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(54) **COPPER FOIL WITH CARRIER, COPPER-CLAD LAMINATE AND PRINTED WIRING BOARD.**

(57) There is provided a copper foil with a carrier capable of significantly reducing the generation of blisters caused by hot pressing for stacking to a resin substrate. The copper foil with a carrier includes, in sequence, a carrier, a release layer and an extremely thin copper foil. The release layer comprises a carboxyl group-containing compound and a derivative thereof. The number of H_2O molecules per unit area in the copper foil with a carrier is $3.44*10^{16}/cm^2$ or less, and the number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39x10^{16}/cm^2$ or less.

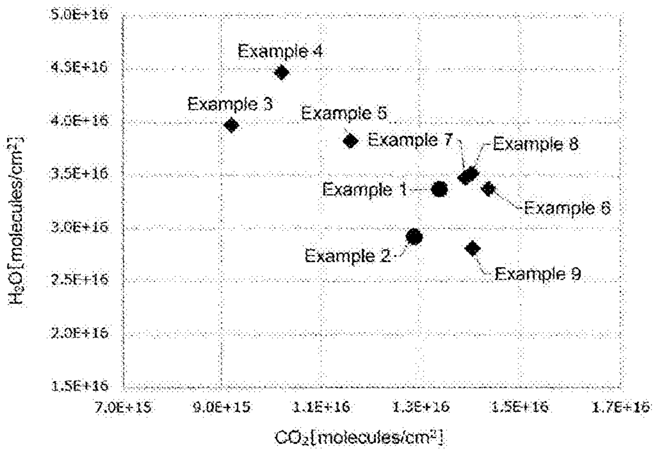

FIG. 1

COPPER FOIL WITH CARRIER, COPPER-CLAD LAMINATE AND PRINTED WIRING BOARD

TECHNICAL FIELD

[0001]

The present invention relates to a copper foil with a carrier, a copper-clad laminate and a printed wiring board.

BACKGROUND ART

[0002]

A copper foil with a carrier has been widely used as a material for manufacturing a printed wiring board. The copper foil with a carrier is bonded to an insulating resin substrate, such as a glass-epoxy substrate, a phenol substrate, a polyimide substrate by hot pressing into a copper-clad laminate, which is used for manufacturing a printed wiring board.

[0003]

A copper foil with a carrier typically has, in sequence, a carrier, a release layer, and an extremely thin copper foil, and the use of an organic release layer containing an organic compound has been proposed for the release layer. For example, PTL 1 (JP2003-328178A) discloses a method of manufacturing a copper foil with a carrier. The method comprises pickling and dissolving a surface of the carrier with a pickling acid solution containing an organic agent of 50 ppm to 2000 ppm, and simultaneously forming an organic film, as an organic release layer, containing the adsorbed organic agent after the pickling, and discloses the use of carboxybenzotriazole (CBTA) as the organic agent. In addition, PTL 2 (JP5842077B) also discloses a copper foil with a carrier through the use of carboxybenzotriazole (CBTA) as an organic release layer.

[0004]

Meanwhile, when a copper foil with a carrier is bonded to a resin substrate by hot pressing, blisters (air bubbles) may be generated between the extremely thin copper foil and the carrier. Since the blisters adversely affects the formation of circuits, the product yield decreases. Techniques for reducing the amount of moisture in a release layer have been proposed in order to address such a problem. For example, PTL 3 (JP2015-199355A) discloses a copper foil with a carrier having a moisture content of 160 ppm in weight or less generated when being heated at 30 °C/min up to 500 °C, and indicates that the copper foil with a carrier in which the production of moisture is reduced can effectively restrain the generation of the blisters.

CITATION LIST

PATENT LITERATURES

[0005]

PTL 1: JP2003-328178A

PTL 2: JP5842077B

PTL 3: JP2015-199355A

SUMMARY OF INVENTION

[0006]

However, a further improvement is desired since the prior art as disclosed in PTL 3 is not still a satisfactory solution to a problem in a yield reduction due to the generation of blisters.

[0007]

The present inventors have now found that a copper foil with a carrier provided with a release layer including a carboxyl group-containing compound and a derivative thereof can remarkably decrease the generation of blisters caused by hot pressing for stacking to a resin substrate by lowering the number densities of H_2O molecules and CO_2 molecules to predetermined values or less.

[0008]

Accordingly, an object of the present invention is to provide a copper foil with a carrier capable of significantly reducing the generation of blisters caused by hot pressing for stacking to a resin substrate.

[0009]

One embodiment of the present invention provides a copper foil with a carrier including, in sequence, a carrier, a release layer, and an extremely thin copper foil, wherein the release layer comprises a carboxyl group-containing compound and a derivative thereof, and the number of H_2O molecules per unit area in the copper foil with a carrier $3.44\times10^{16}/cm^2$ or less, and the number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39\times10^{16}/cm^2$ or less.

[0010]

Another embodiment of the present invention provides a copper-clad laminate including a copper foil with a carrier.

[0011]

Another embodiment of the present invention provides a printed wiring board including a copper foil with a carrier.

[0012]

Another embodiment of the present invention provides a method of manufacturing a printed wiring board using a copper foil with a carrier.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

FIG. 1 is a graph illustrating the numbers of H_2O molecules and CO_2 molecules per unit area in a copper foil with a carrier of Examples 1 to 9.

FIG. 2 is a diagram illustrating a thermal desorption profile of linoleic acid.

DESCRIPTION OF EMBODIMENTS

[0014]

Copper foil with carrier

A copper foil with a carrier of the present invention comprises, in sequence, a carrier, a release layer, and an extremely thin copper foil. The release layer comprises a carboxyl group-containing compound (typically, an organic compound having a carboxyl group) and a derivative thereof. The number of H_2O molecules per unit area in the copper foil with a carrier is $3.44\times10^{16}/cm^2$ or less. In addition, the number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39\times10^{16}/cm^2$ or less. Accordingly, a copper foil with a carrier provided with a release layer comprising a carboxyl group-containing compound and a derivative thereof can remarkably decrease the generation of blisters caused by hot pressing for bonding to a resin substrate by lowering the number densities of the H_2O molecules and the CO_2 molecules to predetermined values or less. The reduction in the blisters contributes to an increase in production yield because the blisters adversely affects the formation of circuits.

[0015]

Although the mechanism by which blisters generate is not clear, the following hypothesis is made: FIG. 2 shows a thermal desorption profile of linoleic acid that is a typical carboxyl group-containing compound. The thermal desorption profile shown in FIG. 2 illustrates the numbers, as a function of the temperature, of H_2O molecules and CO_2 molecules desorbed from the surface of a sample (linoleic acid) heated at a predetermined rate. As shown in FIG. 2, three major peaks corresponding to the desorption of water are observed, which include, in sequence from a low temperature side, i) a peak resulting from the desorption of water adsorbed on the sample surface (desorption of adsorbed water) , ii) a peak resulting from the desorption of water resonated with the carboxyl group (desorption of resonated water), and iii) desorption of water caused by a dehydration condensation reaction between adjacent linoleic acids (an esterification reaction). Meanwhile, one major peak corresponding to the desorption of carbon dioxide is observed at around 180 °C. This peak is caused by a decarboxylation reaction involving dissociation of carbon dioxide from the carboxyl group of the linoleic acid. The decarboxylation reaction generally occurs at 150 °C or higher, although the temperature of the reaction varies depending on the type of the organic compound. In this manner, large amounts of water and carbon dioxide are generated from an organic compound containing the carboxyl group even at a temperature (for example, 110 to 200 °C) higher than that at which adsorbed water is desorbed (for example, around 90 °C). Accordingly, when a copper foil with a carrier provided with a release layer including a carboxyl group-containing compound is bonded to a resin substrate by hot pressing, the above-described reaction occurs in the release layer heated, and water and carbon dioxide are abundantly generated. As a result, it is believed that blisters due to the water and carbon dioxide gas generates between the extremely thin copper foil and the carrier. In contrast, the present invention can reduce the number densities of the H_2O molecules and the CO_2 molecules in the copper foil with a carrier to predetermined values or less in advance, prevent the production of large amounts of water and carbon dioxide from the release layer during hot pressing for bonding to a resin substrate, and thus significantly reduce the generation of the blisters.

[0016]

Accordingly, the number of H_2O molecules per unit area in the copper foil with a carrier is $3.44\times10^{16}/cm^2$ or less, preferably $3.38\times10^{16}/cm^2$ or less, more preferably $3.30\times10^{16}/cm^2$ or less. The minimum number of H_2O molecules per unit area may be any value, and is typically $1.00\times10^{15}/cm^2$, more typically $1.50\times10^{15}/cm^2$, further more typically $1.04\times10^{16}/cm^2$. The number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39\times10^{16}/cm^2$ or less, preferably $1.34\times10^{16}/cm^2$ or less, more preferably $1.32\times10^{16}/cm^2$ or less. The minimum number of CO_2 molecules per unit area may be any value, and is typically $1.00\times10^{15}/cm^2$, more typically $1.50\times10^{15}/cm^2$, further more typically $9.17\times10^{15}/cm^2$. Each number of H_2O molecules and CO_2 molecules in the copper foil with a carrier can be preferably measured by thermal desorption spectrometry (TDS), as mentioned in the examples described later.

