

TITLE OF INVENTION

WHOLLY AROMATIC POLYAMIDE FIBER PAPER AND LAMINATED SHEET THEREFORM

5

BACKGROUND OF THE INVENTION

The present invention pertains to a completely aromatic polyamide fiber paper that comprises completely aromatic polyamide fiber. The paper can be used to
10 manufacture the substrate of an electric circuit. The fiber paper of the present invention is useful in the fields, which have high requirements for electric insulation reliability under high humidity, dimensional stability, soldering heat resistance, and strength.

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SUMMARY OF THE INVENTION

A base material made of completely aromatic polyamide fiber paper characterized by the following facts: the fiber paper is mainly composed of completely
20 aromatic polyamide fiber formed by spinning from an anisotropic polymer solution and which is capable of deionization; the crystallinity of the fiber paper is 45% or higher; and the crystal size (ACS: Apparent Crystallinity Size (plane 110) is 50 Å or larger.

25

DETAILED DESCRIPTION OF THE INVENTION

Completely aromatic polyamide fiber is widely used in industry and daily life because of its high strength, high modulus, high heat resistance, and other excellent
30 mechanical and thermal properties. Typical examples of such synthetic fiber include polyparaphenylene terephthalamide fiber and polyparaphenylene benzobisoxazole fiber.

An example of using para-aromatic polyamide fiber is
35 the aromatic polyamide fiber paper disclosed in Japanese Kokai Patent Application No. Hei 1[1989]-281790 which is composed of an organic resin binder and a para-aromatic polyamide fiber, such as the

paraphenylene/oxydiphenylene/terephthalamide copolymer fiber spun from an isotropic solution (Technora, product of Teijin Ltd.) and polyparaphenylene/terephthalamide fiber formed by air gap spinning from an anisotropic polymer solution (Kevlar, product of Toray DuPont Co., Ltd.). A manufacturing method for aromatic polyamide fiber paper was disclosed in Japanese Kokai Patent Application No. Hei 2[1990]-203589). Although the content of ionic substance in the former para-aromatic polyamide fiber, that is, the copolymer para-aromatic polyamide fiber having ether bonds and formed by spinning from other than anisotropic polymer solutions is smaller than that in the latter para-aromatic polyamide fiber formed by spinning from anisotropic polymer solutions, the fiber paper made of the former fiber has a low heat resistance because the fiber starts to show thermal shrinkage at a temperature as low as about 200°C. As a result, when the fiber paper is used as the base material of a circuit substrate, the substrate will be deformed when parts are installed on the substrate by means of reflow soldering performed at a high temperature. Also, the former fiber has a larger coefficient of thermal expansion in the radial direction than the latter fiber formed by spinning from anisotropic polymer solutions. When the fiber paper made from the former fiber is used as the base material of a circuit substrate, the dimensional change percentage in the thickness direction of the substrate increases, causing a problem in the reliability of through-hole connections for realizing electric conduction in the thickness direction in the substrate. Also, as described above, an organic thermosetting resin binder is used together with the aforementioned fibers to manufacture paper. Since the glass transition point of the resin is much lower than that of the para-aromatic polyamide fiber, when a pre-preg made of the paper is laminated under heat and pressure as the base material of a substrate for an

electric circuit, the resin binder in the substrate is remelted, leading to unstable bonding among the fibers that form the paper. As a result, a significant
5 dimensional change occurs in the laminated substrate.

In order to reduce the aforementioned dimensional change, Japanese Kokai Patent Application No. Sho 61[1986]-160500 and US Patent No. 4,729,921 disclosed a type of fiber paper manufactured by binding a
10 para-aromatic polyamide fiber with meta-aromatic polyamide fibrids with a high heat resistance (US Patent No. 3,018,091) instead of the aforementioned resin binder. It is preferable to use a para-aromatic polyamide fiber with high heat resistance and small
15 dimensional change and spun from anisotropic polymer solution, such as a homopolymer-type para-aromatic polyamide fiber (polyparaphenylene/terephthalamide fiber (Kevlar, product of Toray DuPont Co., Ltd.)), in this case. The fiber paper formed using the aforementioned
20 polyamide fibrids has high heat resistance and excellent post-heating dimensional stability. However, the aforementioned fiber is manufactured using a spinning method, in which the polymer is spun in an acidic anisotropic polymer solution, followed by neutralization.
25 During neutralization, the ionic substances in the fibers are changed into salts. The content of the salt is usually in the range of 0.5-1 wt% after the spinning operation, and the content of the salt is maintained on that same level even when the fibers are processed into
30 paper. As a result, when the fiber paper is used as the base material of a substrate for an electric circuit, a problem can occur in the electric insulation property at high humidity. This is a problem that must be solved.

