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Copper foil provided with carrier, copper-clad laminate, and printed wiring board.

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A copper foil provided with a carrier includes a carrier foil, a release layer, and an ultra-thin copper foil disposed in this order. The release layer contains 5-carboxybenzotriazole (5CBTA) and/or 4-carboxybenzotriazole (4CBTA) and the ratio of the amount of deposited 5-carboxybenzotriazole to the amount of deposited 4-carboxybenzotriazole i.e., 5CBTA/4CBTA ratio, in the release layer is 3.0 or more. The copper foil provided with a carrier can prevent an increase in release strength of a carrier foil after long-time high-temperature thermal history, and thus can stabilize the release strength

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

TECHNICAL FIELD

5 [0001]

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

BACKGROUND ART

10 [0002]

Copper foils provided with carriers have been widely used as material for manufacturing printed wiring boards. A copper foil provided with a carrier is laminated with an insulating resin substrate, such as a glass-epoxy substrate, a phenolic substrate, and a polyimide substrate by hot press molding into a copper-clad
15 laminate used in the manufacture of printed wiring boards.

[0003]

The copper foil provided with the carrier typically is a laminate of a carrier foil, a release layer, and an ultra-thin copper foil disposed in this order. For example, PTL 1 (JPH11-317574A) discloses an organic release layer containing an organic
20 compound, such as nitrogen-containing compounds, and describes various advantages: 1) the release layer can be readily formed; 2) the release strength (A) between the ultra-thin copper foil and the support metal layer (hereinafter, referred to as a carrier) is uniform and is lower than the peel strength (B) of the ultra-thin copper foil from a substrate after the foil is laminated to the substrate; 3) the inorganic
25 material-free release layer requires no mechanical polishing process or pickling process for removing inorganic material remaining on the surface of the ultra-thin copper foil and thus simplifies the formation of the wiring pattern due to the reduced number of processing steps; 4) the release strength (A), although small, is sufficient to prevent the separation of the ultra-thin copper foil from the carrier at the time of
30 handling the composite copper foil; (5) the peel strength (B) of the composite copper

foil from the laminated substrate is sufficient to prevent the peel-off from the substrate during processing the ultra-thin copper foil into the printed wiring substrate; (6) the carrier can be separated from the ultra-thin copper foil even after being laminated at high temperatures; and (7) the carrier can be reused without difficulty because the release layer remaining on the carrier is readily removable.

[0004]

PTL 2 (JP2003-328178A) discloses a method of manufacturing a copper foil provided with a carrier. This method involves pickling and dissolving the surface of the carrier foil with a pickling solution containing 50 ppm to 2000 ppm of an organic agent while simultaneously allowing the organic agent to adsorb thereon to form an organic release layer, i.e., an organic film by pickling and adsorption.

[0005]

PTLs 1 and 2 each disclose the use of carboxybenzotriazole (CBTA) as an organic agent for forming the organic release layer. Carboxybenzotriazole (CBTA) has two isomers, i.e., 5-carboxybenzotriazole (5CBTA) and 4-carboxybenzotriazole (4CBTA). PTLs 1 and 2 do not mention 5CBTA or 4CBTA.

[0006]

In recent years, multilayer printed wiring boards have gradually been prevalent to meet a decrease in size of and an increase in mounting density on the printed wiring board. Such multilayer printed wiring boards have been used for reductions in weight and size of many portable electronic devices. Requirements for the multilayer printed wiring boards include a further reduction in thickness of the insulating interlayer and a further reduction in weight of the wiring board itself. To meet such requirements, a recent method of manufacturing a multilayer printed wiring board employs a coreless build-up process which alternately laminates insulating resin layers and conductive layers without use of a so-called core substrate.

CITATION LIST

[PATENT DOCUMENTS]

30 [0007]

PTL 1: JPH11-317574A

PTL 2: JP2003-328178A

SUMMARY OF INVENTION

5 [0008]

Unfortunately, repeated long-time high-temperature thermal histories during multiple lamination steps, for example, in the coreless build-up process inevitably increase the release strength between the carrier foil and the ultra-thin copper foil. Accordingly, a copper foil provided with a carrier, in which the release strength
10 between the carrier foil and the ultra-thin copper foil barely increases, even if a long-time high-temperature thermal history are applied, that is, a copper foil provided with a carrier having a stable release strength is desired.