[0017]

The release layer has a function to decrease a release strength between the carrier and the extremely thin copper foil, to ensure the stability of the strength, and further restrain the interdiffusion which may occur between the carrier and the copper foil during hot pressing. The release layer is generally formed on one side of the carrier, or may be formed on two sides. The release layer contains a carboxyl group-containing compound and/or a derivative thereof. Accordingly, the release layer is typically an organic release layer, or may be a composite release layer of an organic release sublayer and an inorganic release sublayer, or a mixed release layer containing an organic release agent and an inorganic release agent. The derivative of the carboxyl group-containing compound includes a compound in which a portion in the molecule of the carboxyl group-containing compound is modified by, for example, a dissociation reaction or a substitution reaction, or a compound in which an atomic group is added to a portion in the molecule of the carboxyl group-containing compound by, for example, an additive reaction. Examples of such derivatives include a compound in which a carboxyl group-containing compound is converted into an acid anhydride (typically dimer) by a dehydration condensation reaction; a compound in which a CO_2 molecule is eliminated from a carboxyl group by a decarboxylation reaction; or a compound in which a substituent such as a methyl group is added to a carboxyl group-containing compound. Accordingly, the release layer may contain a carboxyl group-containing compound and a derivative thereof from an initial stage in forming a layer, or a portion of the carboxyl group-containing compound may be preferably converted into a derivative afterwards or unavoidably by heat treatment described later. That is, the release layer initially contains a carboxyl group-containing compound without a derivative thereof, and may be thereafter subjected to the heat treatment described later to react a portion of the carboxyl group-containing compound (for example, a dehydration condensation reaction, or a decarboxylation reaction) so as to contain a carboxyl group-containing compound and a derivative thereof.

[0018]

The carboxyl group-containing compound is preferably carboxybenzotriazole (CBTA). Alternatively, the carboxyl group-containing compound may be monocarboxylic acid and/or dicarboxylic acid. Preferred examples of the monocarboxylic acid include linoleic acid, oleic acid, linolenic acid, thioglycolic acid, and 3-mercapto-2-pyridinecarboxylic acid. Preferred examples of the dicarboxylic acid include thiomalic acid, diisopropyl azodicarboxylate, and diethyl azodicarboxylate. The release layer can further retain a state ready for separation of a carrier even when the release layer is subjected to hot pressing (for example, 250 °C or more) or long baking treatment (for example, at 200 °C for eight hours), because the release layer contains the carboxyl group-containing compound as described above.

[0019]

The carrier is a support for improving the support and handling of an extremely thin copper foil, and a typical carrier is a metal layer. Examples of such carriers include aluminum foil, copper foil, stainless steel (SUS) foil, and resin films and glass surface-coated with metal, such as copper. Preferred is copper foil. The copper foil may be either a rolled copper foil or an electrodeposited copper foil. The carrier typically has a thickness of 250 μm or less, preferably 9 to 200 µm.

[0020]

The extremely thin copper foil may be any foil, and have a known structure employed in the extremely thin copper foil with a carrier. For example, the extremely thin copper foil may be produced by a wet process of film formation such as copper electroless plating and copper electroplating, a dry process of film formation such as sputtering and chemical vapor deposition, or a combination thereof. The extremely thin copper foil has a thickness of preferably 0.1 to 7.0 µm, more preferably 0.5 to 5.0 µm, further more preferably 1.0 to 3.0 µm.

[0021]

The outermost surface of the extremely thin copper foil (that is, the surface remote from the release layer) is preferably a roughened surface. One surface of the extremely thin copper foil is preferably roughened. Such roughening can improve the adhesiveness to a resin layer in a manufacturing process of a copper-clad laminate or a printed wiring board. This roughening treatment is preferably performed by a known plating procedure through at least two plating processes, i.e., a burning plating process for depositing and fixing fine copper particles on the extremely thin copper foil and a covering plating process for preventing dropping-off of the fine copper particles.

[0022]

Another functional layer may be provided between the release layer and the carrier and/or the extremely thin copper foil. An example of such a functional layer is an auxiliary metal layer. The auxiliary metal layer is preferably composed of nickel and/or cobalt. Interdiffusion which may occur between the carrier and the extremely thin copper foil during hot pressing at high temperature or for long time can be further restrained and the release strength stability of the carrier can be ensured by stacking such an auxiliary metal layer on the surface side of the carrier and/or the surface side of the extremely thin copper foil. The auxiliary metal layer has a thickness of preferably 0.001 to 3 µm.

[0023]

The extremely thin copper foil may be optionally subjected to rust proofing treatment. The rust proofing treatment preferably includes a plating process with zinc. The plating process with zinc may be either a zinc plating process or zinc alloy plating process, and the alloy particularly preferred in the zinc alloy plating process is a zinc-nickel alloy. The zinc-nickel alloy contains at least Ni and Zn, and may further contain other elements, such as Sn, Cr, and Co. The deposited Ni/Zn mass ratio in the zinc-nickel alloy plating is preferably 1.2 to 10, more preferably 2 to 7, further more preferably 2.7 to 4. Preferably, the rust proofing treatment further includes a chromate process. More preferably, the chromate process is performed on the surface of a plated layer containing zinc after plating process with zinc. Such a process further improves rust proofing characteristics. A particularly preferred rust proofing treatment is a combination of zinc-nickel alloy plating and subsequent chromate process.

[0024]

The surface of the extremely thin copper foil may be subjected to a treatment with a silane coupling agent, as desired, to form a layer of a silane coupling agent, which improves the moisture resistance, chemical resistance, and adhesion to, for example, an adhesive. The silane coupling agent may be appropriately diluted, applied and then dried to form a layer of the silane coupling agent. Examples of the silane coupling agent include epoxy-functional silane coupling agents, such as 4-glycidylbutyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane; amino-functional silane coupling agents, such as 3-aminopropyltrimethoxysilane, N-2(aminoethyl)3-aminopropyltrimethoxysilane, N-3-(4-(3-amino-propoxy)butoxy)propyl-3-aminopropyltrimethoxysilane, and N-phenyl-3-aminopropyltrimethoxysilane; mercapto-functional silane coupling agents, such as 3-mercaptopropyltrimethoxysilane; olefin-functional silane coupling agents, such as vinyl trimethoxysilane and vinyl phenyl trimethoxysilane; acryl-functional silane coupling agents, such as 3-methacryloxypropyl trimethoxysilane; imidazole-functional silane coupling agents, such as imidazole silane; and triazine-functional silane coupling agents, such as triazine silane.

[0025]

Method of manufacturing copper foil with carrier

A copper foil with a carrier in the present invention can be preferably manufactured by the steps of: producing the copper foil with a carrier that, in sequence, a release layer, an extremely thin copper foil and other layers are bonded on the carrier in accordance with known techniques; and then facilitating the generation and discharge of water and carbon dioxide from the release layer through heat treatment in two stages as described below.

[0026]

The first stage in the heat treatment involves proceeding the above-mentioned reaction that generates water and carbon dioxide by high temperature treatment. Preferred heat treatment conditions may vary depending on, for example, the size and shape of the copper foil with a carrier, and the type of oven furnace used. Accordingly, the heat treatment conditions may be appropriately determined depending on these variable factors. Such conditions can promote the generation of enough water and carbon dioxide, i.e., not only the desorption of adsorbed water but also the desorption of resonated water from the carboxyl group-containing compound contained in the release layer and the desorption of water and carbon dioxide caused by a dehydration condensation reaction and a decarboxylation reaction. A heat treatment temperature in the first stage is typically higher than 180 °C, preferably 200 to 280 °C, more preferably 220 to 250 °C. A heat treatment time in the first stage is typically 0.5 to 40 hours, preferably 1 to 30 hours, more preferably 2 to 24 hours. Through this treatment, water and carbon dioxide can be adequately generated from a copper foil with carrier (typically, a release layer) while effectively preventing the deterioration of the copper foil and the separation of the optional layer of silane coupling agent. In particular, the heat treatment in the first stage at a temperature close to hot pressing for bonding to the resin substrate contributes to effectively restrain the generation of blisters caused by hot pressing. Typically, a portion of the carboxyl group-containing compound contained in the release layer transforms into derivatives thereof (for example, a dimer or a compound from which CO_2 molecules are eliminated) during the high temperature treatment in the first stage.

[0027]

The second stage in the heat treatment involves discharging water and carbon dioxide generated in the first stage of the heat treatment from the copper foil with a carrier by heat treatment at a relatively low temperature for a long time. That is, since water and carbon dioxide generated from the copper foil with a carrier in the first stage of the heat treatment are typically derived from the release layer comprising the carboxyl group-containing compound, water and carbon dioxide remain within the copper foil with a carrier (for example, between the carrier and the extremely thin copper foil), and cause the generation of the blisters. The second stage in the heat treatment may desirably discharge water and carbon dioxide remained within the copper foil with a carrier to the outside of the system. As a result, this heat treatment can modify into the copper foil with a carrier (in particular, the release layer) such that the number of H_2O molecules per unit area is $3.44\times10^{16}/cm^2$ or less and the number of CO_2 molecules per unit area is $1.39\times10^{16}/cm^2$ or less. At this time, a heating temperature in the second stage is preferably lower than that in the first stage from the viewpoint of preventing further generation of water and carbon dioxide from the release layer. The heating temperature in the second stage is typically 180 °C or less, preferably 90 to 180 °C, more preferably 100 to 180 °C. In addition, the heating treatment time in the second stage is typically 3 to 40 hours, preferably 5 to 35 hours, more preferably 5 to 30 hours. Through the heat treatment in the second stage within such ranges of temperature and time, water and carbon dioxide generated in the first stage can be effectively discharged from the copper foil with a carrier. Similar to the heat treatment conditions in the first stage, preferred conditions in the second stage may also vary depending on, for example, the size and shape of the copper foil with a carrier, and the type of oven furnace used.