The purpose of the present invention is to provide a
35 type of completely aromatic polyamide fiber paper characterized by the following facts: the paper is made of completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution; the paper can be used as

the base material for an electric circuit substrate; the fiber paper contains a small amount of ionic substance with little deposition of ionic substance; the fiber paper shows excellent electric insulation at high humidity and has high heat resistance and high post-heating stability; and the inflection point temperature of dimensional change percentage of the fiber paper is high.

10 In order to realize the aforementioned objectives, the present invention uses a type of completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution and having high heat resistance and excellent dimensional stability. In this case, the ionic substance
15 contained in the fibers can be washed out with water, and the fiber can be deionized if spinning is carried out under such a condition that the crystal size of the fiber is smaller than a certain level. The deionized fiber of this invention can be processed into a pulp consisting of
20 short fibers or fibrils, which are combined with a binder having high heat resistance. In this way, it is possible to perform a heat treatment for the obtained fiber paper at a high temperature. Also, the crystallinity, heat resistance, dimensional stability, and moisture
25 resistance of the fiber paper can be improved. The content of the ionic substance and deposition of the ionic substance can be reduced. The fiber paper of the present invention shows excellent electric insulation in an environment with high humidity.

30 Any completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution can be used in the present invention.

The aromatic polyamide fiber used in the present invention is aromatic polyamide obtained by spinning an
35 anisotropic polymer solution. It is preferable to manufacture the fiber from a polymer with a number-average molecular weight in the range of 20,000-25,000 and formed by condensation polymerization of

paraphenylenediamine and terephthalic dichloride. The conventional air gap spinning of an anisotropic solution can be used to form the fiber from the polymer. In the case of a para-aromatic polyamide fiber, a viscous solution, prepared by dissolving the polymer in a concentrated sulfuric acid solvent, is spun from a spinning nozzle through an air gap and into a coagulating bath. In this case, when the fiber is discharged from the spinning nozzle, the shearing speed is preferably in the range of 25,000-50,000 sec^{-1} . The fiber is washed with water after the sulfuric acid used as the solvent is neutralized with an aqueous solution of sodium hydroxide immediately after the spinning operation. Subsequently, the fiber is wound after it is dried/heat treated at 150-500°C (U.S. Patent No. 3,767,756). The crystal size of the obtained fiber is usually larger than 50 Å and in the range of 55-75 Å. Also, as an ionic substance, sodium sulfate is contained in the fiber during the neutralization treatment, and its content is in the range of 0.5-1.0 wt% in this stage.

In order to use the fiber in the present invention, it is necessary to spin the fiber under appropriate drying/heat treating conditions so that the crystal size is smaller than 50 Å, preferably in the range of 35-45 Å. If the fiber has a crystal size in the aforementioned range, although the ionic substance is still contained in the fiber, it can be almost completely washed out of the fiber when the fiber is brought into contact with water or other liquids. As a result, when the obtained fiber is used for an electric circuit substrate, the electric insulation at high humidity is improved.

The size of the aromatic polyamide fiber used in the present invention should be in the range of 0.1-5 denier, or preferably in the range of 0.3-3 denier from the viewpoint of spinnability, cost effectiveness, and papermaking properties during the papermaking operation. If the fiber size is too large, papermaking properties

and texture are poor. On the other hand, if the fiber size is too small, it is difficult to spin the fiber, leading to poor cost effectiveness.

- 5 The length of the short fiber used to manufacture the aromatic polyamide fiber paper of the present invention is preferably in the range of 1-50 mm, or in the range of 2-14 mm when the paper is manufactured using a wet method. If the fiber is too long, it is difficult
10 to disperse the fibers during the papermaking operation, and the texture surface is not good enough to make the fiber paper a qualified base material for a circuit board substrate. On the other hand, if the fiber is too short, the fibers cannot be sufficiently interwoven. As a
15 result, the paper strength and other mechanical properties are poor.