[0009]

The present inventor has found that a ratio of the amount of deposited
15 5-carboxybenzotriazole to the amount of deposited 4-carboxybenzotriazole, i.e., 5CBTA/4CBTA ratio of 3.0 or more in the release layer of the copper foil provided with a carrier can prevent the increase in the release strength of the carrier foil even after a long-time high-temperature thermal history, and thus can achieve a stable release strength.

20 [0010]

It is an object of the present invention to prevent an increase in release strength of a carrier foil after long-time high-temperature thermal history, and to provide a copper foil provided with a carrier having a stable release strength.

[0011]

25 According to a first aspect of the present invention, there is provided a copper foil provided with a carrier. The copper foil includes a carrier foil, a release layer, and an ultra-thin copper foil disposed in this order, wherein the release layer contains 5-carboxybenzotriazole (5CBTA) and/or 4-carboxybenzotriazole (4CBTA) and the ratio of the amount of deposited 5-carboxybenzotriazole to the amount of deposited
30 4-carboxybenzotriazole i.e., 5CBTA/4CBTA ratio, in the release layer is 3.0 or more.

[0012]

According to a second aspect of the present invention, there is provided a copper-clad laminate prepared with the copper foil provided with a carrier of the first aspect.

[0013]

- 5 According to a third aspect of the present invention, there is provided a printed wiring board prepared with the copper foil provided with a carrier of the first aspect.

DESCRIPTION OF EMBODIMENT

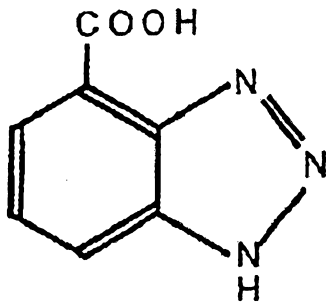
[0014]

- 10 <Copper foil provided with a carrier>

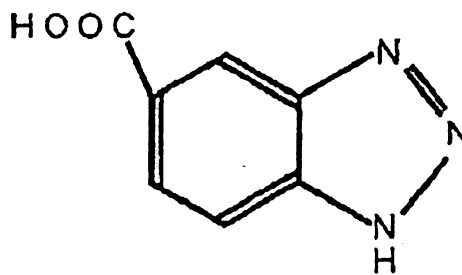
The copper foil provided with a carrier according to the present invention includes a carrier foil, a release layer, and an ultra-thin copper foil disposed in this order. The release layer contains 5-carboxybenzotriazole (hereinafter referred to as 5CBTA) and/or 4-carboxybenzotriazole (hereinafter referred to as 4CBTA). The chemical

- 15 formula of 4CBTA and 5CBTA are as follows:

[Chemical Formula 1]



4CBTA



5CBTA

[0015]

- 20 The copper foil provided with a carrier according to the present invention has a ratio of the amount of deposited 5CBTA to the amount of deposited 4CBTA, i.e., the 5CBTA/4CBTA ratio, in the release layer of 3.0 or more. Thus, the 5CBTA is an

essential component, while the 4CBTA is an optional component. In any case, the copper foil provided with a carrier of the present invention includes the release layer and can have a known layer structure.

[0016]

5 Thus, in the release layer of the copper foil provided with a carrier of the present invention, a 5CBTA/4CBTA ratio of 3.0 or more can unexpectedly prevent an increase in the release strength of the carrier foil after long-time high-temperature thermal history and thus can stabilize the release strength. In this context, although CBTA has been conventionally used as described above in the organic release layer, the organic release layer having a 5CBTA/4CBTA ratio of 3.0 or more is not yet known. To the knowledge of the inventor, commercially available CBTA mixtures contain 5CBTA and 4CBTA in a ratio of about 6:4 (5CBTA:4CBTA ratio), and thus the 5CBTA/4CBTA ratio is only about 1.5. The release layers containing CBTA mixtures having such a low ratio of 5CBTA/4CBTA have a problem in that repeated long-time high-temperature thermal histories through multiple lamination steps in, for example, a coreless build-up process can significantly increase the release strength between the carrier foil and the ultra-thin copper foil. The recent findings of the present inventor indicate that the above problem can be unexpectedly solved by a 5CBTA/4CBTA ratio of 3.0 or more in the release layer in the copper foil provided with a carrier. Consequently, in the lamination process of printed wiring boards, such as a coreless build-up process, involving repeated long-time high-temperature thermal histories through multiple stacking steps, the copper foil provided with a carrier according to the present invention has a release strength which does not increase much from the release strength under normal conditions (prior to the repeated long-time high-temperature thermal histories), and thus can exhibit a stable release strength (for example, 10 to 20 gf/cm). Accordingly, the copper foil provided with a carrier of the present invention is significantly useful in a lamination process, such as a coreless build-up process, of the printed wiring board.