[0028]

Copper-clad laminate

The copper foil with a carrier in the present invention is preferably used for manufacturing a copper-clad laminate for printed wiring boards. That is, a preferred embodiment of the present invention provides a copper-clad laminate comprising the copper foil with a carrier as described above. This copper-clad laminate comprises the copper foil with a carrier of the present invention and a resin layer provided in close contact with the extremely thin copper foil of the copper foil with a carrier. The copper foil with a carrier may be provided on one side or on two sides of the resin layer. The resin layer contains a resin, preferably an insulating resin. The resin layer is preferably a prepreg and/or a resin sheet. The "prepreg" is a generic term for a composite material prepared by impregnating a substrate, such as a synthetic resin plate, a glass plate, a glass woven fabric, a glass nonwoven fabric, or paper, with a synthetic resin. Preferred examples of the insulating resin include epoxy resins, cyanate resins, bismaleimide triazine resins (BT resins), polyphenylene ether resins, and phenol resins. Examples of the insulating resin constituting the resin sheet include epoxy resins, polyimide resins, and polyester resins. The resin layer may contain filler particles or other additives composed of various inorganic particles, such as silica and alumina from the viewpoint of, for example, improving the insulating property. The resin layer may have any thickness, but a thickness of preferably 1 to 1000 μm, more preferably 2 to 400 μm, further more preferably 3 to 200 μm. The resin layer may be composed of a plurality of sublayers. The resin layer composed of, for example, the prepreg and/or the resin sheet may be provided on a primer resin layer preliminarily applied onto the surface of the extremely thin copper foil with a carrier.

[0029]

Printed Wiring Board

The copper foil with a carrier of the present invention is preferably used for manufacturing a printed wiring board. A preferred embodiment of the present invention provides a printed wiring board comprising the copper foil with a carrier, or a method of manufacturing the printed wiring board. The printed wiring board according to the embodiment includes a stack of a resin layer and a copper layer. The resin layer is as described above in the explanation of the copper-clad laminate. In any case, any known layer structure can be employed in the printed wiring board. Specific examples of the printed wiring board include a single- or double-sided printed wiring board in which circuits are formed by bonding the extremely thin copper foil of the present invention on one side or two sides of a prepreg to form a cured laminate, and a multilayered printed wiring board in which these single- or double-sided printed wiring board are stacked. Other specific examples include flexible printed wiring boards, COF tapes, and TAB tapes which include the extremely thin copper foil of the present invention formed on a resin film and circuits formed thereon. Further specific examples include a build-up wiring board in which circuits are formed by, for example, a modified semi-additive process (MSAP) or a subtractive process using the extremely thin layer as all or part of the wiring layer after forming a resin-coated copper foil

(RCC) coated with the above resin layer on the extremely thin copper foil of the present invention and stacking the resin layer as an insulating adhesive layer on the printed wiring board; a build-up wiring board in which circuits are formed by a semi additive process (SAP) after removing the extremely thin copper foil; and a direct build-up-on-wafer wiring board in which the stacking of a resin-coated copper foil and the formation of circuits are alternately repeated on a semiconductor integrated circuit. The copper foil with a carrier of the present invention can also be preferably employed in a manufacturing method including a coreless buildup process in which insulating resin layers and conducting layers are alternately stacked without use of a so-called core substrate.

EXAMPLES

[0030]

The present invention will be described more specifically with reference to the following examples.

[0031]

Examples 1, 2 and 4 to 8

Each copper foil with a carrier was produced and evaluated as follows.

[0032]

(1) Provision of a career

An electrodeposited copper foil having a thickness of 18 μm, classified as Grade 3 in accordance with the IPC standard, was provided as a carrier. The electrodeposited copper foil as the carrier was a copper foil produced electrolytically as it is (a so-called plain foil), and was not subjected to the surface treatment such as rust proofing treatment or roughening treatment. The surface of the carrier was pickled to remove grease components and surface oxide film.

[0033]

(2) Formation of release layer

The electrode surface of the pickled carrier was immersed in an aqueous CBTA solution composed of 1 g/L CBTA (carboxybenzotriazole), 150 g/L sulfuric acid and 10 g/L copper at 30 °C for 30 seconds, and the components of CBTA were adsorbed on the electrode surface of the carrier. A CBTA layer, as a release layer, was formed on the electrode surface of the carrier.

[0034]

(3) Formation of auxiliary metal layer

The carrier provided with the release layer was immersed in the solution which was prepared using nickel sulfate and composed of 20 g/L nickel to deposit nickel having a thickness of 0.001 μm on the release layer of the carrier under the conditions of a liquid temperature of 45 °C, pH of 3 and a current density of 5 A/dm^2. A nickel layer, as an auxiliary metal layer, was formed on the release layer.

[0035]

(4) Formation of extremely thin copper foil

The carrier on which the auxiliary metal layer was formed was immersed in a copper sulfate solution having 60 g/L copper and 200 g/L sulfuric acid, and electrolyzed under the conditions of a liquid temperature of 50 °C and a current density of 5 to 30 A/dm^2 to form an extremely thin copper foil having a thickness of 1.5 μm on the auxiliary metal layer.

[0036]

(5) Roughening treatment

The surface of the extremely thin copper foil was roughened. This roughening treatment was performed in the following two plating stages: In the first plating stage, the surface was electroplated under the plating conditions of a liquid temperature of 40 °C and a current density of 30 A/dm^2 with an acidic copper sulfate solution containing 10 g/L copper and 120 g/L sulfuric acid. In the second plating stage, the surface was electroplated under the plating conditions of a liquid temperature of 40 °C and a current density of 30 A/dm^2 with an acidic copper sulfate solution containing 70 g/L copper and 120 g/L sulfuric acid.

[0037]

(6) Rust proofing treatment

Rust proofing treatment consisting of inorganic rust proofing treatment and chromate treatment was performed on the two surfaces of the copper foil with a carrier after the roughening treatment. The inorganic rust proofing treatment was carried out with a zinc-nickel alloy in a pyrophosphoric acid bath containing 80 g/L potassium pyrophosphate, 0.2 g/L zinc and 2 g/L nickel under the conditions of a liquid temperature of 40 °C and a current density of 0.5 A/dm^2. A chromate layer was further deposited on the zinc-nickel alloy (the chromate treatment). This chromate treatment was carried out under the conditions of 1 g/L chromic acid, a pH of 11, a liquid temperature of 25 °C and a current density of 1 A/dm^2.

[0038]

(7) Silane coupling agent treatment

The copper foil subjected to the rust proofing treatment was washed with water and immediately treated with a silane coupling agent, and the silane coupling agent was adsorbed on the roughened surface of the rust proofing layer. In this silane coupling agent treatment, the adsorption treatment was carried out by showering a solution that contains pure water as a solvent and 3 g/L 3-aminopropyltrimethoxysilane onto the roughened surface. After the adsorption of the silane coupling agent, water was finally evaporated with an electric heater to give a roughened copper foil with a carrier having a total thickness of 1.5 μm.

[0039]

(8) Heat treatment

The resultant copper foil with carrier was subjected to one or two stages of heat treatment under the conditions shown in Table 1 in an air oven. At this time, various samples with different contents of moisture and carbon dioxide in the release layer were prepared by appropriate changes of the heating conditions in Examples 1, 2 and 4 to 8 as shown in Table 1. It should be appreciated that the conditions of the heat treatment vary depending on, for example, the size of the sample and the type of the oven, and the present invention should not be limited at all by these conditions.

[0040]

(9) Evaluations of copper foil with carrier

The resultant copper foils with a carrier were evaluated as follows.

[0041]

<Evaluation 1: Measurement of moisture and carbon dioxide>

The amounts of moisture and carbon dioxide contained in the resultant copper foils with carriers (in particular, the release layer) were measured by thermal desorption spectrometry (TDS) as follows. In order to remove moisture adsorbed on the surface of the copper foil with a carrier subjected to the heat treatment in the above item (8), the copper foil with a carrier was dried in a vacuum thermostatic oven at 50 °C and at -0.1 MPa against the atmospheric pressure for seven days. The copper foil with a carrier dried in vacuum was then stamped out with a puncher to produce a test piece with a size of 1 cm in diameter, and this test piece was quickly weighed. The test piece was placed in a chamber of a thermal desorption spectrometer (TDS 1200II, manufactured by Electronic Science Co., Ltd.) in a state where the carrier and the extremely thin copper foil were separated (that is, a state where the release layer was exposed), and the chamber is purged with nitrogen gas for 3 minutes and then evacuated for 5 minutes. After that, the test piece was irradiated with lamp light, and the temperature of the test piece was raised up to 400 °C at a heating rate of 30 °C/min by light absorption. During this step, the gas generated from the test piece was measured qualitatively and quantitatively by mass spectrometer. In this measurement, the H_2O gas and CO_2 gas were analyzed, respectively, at $m/z = 18$ and at $m/z = 44$, and the numbers of H_2O molecules and CO_2 molecules were calculated in a circle with 1 cm diameter of the copper foil with a carrier. The resultant numbers were divided by the area of a circle having a diameter of 1 cm (0.785 cm^2) into the numbers of H_2O molecules and CO_2 molecules per unit area. The results are as shown in Table 1 and FIG. 1. For reference, Table 1 illustrates the weight ratios (ppm) of H_2O and CO_2 of the copper foil with a carrier, which are calculated by dividing each weight of H_2O and CO_2 (converted from each number of molecules) by the weight of the test piece.