- It is preferable to use meta-aromatic polyamide fibrids as the binder in the present invention from the viewpoint of heat resistance and dimensional stability.
- 20 An example of meta-aromatic polyamide fibrids is polymetaphenylene isophthalamide or a copolymer or mixed polymer mainly composed of polymetaphenylene isophthalamide. Although it is also possible to copolymerize terephthalic acid, paraphenylenediamine, and
25 the like as a third component with the meta-aromatic polyamide, the content of the third component should be 20 mol% or lower. Moreover, it is also possible to add organic resin, especially, thermosetting resin, such as epoxy resins, phenol resins, and melamine resins, as the
30 binder component in addition to the meta-aromatic polyamide fibrids as long as the purpose of the present invention is not affected by this resin.

- When para-aromatic polyamide short fiber and meta-aromatic polyamide fibrids are used to manufacture
35 the aromatic polyamide fiber paper of this invention, the mixing ratio should be such that the amount of the para-aromatic polyamide short fiber is in the range of 60-97 wt%, and the amount of the meta-aromatic polyamide

fibrids is in the range of 3-40 wt% with respect to the total weight of the aromatic polyamide fiber paper. If the content of the meta-aromatic polyamide fibrids is too low, the paper strength will be low during the papermaking process and the heat treatment, and the paper will be difficult to wind up. Also, the para-aromatic polyamide short fibers will fall off, and fuzz will occur on the surface of the paper, leading to a problem in quality. It is preferable that the content of the binder be at least 5 wt%. The meta-aromatic polyamide fibrids are softened and thus expand at high temperature during the heat treatment, to bond the para-aromatic polyamide fibers together. However, if the content of the binder is too high, the porosity of the paper will be too low leading to poor impregnation by the resin impregnant and resultant low quality. Consequently, the content of the binder should be 30 wt% or less.

In addition to the para-aromatic polyamide short fiber, it is also possible to add copolymer-type para-aromatic polyamide short fibers such as paraphenylene/3,4-diphenylene copolymer ether terephthalamide short fiber (Technora, product of Teijin Ltd.) and polyparaphenylene benzobisoxazole short fiber, glass short fibers, ceramic short fibers and the like as long as the purpose of the present invention is not affected by these fibers. In this case, the content of the aforementioned materials should be 45 wt% or lower, or preferably 35 wt% or lower.

In the following, the method used for manufacturing paper made of completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution will be explained. First, para-aromatic polyamide short fibers and meta-aromatic polyamide fibrids are dispersed in water in an aforementioned ratio to obtain a homogeneous papermaking slurry. At that time, the concentration of fiber in the dispersion is kept in the range of 0.1-1.0 wt%. If the concentration of fiber is too high, the

fiber may not be well dispersed. Paper is manufactured from the obtained dispersion using a flat wire type papermaking machine, cylinder wire type papermaking machine, inclined wire type papermaking machine, and the like. The ionic substance contained in the para-aromatic polyamide short fiber used in the present invention is ionized when it contacts water and is then extracted from the fiber. As a result, the ionic substance is discharged together with the water used in the papermaking process and the fiber is deionized. In this stage, the content of the ionic substance in the short fiber can be reduced to a level lower than 0.5 wt%. In particular, when the content of the ionic substance is reduced to a level lower than 0.2 wt%, the obtained fiber paper can display excellent electric insulation even at high humidity when it is used for an electric circuit substrate.

When the aromatic polyamide fiber paper of the present invention is used as an electric circuit substrate, it is preferable that the paper has the following properties including density and strength, which have influence on the operation for manufacturing the substrate and the properties of the substrate. The density of the paper is preferably in the range of 0.40-0.85 g/cm³. If the density is too low, it is difficult to obtain a high strength. Also, the dimensional stability is poor. Therefore, it is preferable that the density of the paper be 0.50 g/cm³ or higher. On the other hand, if the density is too high, when the resin-impregnated pre-preg is manufactured, the resin enters the interior of the paper with difficulty, which adversely affects the properties of the substrate. Consequently, the density of the paper is preferably 0.75 g/cm³ or lower. It is preferable that the strength of the paper be 1.5 kg/cm or higher so that the paper will not tear easily in the resin-impregnating operation to be described later.