[0017]

30 The release layer decreases the release strength between the carrier foil and the

ultra-thin copper foil to ensure the stability of the release strength and to inhibit the interdiffusion which may occur between the carrier foil and the copper foil during press molding at a high temperature. The release layer is generally formed on one surface of the carrier foil, but may be formed on two surfaces thereof. The release layer is
5 an organic release layer and contains 5CBTA and optional 4CBTA. In addition to 5CBTA and 4CBTA, the release layer may contain any other known component for the organic release layer.

[0018]

In the release layer, the 5CBTA/4CBTA ratio is 3.0 or more, preferably 3.5 to 30.
10 Such a ratio can lead to more stable release strength of the release layer. The release layer may contain 5CBTA alone (containing no 4CBTA).

[0019]

The release layer contains deposited 5CBTA and optional 4CBTA in total amount of preferably 3 mg/m² or more, more preferably 5 mg/m² or more, still more preferably 8
15 mg/m² or more. Although the upper limit of the deposited amount is not defined, the release layer contains deposited 5CBTA and optional 4CBTA in a total amount of preferably 80 mg/m² or less, more preferably 50 mg/m² or less, still more preferably 30 mg/m² or less in view of an improvement in handling characteristics of the copper foil provided with a carrier and further stabilization of the release strength.

20 [0020]

The release layer is formed, for example, such that the CBTA solution containing 5CBTA and optional 4CBTA is put into contact with at least one surface of the carrier foil to fix the CBTA components on the surface of the carrier foil. The CBTA solution contains preferably 5CBTA in an amount of 50 to 6000 ppm and 4CBTA in an amount
25 of 0 to 3000 ppm, having a 5CBTA/4CBTA ratio of 2 or more, more preferably 5CBTA in an amount of 300 to 800 ppm and 4CBTA in an amount of 0 to 150 ppm, having a 5CBTA/4CBTA ratio of 2 to 8. The liquid temperature of the CBTA solution is within the range of preferably 20 to 60°C, more preferably 30 to 40°C. The treatment time with CBTA solution is within the range of preferably 5 to 120 sec, more preferably 30
30 to 60 sec. The carrier foil may be put into contact with the CBTA solution by, for

example, immersion in the CBTA solution, spray of the CBTA solution, and falling or dropping of the CBTA solution. The CBTA may be fixed to the surface of the carrier foil by, for example, adsorption or drying of the CBTA solution, electrodeposition of CBTA components of CBTA solution. For example, in the case where a copper carrier foil is used, it is preferred that the release layer be formed by pickling the carrier foil and allowing CBTA components to be deposited on the surface of the foil simultaneously, and the CBTA solution has preferably a sulfuric acid content of 50 to 250 g/L and a copper content of 2 to 20 g/L, more preferably a sulfuric acid content of 100 to 200 g/L and a copper content of 5 to 15 g/L. Thus, while the surface of the carrier foil is pickled and dissolved, the dissolved metal ions and the CBTA components form metal complexes, which can precipitate and adsorb on the carrier foil. As a result, the CBTA components which are precipitated and adsorbed have a fine structure and can be more uniformly deposited compared to the case where the CBTA components are precipitated and deposited by contact with an aqueous dispersion in which the CBTA components are merely dispersed.

[0021]

The carrier foil supports an ultra-thin copper foil to improve the handling characteristics of the ultra-thin copper foil. Examples of the carrier foil include an aluminum foil, a copper foil, a stainless steel foil, and a metal-coated resin film, preferably a copper foil. The copper foil may be either a rolled copper foil or an electrodeposited copper foil. The carrier foil typically has a thickness of 250 μm or less, preferably 9 μm to 200 μm .

[0022]

The ultra-thin copper foil may have any known structure employed in the ultra-thin copper foil provided with a carrier. For example, the ultra-thin copper foil may be formed by a wet process, for example, electroless-copper plating or electro-copper plating; a dry process, for example, sputtering vapor deposition or chemical vapor deposition; or a combination thereof. The ultra-thin copper foil has a thickness of preferably 0.1 to 7.0 μm , more preferably 0.5 to 5.0 μm , still more preferably 1.0 to 3.0 μm .