[0042]

<Evaluation 2: Measurement of blisters>

A prepreg with a thickness of 100 μm (GHPL-830 NSF, manufactured by Mitsubishi Gas Chemical Company, Inc.) was provided as a resin substrate. The copper foil with a carrier subjected to the heat treatment in the above item (8) was stacked onto the resin substrate such that the copper foil with a carrier was in contact with the resin substrate at the side of the extremely thin copper foil, and hot-pressed at a pressure of 2.4 MPa and at 250 °C for 90 minutes, followed by the baking treatment in an oven at 200 °C for eight hours to give a sample of copper-clad laminate. After the carrier was released from the sample of copper-clad laminate, the surface of the extremely thin copper foil was observed under the conditions of a magnification of 20 folds and a visual measured field of 18 mm×13.5 mm with an optical microscope (VHX-5000, manufactured by Keyence Corporation), and the number of dimples was counted to give a mean value of three different visual fields as the number of blisters. In other words, since the dimples are formed on the surface of the sample of copper-clad laminate after releasing of the carrier (that is, the surface of the extremely thin copper foil) as the traces caused by the blisters generated between the carrier and the extremely thin copper foil, the number of dimples was regarded as the number of blisters generated. The results are shown in Table 1.

[0043]

Example 3 (comparative)

A copper foil with a carrier was prepared and evaluated in the same process as in Example 1 except that the copper foil with a carrier was not subjected to heat treatment. The result is as shown in Table 1 and FIG. 1.

[0044]

Example 9 (comparative)

A copper foil with a carrier was prepared and evaluated in the same process as in Example 2 except that an aqueous linoleic acid solution containing 1000 ppm by weight linoleic acid was used instead of the CBTA aqueous solution in the step of forming the release layer. The result is as shown in Table 1 and FIG. 1.

[0045]

Table1

	Component of release layer	Heat treatment					Evaluations				
	Carboxyl group-containing compound	Heating	Heat treatment in the first stage		Heat treatment in the second stage		Measurement of water and carbon dioxide				Measurement of blisters
							Numbers of H_2O molecules and CO_2 molecules per unit area		Weight ratios of H_2O and CO_2 on φ1cm sample		Number of blisters
			Temp. [°C]	Time [hr]	Temp. [°C]	Time [hr]	H_2O [/cm^2]	CO_2 [/cm^2]	H_2O [ppm]	CO_2 [ppm]	[Number]
Ex. 1	CBTA	2 stage	230	2	120	8	3.38×10^{16}	1.34×10^{16}	58	56	15
Ex. 2		2 stage	230	2	180	5.3	2.93×10^{16}	1.29×10^{16}	50	54	2
Ex. 3*		Non	n/a		n/a		3.97×10^{16}	9.21×10^{15}	68	39	162
Ex. 4*		1 stage	120	23.6	n/a		4.47×10^{16}	1.02×10^{16}	77	43	150
Ex. 5*		1 stage	180	5.3	n/a		3.82×10^{16}	1.16×10^{16}	66	49	148
Ex. 6*		1 stage	230	2	n/a		3.38×10^{16}	1.44×10^{16}	58	60	132
Ex. 7*		2 stage	230	2	180	2.7	3.48×10^{16}	1.39×10^{16}	60	58	78
Ex. 8*		2 stage	180	5.3	230	2	3.52×10^{16}	1.40×10^{16}	60	59	91
Ex. 9*	Linoleic acid	Non	n/a		n/a		2.81×10^{16}	1.40×10^{16}	48	59	143

* : Comparative example

ANSPRÜCHE

1. Kupferfolie mit einem Träger, der nacheinander einen Träger, eine Freisetzungsschicht und eine extrem dünne Kupferfolie umfasst, wobei die Freisetzungsschicht eine carboxylgruppenhaltige Verbindung und ein Derivat davon umfasst und die Anzahl der H_2O-Moleküle pro Flächeneinheit in der Kupferfolie mit einem Träger $3{,}44\times10^{16}/cm^2$ oder weniger beträgt und die Anzahl der CO_2-Moleküle pro Flächeneinheit in der Kupferfolie mit einem Träger $1{,}39\times10^{16}/cm^2$ oder weniger beträgt.

2. Kupferfolie mit einem Träger nach Anspruch 1, wobei die carboxylgruppenhaltige Verbindung Carboxybenzotriazol (CBTA) ist.

3. Kupferfolie mit einem Träger nach Anspruch 1, wobei die carboxylgruppenhaltige Verbindung Monocarbonsäure und/oder Dicarbonsäure ist.

4. Kupferfolie mit einem Träger nach einem der Ansprüche 1 bis 3, wobei der Träger eine Metallschicht beinhaltet.

5. Kupferfolie mit einem Träger nach einem der Ansprüche 1 bis 4, ferner umfassend eine Hilfsmetallschicht zwischen der Freisetzungsschicht und dem Träger und/oder der extrem dünnen Kupferfolie.

6. Kupferbeschichtetes Laminat, umfassend die Kupferfolie mit einem Träger nach einem der Ansprüche 1 bis 5.

7. Leiterplatte, umfassend die Kupferfolie mit einem Träger nach einem der Ansprüche 1 bis 5.

8. Verfahren zur Herstellung einer Leiterplatte, wobei die Leiterplatte mit der Kupferfolie mit einem Träger nach einem der Ansprüche 1 bis 5 hergestellt wird.

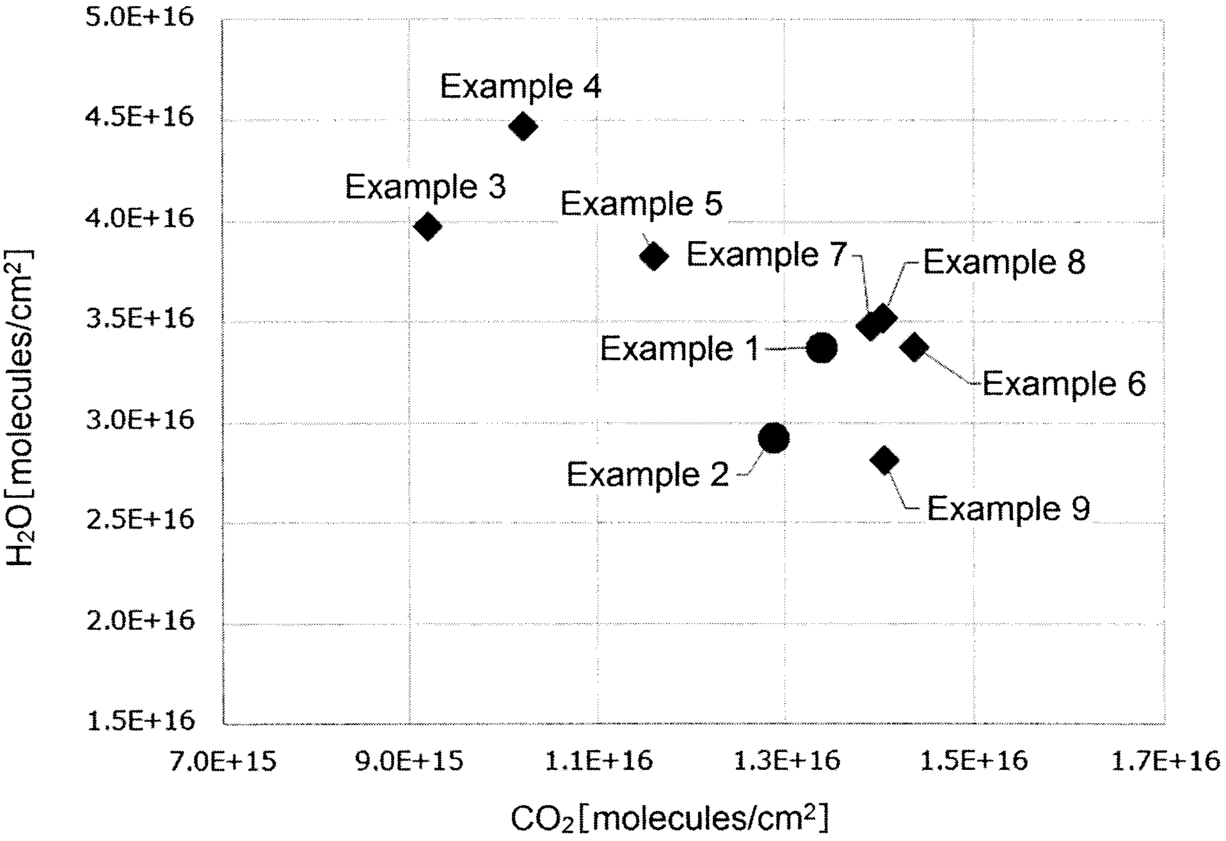
5.0E+16
4.5E+16
4.0E+16
3.5E+16
3.0E+16
2.5E+16
2.0E+16
1.5E+16
H_2O[molecules/cm^2]
7.0E+15
9.0E+15
1.1E+16
1.3E+16
1.5E+16
1.7E+16
CO_2[molecules/cm^2]
Example 4
Example 3
Example 5
Example 7
Example 8
Example 1
Example 6
Example 2
Example 9