When the aromatic polyamide fiber paper with the
aforementioned composition is used as an electric circuit
substrate, in order to fully display heat resistance,
5 post-heating dimensional stability, and
post-humidification stability, it is necessary to perform
a heat treatment after the paper is manufactured and to
process the paper appropriately so that the
characteristics of the paper are in the aforementioned
10 ranges, respectively. For example, it is possible to use
a calender machine to process the paper and control the
temperature and pressure. In this case, the paper is
passed between calender rolls made from one-stage or
multistage metal rolls under heat and pressure. When the
15 meta-aromatic polyamide fibrids are used as the binder,
the temperature and pressure for softening the binder are
in the range of 140-400°C and 30 kg/cm or higher,
respectively. If the temperature and pressure are not
kept in the aforementioned ranges, a fine paper structure
20 cannot be obtained, and the strength of the paper reaches
the aforementioned level with difficulty. Also, the
conditions of the heat treatment should be set
appropriately so that the crystallinity of the aromatic
polyamide fiber paper of the present invention is 45 or
25 higher, and the crystal size (ACS: Apparent Crystallinity
Size (plane 110)) is 50 Å or larger. By promoting
crystallization of the fiber paper, it is possible to
restrain ionization of a small amount of the ionic
substance left in the aromatic polyamide fiber at high
30 humidity when the paper is used as an electric circuit
substrate. Also, the heat resistance, dimensional
stability, and moisture resistance of the fiber paper
used as the base material for a circuit substrate can be
improved significantly by forming a fine aromatic
35 polyamide fiber crystal structure.

In the following, this invention will be explained
in more detail with reference to application examples.

The present invention, however, is not limited to these application examples.

TEST METHODS

5 1. Crystallinity and crystal size.

The diffraction intensity of a paper sample cut in a size of about 3 cm x 4 cm is measured using an X-ray diffraction device (PW1075/00, product of Philips Co.) under the conditions of 40 kv and 40 mA in a reflection
10 mode. The crystal size (ACS: Apparent Crystallinity Size) is equivalent to the diffraction intensity at a scanning angle of 20-21°. It is calculated from the following equation using the half-value width of the diffraction peak of plane (110).

15 $ACS = (Kx) / \beta \cos TH$

$K = 1$

$x = \text{Wavelength of X-ray (1.5418 \AA in this case)}$

$\beta = \text{Correction factor}$

20 $TH = \text{Half of the Bragg angle of plane (110) obtained from the diffraction pattern (half of the scattering angle)}$

The crystallinity (CI: Crystallinity Index) is calculated from the following equation.

$CI = [(A - C) \times 100] / A$

$A = \text{Diffraction peak intensity of plane (200) at about } 23^\circ$

25 $C = \text{The lowest diffraction intensity at about } 22^\circ$

In the case of fiber, the crystal size and crystallinity are calculated in the same way using the aforementioned method except that a paper sample with a length of 4 cm and a weight of 20 mg is fixed with a
30 collodion solution before measurement is carried out.

2. Content of ionic substance in the paper

About 0.3 g of paper is placed in a platinum dish. After dissolution in sulfuric acid, the paper sample is
35 incinerated with a gas burner or an electric oven. The obtained incinerated substance is pyrolyzed in sulfuric acid, nitric acid, or hydrofluoride acid and is then dissolved in diluted nitric acid to obtain a solution.

The amount of cationic substance in the obtained solution is measured using the atomic absorption method.

5 3. Density of the paper

The density of the paper is measured according to JIS P-8118.

10 4. Dimensional change percentage of the paper during heating

The change in the length of a paper sample with a length of 200 mm and a width of 30 mm is measured. The length of the paper sample is measured with an X-Y coordinate measuring device before the sample is heated and after the sample is heated at 300°C for 10 min. After the paper sample is heated, the dimensional change percentage (%) of both MD and CD are calculated.

15 Dimensional change percentage (%) = $100 \times (\text{length measured after heating} - \text{length measured before heating}) / (\text{length measured before heating})$

20

5. Inflection point temperature of dimensional change of the paper during heating

The temperature at which the dimensional change of a paper sample with a length of 5 mm and a width of 2 mm increases significantly is measured. The measurement is carried out using TMA (thermomechanical analysis device: product of TA Instrument Co.). The temperature is raised from room temperature to 150°C at a heating rate of 10°C/min under a load of 2 g, it is then dropped and then raised again at a rate of 10°C/min. The paper sample is heated to 350°C. As the temperature rises, the temperature at which the constant dimensional change rate varies significantly is taken as the inflection point temperature of dimensional change.