[0023]

It is preferred that the ultra-thin copper foil have a roughened surface on a side opposite to the surface on which the release layer is disposed. That is, it is preferred that one surface of the ultra-thin copper foil be subjected to a roughening treatment, which can improve the adhesion to the resin layer during manufacturing the copper-clad laminate and the printed wiring board. The roughening treatment is preferably performed according to known plating techniques involving at least two plating processes, i.e. burning plating for depositing and fixing fine copper particles on the ultra-thin copper foil and covering plating for preventing the fine copper particles from detaching.

[0024]

Any other functional layer may be provided between the release layer and the carrier foil, and/or the release layer and the ultra-thin copper foil. Examples of such a functional layer include an auxiliary metal layer. The auxiliary metal layer is preferably composed of nickel and/or cobalt. Such an auxiliary metal layer is formed on the front side of the carrier foil and/or on the front side of the ultra-thin copper foil to inhibit interdiffusion which may occur between the carrier foil and the ultra-thin copper foil during high-temperature or long-time hot press molding, and thereby the stability of the release strength of the carrier foil can be ensured. The auxiliary metal layer has a thickness of preferably 0.001 to 3 μm .

[0025]

If desired, the ultra-thin copper foil may be subjected to rust proofing treatment. The rust proofing treatment preferably involves plating with zinc. The plating with zinc may be either zinc plating or zinc alloy plating, and the zinc alloy plating is particularly preferably zinc-nickel alloy plating. Zinc-nickel alloy plating may be any plating process including at least Ni and Zn, and may further include other elements such as Sn, Cr, and Co. The deposited Ni/Zn ratio by mass in zinc-nickel alloy plating is preferably 1.2 to 10, more preferably 2 to 7, still more preferably 2.7 to 4. Furthermore, the rust proofing treatment preferably further involves chromate treatment. More preferably, the chromate treatment is performed on the plated

surface containing zinc after the plating with zinc, and thus the rust proofing properties are further improved. Particularly preferred rust proofing treatment is a combination of zinc-nickel alloy plating process and subsequent chromate treatment.

[0026]

5 Optionally, a silane coupling agent treatment is applied on the surface of the ultra-thin copper foil to form a silane coupling agent layer, which can improve moisture resistance, chemical resistance, and adhesion to, for example, adhesive. The silane coupling agent layer can be formed by coating an appropriately diluted silane coupling agent and then allowing the coating to dry. Examples of the silane coupling agent
10 include epoxy functional silane coupling agents, such as 4-glycidylbutyltrimethoxysilane and γ -glycidoxypropyltrimethoxysilane; amino-functional silane coupling agents, such as γ -aminopropyltrimethoxysilane, N- β (aminoethyl) γ -aminopropyltrimethoxysilane, N-3-(4-(3-amino-propoxy)butoxy)propyl-3-aminopropyltrimethoxysilane, and
15 N-phenyl- γ -aminopropyltrimethoxysilane; mercapto-functional silane coupling agents, such as γ -mercaptopropyltrimethoxysilane; olefinic functional silane coupling agents, such as vinyltrimethoxysilane and vinyl phenyl trimethoxysilane; acrylic functional silane coupling agents, such as γ -methacryloxypropyl trimethoxysilane; imidazole functional silane coupling agents, such as imidazole silane; and triazine functional
20 silane coupling agents, such as triazine silane.

[0027]

<Copper-clad laminate>

The carrier copper foil provided with a carrier of the present invention is preferably used in production of a copper-clad laminate for the printed wiring board. That is,
25 according to a preferred embodiment of the present invention, a copper-clad laminate can be prepared using the copper foil provided with a carrier. The copper-clad laminate includes a copper foil provided with a carrier and a resin layer in tight contact with the ultra-thin copper foil of the copper foil provided with a carrier. The copper foil provided with a carrier may be provided on one or two surfaces of the resin layer.
30 The resin layer is composed of a resin, preferably an insulating resin. It is preferred

that the resin layer be a prepreg and/or a resin sheet. The prepreg is a general term for composite material which is prepared by impregnating a substrate, such as a synthetic resin plate, a glass plate, a glass woven fabric, a glass non-woven fabric, and 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 phenolic resins. Examples of the insulating resin composing the resin sheet include epoxy resins, polyimide resins, and polyester resins. Furthermore, the resin layer contains, for example, filler particles made of various inorganic particles, such as silica and alumina, in view of improving the insulating properties. The resin layer may have any thickness, for example, preferably 1 to 1,000 μm , more preferably 2 to 400 μm , still more preferably 3 to 200 μm . The resin layer may be composed of a plurality of layers. The resin layer, such as a prepreg and/or a resin sheet, may be disposed on the ultra-thin copper foil provided with a carrier through a primer resin layer preliminarily applied on the copper foil surface.