FIG. 1

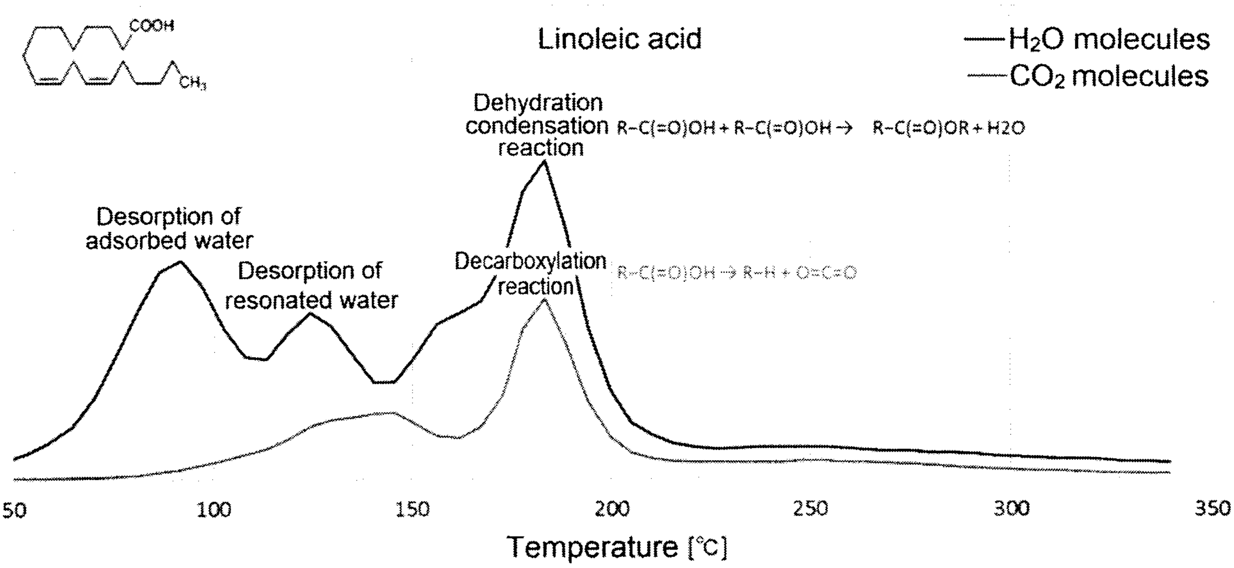
COOH
CH₃
Linoleic acid
—H_2O molecules
—CO_2 molecules
Dehydration condensation reaction
R-C(=O)OH + R-C(=O)OH → R-C(=O)OR + H2O
Desorption of adsorbed water
Desorption of resonated water
Decarboxylation reaction
R-C(=O)OH → R-H + O=C=O
50
100
150
200
250
300
350
Temperature [℃]

FIG. 2

ABSTRACT

There is provided a copper foil with a carrier capable of significantly reducing the generation of blisters caused by hot pressing for stacking to a resin substrate. The copper foil with a carrier includes, in sequence, a carrier, a release layer and an extremely thin copper foil. The release layer comprises a carboxyl group-containing compound and a derivative thereof. The number of H_2O molecules per unit area in the copper foil with a carrier is $3.44\times10^{16}/cm^2$ or less, and the number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39\times10^{16}/cm^2$ or less.

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

National Application Number

LO 2188
LU 101147

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	JP 2017 013385 A (MITSUI MINING & SMELTING CO) 19 January 2017 (2017-01-19) * examples 1-9 * * claim 1 * -----	1-8	INV. C23C18/16 C25D5/10 C25D7/06 H05K3/02 B32B15/08 ADD. C23C18/38 C25D3/56 C25D3/38 H05K3/38 C25D1/04
A	JP H04 30595 A (SHOWA DENKO KK) 3 February 1992 (1992-02-03) * the whole document * -----	1-8	
A	JP 2015 199355 A (JX NIPPON MINING & METALS CORP) 12 November 2015 (2015-11-12) * paragraph [0095] - paragraph [0100] * -----	1-8	
A	US 2005/089709 A1 (BRENNEMAN WILLIAM L [US] ET AL) 28 April 2005 (2005-04-28) * paragraph [0014] - paragraph [0020] * -----	1-8	

TECHNICAL FIELDS SEARCHED (IPC)
C23C H05K C25D B32B

The present search report has been drawn up for all claims

1

	Date of completion of the search	Examiner
	17 September 2019	Le Hervet, Morgan

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE SEARCH REPORT ON LUXEMBOURG PATENT APPLICATION NO.

LO 2188
LU 101147

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-09-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP 5842077 B1	13-01-2016
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		LU 93050 B1	08-06-2017
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		US 2007141380 A1	21-06-2007
		US 2011008616 A1	13-01-2011
		WO 2005042807 A1	12-05-2005

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO2188	04.03.2019	23.03.2018	LU101147

International Patent Classification (IPC)
INV. C23C18/16 C25D5/10 C25D7/06 H05K3/02 B32B15/08 ADD. C23C18/38 C25D3/56 C25D3/38 H05K3/38 C25D1/04

Applicant
MITSUI MINING & SMELTING CO., LTD.

This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the application
☒	Box No. VIII	Certain observations on the application

Examiner
Le Hervet, Morgan

Application No.
LU101147

WRITTEN OPINION

Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

a. type of material:

☐ a sequence listing

☐ table(s) related to the sequence listing

b. format of material:

☐ on paper

☐ in electronic form

c. time of filing/furnishing:

☐ contained in the application as filed.

☐ filed together with the application in electronic form.

☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-8
	No:	Claims	
Inventive step	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Box No. VIII Certain observations on the application

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1	JP 2017 013385 A (MITSUI MINING & SMELTING CO) 19 January 2017 (2017-01-19)
D2	JP H04 30595 A (SHOWA DENKO KK) 3 February 1992 (1992-02-03)
D3	JP 2015 199355 A (JX NIPPON MINING & METALS CORP) 12 November 2015 (2015-11-12)
D4	US 2005/089709 A1 (BRENNEMAN WILLIAM L [US] ET AL) 28 April 2005 (2005-04-28)

2 Disclosure of the prior art

2.1 D1 discloses a copper foil with a carrier comprising, in sequence, a carrier, a release layer, and an extremely thin copper foil, wherein the release layer comprises a carboxyl group-containing compound (see D1, examples 1-9; claim 1).

2.2 D2 discloses a board comprising in this order an aluminium metal plate, a thermoplastic resin film and a copper foil. This composite board is thermocompressed under vacuum in order to evacuate the bubbles (moisture and carbon dioxide) confined in the interfaces between the layers (see D2, description, claim 1).

2.3 D3 discloses a copper foil with a carrier comprising in this order a copper foil carrier, an intermediate nickel plated layer and an ultra-thin copper layer. The moisture content is controlled by depositing a uniform nickel layer without defects and by removing water by heat processing (see D3, paragraphs [0095]-[0100]).

2.4 D4 discloses a copper foil with a carrier comprising in this order a copper-based, aluminium-based or iron-based carrier foil, an inorganic release layer (e.g. a mixture chromium oxide, chromium and chromium hydroxide) and a copper foil layer. Blistering is limited due to the reaction of the substrate alloy or his constituents with gaseous compounds or moisture (see D4, paragraphs [0014]-[0020]).

3 Novelty and inventive step

3.1 D1 is regarded as being the prior art closest to the subject-matter of claim 1.

3.2 The subject-matter of claim 1 therefore differs from the copper foil with carrier of D1 in that the the number of H_2O molecules per unit area in the copper foil with a carrier is $3.44x10^{16}$ /cm^2 or less, and the number of CO_2 molecules per unit area in the copper foil with a carrier is $1.39x10^{16}$ /cm ^{2} or less, and is therefore new.

It is noted that the specific heat treatment applied to the copper foil with carrier, as described in the description of the present application, provides the desired low water and carbon dioxide contents. It is thus clear that the product as disclosed in D1 cannot be within the ranges specified in the claim.

3.3 The problem to be solved by the present invention may be regarded as to prevent the formation of blisters.

3.4 The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step for the following reasons.

D2 describes a thermocompression process for bonding two metal foils by means of an adhesive layer comprising polysulfone, polyether sulfone, polyamide imide, polyether ketone or polyimide. Therefore, it does not relate to an ultra-thin copper foil deposited on a release layer. Furthermore, D1 discloses a first heating step at a relatively low temperature followed by a second step at a relatively high temperature. The process features are thus so different from those disclosed in the present application, that there is actually no evidence that the procedure of D2 could lead to the desired water and carbon dioxide contents.

D3 and D4 do not relate to an organic release layer and thus provide no hint at the claimed solution.

Therefore, starting from D1, it can be concluded that the skilled person would find no incentive in the prior art at hand or in common general knowledge to arrive at the subject matter of claim 1 when aiming at solving the problem posed.