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6. Coefficient of thermal expansion in the thickness direction of the paper

The coefficient of thermal expansion of a paper sample cut in a size of 10 mm x 10 mm is measured. The measurement is carried out using TMA (thermomechanical analysis device: product of TA Instrument Co.). The temperature is raised from room temperature to 150°C at a heating rate of 10°C/min under a load of 2 g, then it is dropped and then raised again to 350°C at a rate of 10°C/min. The average coefficient of thermal expansion in the range from room temperature to 250°C is calculated.

7. Tensile strength of the paper (paper force)

The tensile strength of the paper is measured according to JIS P-8113.

8. Extraction electroconductivity of the paper

The insulation reliability of the fiber paper used as an electric circuit substrate at high humidity is determined by evaluating the extraction state of the ionic substance as ions. The ionic substance is extracted using the following method. About 5 g of paper sample are cut out and weighed accurately. After the paper sample is loaded in a flask, about 180 mL of ion exchange water are added. The flask is heated for 24 h, and the ions are extracted into the water. After cooling, the electroconductivity of the extracted liquid is measured with a conductivity meter and calculated as the value for every 5 g of sample.

Characteristics of the electric circuit substrate

9. Insulation reliability after moisture absorption

An epoxy resin composition is prepared by adding dicyandiamide as curing agent and benzyl methyl amine as curing promoter in cresol novolac epoxy resin and bisphenol A epoxy resin used as the epoxy resin with which the aromatic polyamide fiber paper is impregnated. After the aromatic polyamide fiber paper is impregnated

with a varnish prepared by dissolving the aforementioned epoxy resin composition in a methyl ethyl ketone solution, the paper is dried to obtain a B-stage pre-preg containing 53 wt% of resin. After 18- μ m thick copper foil is arranged on both sides of the pre-preg, the pre-preg is pressed by a vacuum heating press machine at 170°C under a pressure of 30 kg/cm² for 60 min to obtain a laminate. A comb electrode pattern is formed by means of etching at a line width and interval of 200 μ m on one side of the laminate. Then, B-stage pre-pregs impregnated with the aforementioned resin are arranged on both sides of the laminate, followed by pressing at 170°C under a pressure of 30 kg/cm² for 60 min using a vacuum heating press machine to obtain another laminate. The substrate is allowed to stand at 110°C and 85%RH for 500 h and 1000 h while a DC voltage of 20 V is applied to the substrate. After the substrate is removed from the aforementioned high-temperature and high-humidity environment, it is allowed to stand at 20°C and 60%RH to recover to a normal state. Then, a DC voltage of 35 V is applied between the comb electrodes for 60 sec, and the insulating resistance of the substrate after treatment in the high-humidity environment is measured. The lowest resistance of each comb electrode is taken as the measured value.

10. Dimensional stability

Five pieces of the B-stage resin-impregnated pre-pregs obtained in item 9, above, are overlapped to make a sheet. Copper foil with a thickness of 18 μ m is arranged on each side of the sheet, which is then pressed at 180°C under a pressure of 30 kg/cm² for 60 min. using a vacuum heating press machine to obtain a laminate. The copper foil laminate is cut to a size of 250 mm x 250 mm. Four of the aforementioned laminate samples are prepared. The dimensions in the longitudinal and lateral directions of each substrate are measured at a measurement interval

of 200 mm x 200 mm. The measurement is carried out under normal conditions (measurement 1), after a copper foil etching treatment (measurement 2), and after a heat treatment (measurement 3). The dimensional change percentage from the normal state is calculated from the maximum and minimum changes.

11. Soldering heat resistance

The soldering heat resistance of the copper foil laminate obtained in item 9, above, is measured according to JIS C-6481.

12. Coefficient of thermal expansion in the thickness direction

A sample with a size of 10 mm x 10 mm is cut out from the substrate after the copper foil on each side of the copper foil laminate obtained in item 9, above, is removed by means of etching. The coefficient of thermal expansion in the thickness direction is measured using TMA (thermomechanical analysis device: product of TA Instrument Co.). The temperature is raised from room temperature to 150°C at a heating rate of 10°C/min under a load of 2 g, then it is dropped and then raised again to 300°C at a rate of 10°C/min. The average coefficient of thermal expansion in the range from room temperature to 250°C is calculated.