15 [0028]

<Printed wiring board>

The copper foil provided with a carrier of the present invention is preferably used in production of printed wiring boards. That is, according to a preferred embodiment of the present invention, there is provided a printed wiring board prepared with a copper foil provided with a carrier. The printed wiring board has a layer structure including a resin layer and a copper layer laminated in this order. The resin layer is described above in connection with the copper-clad laminate. In any case, the printed wiring board may have any known layer structure. Specific examples of the printed wiring board include a single-sided or double-sided printed wiring board which is prepared by forming a circuit after bonding the ultra-thin copper foil of the present invention to one or each surface of the prepreg into a cured laminate or a multilayer printed wiring board consisting of these printed wiring boards. Other specific examples thereof include flexible printed wiring boards, chip-on-film (COF) boards and tape-automated-bonding (TAB) tapes which includes the ultra-thin copper foils of the present invention formed on the resin films and the circuits formed thereon. Further

specific examples include a build-up wiring board formed such that the ultra-thin copper foil is coated with the resin layer described above to form a resin-coated copper foil (RCC) which is then laminated on the printed wiring board through the resin layer which functions as an insulating adhesive layer, and subsequently a circuit
5 is formed with the ultra-thin copper foil as all or part of the wiring layer by a technique such as a modified semi-additive process (MSAP) or a subtractive process; another build-up wiring board in which the ultra-thin copper is removed to form a circuit by a semi-additive process (SAP); and a direct build-up-on-wafer formed such that lamination of the resin-coated copper foil and circuit formation are alternately
10 repeated on the semiconductor integrated circuit. The copper foil provided with a carrier of the present invention can be preferably also used in the manufacturing method which uses a coreless build-up process, in which insulating resin layers and conductive layers are alternately laminated without a so called core substrate.

15

EXAMPLES

[0029]

The present invention will be further described in detail with reference to the following examples.

[0030]

20 Examples 1 to 9

Copper foils provided with carriers were prepared and evaluated as follows.

[0031]

(1) Provision of carrier foil

An electrodeposited copper foil with a thickness of 18 μm not subjected to roughening
25 and rust proofing treatments (Mitsui Mining & Smelting Co., Ltd., Class-III) was provided for a carrier foil.

[0032]

(2) Formation of release layer

The electrode surface of the pickled carrier foil was immersed in an aqueous CBTA
30 solution of a sulfuric acid content of 150 g/L and a copper content of 10 g/L containing

5CBTA and/or 4CBTA having a content shown in Table 1 below at a liquid temperature of 30°C (Examples 1 to 4, 7 and 8) or 40°C (Examples 5, 6 and 9) for 30 sec to allow CBTA components to be adsorbed on the electrode surface of the carrier foil. A CBTA layer i.e. an organic release layer was formed on the electrode surface of the carrier foil. Example 7 corresponds to the composition of Example 3 disclosed in PTL 2 (JP2003-328178A).

[0033]

[Table 1]

Table 1

	Content of 5CBTA (ppm)	Content of 4CBTA (ppm)	Total content of CBTA(5CBTA+4CBTA) (ppm)
Ex. 1	300	150	450
Ex. 2	300	120	420
Ex. 3	300	100	400
Ex. 4	450	100	550
Ex. 5	600	80	680
Ex. 6	800	0	800
Ex. 7*	450	350	800
Ex. 8*	300	200	500
Ex. 9*	300	200	500

10

[0034]

(3) Formation of auxiliary metal layer

The carrier foil having an organic release layer formed thereon was immersed in a nickel sulfate solution having a nickel content of 20 g/L under the condition of a liquid temperature of 45°C, a pH of 3, and a current density of 5 A/dm² to deposit nickel in an amount equivalent to that of a 0.001 μm thick layer on the organic release layer. The nickel layer as an auxiliary metal layer was formed on the organic release layer.

[0035]

(4) Formation of ultra-thin copper foil

20 The carrier foil having the auxiliary metal layer formed thereon was immersed in a copper solution having a composition described below and electrolyzed under the condition of a solution temperature of 45°C, and a current density of 5 to 30 A/dm² to form an ultra-thin copper foil having a thickness of 3 μm.