3.5 Claims 2 to 7 are dependent on claim 1 and as such also meet the requirements of novelty and inventive step.

3.6 Claim 8 relates to a method using the copper foil with carrier of claim 1 and as such also meets the requirements of novelty and inventive step.

Re Item VIII

Certain observations on the application

4 Claim 1 is not clear.

4.1 In claim 1 the expression "derivative thereof" adds to specifically defined compounds, i.e. a carboxyl group-containing compound, those which are "derived" from said compounds. There is, however, no clear definition to which extent said carboxyl-containing compounds may be modified while still being regarded as derivatives. This has the effect that the person skilled in the art cannot decide clearly which compounds are to be covered by the claims and which are not.

4.2 Claim 1 is not supported by the description, as its scope is broader than justified by the description.

4.2.1 Claim 1 mentions a compound which can be any derivative of a carboxyl group-containing compound. In paragraph [0017], the description suggests that it could be a compound in which a substituent such as a methyl group is added to a carboxyl group-containing compound. However, claim 1 is restricted to release layers fulfilling the criteria relating to the number of H_2O molecules per unit area and the number of CO_2 molecules per unit area. The present application has not shown that those criteria could be fulfilled by an additive reaction only. The examples concern only the use of a heat treatment. Therefore, it is essential that the release layer comprises a derivative of said carboxyl group-containing compound obtained by a dehydration condensation reaction and a derivative of said carboxyl group-containing compound obtained by a decarboxylation reaction.

4.2.2 Furthermore, the description does not convincingly show that the number of H_2O molecules per unit area can be made lower than 2.93×10^{16} and the number of CO_2 molecules per unit area lower than 1.29×10^{16} (see example 2). The ranges provided in present claim 1 should thus have those values as lower limits.

4.3 The number of H_2O molecules per unit area and the number of CO_2 molecules per unit area are unusual parameters.

The method of measurement provided in the description in paragraph [0041] appears to be necessary for the unambiguous definition of these parameters and should therefore be included in claim 1, at least by reference to the description.

4.4 The sample of example 3 shows the lowest number of CO2 molecules, although it was not subjected to a heat treatment. This contradicts the idea that the present application would provide a reliable method for decreasing the amount of CO_2 molecules.

JP2017013385A 20170119

EPO Machine Translation XML

SUBJECT OF THE INVENTION
Copper with the carrier, copper clad laminate and printed wiring board

[0001] The present invention provides a copper foil with a carrier, to a copper-clad laminate and a printed wiring board.

[0002] As a material for the printed wiring board manufacturing, copper foil is widely used with the carrier. Copper foil with carrier is a glass - epoxy substrate, phenolic substrates, are bonded together by an insulating resin base material and the hot press forming such as polyimide is a copper-clad laminate, is used in the manufacture of printed circuit boards .

[0003] Copper foil with carrier has a carrier foil, a structure having a release layer and the ultra-thin copper foil in this order, typically. As the peeling layer, Patent Document 1 (JP-A-11-317574), an organic release layer comprising an organic compound of a nitrogen-containing compound and the like have been proposed, it is easy to form the (1) release layer, (2) ultra-thin copper foil and the support metal layer (hereinafter, carrier) peel strength between (a) a uniform, compared to the peel strength of the ultra-thin copper foil after lamination to a substrate (B) It shows a low value, (3) because it does not use an inorganic material, without requiring a mechanical polishing process and pickling step to remove the inorganic material remaining on the surface of the ultra-thin copper foil, therefore, the wiring formation of a pattern can be simplified by reducing the number of processing steps, (4) peel strength (a), although small, to prevent the ultra-thin copper foil from the carrier during handling of the composite copper foil is separated is sufficient, (5) the composite foil has sufficient peel strength after lamination to a substrate (Bs), never peeled off from the substrate during processing into ultra-thin copper foil printed wiring board, (6) carriers, even after lamination at high temperatures, can be separated from the ultra-thin copper foil, (7) because it is easy to remove the separation layer remaining on the carrier, reusing the carrier it is easy, it is disclosed that there are various advantages such.

[0004] Further, Patent Document 2 (JP 2003-328178), that with a pickling solution 50ppm~2000ppm containing an organic material, while the surface of the carrier foil pickled dissolved, adsorbing the organic material at the same time and forming a pickling adsorption organic film as an organic release layer, a manufacturing method of a copper foil with a carrier is disclosed by.

[0005] In any of Patent Documents 1 and 2 also as an organic agent for the organic release layer formation, the use of carboxy benzotriazole (CBTA) is disclosed. Relates carboxybenzotriazole (CBTA), 5- carboxy Although two chemical structures of benzotriazole and (5CBTA) 4- carboxy benzotriazole (4CBTA) is known to be present, in Patent Documents 1 and 2 5CBTA and description of 4CBTA has not been made at all.

[0006] In recent years, in order to miniaturize and increase the mounting density of the printed wiring board, it has become multi-layered printed wiring board is widely performed. Such multilayer printed wiring board, a number of portable electronic devices, have been utilized for the purpose of weight reduction and size reduction. Then, this multilayer printed wiring board, reduce further the thickness of the interlayer insulating layer, and more weight reduction as a wiring board is required. Therefore, the production method of the recent multi-layer printed wiring board, without using a so-called core board, manufacturing method using the coreless build-up method in which the insulating resin layers and conductor layers are alternately laminated is employed.

[0007] 特開平１１−３１７５７４号公報
特開２００３−３２８１７８号公報

[0008] By the way, there is a problem of the peeling strength between multiple high temperatures and provide long-time thermal history when the carrier foil and the ultrathin copper foil may increase considerably by stacking a plurality of times in a coreless build-up method or the like . Therefore, high-temperature and peel strength between long carrier foil can give a heat history and ultrathin copper foil is hardly increased, i.e. copper foil carrier peel strength is stabilized is desired.

[0009] The present inventors have now, in the peeling layer of copper foil with a carrier, 5-carboxylate which is the ratio of the amount of adhesion of adhesion amount of 4-carboxy benzotriazole of benzotriazole, to 3.0 or more 5CBTA / 4CBTA ratio by, it is possible to suppress an increase in peel strength of the carrier foil can give a high-temperature and long-time thermal history, namely the peel strength was obtained a finding with stabilized.

[0010] Accordingly, an object of the present invention can suppress an increase in peel strength of the carrier foil can give a high-temperature and long-time thermal history, namely the peel strength is to provide a stabilized copper foil carrier.

[0011] According to one aspect of the present invention, the carrier foil, a copper foil carrier with a release layer and the ultra-thin copper foil in this order, the release layer, 5-carboxyfluorescein-benzotriazole (5CBTA) and / or 4- comprises a carboxybenzotriazole (4CBTA), made in the above is the ratio of the amount of adhesion of peeling in the 5-carboxylate of benzotriazole amount of adhesion of layer 4 carboxybenzotriazole, 5CBTA / 4CBTA ratio is 3.0 or more, the carrier Tsukedohaku is provided.

[0012] According to another aspect of the present invention, copper-clad laminate obtained using the copper foil carrier of the above aspects are provided.

[0013] According to another aspect of the present invention, a printed wiring board obtained using copper foil carrier of the above aspects are provided.

[0014] Copper foil with a carrier

Copper foil with carrier of the present invention is a carrier foil, a release layer and the ultra-thin copper foil that in this order. The release layer, 5-carboxyfluorescein benzotriazole (hereinafter, 5CBTA hereinafter) and / or 4-carboxy benzotriazole (hereinafter, referred 4CBTA) comprising. Chemical structural formula of 4CBTA and 5CBTA are as follows.

[2017013385.tif-000002]

[0015] Copper foil with carrier of the present invention is the ratio adhesion amount of adhering amount of 4CBTA of 5CBTA in the release layer is 5CBTA / 4CBTA ratio of 3.0 or more. Thus, while 5CBTA is an essential component, it can be said that the 4CBTA is an optional component. In any case, the copper foil with carrier, except employing the present invention specific to the release layer, a known layer configuration can be adopted.

[0016] Thus, in the release layer of the copper foil carrier of the present invention, by the 5CBTA / 4CBTA ratio 3.0 or higher, unexpectedly, the carrier foil can give a high-temperature and long-time thermal history it is possible to suppress an increase in peel strength, i.e. the peel strength can be stabilized. In this regard, although the CBTA conventionally as described above have been used in the organic release layer, which was the 5CBTA / 4CBTA ratio of 3.0 or more it is not yet known. Because, as long as the knowledge of the applicant, the CBTA mixture that is commercially available, the 5CBTA and 4CBTA, about 6: 4 ratio: are those that contain at (5CBTA 4CBTA ratio), 5CBTA / 4CBTA ratio of the mixture only about 1.5. The peeling layer using CBTA mixture of such low 5CBTA / 4CBTA ratio, among the plurality of times of high temperature and gives a long-time thermal history when the carrier foil and the ultrathin copper foil by stacking a plurality of times in a coreless build-up method or the like peel strength there was a problem with the device may be increased significantly. In contrast, according to the recent findings of the present inventors, in the separation layer of the copper foil carrier, by the 5CBTA / 4CBTA ratio 3.0 or more, it can be eliminated unexpectedly the above problems . Thus, the copper foil with carrier of the present invention, in the plurality of times of lamination process of a printed wiring board of the coreless buildup method in which high-temperature and long-time heat history is given more than once by lamination, normal (high temperature and long-time heat low rate of increase in peel strength to peel strength before) the history is given, that is, to exhibit a stable peel strength (e.g. 10~20gf / cm). Therefore, the copper foil with carrier of the present invention can be said to be very useful in the lamination process of a printed wiring board such as a coreless build-up method.