DESCRIPTION OF PREFERRED EMBODIMENTS

Application Example 1

The para-aromatic polyamide short fiber used for the completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution was made of polyparaphenylene terephthalamide. The content of the ionic substance in the short fiber was 0.36 wt% after spinning, and the short fiber was processed appropriately

so that the crystal size on plane (110) was 40 Å. The size and length of the short fiber were 1.5 denier and 3 mm, respectively. A polymetaphenylene isophthalamide solution was precipitated in a coagulating solution under high shear to obtain meta-aromatic polyamide fibrils. The short fibers and the fibrils were dispersed homogeneously together with a dispersant in water to obtain a papermaking slurry with a fiber concentration of 0.2 wt%. The short fiber was 90 wt% of the total short fibers and fibrils. The slurry was processed with a TAPPI type square sheet machine, followed by dehydration to obtain a type of aromatic polyamide fiber paper with a basis weight of 70 g/cm². Subsequently, the fiber paper was subject to calender processing carried out under a linear pressure of 60 kg/cm² using a calender machine made of a pair of metal rolls heated to 300°C. Then, the paper was heated in a hot blast stove at 300°C for about 2 min. A resin-impregnated pre-preg was formed using the obtained fiber paper following the method described above. A substrate for an electric circuit was formed using the obtained pre-preg. The characteristics of the completely aromatic, synthetic fiber paper and the characteristics of the substrate used for an electric circuit are listed in Table I.

Application Example 2

The para-aromatic polyamide short fiber used for the completely aromatic polyamide fiber formed by means of liquid crystal spinning was made of polyparaphenylene terephthalamide. The content of the ionic substance in the short fiber was 0.36 wt% after spinning, and the short fiber was processed appropriately so that the crystal size on plane (110) was 40 Å. The size and length of the short fiber were 1.5 denier and 3 mm, respectively. Para-aromatic polyamide fiber paper was manufactured in the same way as described in Application

Example 1 except instead of meta-aromatic polyamide fibrids, that the paper was coated with an aqueous solution of bisphenol-type water dispersible epoxy resin and processed appropriately so that the amount of the attached epoxy resin was 10 wt%. The content of the short fiber in the coated paper system was 90 wt%. A resin-impregnated pre-preg was formed using the obtained fiber paper following the method described above. A substrate for an electric circuit was formed using the obtained pre-preg. The characteristics of the completely aromatic polyamide fiber paper and the characteristics of the substrate used for an electric circuit are listed in Table I.

Comparative Example 1

A type of para-aromatic polyamide fiber paper was manufactured in the same way as described in Application Example 1 except for using a different type of short fiber. In this case, the para-aromatic polyamide short fiber (Kevlar, product of Toray DuPont Ltd.) used for the completely aromatic polyamide fiber formed by spinning an anisotropic polymer solution was made of polyparaphenylene terephthalamide. The content of the ionic substance that had gone through drying heat treatment after spinning was 0.5 wt%. The crystal size on plane (110) was 55 Å. The size and length of the short fiber were 1.5 denier and 3 mm, respectively. The content of the short fibers in the resulting paper was 90 wt% of the total short fibers and fibrids. A resin-impregnated pre-preg was formed using the fiber paper following the method described above. A substrate for an electric circuit was formed using the obtained pre-preg. The characteristics of the completely aromatic polyamide fiber paper and the characteristics of the substrate used for an electric circuit are listed in Table I.

Comparative Example 2

5 A type of para-aromatic polyamide fiber paper was
manufactured in the same way as described in Application
Example 1 except for using a different type of short
fiber. The para-aromatic polyamide short fiber used in
this case was manufactured using a method other than by
10 spinning an anisotropic polymer solution. The short
fiber was made of
paraphenylene/3,4-oxydiphenylene/terephthalamide
copolymer (Technora, product of Teijin Ltd.). The size
and length of the short fiber were 1.5 denier and 3 mm,
15 respectively. The content of the short fiber in the
resulting paper was 90 wt% of the total short fibers and
fibrils. A resin-impregnated pre-preg was formed using
the obtained fiber paper following the method described
above. A substrate for an electric circuit was formed
20 using the obtained pre-preg. The characteristics of the
completely aromatic polyamide fiber paper and the
characteristics of the substrate used for an electric
circuit are listed in Table I.