<Composition of solution>

- Copper content: 65 g/L
- Sulfuric acid content: 150 g/L

[0036]

(5) Roughening treatment

5 The resulting surface of the ultra-thin copper foil was subjected to roughening treatment. The roughening treatment consists of a burning plating step for depositing and fixing fine copper particles on the ultra-thin copper foil and a covering plating step for preventing the fine copper particles from detaching. In the burning plating step, a roughening treatment was performed with an acidic copper sulfate
10 solution having a copper content of 18 g/L and sulfuric acid content of 100 g/L under the condition of a liquid temperature of 25°C and a current density of 10 A/dm². In the subsequent covering plating step, electrodeposition was performed with a copper solution having a copper content of 65 g/L and sulfuric acid content of 150 g/L under the smooth plating condition of a liquid temperature of 45°C and a current density of
15 15 A/dm²

[0037]

(6) Rust proofing treatment

The rust proofing treatment consisting of an inorganic rust proofing treatment and chromate treatment was applied on the both surfaces of the copper foil provided with
20 a carrier after roughening treatment. First, in the inorganic rust proofing treatment, zinc-nickel alloy rust proofing treatment was performed in a pyrophosphate bath under the conditions of a potassium pyrophosphate content of 80 g/L, a zinc content of 0.2 g/L, a nickel content of 2 g/L, a liquid temperature of 40°C and a current density of 0.5 A/dm². Then, in chromate treatment, chromate layers were formed on the both
25 surfaces having been subjected to the zinc-nickel alloy rust proofing treatment. The chromate treatment was performed under the conditions of a chromic acid content of 1 g/L, a pH of 11, a solution temperature of 25°C, and a current density of 1A/dm².

[0038]

(7) Silane coupling agent treatment

30 The rust proof treated copper foil was washed with water and was immediately

subjected to silane coupling agent treatment to adsorb the silane coupling agent on the rust proof treated layer of the roughened surface. The silane coupling agent treatment was performed such that a solution of 3-aminopropyltrimethoxysilane (3 g/L) in pure water was sprayed by showering to adsorb the silane coupling agent on the roughened surface. After the adsorption of the silane coupling agent, water was finally vaporized with an electric heater to prepare a copper foil provided with a carrier.

[0039]

(8) Evaluation of copper foil provided with carrier

The resulting copper foil provided with a carrier was evaluated in the following manner.

[0040]

<Analysis of release layer>

The carrier foil was peeled off from the copper foil provided with a carrier. The peeled-off carrier foil and the ultra-thin copper foil were immersed in 1 mol/L hydrochloric acid solution at 40°C for 60 min to extract CBTA, wherein surfaces of the carrier foil and the ultra-thin copper foil on the opposite side of the release layer were masked so that only the surfaces in contact with the release layer were subjected to extraction of CBTA. The resulting CBTA-containing extract was analyzed by a high-performance liquid chromatography, HPLC LC10 series (manufactured by Shimadzu Corporation) to measure each content of 5CBTA and 4CBTA. The amount (mg/m²) of deposited 5CBTA, the amount (mg/m²) of deposited 4CBTA, the total amount (mg/m²) of deposited CBTA, and the ratio of 5CBTA/4CBTA were thereby calculated. The result are shown in Table 2.

[0041]

<Measurement of release strength>

The release strength in the copper foil provided with a carrier under the normal conditions was measured as follows. The double-sided tape was bonded to the ultra-thin copper foil side of the copper foil provided with a carrier, which was then bonded and fixed to the substrate, resulting in a sample for measurement. The

release strength RS_0 (gf/cm) under the normal conditions for peeling off the carrier foil was measured in accordance with JIS C 6481-1996, where the width and length for measurement were 50 mm and 20 mm, respectively.

[0042]

- 5 The release strength after one or two hot pressing operations was measured as follows. A prepreg (manufactured by Mitsubishi Gas Chemical Co., Ltd., GHPL830NX-A) having a thickness of 100 μm was prepared as the resin substrate. The copper foil provided with a carrier was laminated to the resin substrate such that the ultra-thin copper foil was in contact with the resin substrate. The laminate was
- 10 hot-press molded once or twice at a pressure of 2.5 MPa and a temperature of 230°C for 60 min to form a copper-clad laminate sample after hot pressing. The release strength RS_1 (after one hot pressing) and the release strength RS_2 (after two hot pressings) (gf/cm) of the copper-clad laminate sample were measured by peeling the carrier foil from the ultra-thin copper foil laminated on the surface of the resin
- 15 substrate in accordance with JIS C 6481-1996, where the width and length for measurement were 50 mm and 20 mm, respectively. The ratio of the release strength RS_0 of the normal state to the release strength RS_2 (after two hot pressings) ($(RS_2 - RS_0) / RS_0$) was multiplied by 100 to calculate the increase rate of the release strength (%). The results were as shown in Table 2.