[0017] The release layer is to weaken the peel strength between the carrier foil and the ultrathin copper foil, and ensure the stability of the intensity, further suppressing the interdiffusion can occur between the carrier foil and the copper foil during press molding at a high temperature a layer having a function of. Peeling layer is being formed on one surface of the carrier foil is generally, it may be formed on both surfaces. The release layer is an organic release layer comprises 4CBTA by 5CBTA and optionally. Release layer, in addition to 5CBTA and 4CBTA, may contain other ingredients known as a component of the organic release layer.

[0018] 5CBTA / 4CBTA ratio in the release layer is 3.0 or more, and preferably 3.5 to 30. When it is within this range, it tends to more exhibit stable peeling strength. Incidentally, the peeling layer may comprise a 5CBTA alone (without 4CBTA).

[0019] The release layer preferably comprises at deposition amount of 3mg / m 2 or more in total 4CBTA if 5CBTA and present, more preferably 5mg / m 2 or more, still more preferably 8 mg / yd 2 or more. Upper limit of the coating weight is not particularly limited, for further stabilization improved and the peeling strength of the handling of the copper foil with carrier, release layer, 80 mg in total of 4CBTA if 5CBTA and present / m 2 preferably comprises the following coating weight, more preferably 50mg / m 2 or less, further preferably 30mg / m 2 or less.

[0020] On at least one surface of the formed carrier foil of the release layer, the 5CBTA and optionally contacting the CBTA solution containing 4CBTA, it can be carried out such as by being fixed to CBTA components on the surface of the carrier foil. CBTA solution, 50~6000ppm the 5CBTA, containing 0~3000ppm the 4CBTA, it is preferably the concentration ratio of 5CBTA / 4CBTA is 2 or more, more preferably, 300~800ppm the 5CBTA, the 4CBTA contain 0~150ppm , the concentration ratio of 5CBTA / 4CBTA is 2-8. Is preferably liquid temperature of CBTA solution is in the range of 20 to 60 ° C., more preferably from 30 to 40 ° C.. Is preferably duration of the treatment with CBTA solution is in the range of 5 to 120 seconds, more preferably 30 to 60 seconds. Contact to the CBTA solution of the carrier foil, dipping to the CBTA solution, spray of CBTA solution, may be carried out by a falling or dropping, etc. of the CBTA solution. In addition, fixed to the carrier foil surface of the CBTA, the adsorption and drying of CBTA solution, may be carried out by electrodeposition, etc. of CBTA component of CBTA solution. For example, in the case of using the copper foil as the carrier foil, formation of the release layer is preferably performs carrier foil simultaneously adsorb CBTA components while pickling treatment, in which case, CBTA solution, a sulfuric acid concentration 50 it is preferably from 250 g / L and the copper concentration 2~20g / L, and more preferably sulfuric acid concentration 100 to 200 g / L and the copper concentration 5 to 15 g / L. While the surface of the carrier foil was pickled dissolved in doing so, to form a metal complex with the eluted metal ion and CBTA component, it may be precipitated adsorbed on the carrier foil. As a result, precipitation adsorption tissue CBTA component is fine to adsorb, and to simply as compared with the case of precipitating adsorbed by contact with an aqueous solution obtained by dispersing CBTA components can be uniformly adsorbed CBTA components.

[0021] The carrier foil is a foil to improve its handling properties and supports the ultrathin copper foil. Examples of the carrier foil, aluminum foil, copper foil, stainless (SUS) foil, a surface resin film or the like metal coatings can be mentioned, and preferably a copper foil. Copper foil may be either rolled copper foil and electrolytic copper foil. The thickness of the carrier foil is typically at 250μm or less, preferably 9μm~200μm.

[0022] Ultrathin copper foil is not particularly limited and may be a known structure employed in ultra-thin copper foil carrier. For example, ultrathin copper foil, an electroless copper plating method and wet film-forming method such as electrolytic copper plating method, a dry film formation method such as sputtering and chemical vapor deposition, or may be one formed by a combination thereof. The preferred thickness of the ultra-thin copper foil was 0.1~7.0μm, more preferably 0.5 to 5.0 m, more preferably from 1.0 to 3.0 m.

[0023] Pole opposite side of the release layer of thin copper foil is preferably roughened. That is, it is preferable that the the roughening treatment on one surface of the ultrathin copper foil. It is possible to improve the adhesion between the resin layer in the copper-clad laminate and a printed wiring board during manufacture by this way. This roughening treatment is subjected at least two plating step comprises a burnt plating step of depositing deposited copper microparticles on the ultra-thin copper foil, and a covering plating step to prevent dropping off of the fine copper particles preferably carried out in accordance with known plating technique.

[0024] It may be provided other functional layer between the release layer and the carrier foil and / or ultra-thin copper foil. Examples of such other functional layer include an auxiliary metal layer. Auxiliary metal layer is preferably made of nickel and / or cobalt. By forming such auxiliary metal layer on the surface side of the surface side and / or the ultra-thin copper foil carrier foil, may occur between the carrier foil and the ultrathin copper foil at high temperatures or prolonged hot press forming suppressing the mutual diffusion, it is possible to ensure the stability of the peel strength of the carrier foil. Thickness of the auxiliary metal layer is preferably in the 0.001~3μm.

[0025] If desired, it may anticorrosive treatment is applied to the ultrathin copper foil. Rustproofing preferably includes a plating treatment with zinc. Plating with zinc, may be any of the zinc plating or zinc alloy plating, zinc alloy plating zinc - nickel alloy treatment is particularly preferred. Zinc -

may be a plating process nickel alloy treatment including at least Ni and Zn, Sn, Cr, may further comprise other elements such as Co. Zinc - Ni / Zn adhesion ratio in the nickel alloy plating, the mass ratio, preferably from 1.2 to 10, more preferably 2-7, even more preferably from 2.7 to 4. In addition, it is preferable that anti-rust treatment further comprises a chromate treatment. After this chromate treatment is plating treatment with zinc, and more preferably carried out in a plating surface containing zinc. It is possible to further improve the rust resistance in doing so. Particularly preferred anti-rust treatment, zinc - is a combination of a nickel alloy plating process and subsequent chromate treatment.

[0026] If desired, the process silane coupling agent is applied to the surface of the ultra-thin copper foil, a silane coupling agent layer may be formed. This makes it possible to improve the adhesiveness or the like of the humidity resistance, chemical resistance and adhesive. Silane coupling agent layer, the silane coupling agent suitably diluted by coating can be formed by drying. Examples of the silane coupling agent, 4-glycidyl butyl trimethoxysilane, epoxy-functional silane coupling agent such as γ– glycidoxypropyltrimethoxysilane, or γ– aminopropyltrimethoxysilane, N-β (amino ethyl) .gamma.-aminopropyltrimethoxysilane, N-3- (4- (3- amino-propoxy) butoxy) propyl-3-aminopropyltrimethoxysilane, N- phenyl-- γ– aminopropyl trimethoxy amino functional such as a silane sex silane coupling agent, or γ– mercaptopropyltrimethoxysilane mercapto functional silane coupling agent or vinyltrimethoxysilane such, olefin functional silane coupling agent such as vinyl phenyl trimethoxysilane, or γ– methacryloxypropyl acrylic-functional silane coupling agent such as trimethoxysilane, or imidazole functional silane coupling agent such as imidazole silane, or triazine-functional silane coupling agents such as triazine silane.

[0027] <u>Copper-clad laminate</u>

Copper foil with carrier of the present invention is preferably used for the production of copper - clad laminates for printed wiring boards. That is, according to a preferred embodiment of the present invention, copper-clad laminate obtained using the copper foil the carrier is provided. The copper-clad laminate, it comprises a copper foil carrier of the present invention, a resin layer provided in close contact with ultrathin copper foil of the copper foil carrier. Copper foil with carrier may be provided on one surface of the resin layer may be provided on both surfaces. Resin layer, the resin preferably comprises an insulating resin. Preferably the resin layer is a prepreg and / or resin sheet. A prepreg, a synthetic resin plate, a glass plate, is a general term for woven glass fabric, nonwoven glass fabric, composite material impregnated substrate to a synthetic resin, such as paper. Preferred examples of the insulating resin, epoxy resin, cyanate resin, bismaleimide triazine resin (BT resin), polyphenylene ether resins, phenolic resins. Further, examples of the insulating resin that constitutes the resin sheet include epoxy resin, polyimide resin, and an insulating resin such as polyester resin. Further, the resin layer may contain the filler particles or the like consisting of various inorganic particles such as silica, alumina from the viewpoint of improving the insulating property. The thickness of the resin layer is not particularly limited, but is preferably 1 to 1000 m, more preferably from 2～400Myuemu, more preferably from 3~200μm. Resin layer may be composed of a plurality of layers. Prepreg and / or resin layer of the resin sheet or the like may be provided to the ultra-thin copper foil carrier through a primer resin layer applied in advance a copper foil surface.

