 5% by mass or more and less than 100% by mass of water, and more than 0% by mass to 95% by mass or less, of an organic polar solvent.

4. The method for producing a porous polyimide film according to any one of claims 1 to 3, further comprising the step of subjecting at least one surface of the porous polyimide film obtained in the step (2) to plasma treatment.

5. A method for producing a porous polyimide film, the method comprising the steps of:

(1) casting a poly(amic acid) solution consisting of 3 to 60% by mass of a poly(amic acid) having an limiting viscosity number, determined by the method of measurement according to paragraphs [0082] to [0085] of the description, of 1.0 to 3.0, the poly(amic acid) consisting of tetracarboxylic acid unit and diamine unit, and 40 to 97% by mass of an organic polar solvent into a film-like shape, and dipping in or bringing it into contact with a coagulating solvent comprising water as an essential component to prepare a porous film of poly(amic acid);

(2) imidizing the porous film of a poly(amic acid) obtained in the step (1) by heat treatment, and

(3) subjecting at least one surface of the porous polyimide film obtained in the step (2) to plasma treatment,

wherein the porous polyimide film is a three-layer structure porous polyimide film having two surface layers (a) and (b), and a macrovoid layer sandwiched between the surface layers (a) and (b),

the macrovoid layer has partition walls bonded to the surface layers (a) and (b), and a plurality of macrovoids surrounded by the partition walls and the surface layers (a) and (b) and having a mean pore size in the film plane direction of from 10 to 500 μm,

the partition walls of the macrovoid layer have a thickness of 0.1 μm to 50 μm,

at least one partition walls have one or a plurality of pores communicating adjacent macrovoids,

each of the surface layers (a) and (b) has a thickness of 0.1 μm to 50 μm,

at least one of the surface layers (a) and (b) has a plurality of fine pores having an average pore diameter of more than 5 μm and not more than 200 μm, while the other has a plurality of fine pores having an average pore diameter of 0.01 μm to 200 μm;

the surface opening ratio of at least one of the surface layer is not less than 10%, while that of the other surface layer is not less than 5%;

the fine pores in the surface layers (a) and (b) communicate with the macrovoids; and

the porous polyimide film has a total film thickness of 5 μm to 500 μm, the Gurley value, determined by the method of measurement according to paragraph [0075] of the description, being not more than 20 sec/100 cc, and a porosity being 60% to 95%.