25 Comparative Example 3

A type of para-aromatic polyamide fiber paper was
manufactured in the same way as described in Application
Example 1 except for the following facts. The
30 para-aromatic polyamide short fiber used in this case was
manufactured using a method other than by spinning an
anisotropic polymer solution. The short fiber was made
of paraphenylene/3,4-oxydiphenylene/terephthalamide
copolymer (Technora, product of Teijin Ltd.). The size
35 and length of the short fiber were 1.5 denier and 3 mm,
respectively. The content of the short fiber in the
resulting paper was 90 wt% of the total short fibers and
fibrils. Instead of meta-aromatic polyamide, the paper

was coated with an aqueous solution of bisphenol-type water dispersible epoxy resin and processed appropriately so that the amount of the attached epoxy resin was 10 wt%. A resin-impregnated pre-preg was formed using the obtained fiber paper following the method described above. A substrate for an electric circuit was formed using the obtained pre-preg. The characteristics of the completely aromatic polyamide fiber paper and the characteristics of the substrate used for an electric circuit are listed in Table I.

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Table I.

	Characteristics of the paper									Characteristics of the electric circuit substrate					
	Crystallinity %	Crystal size (plane 110) Å	Content of ionic substance (wt%)	Density g/cm³	Dimensional change during heating %	Inflection point of dimensional change °C	Coefficient of thermal expansion in thickness direction ppm/°C	Strength of paper Kg/cm	Extraction electroconductivity µs/cm	Insulation reliability at high humidity (minimum value)		Dimensional stability		Soldering heat resistance sec	Coefficient of thermal expansion thickness ppm/°C
										500 h	1000 h	After molding	After etching		
										Ω	Ω	%	%		
Application example 1	52.9	73.0	0.03	0.53	0.030	275	140	4.4	3	3.7 X 10⁸	6.7 X 10⁸	0.08	0.15	1500	160
Application example 2	53.0	70.0	0.03	0.53	0.030	170	340	8.0	3	3.7 X 10⁸	6.7 X 10⁸	0.08	0.15	1500	180
Comparative example 1	54.0	74.0	0.50	0.53	0.036	275	150	4.2	40	7.3 X 10⁸	Short circuit	0.07	0.17	1400	160
Comparative example 2	Cannot be measured	50 or smaller	0.02	0.47	0.046	255	170	6.0	4	6.4 X 10⁸	2.2 X 10¹⁰	0.12	0.35	500	230
Comparative example 3	Cannot be measured	50 or smaller	0.02	0.47	0.046	170	1200	9.7	5	1.0 X 10⁸	3.5 X 10⁸	0.15	0.33	500	250

CLAIM(S)

What is claimed is :

1. Completely aromatic polyamide fiber paper
5 characterized in that: the completely aromatic polyamide fiber paper comprises 60-97 wt% of completely aromatic polyamide fiber and 3-40 wt% of a binder; the content of ionic substance in the aforementioned fiber paper is less than 0.5 wt%; the crystallinity of the aromatic polyamide
10 fibers is 45% or higher; and the crystal size (ACS: Apparent Crystallinity Size (plane 110)) of the aromatic polyamide fibers is 50 Å or larger.
2. The completely aromatic polyamide fiber paper of Claim 1 characterized by the fact that the completely
15 aromatic polyamide fiber is polyparaphenylene terephthalamide.
3. The fiber paper of Claim 1 characterized by the fact that the length of the completely aromatic polyamide fibers is 2-14 mm.
- 20 4. The completely aromatic polyamide fiber paper of Claim 1 characterized by the fact that the density of the paper is 0.45-0.85 g/cm³.
5. The completely aromatic polyamide fiber paper of Claim 1 characterized by the fact that the dimensional
25 change in the paper is 0.03% or less after heating the paper at 300°C for 10 minutes.
6. The completely aromatic polyamide fiber paper of Claim 1 characterized by the fact that the coefficient of thermal expansion of the paper in the thickness
30 direction is in the range of 50-400 ppm/°C.
7. The completely aromatic polyamide fiber paper of Claim 1 characterized by the fact that the extraction conductivity of the paper is 10 μS/cm or lower.
8. The completely aromatic polyamide fiber paper
35 of Claim 1 characterized by the fact that the tensile strength is 1.5 kg/cm or higher.
9. A laminated sheet comprising at least one layer of the fiber paper of Claim 1 impregnated with a



thermosetting resin, wherein the coefficient of thermal expansion of the laminated sheet is 200 ppm/°C or less.