[0028] Printed-wiring board

Copper foil with carrier of the present invention is preferably used for the production of a printed wiring board. That is, according to a preferred embodiment of the present invention, a printed wiring board obtained using copper foil the carrier is provided. A printed wiring board according to the present embodiment comprises a resin layer, and the copper layer is a stacked layer in this order. Further, the resin layer is as described above with respect to copper-clad laminate. In any case, the printed wiring board known layer configuration can be adopted. Specific examples of the printed wiring board, and one side or both sides printed wiring board circuits forming the ultrathin copper foil on which a laminated body obtained by curing adhered of the present invention one or both surfaces of the prepreg, multilayer these were multilayered a printed wiring board, and the like. As another embodiment, the flexible printed wiring board for forming a circuit by forming a ultrathin copper foil of the present invention on a resin film, COF, TAB tapes, etc. may be mentioned. As yet another embodiment, to form a resin coated copper foil coated with resin layers mentioned above to the ultrathin copper foil of the present invention (RCC), was laminated resin layer of the above printed wiring board as the insulating adhesive layer after, modified semi-additive (MSAP) method ultra-thin copper foil as all or part of the wiring layer, a subtractive method approach and build-up wiring board obtained by forming a circuit in such, by removing the ultra-thin copper foil semi additive (SAP) method build-up wiring board to form a circuit, the direct build-up-on-wafer or the like repeated alternately laminating a circuit formed of the resin coated copper foils to a semiconductor integrated circuit. Copper foil with carrier of the present invention, without using a so-called core substrate, can also be preferably used in the production method of the insulating resin layer and the conductive layer using a coreless build-up method which are alternately laminated.

[0029] More specifically illustrated by the following examples of the present invention.

[0030] Examples 1-9

The production and evaluation of the copper foil with the carrier was carried out in the following manner.

[0031] (1) as prepared carrier foil of the carrier foil, 18μm thick electrolytic copper foil not subjected to roughening treatment and anti-rust treatment of (Mitsui Mining & Smelting Co., Ltd., Class-III) was prepared.

[0032] (2) the electrode surface side of the forming pickled treated carrier foil peeling layer comprises 5CBTA and / or 4CBTA of concentrations indicated in Table 1, CBTA solution of sulfuric acid concentration 150 g / L and the copper concentration 10g / L in, was immersed for 30 seconds at a liquid temperature of 30 ° C. (examples 1∼4,7 and 8) or 40 ° C. (examples 5 and 6 and 9), to adsorb the CBTA component to the electrode surface of the carrier foil. Thus, the CBTA layer on the surface of the electrode surface of the carrier foil was formed as an organic release layer. The example 7 is a composition corresponding to Example 3 disclosed in Patent Document 2 (JP 2003-328178).

[0033]

[0034] (3) the carrier foil to form an organic release layer is formed of the auxiliary metal layer is immersed in a solution of the fabricated nickel concentration 20 g / L using a nickel sulfate solution temperature 45 ° C., pH 3, the current density. 5A / under the conditions of dm 2, it was deposited thickness 0.001μm equivalent of adhesion amount of nickel in the organic release layer on. Thus forming a nickel layer as an auxiliary metal layer in the organic release layer.

[0035] (4) a carrier foil forming the auxiliary metal layer is formed of ultra-thin copper foil is immersed in a copper solution having the composition shown below, a solution temperature of 45 ° C., and electrolysis at a current density of 5~30A / dm 2, the ultra-thin copper foil with a thickness of 3μm was formed on the auxiliary metal layer. <Composition of the solution> - copper concentration: 65g / L - sulfuric acid concentration: 150g / L

[0036] (5) The roughening treatment was carried out a roughening treatment thus formed surface of the ultra-thin copper foil. This roughening treatment is composed of a burnt plating step of depositing deposited copper microparticles on the ultra-thin copper foil, and covering the plating step to prevent dropping off of the fine copper particles. The burnt plating process, using an acidic copper sulfate solution comprising copper 18 g / L and sulfuric acid 100 g / L, a solution temperature of 25 ° C., was subjected to roughening treatment at a current density of 10A / dm 2. In subsequent covering plating step, using a copper solution containing a copper 65 g / L and sulfuric acid 150 g / L, liquid temperature 45 ° C., was electrodeposition smooth plating a current density of 15A / dm 2.

[0037] (6) on both sides of a copper foil with a carrier after anti-rust treatment roughening treatment was carried out anti-rust treatment composed of an inorganic anti-rust treatment and chromate treatment. First of all, as the inorganic anti-rust treatment, using a pyrophosphate bath, potassium pyrophosphate concentration 80g / L, zinc concentration 0.2g / L, nickel concentration 2g / L, a liquid temperature of 40 ℃, at a current density of 0.5A / dm 2 zinc - were nickel alloy anti-rust treatment. Then, the chromate treatment, zinc - on the nickel alloy rustproofing was further form a chromate layer. This chromate treatment, chromic acid concentration of 1g / L, pH11, solution temperature 25 °C, was carried out at a current density of 1A / dm 2.

[0038] (7) a silane coupling agent treatment the anti-rust treatment is washed with water copper foil that has been subjected to, to then immediately performs a silane coupling agent treatment, adsorption of the silane coupling agent on the rust-proofing layer of roughened surface It was. The silane coupling agent treatment, pure water as a solvent, 3-aminopropyltrimethoxysilane concentration using a solution of 3 g / L, by adsorption treatment by spraying the solution on the roughened surface by showering went. After adsorption of the silane coupling agent, finally moisture to Eat the by the electric heater to obtain a copper foil with a carrier.

[0039] (8) Evaluation obtained copper foil carrier of the copper foil carrier was evaluated as follows.

[0040] Peeling the carrier foil from the copper foil carrier <Analysis of the release layer>. The peeled carrier foil and the ultra-thin copper foil was immersed for 60 minutes at 40 ° C. in hydrochloric acid 1 mol / L, were extracted CBTA. At that time, by masking the surface opposite to the release layer of the carrier foil and the ultrathin copper foil, and to be subjected only to the extraction of CBTA surface in contact with the release layer. Thus obtained CBTA containing extract by high performance liquid chromatography (manufactured by Shimadzu Corporation, HPLC LC10 series) are analyzed by, by measuring the respective concentrations of 5CBTA and 4CBTA, the adhesion amount of 5CBTA (mg / m 2), the adhesion amount of 4CBTA (mg / m 2), the total deposition amount of the CBTA (mg / m 2), and were calculated 5CBTA / 4CBTA ratio. The results were as shown in Table 2.

[0041] <Measurement of peeling strength> First, was measured in the peel strength of a normal state in the copper foil with a carrier as follows. Paste the double-sided tape to the ultra-thin copper foil side of the copper foil with the carrier, which was fixed and paste to the substrate, to obtain a measurement sample. For this measurement sample, in conformity with JIS C 6481-1996, the peel strength was measured in normal when the carrier foil was peeled RS 0 (gf / cm). At this time, the measurement width is set to 50 mm, the measurement length was set to 20 mm.

[0042] Then, it was measured once or twice peel strength after hot pressing as follows. As the resin base material, it was prepared having a thickness of 100μm prepreg (Mitsubishi Gas Chemical Co., GHPL830NX-A). This with the carrier in the resin base material copper foil the ultra-thin copper foil side is stacked so as to be in contact with the resin base material, once the hot press forming of pressure 2.5MPa and temperature 230 °C for 60 minutes or twice go to give the copper-clad laminate samples after hot pressing. For copper-clad laminate samples, in compliance with JIS C 6481-1996, peel strength from the ultra-thin copper foil laminated to a resin substrate surface by peeling the carrier foil RS 1 (after hot pressing once) and the peel strength was measured

RS 2 (after hot press twice) (gf / cm). At this time, the measurement width is set to 50 mm, the measurement length was set to 20 mm. For peel strength RS 0 of normal before hot press, the ratio of the peel strength RS 2 after hot press twice ((RS 2 -RS 0) / RS 0) to peel strength increase rate multiplied by 100 (%) It was calculated. The results were as shown in Table 2.

[**0043**]

1. Carrier foil, a copper foil carrier with a release layer and the ultra-thin copper foil in this order, the release layer, 5-carboxyfluorescein-benzotriazole (5CBTA) and / or 4-carboxy include benzotriazole (4CBTA) becomes a ratio of the adhesion amount of adhering amount of 4-carboxy benzotriazole of 5-carboxy benzotriazole of the release layer is 5CBTA / 4CBTA ratio is 3.0 or more, the copper foil with carrier.
2. It said 5CBTA / 4CBTA ratio is 3.5 to 30, copper foil with carrier according to claim 1.
3. The release layer, 5-carboxyfluorescein comprises at 4-carboxybutyl benzotriazole (4CBTA) attached amount of 3 mg / yd 2 or more in total in the case of benzotriazole (5CBTA) and presence, carrier according to claim 1 or 2, Tsukedohaku.
4. The peeling layer, 5-carboxymethyl when benzotriazole (5CBTA) and present, including a 4-carboxy benzotriazole (4CBTA) in the amount of deposition of 80mg / m 2 or less in total, one of the claims 1 to 3 one copper foil with carrier according to section.
5. Wherein between the release layer and the carrier foil and / or said ultra-thin copper foil and an auxiliary metal layer further copper foil with carrier according to any one of claims 1 to 4.
6. Copper-clad laminates obtained using the copper foil carrier according to any one of claims 1-5.
7. A printed circuit board obtained using copper foil carrier according to any one of claims 1-6.