20 [0043]

[Table 2]

Table 2

	Compositional analysis of release layer			Release strength				
	Amount of deposited 5CBTA (mg/m ²)	Amount of deposited 4CBTA (mg/m ²)	Total amount of deposited CBTA (5CBTA+4CBTA) (mg/m ²)	5CBTA/4CBTA ratio	Release strength in normal state (before hot pressing) RS ₀ (gf/cm)	Release strength after one pressing operation at 230°C for 1hr RS ₁ (gf/cm)	Release strength after two pressing operations at 230°C for 1hr RS ₂ (gf/cm)	Increase rate of release strength 100×(RS ₂ -RS ₀)/RS ₀ (%)
Ex. 1	15.5	5.2	20.7	3.0	13	16	19	46
Ex. 2	10.2	2.6	12.8	3.9	11	12	13	18
Ex. 3	8.1	1.2	9.3	6.8	12	13	14	17
Ex. 4	14.8	1.4	16.2	10.6	13	14	14	8
Ex. 5	28.7	1.1	29.8	26.1	11	11	13	18
Ex. 6	15.3	0.0	15.3	∞	12	14	17	42
Ex. 7*	15.8	10.2	26.0	1.5	12	18	37	208
Ex. 8*	6.2	3.1	9.3	2.0	14	19	30	114
Ex. 9*	10.3	4.3	14.6	2.4	11	15	22	100

“*” represents comparative example

CLAIMS

1. A copper foil provided with a carrier comprising:
a carrier foil, a release layer, and an ultra-thin copper foil disposed in this
5 order, wherein the release layer contains 5-carboxybenzotriazole (5CBTA) and
optionally 4-carboxybenzotriazole (4CBTA) and the ratio of the amount of deposited
5-carboxybenzotriazole to the amount of deposited 4-carboxybenzotriazole i.e.,
5CBTA/4CBTA ratio, in the release layer is 3.0 or more.
- 10 2. The copper foil provided with a carrier according to claim 1, wherein the
5CBTA/4CBTA ratio is 3.5 to 30.
3. The copper foil provided with a carrier according to claim 1 or 2, wherein the
release layer contains deposited 5-carboxybenzotriazole (5CBTA) and optional
15 4-carboxybenzotriazole (4CBTA) in a total amount of 3 mg/m² or more.
4. The copper foil provided with a carrier according to any one of claims 1 to 3,
wherein the release layer contains deposited 5-carboxybenzotriazole (5CBTA) and
optional 4-carboxybenzotriazole (4CBTA) in a total amount of 80 mg/m² or less.
20
5. The copper foil provided with a carrier according to any one of claims 1 to 4,
further comprising at least one auxiliary metal layer between the release layer and the
carrier foil, and/or the release layer and the ultra-thin copper foil.
- 25 6. A copper-clad laminate prepared with the copper foil provided with a carrier
according to any one of claims 1 to 5.
7. A printed wiring board prepared with the copper foil provided with a carrier
according to any one of claims 1 to 6.

ABSTRACT

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A copper foil provided with a carrier includes a carrier foil, a release layer, and an ultra-thin copper foil disposed in this order. The release layer contains
5 5-carboxybenzotriazole (5CBTA) and/or 4-carboxybenzotriazole (4CBTA) and the
ratio of the amount of deposited 5-carboxybenzotriazole to the amount of deposited
4-carboxybenzotriazole i.e., 5CBTA/4CBTA ratio, in the release layer is 3.0 or more.
The copper foil provided with a carrier can prevent an increase in release strength of a
carrier foil after long-time high-temperature thermal history, and thus can stabilize the
10 release strength.



SEARCH REPORT

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

LO 1341
LU 93050

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 5 842077 B1 (MITSUI MINING & SMELTING CO) 13 January 2016 (2016-01-13) * claims 1-7 *	1-7	INV. C25D1/04 C25D1/22
X	JP 2004 131836 A (MITSUI MINING & SMELTING CO) 30 April 2004 (2004-04-30) * abstract * * claims 1, 8 * * paragraphs [0002], [0024] *	1,3,4,6,7	
A	WO 2009/117734 A1 (ENTHONE [US]; ABYS JOSEPH A [US]; ANTONELLIS THEODORE [US]; SUN SHENLI) 24 September 2009 (2009-09-24) * abstract * * example 6 * * claim 1 * * paragraph [0012] *	1	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25D
The present search report has been drawn up for all claims			
		Date of completion of the search	Examiner
		6 January 2017	Lange, Ronny
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	

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EPO FORM 1503 03.82 (P04C55)

**ANNEX TO THE SEARCH REPORT
ON LUXEMBOURG PATENT APPLICATION NO.**

LO 1341
LU 93050

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.

06-01-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 5842077 B1	13-01-2016	JP 5842077 B1	13-01-2016
		TW 201622495 A	16-06-2016

JP 2004131836 A	30-04-2004	JP 3812834 B2	23-08-2006
		JP 2004131836 A	30-04-2004

WO 2009117734 A1	24-09-2009	CN 102037157 A	27-04-2011
		EP 2274460 A1	19-01-2011
		EP 2546387 A1	16-01-2013
		JP 5620365 B2	05-11-2014
		JP 2011515542 A	19-05-2011
		KR 20100128335 A	07-12-2010
		US 2012168075 A1	05-07-2012
		WO 2009117734 A1	24-09-2009



WRITTEN OPINION

File No. LO1341	Filing date (day/month/year) 27.04.2016	Priority date (day/month/year)	Application No. LU93050
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International Patent Classification (IPC)
INV. C25D1/04 C25D1/22

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

Lange, Ronny

WRITTEN OPINION

Application No.

LU93050

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	
	No: Claims	1-7
Inventive step	Yes: Claims	
	No: Claims	1-7
Industrial applicability	Yes: Claims	1-7
	No: Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Application No.

LU93050

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

Reference is made to the following documents:

- D1 JP 5 842077 B1 13 January 2016 (2016-01-13) and a machine translation in English provided by ThomsonReuters
- D2 JP 2004 131836 A (MITSUI MINING & SMELTING CO) 30 April 2004 (2004-04-30) and a machine translation in English.

The translations were used for the interpretation of the relevance of documents D1 and D2. A copy of the translation used is annexed.

1 Novelty

The present application does not meet the criteria of patentability, because the subject-matter of claims 1-7 is not new.

1.1 Independent claim 1

Document D1 (Claim 1) discloses a copper foil laminate comprising a carrier foil, a release layer and an ultra-thin copper foil in this order, wherein the release layer contains 5CBTA and/or 4CBTA whilst the 5CBTA/4CBTA ratio is 3.0 or more.

Furthermore document D2 (Claim 1 and Paragraph 0024 - Paragraph 0024 shows that 5CBTA is used) also teaches such a laminate.

1.2 Dependent claim 2-5

Document D1 also reveals a laminate wherein the 5CBTA/4CBTA ratio is between 3.5 and 30 (Claim 2 in D1) and wherein the total amount of 5CBTA and CBTA is between 3mg/m² (Claim 3 in D1) and 80mg/m² (Claim 4 in D1), wherein the laminate comprises at least one auxiliary metal layer between the release layer and the carrier foil and/or the release layer and the ultra-thin copper foil (Claim 5 in D5).

Moreover document D2 describes a laminate wherein the total amount of 5CBTA and 4CBTA is between 3mg/m² and 80mg/m² (Paragraph 0033 - *the method to prepare the laminate in D2 is identical to the method used in the present application, e.g. the same amount of 5CBTA is used in the deposition solution* - in D2)

1.3 Dependent claims 6 and 7

Documents D1 and D2 also show a copper-clad laminate prepared with the copper foil laminate (Claim 6 in D1, Claim 8 in D2) and a printed wiring board prepared with said copper foil laminate (Claim 7 in D1, Paragraph 0002 in D2)

2 Inventive step

The present application does not meet the criteria of patentability, because the subject-matter of claim 1-7 does not involve an inventive step.

Claims 1-7

The subject-matter of claims 1-7 is not new. Therefore it does involve neither an inventive step.

3 Industrial applicability

The subject-matter of claims 1-7 is industrially applicable.

Re Item VIII

Certain observations on the international application

4 Clarity

Claim 1 is not clear.

The wording "A copper foil provided with a carrier comprising [...] an ultra-thin copper foil" is unclear. It is not apparent whether the copper foil and the ultra-thin copper foil is the same or different. In addition it not clear whether the carrier and the carrier foil are the same or different.

Furthermore the wording "5-carboxybenzotriazole (5CBTA) and/or 4-carboxybenzotriazole" is unclear. According to the description (Paragraph 0018) the release layer may either only contain 5CBTA or a mixture of 5CBTA and 4CBTA. The wording above also includes a release layer comprising only 4-carboxybenzotriazole. Claim 1 is not therefore not supported by the description, as its scope is broader than justified by the description and drawings.